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THÈSE PRÉSENTÉE POUR OBTENIR LE GRADE DE

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SPÉCIALITÉ CHIMIE ORGANIQUE

Christiaan J.F. de Vet

Auto-assemblage d'un anthracène fluorescent aux échelles nano- et micrométriques par photoréaction contrôlée

Photocontrolled self-assembly of a fluorescent anthracene at nano- and microscales

Sous la direction de: Prof. André DEL GUERZO

Soutenue le 9 Décembre 2016

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Voor ome Ad...

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Résumé

Les gels supramoléculaires, grâce à leurs propriétés uniques comme la réversibilité ou la dynamique, permettent d'envisager de nouvelles gammes de matériaux plus sophistiqués comme par exemple des matériaux s'auto-réparant. Cependant, un des défis majeurs à relever dans ce domaine est de mieux contrôler leur morphologie aux échelles nano- et micrométriques ainsi que la possibilité de contrôler précisément l'emplacement de la croissance des nanostructures formant ces gels. Dans cette thèse, nous présentons les principaux résultats obtenus sur l'auto-assemblage photo-induit des *n*-acènes. Plus précisément, nous traiterons du contrôle de la nucléation et de la croissance de 2,3-didecyloxyanthracène (ou DDOA) à différentes échelles, pour permettre le photo-patterning d'objets anisotropes. Le concept présenté ici a pour objectif global d'avancer sur le contrôle de la formation de nanofibres en 3D. L'utilisation d'acènes fluorescents permet simultanément de pouvoir étudier grâce à la microscopie de fluorescence les mécanismes fondamentaux de l'auto-assemblage photo-induit, ainsi que l'impact de cette approche sur la fabrication de matériaux pour la photonique à nanostructure contrôlée.

Le premier chapitre est consacré à la présentation des notions essentielles à la compréhension et à la mise en relief des résultats discutés dans la thèse. Celles-ci comprennent à la fois l'auto-assemblage moléculaire, les gélifiants de faible poids moléculaire (GFPM) (principes et état-de-l'art) ainsi que les bases de la photochimie.

Le deuxième chapitre introduira le 1,2-dicétone-2,3-didecyloxyanthracène (dkDDOA), le pro-gélifiant du DDOA, et ses propriétés photo-chimiques et photo-physiques en solution. Ensuite, la gélification photo-induite du DDOA dans le DMSO sera présentée. Les propriétés physiques du gel induit par réaction photochimique sont comparées à celles du gel standard, induit par refroidissement. Une attention particulière a été apportée à l'étude des interactions entre le DDOA et le dkDDOA en solution. Enfin, nous présenterons le dkG10, un diphenyl-tetracène photoactivable, et son utilisation pour le contrôle spatial de la couleur de l'émission des fibres grâce à un transfert d'énergie entre DDOA et G10 pendant la photoconversion.

Dans le troisième chapitre, avant de discuter du photo-patterning des fibres de DDOA, différentes techniques de contrôle de la croissance des matériaux auto-assemblables pour l'obtention de propriétés anisotropes seront présentées. Ensuite nous discuterons des conditions expérimentales pour l'obtention des patterns de fibres alignées de DDOA grâce à un faisceau laser focalisé.

Au cours du chapitre 4, la stratégie de synthèse adoptée pour avoir des acènes autoassemblables avec les propriétés photo-physiques souhaitées sera détaillée.

Le dernier chapitre présente les travaux concernant le contrôle des propriétés mécaniques d'un hydrogélifiant, d'abord via l'auto assemblage contrôlée cinétiquement par le pH et ensuite via un post-traitement comprenant la réticulation photo-initiée des fibres supramoléculaires. Les propriétés mécaniques sont mesurées par rhéologie.

Chapitre 1 Introduction

L'auto-assemblage se réfère à l'organisation spontanée des composants individuels dans des motifs ou des structures ordonnées. En d'autres termes, les structures sont formées à l'équilibre thermodynamique ou dans un état métastable. Aucun apport d'énergie n'est nécessaire pour maintenir la structure dans le temps. L'auto-assemblage moléculaire est gouverné par des interactions non-covalentes faibles comme les liaisons hydrogène, les interactions π - π , de transfert de charge ou de van der Waals. Un point très important est le fait que l'auto-assemblage des molécules est toujours gouverné par une multitude d'interactions faibles.

Les GFPMs sont une classe de molécules pouvant s'auto-assembler. Les molécules forment des fibres 1D qui croissent et forment un réseau maintenu par des liaisons physiques faibles qui piège le solvant. L'auto-assemblage des gels est gouverné par deux étapes clé: la nucléation et la croissance. Celles-ci sont initialisées quand la solution est supersaturée, c'està-dire que la concentration en gélifiant est suffisante pour provoquer une nucléation. Pour un échantillon classique, la supersaturation est provoquée par un refroidissement après une dissolution à chaud. Dans ce cas, le gel contient 98 à 99%mol du solvant, les 1 à 2 %mol restants étant le gélifiant. Du fait que le solvant soit piégé, le matériau possède les caractéristiques mécaniques d'un solide visco-élastique.



Figure I: Mécanisme d'auto-assemblage d'un gélifiant à faible poids moléculaire. Monomer = monomère ; nucleus = noyau, fibril = fibrile ; fiber = fibre ; entanglement = enchevêtrement.

Les gélifiants moléculaires sont des molécules dont le poids moléculaire est inférieur à 1000 Da, et peuvent donc être facilement modifiées par synthèse organique pour être

adaptées à d'autres stimuli que la température. En effet, la maîtrise de la gélification par la lumière introduit de nombreux avantages comme le contrôle spatial et temporel, la possibilité de travailler à température ambiante et enfin la lumière est un des seuls réactifs qui ne laisse pas de traces. En autres termes, synthétiser un gélifiant photo-sensible est un concept pour gouverner la position et la croissance de nos *n*-acènes à température ambiante. De plus, le DDOA est un supergélifiant formant des gels à faible concentration et dans une large gamme de solvants comme des alcools primaires linéaires et le DMSO, par exemple. C'est pour cette raison que nous avons synthétisé un des précurseurs photo-réactifs du DDOA.

Chapitre 2 Gélification du DDOA par photoréaction contrôlée

La 1,2-dicétone est un groupement fonctionnel photosensible. Quand la molécule est irradiée avec de la lumière bleue à 450 nm (transition $n-\pi^*$ entre 420-550 nm), deux molécules de monoxyde de carbone et un groupement aromatique sont libérés. La photo-conversion est quantitative pour plusieurs dérivés d'anthracène. L'efficacité globale de la réaction est favorisée par l'absence de chevauchement des spectres d'absorption du photo-produit et du groupement photosensible, comme c'est le cas pour le dkDDOA. La 1,2-dicétone est une cétone active et pour cette raison elle est sensible à l'humidité et aux nucléophiles comme les alcools. En conséquent, le DMSO est, de préférence, utilisé comme solvant. Deux autres raisons justifient l'utilisation du DMSO: la solubilité du monoxyde de carbone est quasi nulle dans ce solvant et les nanofibres du gel de DDOA présentent un caractère cristallin dans ce solvant. Cette cristallinité est une des caractéristiques engendrant une émission polarisée dans les nanofibres auto-assemblées. Cette particularité est intéressante pour l'analyse du photo-patterning et l'exploitation de ces matériaux optiques nanostructurés (c.f. Chapitre 3).

Le groupement fonctionnel 1,2-dicétone est ajouté au DDOA en trois étapes de synthèse. La première est une réaction de Diels-Alder entre le DDOA et le carbonate de vinylène sous haute température. La seconde étape est une hydrolyse qui donne le 1,2-diol et enfin une oxydation de Swern qui donne le dkDDOA avec un rendement global de 56%. Le dkDDOA est une molécule solvatochrome dû à une transition de transfert de charge qui répond par un déplacement bathochrome à la polarité croissante du solvant. La fluorescence présente également un déplacement bathochrome et le rendement quantique de fluorescence (Φ_F) se situe entre 0.4% et 0.8% selon les solvants. En revanche, le Φ_F du DDOA est de 24%, ce qui donne la possibilité d'analyser la photoconversion grâce à l'activation de sa fluorescence.



Figure II: Photodecarbonylation du dkDDOA sous irradiation.

Le suivi par UV-vis et ¹H-RMN de la photoconversion du dkDDOA dans le DMSO sous irradiation (à 450 nm) vérifie qu'elle est quantitative et ne forme pas d'autres produits secondaires que le monoxyde de carbone, comme décrit précédemment. De plus, la formation d'un gel est confirmée par une augmentation à 384 nm de l'absorption de la transition 0-0 du DDOA à des concentrations aussi basses que 1 mM de dkDDOA.

Le rendement quantique de photoréaction a une valeur basse dans le DMSO : 0.2%. Cette valeur est sept fois plus basse que la valeur dans le toluène (14%), un solvant apolaire. En effet, un état compétitif de transfert de charge, peu propice à la photodécarbonylation, est stabilisé dans le DMSO.

La comparaison des propriétés photo-physiques d'un gel photoinduit avec celles d'un gel obtenu par refroidissement montre que les deux sont identiques, à l'exception d'une composante bathochrome mineure dans l'émission du gel photoinduit. La durée de vie de fluorescence nous a permis de confirmer que cette composante bathochrome est dû à une légère augmentation des défauts émissifs. Ceux-ci sont sensibilisés par des sauts d'excitons efficace dans les gels. Effectivement, il a été démontré précédemment qu'un accepteur d'énergie, tel que par exemple une molécule de 2,3-didecyloxytetracene (DDOT), peut désactiver 100-1000 excitons de DDOA. Le mécanisme responsable de la formation de défauts est attribué à l'inclusion partielle de dkDDOA dans les fibres de DDOA pendant l'auto-assemblage. Ceci a été confirmé par une mesure de l'absorption à différentes températures et par l'analyse de l'émission par la procédure de Stern-Volmer.

L'ajout de seulement 2 %mol d'un tetracène photoactivable synthetisé par la même voie que celle du dkDDOA (rendement global : 38%) peut changer la couleur d'émission du DDOA par un transfert d'énergie efficace. Cette méthode est un premier pas vers la possibilité de fabriquer des motifs de différentes couleurs (color-patterning) (Figure III).



Figure III: (a) Un gel de DDOA sans accepteur. La concentration de DDOA est de 2 mM. (b) Un gel de DDOA et G10 photoinduit (photoconversion de dkDDOA et de dkG10). Concentration à 2 mM pour le dkDDOA et 0.04 mM pour le dkG10. La source d'excitation est une LED à 450 nm.

Chapitre 3 Auto-assemblage contrôlé aux échelles nano- et micrométriques: photopatterning des nanofibres de DDOA.

Les structures alignées sans défauts sont très recherchées dans différents domaines, comme par exemple les transistors à effet de champ monocristallin (SCFETs) et les cristaux liquides (LCs). Les SCFETs sont très étudiés car la minimisation de défauts dans la structure cristalline permettrait une augmentation sensible de la mobilité des charges. Cependant, l'obtention de couches monocristallines sans défauts représente encore un défi. En effet, un simple joint de grain sera dommageable aux performances d'un transistor à effet de champ. Les techniques décrites dans le chapitre 3, par exemple 'droplet pinned cristallisation' et 'solution shearing', pourraient être intéressantes pour ce type d'applications.

Les LCs sont des matériaux intermédiaires entre un liquide et un solide cristallin. Les interactions non-covalentes faibles entre les molécules de forme ovale permettent à la fois d'organiser un film de LCs et d'avoir des propriétés anisotropes. Une des méthodes les plus innovantes exploitées ces dernières années comporte l'utilisation de la lumière. Les couches photosensibles peuvent diriger l'alignement du LCs par des interactions non-covalentes faibles. L'anisotropie est dans ce cas obtenue par l'utilisation de lumière polarisée linéairement. La molécule utilisée de préférence pour cette technique est l'azobenzene.

Les GFPMs ont un avantage sur les autres matériaux détaillés précédemment, car leur croissance est orientée dans une direction à cause des liaisons faibles, ce qui permet de former une fibre. En revanche, les réseaux de fibres formés sont macroscopiquement isotropes. Cependant, un stimulus externe peut guider la croissance vers une direction commune et ainsi permettre une certaine anisotropie. Une multitude de stimuli externes a été utilisée comme des champs électriques ou magnétiques, des gradients chimiques ou des films de Langmuir-Blodgett. Dans ce travail, nous utilisons un faisceau laser focalisé.

Une extrapolation directe des conditions utilisées pour la gélification photo-induite en volume n'était pas satisfaisante. Malgré le fait que le laser permettre un contrôle spatial, les fibres formées ne sont pas stables (elles se dissolvent dans le noir) et leur formation n'est ni reproductible ni contrôlée. Le DMSO est un solvant hygroscopique et le dkDDOA, une molécule sensible à l'humidité. Il est apparu lors d'essais préliminaires que la quantité d'eau présente est potentiellement un paramètre crucial pour contrôler la photo-nucléation et la croissance des fibres de DDOA.

L'addition contrôlée d'eau a plusieurs effets sur le photo-patterning. Une augmentation graduelle d'eau en petites quantités (de 0 jusqu'à 10 %vol) cause une augmentation de la densité de noyaux et donne des fibres de plus en plus courtes. Une augmentation jusqu'à 50 %vol crée des nanoparticules de DDOA.

De plus, il y a un effet détectable sur les temps de nucléation : une quantité plus importante en eau réduit le temps pour provoquer la nucléation. La relation entre le volume d'eau et le temps de nucléation est une exponentielle décroissante (Figure IV). Un autre résultat très typique est la diminution de la barre d'erreur. Le temps nécessaire à la nucléation est plus contrôlable avec 3 %vol d'eau que sans.



Figure IV: Les temps moyens de la nucléation de DDOA en fonction de la quantité d'eau avec une concentration de 2 mM de dkDDOA. L'irradiation est une diode laser à 473 nm (2.2 W.cm⁻²). Le volume total de l'échantillon est de 100 μ L.

Une corrélation entre la nucléation de DDOA et la pré-agrégation du précurseur dkDDOA peut être envisagée. En effet, l'augmentation de la concentration de dkDDOA dans le DMSO à volume d'eau constant (5 %vol) induit la formation d'agrégats de dkDDOA (concentration de 4 mM ou plus). Nous pouvons donc en déduire que l'agrégation du dkDDOA joue un rôle important dans l'augmentation de la densité de sites de nucléation du DDOA. En effet, elle doit permettre une concentration locale élevée de DDOA pendant la

photoconversion, ce qui favorise la nucléation. En plus, le DDOA et très peu soluble dans l'eau. Par conséquent, l'addition d'eau dans le DMSO diminue la solubilité du DDOA, ce qui favorise l'agrégation. La pré-agrégation et une diminution de la solubilité du DDOA aident à densifier la quantité de points de nucléation sur le substrat lors d'une irradiation sur du verre. Ce paramètre est également important pour favoriser l'alignement de fibres.

Comme dans le cas du photo-patterning de polymères covalents ou la cristallisation sur surfaces, l'affinité des molécules photo-converties avec le substrat joue également un rôle important dans la couverture de la surface. En conséquent, nous avons testé trois substrats avec une hydrophobicité/hydrophilicité différente. Les résultats montrent que la densité de nucléation augmente avec l'hydrophobicité et a un effet sur la croissance. En effet, avec un substrat hydrophobe, les fibres sont plus denses et alignées.

L'optimisation des paramètres a conduit aux choix d'une excitation à deux photons (770 nm), d'un substrat hydrophobe et de l'addition de 5 %vol d'eau afin de contrôler la nucléation spatialement et de diriger la croissance des fibres. Ainsi, des motifs anisotropes de fibres alignées ont été réalisés avec du DDOA résultant en une émission polarisée linéairement. Un des résultats les plus originaux consiste en la possibilité de pouvoir choisir la direction de croissance des fibres simplement avec la direction de balayage du laser. Ainsi, sur une même surface isotrope il est possible d'alterner des micro-surfaces ayant des orientations de croissances différentes, donc par exemple des polarisations d'émission perpendiculaires. (Figure V).



Figure V: (a) Histogramme de polarisation (b) Motifs correspondants (16 x 20 μ m) formées dans la direction YX (carrés bleus) et XY (carrés rouges). L'échelle est de 10 μ m.

Chapitre 4 Stratégie de synthèse pour les *n*-acenes autoassemblables

Les *n*-acènes, un nom générique pour une classe de molécule constituée d'une série linéaire de cycles de benzène polycondensés, sont des molécules très prisées dans différent domaines de recherche, à cause de leurs propriétés exceptionnelles comme la fluorescence, la mobilité de charge et la photochimie. La variabilité des structures des *n*-acènes est très élevée, ce qui permet de concevoir ou adapter certains acènes pour avoir la combinaison de propriétés souhaitées. La stratégie synthétique adoptée dans cette thèse a permis de synthétiser une gamme d'acènes auto-assemblables avec les propriétés photo-physiques d'absorption et de fluorescence requises. La stratégie consiste en trois étapes principales (Figure VI):

- 1. Synthèse de la 2,3-dimethoxyquinone
- 2. Déprotection/alkylation pour introduire les chaines alcoxydes
- 3. Réduction ou réaction de Grignard sur la quinone pour obtenir l'acène fluorescent



Figure VI: Schéma de la rétrosynthèse des 2,3-alcoxyde acènes auto-assemblables

La première étape donne un précurseur stable (qu'il est possible d'obtenir par grammes) et forme la base pour les deux autres étapes. C'est l'addition des chaines alcoxydes qui permet l'auto-assemblage de ces acènes en fibres ou rubans. La dernière étape détermine les propriétés photo-physiques finales. Une extension dans la transition S_0 - S_1 donne la possibilité d'ajuster les propriétés photo-physiques. (voir Figure VII)



Figure VII: Les moments de transitions dans l'anthracène et l'effet d'extension de la transition S_0 - S_1 sur l'absorbance et la fluorescence sur une série des tetracènes.

Cette stratégie a permis de synthétiser une nouvelle gamme d'anthracènes et de tétracènes auto-assemblables.

Chapitre 5 réticulation photochimique des fibres supramoléculaires

Ce chapitre relève d'un travail en collaboration avec l'Université de Technologie de Delft aux Pays-Bas. Le but est de contrôler et renforcer les propriétés mécaniques d'un hydrogélifiant basé sur le 1,3,5-cyclohexanetrisamide (OG2) (Figure VIII) par la réticulation photo-initialisée. Les propriétés mécaniques des gels de GFPM sont souvent faibles, en particulier la résistance aux contraintes.



Figure VIII: La structure moléculaire de l'OG2.

D'abord, une nouvelle méthode a été testée pour mieux contrôler l'auto-assemblage de l'OG2 avant la photo-réticulation. Le contrôle d'auto-assemblage est important pour avoir un système et des résultats comparables. La cinétique de gélification a une influence sur les propriétés finales.

OG2 est soluble dans une solution acide grâce à la 6-aminoquinoline. L'introduction des imines conjuguées qui libère l'amine trishydroxyméthylaminométhane (TRIS) dans des conditions acides (hydrolysation qui donne une amine et un aldéhyde) permet de neutraliser la solution et initie la nucléation et la croissance des fibres de façon contrôlée. Différentes imines donnent différentes cinétiques, mais des gels supramoléculaires avec des propriétés mécaniques comparables. Malheureusement, ces imines ne sont pas compatibles avec le photo-amorceur utilisé pour la photo-réticulation.

Les réactions utilisées pour la photo-réticulation sont le thiol-ene et thiol-yne. Ces réactions orthogonales forment des liaisons covalentes entre un alcène (thiol-ene) ou un alcyne (thiol-yne) et des thiols polyvalents. Le photo-amorceur est le lithium phenyl-2,4,6trimethylbenzoylphosphinate, ou LAP. Le LAP crée des radicaux sous irradiation UV et réagit avec des thiols pour créer des thiyl radicaux qui peuvent faire des liaisons covalentes avec un alcène ou un alcyne. Le LAP absorbe très peu, comparé à toutes les imines conjuguées, à cause d'un effet de filtre interne. Par conséquent, l'imine est substituée pour une neutralisation directe avec du NaOH, afin de prouver que la réticulation fonctionne.

Le gélifiant OG2 est mélangé avec 1 à 5 %mol d'un dérivatif fonctionnalisé (Figure IX) avec un alcène ou alcyne pour avoir des sites réactifs pour la future modification avec des réticulateurs polyvalents de thiol.



OG2-norbornene

OG2-alkyne

Figure IX: Les structures moléculaires des dérivées de OG2 pour la photo-réticulation avec des thiols polyvalents.

Les résultats rhéologiques ont montré que 1 %mol du dérivé d'alcyne mélangé avec OG2 était suffisant pour observer une réticulation. Le module de conservation augmente pendant l'irradiation. Malheureusement, la neutralisation directe du NaOH ne permet pas des comparaisons quantitatives, car nous n'obtenons jamais les mêmes modules de conservation.

En ce moment, les optimalisations de ce système sont encore en cours, car ce système peut permettre de mieux étudier l'effet de la réticulation sur la morphologie des gels par la microscopie (à super-résolution). Ce domaine est, pour l'instant, peu étudié, mais est très important pour avoir des gels avec les propriétés mécaniques souhaitées.

Conclusion générale

Nous avons prouvé que la photoconversion du dkDDOA en DDOA est quantitative sous irradiation à 450 nm et permet de gélifier le DMSO à des concentrations aussi basses que 1 mM. Il n'y a pas de formation de produits autres que le monoxyde de carbone. Une étude plus approfondie sur l'impact que le dkDDOA a sur la gélification photo-induite de DDOA montre que les fibres présentent au final un taux légèrement supérieur de défauts structuraux dus à l'inclusion de dkDDOA. Cependant, la différence entre les deux reste anecdotique et nous pouvons valider cette technique comme une alternative a la technique de refroidissement d'une solution de gélifiant.

Le principe de photogélification a pu être étendu afin de contrôler spatialement l'auto-assemblage des molécules en nanostructures. La maîtrise de la nucléation et la croissance dépend de certains paramètres critiques. Ainsi, l'addition de seulement 5 %vol d'eau dans la solution du dkDDOA dans le DMSO et l'utilisation d'un substrat hydrophobe permettent de réaliser des motifs anisotropes sur le substrat. En effet, l'eau induit la diminution de la solubilité du DDOA et la pré-agrégation du dkDDOA, ce qui favorise la supersaturation locale sur le substrat et l'augmentation de la densité de sites de nucléation. Etonnamment, l'addition d'eau favorise le photo-patterning mais n'induit pas l'hydrolysation du précurseur dicétone.

Dans la deuxième partie de cette thèse nous avons montré que la stratégie de synthèse adoptée permet d'obtenir une large gamme de *n*-acenes auto-assemblables. La stratégie permet de changer la longueur du conjugaison sur les transitions S_0 - S_1 et S_0 - S_2 pour avoir les propriétés photophysiques souhaitées.

Enfin, l'utilisation de réaction 'thiol-ene' ou 'thiol-yne' pour la photo-réticulation a prouvé être une méthode valide pour contrôler les propriétés mécaniques d'un GFPM. Malgré tout, la méthode pour contrôler l'auto-assemblage et celles pour contrôler la réticulation sont incompatibles. Il semble donc nécessaire de poursuivre les optimisations.

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List of abbreviations

А	Acceptor
AFM	Atomic force microscope
AIEE	Aggregation-induced enhanced emission
ATP	Adenosine triphosphate
cgc	Critical gel concentration
CLSM	Confocal laser scanning microscope
CMOS	Complementary metal oxide semi-conductor
CT	Charge transfer
D	Donor
DCM	Dichloromethane
DDOA	2,3-didecyloxyanthracene
DDOT	2,3-alkoxytetracene
dkDDOA	Alpha-diketone 2,3-didecyloxyanthracene
DIPEA	N,N-Diisopropylethylamine
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DPC	Droplet pinned crystallization
DTNB	5,5'-dithiobis-(2-nitrobenzoic acid)
EDTA	Ethylenediaminetetraacetic acid
ESI	Electrospray ion source
EtOAc	Ethyl acetate
FLIM	Fluorescence lifetime imaging microscopy
Fmoc	Fluorenylmethoxycarbonyl
GdL	Glucono-δ-lactone
НОМО	Highest occupied molecular orbital
HRMS	High resolution mass spectroscopy
IC	Internal conversion
ICT	Internal charge transfer
I_F	Fluorescence intensity
\mathbf{I}_{t}	Transmitted spectral radiant power
ITT	Inverted tube test
ISC	Intersystem crossing
LAP	$\label{eq:linear} {\it Lithium\ phenyl-2,4,6-trimethyl benzoyl phosphinate}$
LC	Liquid crystal
LED	Light emitting diode
LMWG	Low molecular weight gelator
LUMO	Lowest unoccupied molecular orbital
MS	Mass spectroscopy
n	Refractive index

NIR	Near infrared	
NMR	Nuclear magnetic resonance	
OTS	Octadecyltriethyloxysilane	
Р	Polarization	
pH	Hydrogen potential	
PhLi	Phenyllithium	
pKa	Acid dissociation constant	
PTS	Phenyltrichlorosilane	
Py-CN-TFMBE	2-(3′,5′)-bis(trifluoromethyl) biphenyl-4-yl)-3-(6-(3,5 bis(trifluoromethyl)	
	phenyl) pyridin-3-yl) acrylonitrile	
SAM	Self-assembled monolayer	
SAXS	Small angle X-ray scattering	
S_0	Singlet ground state	
S_1	Singlet excited state	
TEM	Transmission electron microscopy	
TFAA	Trifluoroacetic anhydride	
$\mathrm{T}_{\mathrm{gel}}$	Temperature of gelation	
THF	Tetrahydrofuran	
TIPS-pentacene	6,13-bis(isopropylsilylethynyl)pentacene	
TLC	Thin layer chromatography	
$\mathrm{T}_{\mathrm{melt}}$	Melting temperature	
TRIS	Tris(hydroxymethyl)aminomethane	
T_1	Triplet excited state	
UV-vis	Ultraviolet-visible	
WCA	Water contact angle	
ΔG	Gibbs free energy	
ε	Molar extinction coefficient	
κ^2	Orientation factor	
λ	Wavelength	
τ	Fluorescence lifetime	
$\Phi_{ m F}$	Quantum yield of fluorescence	
$\Phi_{ m R}$	Quantum yield of the photoreaction	

1

Introduction

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In this thesis molecular self-assembly and photochemistry were combined to obtain full control over the organization in space of a fluorescent molecular gelator by using light as an external control. Therefore, this Chapter will introduce the state of the art research in the field of low molecular weight gelators and the basics of photochemistry. In the end, the outline of the thesis will be given.

1.1. Self-assembly

Self-assembly refers to the *spontaneous* organization of individual components into ordered patterns or structures.^[1] In other words, the structures are formed through *thermodynamic equilibrium*, but can also relax into a *metastable state*. No addition of energy is necessary to maintain the structure over time. It is also possible to induce organization to pre-existing components while dissipating energy, i.e. the organization is governed over time by a "fuel" that can be either chemical (e.g. adenosine triphosphate, ATP) or physical (e.g. magnetic fields^[2] or light^[3]) and the structure will decay upon removal of the energy source. This type of self-assembly is defined as out-of-equilibrium or dynamic self-assembly by most chemists, but has been suggested to be described as *self-organization*. The term self-assembly is reserved for autonomous processes leading towards thermodynamic equilibrium.^[4]

Self-assembly can be found in different length scales ranging from the formation of the double helix in DNA^[5], the organization of millimetre sized objects by electrostatic forces^[6] to the ring formation around the planet Saturn.^[7] (Figure 1.1).



Figure 1.1^[5,6]: (a) Self-assembly in different length scales: Double helix of DNA and its base pair interactions, (b) electrostatic self-assembly of Nylon 6,6 and Teflon spheres and (c) the rings around the planet Saturn (Figures are a reprint of ref 5, 6 and www.nasa.gov).

In this thesis, the focus will be on *molecular self-assembly* which describes the autonomous organization of molecules. The attractive forces driving self-assembly are weak non-covalent

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interactions (see paragraph 1.2). The weak nature of these interactions introduces *reversibility* and *dynamics* to the formed structure providing inherent auto-correction due to the continuous exchange between monomers in solution and in the self-assembled structure.^[8] The reversibility in combination with the instinctive organization makes molecular self-assembly a very interesting approach for bottom-up design as exploited in block copolymer self-assembly^[9] or self-assembling monolayers (SAM)^[10].

Molecular self-assembly is a discipline within *supramolecular chemistry* (*supra* coming from Latin meaning above or over). It is based on the pioneering work of Cram, Petersen and Jean-Marie Lehn (Nobel Prize in Chemistry in 1987), on the alkali metal binding spherands, crown ethers and cryptands, respectively (Figure 1.2). It has grown into many disciplines over the years, such as molecular encapsulation^[11–13], molecular machines^[14–16] (Nobel Prize 2016) and dynamic covalent chemistry^[17]. The aspect connecting all these different fields is the use of non-covalent interactions to form functional assemblies.



Figure 1.2: The three molecules which started the field of supramolecular chemistry.

1.2. Non-covalent interactions

An overview of non-covalent interactions which govern self-assembly is given in Table 1.1. Almost all of these interactions possess lower bond strengths than a covalent bond (~ 350 kJ.mol^{-1}) and are of electrostatic character. It is important to consider that it is the interplay of several non-covalent interactions which are responsible for the formation of self-assembled patterns or structures.

Interaction	Bond energy (kJ/mol)
Ion-ion	100-350
Ion-dipole	50-200
Dipole-dipole	5-50
Hydrogen bond	2-167
Ion - π	4-80
π-π	0-50
van der Waals	0.4-20

 ${\bf Table \ 1.1: \ Different \ non-covalent \ (electrostatic) \ interactions \ governing \ self-assembly ^{[18,19]} }$

The weak electrostatic interactions frequently exploited in molecular self-assembly are hydrogen bonding, π - π stacking and charge transfer interactions due to their directionality. Therefore, these interactions will be discussed in more detail.

1.2.1. Hydrogen bonding

The hydrogen bond describes the attraction between a hydrogen bound to a more electronegative atom (H-donor D) and an acceptor (A), typically an electronegative atom such as oxygen, nitrogen or fluorine. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which allows proximal interaction of dipoles or charges. Hydrogen bonds may be an intermolecular or intramolecular interaction. The bond length differs from 2.2 to 4.0 Å between the donor and acceptor (D-H ---A) with typical bond strength between 4-60 kJ/mol. To give some perceptive, the general distance of hydrogen bonds involved in the secondary structures of proteins are close to 3 Å and are considered a moderate interaction. The interesting feature of the hydrogen bond in self-assembly is its directionality which gives orientation to the self-assembled structure (bond angle ranges from 120-180°).^[20] Therefore, many self-assembling molecules made by synthetic chemists contain amide or urea moieties to exploit this directionality. A nice example is the anisotropic growth of the 1,3,5-benzene-trisamide (BTA) by Meijer and co-workers^[8] and the

cis, cis-1,3,5-cyclohexanetriscarboxamides by van Esch and co-workers^[21] where the accumulation of amide groups lead to 1D aggregates or nanofibers, see Figure 1.3.



Figure 1.3: Anisotropic aggregates/nanofibers through hydrogen bonding. (a) Crystal structure of a BTA^[22]. (b) Molecular structure of the BTA and cyclohexanetriscarboxamide. (c) Crystals structure of a cyclohexanetriscarboxamide^[23].

1.2.2. π - π interactions

 $\pi-\pi$ interactions are weak electrostatic interactions between (hetero)aromatic compounds. There are generally two types of π -interactions: face-to-face and edge-to-face (also called T-shape) and leads to the typical "herringbone" arrangement (Figure 1.4). In 1990, Hunter and Sanders^[24] proposed that these stacking geometries are due to the quadrupolar interactions between the aromatic compounds. A centred face-to-face geometry (directly on top of each other) results into repulsion by the partially negatively charged π -electron clouds in non-substituted or neutral conjugated molecules.



Figure 1.4: (a) Description of the quadrupole moment in benzene. In red are the π -clouds and in black is the σ -framework(a). (b) The face-to-face and (c) edge-to-face interaction due to the quadrupole moment.

An example of the importance of π - π stacking can be found in organic electronics. Here, the charge mobility is dependent on the stacking geometry and the proximity of the assembling molecules, as shown by Anthony *et al.*(Figure 1.5).^{[25][26]} The partial fluorination of 6,13-

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bis(isopropylsilylethynyl)pentacene (TIPS-pentacene) allows the slip-stacked molecules to come in closer proximity and enhances the charge mobility through the crystal.



Figure $1.5^{[26]}$: Fluorination of TIPS-pentacene increases the proximity between molecules and subsequently the hole mobility in the crystal structure. (Figure is a reprint from ref 25).

1.2.3. Charge transfer interactions

Charge transfer interactions are weak non-covalent interactions between electron-rich donor molecules (D) and electron-poor acceptor molecules (A). They consist of a partial electronic coupling between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. The partial electronic charge transfer has a stabilizing effect on the complex and creates a ground state with a certain degree of ionic character ($D^{\rho_+}A^{\rho_-}$). This can lead to new transition band, called the internal charge transfer band or ICT band, which can be observed in UV-vis or NIR spectroscopy. The degree of ionic character within the complex is dependent upon the ionization potential of the donor and the electron affinity of the acceptor (see Scheme 1.1).^[27] The interaction is stabilized more strongly by polar solvents.



Scheme 1.1: Energy levels of the donor and the acceptor with the ground state CT transition due to the electronic coupling between the HOMO of the donor and the LUMO of the acceptor. HOMO donor \approx HOMO CT and LUMO acceptor \approx LUMO CT.

Charge transfer interactions are mostly enhanced when the donor and acceptor consist of π conjugated molecules due to the planarity, favouring thereby close proximity of D and A.

Two different packing modes are known for 1:1 charge transfer complexes namely, segregated stacking $(\cdot \cdot DDD \cdot \cdot, \cdot \cdot AAA \cdot \cdot)$ and mixed stacking $(\cdot \cdot DAD \cdot \cdot, \cdot \cdot ADA \cdot \cdot)$. In segregated stacks the donor and acceptor form separated stacks and for mixed stacking there is an alternation between donor and acceptor.

A recent example are the charge transfer complexes based on the so-called lock-arm supramolecular ordering introduced by Stupp and Stoddart.^[28] Here, the CT interactions are supported by additional hydrogen bonding and solvophobic effects due to the inclusion of diethylene glycol chains resulting in large (centimeter sized) mixed-stack co-crystals (Figure 1.6).^[28]



Figure 1.6^[28]: (a) A CT complex based on the lock-arm supramolecular ordering principle. Molecular structure of diethylene glycol substituted pyromellitic diimide and 1,5-diaminonaphthalene. (b) The crystal structure showing the close proximity and mixed stack from the a-axis.

1.3. Self-assembling gelators

A gel is a viscoelastic solid, thus recoverable after deformation by a mechanical stress (up to a certain strain). The viscoelasticity is an important feature as gels are more easily defined by comparison with everyday products (jelly, hair-gel) than in precise terms due to large variety of materials and morphologies. A gel consists of two phases, a liquid phase (solvent) and a solid phase (gelator), where the solvent is immobilized by the three-dimensional interconnecting network of fibers formed by the gelator. The solvent is entrapped by capillary forces and surface tension. The gelator can form a fibrillar network, as in the present study, or worm-like micellar structures. The concentration of a very good gelator is around 0.5 ± 2 wt%, although often higher concentrations are needed.

Gels can be divided into two main classes: chemical and physical gels. In the first class, the three-dimensional network is formed though covalent bonds. As a result, robust and irreversible gels are formed. The materials of choice are cross-linkable polymers. In contrast, physical gels consist of smaller entities which are self-assembled and held together through multiple non-covalent interactions. These demonstrate the characteristics mentioned previously in Chapter 1.1, such as reversibility, dynamics and autonomous organization, in contrast to covalent bonded networks. Both organic solvents and water can be gelled, and

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are referred to as an organogel and hydrogel, respectively. A class of physical gels is based on the assembly of so-called low molecular weight gelators.

1.3.1. Low molecular weight gelators

Low molecular weight gelators (LMWG) are small organic molecules, having a molar mass typically of ≤ 1000 Da, and can form highly anisotropic 1D-like aggregates in solution through weak non-covalent interaction. At sufficiently high concentration, known as the critical gel concentration (cgc), the anisotropic aggregates evolve into a three-dimensional fibrous network interconnecting through branching or entanglements. Typically, a gel forms in a solvent in which the gelator is not soluble at room temperature. Therefore, the LMWG is dissolved by heating and cooled down to obtain a supersaturated solution. The supersaturation causes the immediate formation of fibers and ultimately the gel. In this specific case of performing a heat and cool cycle, the phenomenon is also called *supercooling*. Most supramolecular gelators from a gel by a nucleation-growth mechanism, consisting of a first nucleation step followed by a cooperative assembly^{[29][30]}. The nucleation is the ratedetermining step in the process, because it is an unfavourable event. Explained in thermodynamic terms, the entropic cost (gain in order due to aggregation) is not compensated by an enthalpic gain ($\Delta G > 0$). Therefore, nucleation is characterized as a stochastic process. In contrast, the growth step is "templated" by the formed nuclei and leads to spontaneous polymerization ($\Delta G < 0$). The nucleation-growth mechanism is characterized by two specific features, the temperature of gelation $(T_{\rm gel})$ and the cooperativity parameter ($\sigma = K_n/K_e$). T_{gel} is the temperature where the nuclei are generated and the growth step is initiated. The cooperativity parameter, σ is the ratio between the equilibrium constant of nucleation (K_n) and the equilibrium constant of growth (K_e) and $\sigma > 1$ for a cooperative process (Figure 1.7)



Figure 1.7: Mechanism of gelation. Upon supersaturation/supercooling monomers aggregate into nuclei which initiate the growth of fibrils which can align parallel to from thicker anisotropic fibers. The fibers will entangle and form a 3D-interconnecting network when the concentration is sufficient.

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The structural variety in LMWGs is diverse. However, most were found by serendipity. There is still a lack of a universal understanding of structure-activity relationships that underpin the 1D self-assembly, enabling the straightforward design of novel LMWGs. Small differences in the structure or chirality can already be the difference between a gelator and a 'non-gelator'.^[31] This is due to the delicate balance of interactions in the self-assembly process and the many factors which can affect the aggregation (temperature, concentration, inter- and intermolecular interactions, polarity). The understanding of the gelator-solvent interactions is also of importance. All gelators immobilize only a certain range of solvents and almost never both organic solvents and water, except in rare cases.^[32] Nevertheless, the serendipitous findings have provided rough guidelines in the development of new gelators: (i) the presence of strong self-complementary and unidirectional intermolecular interactions to enforce 1D self-assembly, (ii) control of fiber-solvent interfacial energy to control solubility and to prevent crystallization, and (iii) some factor to induce fiber cross-linking for network formation.^[33] Furthermore, from the variety of LMWGs several functional groups have been characterized as efficient self-assembling synthons. Some are shown in Figure 1.8.



Figure 1.8: Functional groups frequently used in the design of LMWGs. (a) Amides, (b) urea, (c) peptides, (d) 3,4,5-trialkoxybenzamide and (e) cholesterol.

More recently, other more theoretical approaches have made their appearance to better rationalize and predict gelling abilities. A example are the Hansen solubility parameters.^[34] This technique does not predict new gelators, but rationalizes the possible solvents in which the existing gelator will self-assemble by comparing the dispersive, polar and hydrogen bonding interactions of the solvent and molecular gelator. Other methods are the interpretation of crystal structures based on strong directional interactions^[35], screening of combinatorial (dynamic) libraries^{[36][37]} and computational approaches^[38]. Frederix et al.^[39] have given a beautiful example of successfully using molecular dynamics simulations. They predicted new self-assembling tripeptides screening 8000 tripeptides (20³ combinations) through a computational technique. The liable tripeptides proved to be functional in practice.

The research on supramolecular gels is currently evolving towards this direction. The serendipitous findings of new gelators is losing interest and research is more focused on providing a broader perspective and a more fundamental view on what makes a small molecule a LMWG. In addition, the limits of the existing gelators are investigated. The significant advantage of LMWGs over polymer gels is the easy modification of the gelator through standard laboratory and purification techniques. This allows easy fine-tuning of its properties^[40] or insert chemical moieties to control the molecular gelation by an external trigger to gain more functional materials. Smarter materials can provide spatial control, tuneable reversibility, catalysis or multicomponent assemblies.

In brief, studying the rational design of LMWG and incorporating functionality and adaptivity are the new challenges.

1.3.2. Towards functional molecular gelators

As mentioned in the previous paragraph, a large part of the research on molecular gelators is dedicated to develop more functional materials. The introduction of chemical moieties by synthetic modification of the parent gelator can allow new ways to better control the gelation through external stimuli other than temperature. More controlled gelation methods also provide ways to investigate more fundamental aspects of molecular gelation. External stimuli can be divided into two different classes: chemical (pH, enzymes or redox chemistry) or physical (light) stimuli. Here, the chemical stimuli will be discussed, whereas a separate paragraph will consider light as a physical stimulus.

1.3.2.1. pH-responsive gelators

The simplest and frequently used trigger is acid-base chemistry. The introduction of base or acid sensitive groups to the gelator allows to control the self-assembly through pH changes. Functional groups are carboxylic acids or pyridine. In the case of carboxylic acids, the gelator is soluble in water at basic pH (11-14) due to the deprotonation forming the carboxylate. The high pH of 11-14 ensures a complete deprotonation of all carboxylic acids regardless of their actual pKa values. Acidification to neutral or acidic conditions will make the LMWG aggregate and subsequently induce the formation of a gel. Examples are shown in Figure 1.9.



Figure 1.9: Examples of pH sensitive gelators: (a) Fmoc-dipeptide^[41], (b) benzaldehyde protected sorbitol^[42], (c) triscyclohexyl-phenylalanine-glycine^[23], (d) isophthalic acid derivative^[43].
The physical properties of the gel can be very sensitive to the rate of variation of the pH. If the acidic or basic stimulus is added too fast, precipitates can form instead of fibers and the gel properties have a poor reproducibility. In 2009, Adams *et al.* introduced a solution to this problem by using glucono- δ -lactone (GdL).^[41] In the presence of water the lactone slowly hydrolyses to give gluconic acid, which gradually lowers the pH (Scheme 1.2). This method was used for controlled lowering of the pH over time instead of direct quenching with HCl and induces gel formation. As a consequence, quantitative studies could be performed to study the mechanism of gelation.



Scheme 1.2: Hydrolysis of glucono- δ -lactone in the presence of water.

In Chapter 5 of this thesis a similar mechanism will be discussed where a series of hydrolysable imines increase the pH over time. Here, the rate of hydrolysis also has a clear impact on the mechanical properties and their reproducibility. This method is ideal for molecular gelators with basic ionisable groups, such as pyridine or quinoline substituted gelators as shown in Figure 1.10. These gelators are soluble in acidic environment due to protonation and gel at neutral pH.



Figure 1.10: Molecular gelators with basic ionisable groups: (a) pyridine appended value gelator^[44], (b) cyclohexanetriscarboxamide with 6-amino-quinoline^[45] and (c) 2-(3',5')-bis(trifluoromethyl) biphenyl-4-yl)-3-(6-(3,5-bis(trifluoromethyl)phenyl)pyridin-3-yl)acrylonitrile (Py-CN-TFMBE^[46].

The Py-CN-TFMBE reported by Park *et al.* is a very interesting pH responsive molecular gelator for two reasons. It is an organogel whereas most pH sensitive gelators form hydrogels. In addition, it does not only undergo a sol-gel transition upon pH change, but also an increase in fluorescence intensity due to aggregation-induced enhanced emission (AIEE)^[47]. Due to the pyridine unit the highly fluorescent gel becomes a non-fluorescent solution upon addition of a photoacid and irradiation and can be regenerated by adding a base (Figure 1.11).^[46]



Figure 1.11^[46]: (a) Reversible fluorescence enhancement by controlling the sol-gel transition with a pH sensitive low molecular weight gelator. (b) Fluorescence spectra showing the enhancement in the emission in the gel state. (Figure is reproduced from ref 45).

1.3.2.2. Anion and cation-binding

Another approach to influence the gel formation is by binding ions, either anions or cations. Anion-binding gels mainly contain urea groups(s) as binding motif. These type of responsive gels have been studied in detail by Steed and co-workers^[48]. The added anions interact with the urea moiety and break the hydrogen bond interactions thereby disrupting the gel. Extracting the anion from the gel and heating or sonicating the solution reinitiates the gelation (Scheme 1.3).^[49] The same group showed that anion-binding gels are suitable for selective polymorph crystallization of several drugs, such as carbamazepine by performing the crystallization in the gel phase. Afterwards, the crystals are easily obtained by the addition of acetate anions. These interrupt the gel structure and leave a homogeneous solution without co-crystallization of the drug with the anion.^[50] Another anion-binding moiety used is pyrrole^[51].



Scheme 1.3: Principle of anion binding gelators. The addition of an anion can disassemble the gel through anion binding. The anion can be removed to reinitiate the gel formation under heating or sonication.

Next to anion-binding gelators, cations can also stabilise or disassemble the fragile selfassembled gel fibers by complexation. One of the oldest examples is calcium alginate, which is a polymeric gel where the Ca^{2+} ions form the crosslinks between the polymeric fibers creating an interconnecting network. Another type of supramolecular cation-binding gel is the oligothiophene organogelator reported by Shinkai *et al.* with crown ethers (18-crown-6) substituted on the periphery^[52] (Figure 1.12). The addition of alkali metals K⁺ and Cs⁺ disrupted the fiber formation when more than 1 eq of the alkali metal was added. This allows controlling the sol-gel transition by the addition of alkali metals.^[52]



Figure 1.12: Oligothiophene gelator with crown ethers^[52].

A water based cation-binding gelator is the guanosine G-quartet. The association with K⁺ or Na⁺ stabilizes the macrocyle formation of the nucleosides to form transient gels. However, more stable gels can be obtained by mixing the guanosine with the monophosphate derivative^[53] or acetyl derivative^[54] of the ribose. In both examples the guanosine ribose derivative is thought to inhibit the driving force towards crystallization of the guanosine. The only difference is that the monophosphate is more soluble than guanosine, whereas the acetylated version has a lower solubility than guanosine. A more recent example showed excellent stable gels by adding a boron salt which induces the formation of anionic tetravalent borate esters^[55]. The formation of the diesters is said to increase the solubility of the guanosine thereby aiding the gelation.



Figure 1.13: Basic G-quartet structure complex with K^+ and the different discussed riboses attached to the basic skeleton governing the solubility and stability of the hydrogel.

Controlled reversibility with the G-quartet was shown by Ghoussoub *et al.* The gelation of a G-quartet derivative was switched by incorporating a 2,2,2-cryptand which has a strong binding affinity to K^+ , even in neutral and basic conditions. Acidifying the solution, however, protonates the bridgehead amines and the K^+ is released and reinitiates the gelation. Sequential acidification and neutralization allowed controlled reversibility, which could be followed by the naked eye.^[56]

The diversity in ion binding hydrogelators is smaller than the pH dependent gelators due to the competitive interactions with H₂O. Indeed, for the G-quartet hydrogels the concentration is generally > 50 mM and concentrated solutions of KCl (100- 500 mM) are used to overcome the competition with water.^[55]

1.3.2.3. Redox-responsive gelators

The addition of redox active groups can give control over the gelation by a change in oxidation state which can influence the solubility of the gelator or the chemical structure. Frequently used redox moieties are ferrocene, perylene diimide or tetrathiafulvalene (TFF) (Figure 1.14). Several gelators of ferrocene and perylene diimide were realized by attaching it to one of the described self-assembling synthons shown in Figure 1.8. Reversibility for the ferrocene was achieved by oxidation with $(NH_4)_2Ce(NO_3)_6$ which disrupts the gel. A reduction with hydrazine hydrate gives a precipitate which can be reformed into the gel by additional heating or sonication.^[57-59] Perylene diimide gels can be reduced with Na₂S₂O₄ to the radical anion or dianion and oxidizes back in ambient air.^[60] TFF also performed a gel-sol transition when oxidized chemically, which is thought to be due to the induced repulsion between the created radical cations.^[61]



Figure 1.14: Molecular structure of (a) ferrocene, (b) perylene diimide and (c) tetrathiafulvalene.

1.3.2.4. Enzyme-responsive gelators

Another class of chemical stimulus are enzymes. Enzymes are a very useful trigger, because of the catalytic activity and selectivity towards a certain substrate. The use of enzymes can also be extrapolated to actual relevant applications due to the abundance of enzymes used in the human biochemical pathways. This research could result in applications in nanomedicine or biomaterials.

The adopted strategies are the activation of a pro-gelator forming the fibrous interconnecting network upon cleavage or the disassembly of the gel phase to deliver a certain drug attached or embedded into the gel(ator). Xu and co-workers are major contributors to the development of this field and reported several examples over the years on the use of enzymatic active pro-gelators for *in vivo* experiments, as diagnostic test for the screening of inhibitors^[62] or on the use of enzymatically triggered gelators as therapeutic agents.^[63]

1.3.2.5. Kinetic control over the self-assembly with chemical stimuli

The above-mentioned chemical triggers are elegant examples on how to control the sol-gel transition without (in most cases) having to perform a heat-cool cycle. However, they only describe going from state A to B, as a sort of on-off switch. Introducing kinetic control would allow to govern the rate of assembly giving rise to non-equilibrium states which can alter the mechanical properties of the gels.

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van Esch *et al.* recently introduced a new gelator based on hydrazone functional moieties. This is a good hydrogen bonding moiety and its formation is pH dependent, introducing possible kinetic control.^[64] Influencing the rate of assembly by aniline or acid catalysis (pH = 5) gave completely different morphologies and mechanical properties compared to the non-catalysed formation of the hydrazone gel. The catalysed gels formed faster and had more interconnecting fibers and therefore higher mechanical strength. It was proposed that the faster formation creates more defects in the fibers resulting in more branching.

Hirst *et al.* obtained kinetic control over the self-assembly through enzyme catalysed demethylation of a Fmoc dipeptide (Fmoc = fluornylmethoxycarbonyl). The demethylation is dependent on the available amount of catalytic sites and therefore the enzyme concentration can change the kinetics.^[65] At constant gelator concentration, but a gradual increase in enzyme (active catalytic sites) led to an increase in T_{gel} and a pronounced enhancement in fiber-bundling and length affected the mobility of the active sites in solution. This shows that catalytic control through pH or enzymes broadens the control over the gel formation.



Figure 1.15: Kinetic control over supramolecular gelation. (a) Increase in subtilisin (enzyme) increases fiber bundles of a Fmoc-dipeptide.^[65]. (b) Decrease in pH from 7 to 5 increases fiber branching and mechanical properties of a hydrazone hydrogelator.^[64]

The same kinetic control can be achieved by using light as the external trigger. Furthermore, the latter allows spatial structuring of the gel. This paves the way for the development of more sophisticated applications such as tissue engineering or complex photonics, requiring precise spatial control of nanostructures. In the next paragraph the basics of photochemistry will be explained before discussing light-responsive gels.

1.4. Introduction on photochemistry

Photochemistry studies the interaction of matter and light, more precisely, the chemical transformation of molecules in the excited state after the absorption of photons. This is the first law in photochemistry, the Grotthuss-Draper Law. The second law of photochemistry or Stark-Einstein law, states that each absorbed photon activates only one molecule for the subsequent reaction. The minimum energy generally needed to excite a certain organic molecule is around 150- 170 kJ.mol⁻¹ and corresponds to a wavelength in the red region of the visible spectrum at 700-800 nm. The maximum energy for an electronic transition in organic molecules lays around 590 kJ.mol⁻¹ and corresponds to a wavelength of 200 nm. Irradiation with wavelengths lower than 200 nm is energetic enough to induce bond dissociation. The broad range of photochemical reactions known today are mostly induced by UV- or blue-light excitation.

1.4.1. Absorption of light

In organic molecules, upon excitation, an electron is transferred from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) or a higher non-bonding molecular orbital. Upon electronic transition the spin of the initial electron pair is maintained and the exited state reached first is a singlet excited state. Through rapid vibrational relaxation or internal conversion, the lowest singlet excited is then reached. However, via spin-orbit coupling the less energetic triplet excited state can be populated. This process is also called intersystem crossing (ISC). The spin-orbit coupling can be induced by heavy atoms. Excitation from the singlet ground state (S_0) directly in the triplet excited state (T_1) is a spin forbidden transition (Pauli exclusion principle).



Figure 1.16: Excitation of an organic molecule depicted the S_1 and T_1 from the frontier orbitals.

Intermezzo

The unpaired electron of the T_1 excited state resembles the Single Occupied Molecular Orbital (SOMO) of radicals as shown below with the planar configuration of methyl radicals and the pyramidal arrangement of the CF₃-radical. Indeed, photochemical reaction from the T_1 state have a radical character, whereas the S_1 state mostly follows a more "classical" zwitterionic like chemistry.



The difference is best explained illustrating the photochemistry of alkenes. The irradiation of butadiene gives completely different photoproducts in the presence of a triplet sensitizer than without sensitizer. Considering the possible intermediates the radical character of the T_1 and the zwitterionic character of the S_1 can be rationalized.



The absorption of a photon occurs in a faster timescale than molecular vibrations. Therefore, the nucleus is considered to be stationary during the redistribution of the electrons and the vibrational level in the excited state compatible with the state it was excited from, according to the Franck-Condon principle^[66,67]. This makes some transitions more likely than others and is responsible for a difference in the band intensity in the absorption spectrum of an organic molecule.

The different molecular electronic transitions and their intensity can be measured by UV-VIS spectroscopy in solution and are defined as follow:

$$A(\lambda) = \log\left(\frac{I_0}{I_t}\right) = -\log T(\lambda) = \varepsilon(\lambda) * l * c$$
(1.1)

where I_0 is the incident spectral radiant power and I_t is the transmitted spectral radiant power. T is the internal transmittance of the sample at a given wavelength, ε is the molar extinction coefficient in M⁻¹ cm⁻¹, l is the optical path length in cm and c is the concentration in mol.L⁻¹. This is also called the Lambert-Beer law.

1.4.2. Relaxation processes after the absorption of a photon

After light absorption, the excited state formed can follow different relaxation processes. These processes are graphically represented in the Jablonski-Perrin diagram^[68] (Scheme 1.4).



Scheme 1.4: The Jablonski-Perrin diagram. Straight arrows represent an optical transition. Wavy arrows represent a non-radiative relaxation.

If the excited state after absorption is higher in energy than the S_1 state, $S_{2...n+}$, the molecule relaxes back to the singlet exited state by a vibrational relaxation (VR) and internal conversion (IC) according to Kasha's rule. IC occurs with kinetic constants of 10^{11} - 10^9 s⁻¹.

Fluorescence is a radiative process involving the emission of a photon of lower energy than that of the absorption. It occurs from the S_1 state with a kinetic constant, the radiative constant, of around 10⁷ to 10⁹ s⁻¹ and is independent from the excitation process. The difference in energy between the S_0 - S_1 (lowest vibration level, v = 0) transition and the S_1 - S_0 (v = 0) is called the Stokes shift. The Stokes shift corresponds to the loss in energy between the absorbed and emitted photon and can be measured by taking the difference in band maxima of the absorption and fluorescence spectra. The Stokes shift can be influenced by the molecular reorganisation occurring in the excited state, as well as the solvent polarity and its reorganisation.

If the triplet excited state (T_1) is close in energy to the S_1 state, the molecule can relax to the T_1 by intersystem crossing (ISC), as previously explained. The radiative process from the T_1 state is called phosphorescence and has a radiative constant 10^1 to 10^6 s⁻¹ because the transition is spin-forbidden and partially allowed in case of spin-orbit coupling. This process can be observed in favourable conditions, such as low temperatures. In addition, bimolecular processes can occur from an excited state, such as photoinduced electron transfer. This process will not be described since it is not relevant in this work.

1.4.3. Fluorescence lifetime and quantum yield

Electronic excited molecules are very unstable and will decay from the S_1 very rapidly through the above given radiative or radiationless processes. The rate constant for radiative deactivation (fluorescence) is given by k_F . The non-radiative relaxation is given by k_{IC} (internal conversion) and k_{ISC} (intersystem crossing) gathered into k_{nr} , a collective term for all non-radiative processes (from the S_1). When a diluted solution of molecules is excited by a short light pulse, a certain amount of molecules will be electronically excited (t = 0) and return to the ground state radiatively or non-radiatively. The corresponding kinetics of deexcitation are then expressed by the following differential equation:

$$-\frac{d[M^*]}{dt} = (k_F + k_{nr})[M^*]$$
(1.2)

where $[M^*]$ is the concentration of molecules in the S₁ excited state (mol.L⁻¹), k_F and k_{nr} are explained above.

The fluorescence intensity (I_F) measured at time (t) is proportional to the concentration of excited molecules ([M*]). The integration of equation (1.2) gives an exponential dependence of the fluorescence intensity decay, which is characterized by the lifetime (τ_s) of the excited state, the "average" duration of occupying the S_1 state before deexcitation. I_F , the fluorescence intensity in function of time is defined as:

$$I_F = k_F[M^*] = k_F[M^*]_0 * e^{-\frac{t}{\tau}} \quad \text{with} \quad \tau = \frac{1}{k_F + k_{nr}}$$
(1.3)

where $[M^*]_0$ is the initial concentration of molecules in the excited state in mol L⁻¹, τ is the lifetime of the excited state. The lifetime of the singlet excited state for organic molecules varies typically from picoseconds to tens of nanoseconds. The lifetime of a solution of a fluorophore is independent of the wavelength of excitation and emission if only one excited state is involved. Knowing the fluorescence quantum yield (Φ_F , see Experimental section) and the lifetime it is possible to determine the rate constants (k_F and k_{nr}) for molecules with a mono-exponential fluorescence decay.

$$\Phi_F = \frac{emitted \ photons \ per \ mol. \ s^{-1}}{absorbed \ photons \ per \ mol. \ s^{-1}} = \frac{k_F}{k_F + k_{nr}} = k_F * \tau \tag{1.4}$$

In photochemistry it is also important to know the quantum efficiency of the photochemical reactions. The quantum yield of the photoreaction, $\Phi_{\rm R}$, is defined as the ratio of mol.s⁻¹ of

product of reaction formed and mol.s⁻¹ of photons absorbed by the reactant. The method to determine Φ_R is discussed in the Experimental section.

1.5. Light-responsive gelators

Light, a traceless reagent, as external trigger can also induce a sol-gel or gel-sol transition. The photochemically induced transition is mostly associated with a conformational change of the photoreactive molecular gelator. This can be intermolecular or intramolecular and changes the delicate interplay of the non-covalent interactions.

Conformational changes by selective photocaging can mimic enzymatic pathways occurring in biological processes. Haines *et al.* reported the photocaging of a synthetic 20-residue peptide by protecting a cysteine with the negatively charged α -carboxyl-2-nitrobenzyl disrupting the self-assembly. The negative charge inhibits the hydrophobic interactions of the amphiphilic β -hairpin conformation which forms a hydrogel. Upon irradiation with a UV lamp (> 300 nm) the nitrobenzyl is cleaved off providing the peptide that folds into the gel conformation under basic conditions (Figure 1.17).^[69]



Figure 1.17^[69]: Photocontrol over the gelation of an amphiphilic peptide by the addition 2nitrobenzyl photo protecting group.

The photocaging method provides a selective and elegant way to induce conformational changes, but only under the circumstances that such a functionalization is applicable to the LMWG. Furthermore, the photocleavage approach always has secondary reaction products which can have undesired effects. In the case of 2-nitrobenzyl protecting groups, the by-products absorb strongly in the same region as the 2-nitrobenzyl itself leading to inner filter effects.^[70]

Intermolecular reactions, like (photochemically allowed) cycloadditions, are also frequently used to induce a transition or to crosslink the supramolecular fibers to obtain stronger gels (see Chapter 5). Generally, high concentrations are necessary for the reaction to occur due to rotational and translational freedom of the molecule in solution. In the gel state, however, molecules are in close proximity enabling the reaction. Cycloadditions are mostly used for

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gel-sol transitions due to the large conformational change which disrupts the delicate interplay of non-covalent interactions. Full photochemical reversibility is rare in the case of cycloadditions.^[71] Intramolecular rearrangements, however, can provide reversibility since the photoreaction will also work in diluted conditions. Most of these light responsive gelators work via an electrocyclic reaction or *trans-cis* isomerization and are based on the efficient and fatigue resistant photochromic units, like azobenzene^[72] (see also paragraph 3.1.2.), dithienylethenes^[73], spiropyrans^[74] or chromenes^[75] (see Figure 1.18). Photochromism is originally defined as a reversible transformation in one single chemical species between two forms having different absorption spectra, and in these reversible process, at least one pathway is induced by photoexcitation. These transformations, however, go together with a change in polarity and conformation able to induce the sol-gel/gel-sol transition.



Figure 1.18: Selection of common used photochromic molecules for photoresponsive molecular gelators. (a) Dithienylethene, (b) azobenzene and (c) spiropyran.

Gels based on spiropyrans and chromenes are of transient nature and revert back under ambient conditions. Dithienylethenes, on the other hand, are thermostable in closed and open form enabling a real photoswitch and logic gate.^[76]

Qiu *et al.* reported a spiropyran dipeptide hydrogelator of which the merocynanine (open form) produced a dark red gel by adjusting the pH to 3 after UV irradiation. It is the protonation of the phenolate that stabilises the open form inhibiting it from thermally reverting to the parent spiropyran.^[77] The gel was stable at room temperature when kept away from visible light. Irradiating the gel at > 400 nm disassembled the gel by forming a yellow precipitate (the protonated closed form) which could reform the gel after neutralizing the pH, irradiate with the UV and acidify it again. The readjustment of the pH was necessary to go back to the photoreactive spiropyran making the process not truly photoreversible. Replacing the light trigger with 1 equivalent of vancomycin, which binds specifically to the used dipeptide (D-alanine D-alanine) also induces a gel-sol transition.^[78]

In contrast to the previous case, Wezenberg *et al.* reported a fully photoreversible mechanism by synthesizing a series of an overcrowded alkene molecular switch with alkylurea of different chain lengths. The process can be switched on demand with a high

photostationary state of 85:15 for the conversion from the *trans*- to *cis*-conformation (disassembly) at 312 nm and the full recovery of the *trans*-configuration under 365 nm (gelation) in hydrocarbons as solvent. The fibrous network could, however, again only be regenerated by gentle heating of the *trans* configuration after photoisomerisation. In toluene or xylene a concentration was as low as 0.4 mg.mL^{-1} affords transparent gels with the hexyl derivative. The working mechanism is thought to be the blocking of intermolecular hydrogen bonding in the *cis*-state, but was not proven (see Figure 1.19).^[79]



Figure 1.19^[79]: Reversible photoisomerisation of an overcrowded alkene gelator and the predicted intramolecular blocking of the hydrogen bonding in the *cis*-conformation preventing gelation (Figure is a reprint from reference 71).

As mentioned in the beginning, light can provide spatial control and thereby the means to perform photopatterning in the gel state instead of a bulk transition. Nevertheless, studies on photopatterning of LMWGs reported so far are rare.

De Jong *et al.* reported the reversible patterning with a dithienylethene at room temperature through a diffraction grating. The open form of the dithienylethene is a solution at room temperature $(25^{\circ}C)$ whereas the closed form is a gel at the same temperature. A diffraction grating of 313 nm would give continuous lines of fibers whereas the subsequent irradiation with 500-600 nm would dissolve the pattern enabling dynamic spatially controlled self-assembly in a 1 mm quartz cuvette (Figure 1.20).^[80]



Figure 1.20: (a) Dithienylcyclopentene gelator patterned with 313 nm by a diffraction grating. (b) The subsequent erasing of the horizontal lines with 500-600 nm. (c) The boundary between irradiated and non-irradiated surface.

Draper *et al.* reported the first example to control the mechanical properties of a multicomponent LMWG. A photoisomerisable stilbene appended with the amino acid phenylalanine (capable of forming gels in the *trans* formation) was included with another dipeptide gelator. Through sequential gelation of the two gelators having different pKas, a self-sorted interpenetrating fiber network was formed. Photoisomerisation of the stilbene at 365 nm (photostationary state and quantum yield of reaction not given) resulted in the disassembly of the photoreactive gel while the dipeptide was unaffected. More interestingly, the spatial control provided by using a photomask, allowed to convert selective regions of the mixed gel into a single component gel thereby locally changing the mechanical properties of the gel (Figure 1.21).^[81]



Figure 1.21^[81]: (a) Spatial control over a multicomponent gel by pH and light. (b) Naphthalene dipeptide (valine-glycine) gelator and the photoresponsive phenylalanine stilbene conjugate. (Figure is a reprint from reference 80).

Van Esch and co-workers also reported the photopatterning of their hydrazone gel by using a spiropyran as photoacid (proton source) catalyzing the gelation process in the areas not masked by the photomask. In the irradiated areas ($400 < \lambda < 800$ nm) the pH drops to 5.4 making stronger gel patterns than in the non-irradiated areas (pH = 6.6). The size of the patterns achieved with this method was in the order of hundreds of micrometers (Figure 1.22a).^[82]

Furthermore, Hamachi and co-workers reported several studies on spatially controlling the gel-sol transition with a focused laser. In all cases the photopatterning was irreversible. Using the two-photon responsive 7-diethylaminocoumarin-4-yl-methoxycarbonyl as photocleavable moiety gave the possibility to pattern at physiological pH with a spatial resolution of 8 μ m in the Z-axis using a 740 nm, 2 W, 140 femtosecond pulsed laser. The created channels were used to control and guide the motion of immersed *E. Coli* bacteria (Figure 1.22c).^[83,84]



Figure 1.22: (a) Acid catalyzed photopatterning of the cyclohexane hydrazone gel using the photoresponsive spiropyran as photoacid/catalyst. Scale bar is 100 μ m^[82]. (b) Photocontrolled gel-sol transition with a focused 266 nm laser locally performing a *trans-cis* isomerisation. Scale bar is 100 μ m^[83]. (c) Photocontrolled gel-sol transition with a focused 740 nm (2 photon), femtosecond pulsed laser locally performing a photocleavage reaction. Scale bar is 20 μ m.^[84].

Anthracene-based low molecular weight gelators also have been characterized as potential molecular gelators by others by controlling the self-assembly with light as a trigger. As mentioned before, in this thesis we will also investigate the control of the self-assembly of an acene-based gelator with light. Therefore, the general characteristics of acenes and acenebased (functional) gelators will be discussed next.

Introduction

1.6. Self-assembling *n*-acenes

n-acenes is a collective name for the class of organic molecules which consist of linear fused benzene rings and are intensively investigated molecules due to their exceptional properties such as high fluorescence^[85], charge mobility^[26] and photochemistry^[86] in different areas of research. The absorption and emission of benzene, naphthalene, anthracene and tetracene are shown in Figure 1.23.



Figure 1.23: Basic structure of linear fused acenes and the corresponding absorption and emission spectra (spectra of benzene, naphthalene and anthracene spectra are a reprint of omlc.org).

The extension of the linear acene core reduces the band gap (HOMO-LUMO gap). The lowering in energy results in a bathochromic shift in absorption and fluorescence (Figure 1.23). Benzene and naphthalene emit in the far UV and are therefore colourless, whereas anthracene is a blue emitter ($\Phi_{\rm F} = 0.30^{[87]}$) and tetracene a green emitter ($\Phi_{\rm F} = 0.17^{[88]}$). Furthermore, *n*-acenes form crystals with efficient charge mobility as found for the larger acenes such as tetracene and pentacene. Therefore, it is clear that the extension of the acene core leads to interesting material properties. However, the increase in the number of benzene rings largely affects the photostability and solubility of the acene. Pentacene is almost insoluble in all standard organic solvents at room temperature and highly reactive towards singlet oxygen and self-dimerization (paragraph 1.6.1).

Nevertheless, by substituting the acene backbone with bulky or electron withdrawing groups the stability and solubility can be increased. Simultaneously, the addition of bulky groups (phenyl, phenylethylene derivatives) influence the emission properties. This is due to the absorption transition moments in acenes, which are in plane of the molecule. The S_0 - S_1 transition is along the short axis of the molecule and the S_0 - S_2 transition along the long axis (see Figure 1.24.)



Figure 1.24: Absorption transition moments in anthracene.

Extending the conjugation in the S_0 - S_1 transition will further decrease the energy band gap and involve a further bathochromic shift. Furthermore, the increase in conjugation along the short axis will also increase the radiative constant leading to more efficient fluorophores. The extension of the acene core and the substitution of the backbone make acenes a versatile class of molecules allowing custom synthesis (see Chapter 4).

1.6.1. Photo-oxidation

The photo-oxidation reaction can occur through two mechanisms where the acene functions as a photosensitizer. The two principle pathways are denoted a Type I and Type II photooxidation.

Type I photo-oxidation occurs via an electron transfer.^[89] The excited acene donates an electron to the triplet oxygen to form the acene radical cation and the oxygen radical anion, respectively. It is the recombination of the two species which creates the endoperoxide. This type of photo-oxidation can occur when the triplet energy of the sensitizer is too low for energy transfer to occur (Type II). The triplet energy of oxygen is 22,5 kcal.mol⁻¹ (see Scheme 1.5).

Type II photo-oxidation is a [4+2] cycloaddition, with singlet oxygen as the dienophile and the acene as the diene. The reactive singlet excited oxygen is formed by photosensitization of the ground state triplet oxygen initiated by the excited acene. Benzene and naphthalene are inert towards oxygen. On the other hand, for anthracene, tetracene and pentacene, the reaction rate constant increases about two orders of magnitude per fused ring (0.15×10^{-6}) 14×10⁻⁶ to 4200×10⁻⁶ M⁻¹.s⁻¹, respectively).^[90] The mechanism works as follows: the anthracene is excited to the singlet excited state (S_1) upon taking a photon and relaxes (radiationless) through intersystem crossing (ISC) to the spin forbidden triplet state (T_2) which is only 2 kcal.mol⁻¹ lower in energy. From here the anthracene relaxes further to the T_1 state and undergoes an energy transfer with the dioxygen. The dioxygen will be excited from the triplet ground state (T_0) to the singlet excited state (S_1) and subsequently the anthracene goes to the ground state (Figure 1.25). Afterwards the excited dioxygen can react with the ground state acene to form the endoperoxide (Scheme 1.5).^[91] The reaction rate of the last step is solvent dependent.^[92,93] Higher solvent polarity and solvent-solvent interactions increase the rate of photo-oxidation. The suggested reason is the stabilization of the proposed charge transfer complex between the ground state acene and singlet excited oxygen before cycloaddition.



Scheme 1.5: Energy diagram of the photosensitization of oxygen by anthracene and the resulting photoxygenation

The photooxygenation is irreversible for non-substituted acenes leading to the formation of quinones or decomposition products.^[94,95] Nevertheless, efficient reversibility has been reported for the 9,10-phenyl-anthracene at high temperatures $(80-130^{\circ}C)^{[95,96]}$ or more recently, Linker *at al* reported the possible reversibility of different 9,10-phenylethynyl substituted acenes at room temperature.^[89,97] This, however, required to perform the photooxygenation at -20°C.

1.6.2. Photodimerization

The photodimerization is a photochemical $[4_s+4_s]$ cycloaddition, *i.e.* the cycloaddition takes place from the excited state. More precisely, only the singlet excited state can yield the addition since it was shown that the addition of a triplet sensitizer or heavy atoms inhibits the photodimerization. The usual wavelengths to excite anthracene to form the photoadduct are at 366 nm or lower. The cycloreversion can take place by irradiating the adduct with wavelength of higher energy at 270 nm (a photostationary state is created) or by heating. It was shown that prior to the actual cyclization the two monomers of anthracene (when in close proximity) form an emissive or non-emissive excimer. This explains the dimerization only takes place from the singlet excited state. If the 9-position of the anthracene is substituted, two different dimers can be formed: the head to tail (ht) and head to head (hh)

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dimer (Figure 1.25). The ratio between the two compounds will depend on the substituent (steric hinderance, electrostatic interactions) and different lifetimes are observed for the two dimers.^[98]



Figure 1.25: [4+4] cycloaddition of 9-substituted anthracene giving rise to head to tail (ht) and head to head (hh) adducts.

1.6.3. Anthracene based gelators

The photodimerization of anthracene has been extensively used to develop photoreversible gelators, Wang *et al.* synthesized an anthracene substituted with a urea alkylchain on the 9-position which is capable to gelate 1,2-dichloroethane in monomeric form and cyclohexane, hexane and heptanes as photodimer. The configuration of the photodimer was highly selective, 100% ht dimer, and only formed in solution (22 mM in THF, see Figure 1.26). The anthracene monomer gel could be cycled by heating and cooling and showed a tenfold fluorescence increase in the gel state. Nevertheless, no sol-gel transition could be observed by ¹H-NMR while irradiating the anthracene gel nor the gel of the photodimer. Heating of the dimer did also not provide the anthracene showing the stability of the photodimer gel.^[99,100]



Figure 1.26: Selective photodimerization of urea 9-substituted anthracene gelator in THF.

Shinkai *et al.* were the first to report a disassembly of an anthracene gel by photodimerization. The binary organogel of anthracene-9-carboxyl and *n*-decylammonium efficiently gels cyclohexane at 0.5 mM and disassembles when irradiated at > 300 nm forming the photodimer. Heating the solution at 30°C reformed the anthracene giving a precipitate. For the regeneration, the cyclohexane gel needed to be heated till boiling point and cooled down. Nevertheless, it is the first example of a successful photodimerization in the gel state and complete regeneration.^[101]

Bouas Laurent and Desvergne reported a 2,3-dialkoxysubstituted anthracene with interesting self-assembling properties.^[102] The addition of alkyl chains of ten carbons on the 2,3-position of the anthracene, named 2,3-didecyloxyanthracene or DDOA gave the ability to efficiently gel a large number of solvents (alkanes, alcohols, amines, propylene carbonate and DMSO).^[103] Particularly, in alcohols and DMSO low concentrations of 1 mM are enough to entrap the solvent. Therefore, DDOA is called a supergelator. The gelling property was discovered by serendipity, during their research on the photodimerization of di-substituted anthracenes. In contrast to the previously described studies, DDOA does not photodimerize under the irradiation at 300 nm. Furthermore, DDOA is more reactive towards oxygen compared with the parent anthracene due to the higher electron density^[95] induced by the electron donating alkoxy chains. The inactivity towards photodimerization allowed to exploit the self-assembling and fluorescent properties of DDOA extensively, from the formation of composite materials with nanoparticles^[104,105] or other gelators^[106], aerogel formation in supercritical CO₂^[107] to the efficient energy transfer towards tetracene derivatives^{[108][109]}.

The synthesis has also been extended to larger acenes such as 2,3-alkoxytetracene^[110] (DDOT, n = 2) and 2,3-alkoxypentacene^[111] (n = 3), see Figure 1.27. The decyl and hexadecyl derivatives of tetracene form gels in long-chain alcohols, DMSO, alkanes and toluene, whereas the hexadecyl derivatives of pentacene gelates chloroform and dichloroethane.



Figure 1.27: Molecular structure of gelling 2,3-didecyloxyacenes.

The studies by Del Guerzo *et al.* on the fluorescence of DDOA nanofibers have exploited its self-assembly for the control of optical properties. The incorporation of just 1 mol% of the corresponding DDOT as acceptor (Figure 1.29) completely quenched the DDOA emission upon excitation of the anthracene at 405 nm and was sensitized to emit green fluorescence. The complete energy transfer is favoured by a homogeneous incorporation of the tetracene and an additional exciton hopping within the DDOA fibers.

Extending on this study, homogeneous white light emitting nanofibers were obtained through cascade energy transfer incorporating two different emitting tetracene derivatives (Figure 1.28). These emissive properties, including the polarization of the emission, were demonstrated for the first time at the single fiber scale using confocal fluorescence microscopy.



Figure 1.28: Molecular structure 2,3-didecyloxytetracene (DDOT), 2,3-dihexadecyloxy-5,12-diphenyltetracene (G16), 2,3-dihexadecyloxy-5,6,12,13-tetraphenyltetracene (rubrene, R16).

The next step envisioned to go further than controlling the emission properties of the selfassembling acenes is to direct the actual self-assembly with an external trigger. Inspiration on responsive acenes comes from a whole other field, the field of organic electronics. Until today. benchmark for organic pentacene is still the small molecule p-type semiconductors^[112,113], but suffers from high sensitivity towards oxygen and is almost insoluble in all organic solvents at room temperature. Therefore, extensive research has been done in order to search for easier processable organic semiconductors, which can be converted into the parent acene during processing. The substitution of the 6,13-position with triisopropysilylacetylene improved the solubility and stability of the pentacene, as was discussed in the beginning of this paragraph. The chemistry of some of these external triggerable pentacenes will be discussed below rather than the corresponding efficiencies of the devices which are out of the scope of the thesis.

1.6.4. Thermo- and photoresponsive pentacenes

Müllen *et al.* reported a more soluble precursor of pentacene (Figure 1.29a), which would thermally convert into the parent pentacene during annealing.^[114] The solubility however, did not improve largely (1,5 wt% in CH₂Cl₂ and toluene) and precursor requires multistep synthesis. Afzali et al. reported a better performing precursor where the pentacene was masked with N-sulfinylacetamide (Figure 1.29). The resulting adduct had a solubility exceeding 50 g.L⁻¹ in chlorinated solvents, THF and 1,4-dioxane. Heating the adduct provided the pentacene cleanly at temperatures between 120-200°C.^[115] More interestingly, replacing the acetamide with methylacrylamide which had the same the solubility (50 g.L⁻¹) provided photopatterning. Photoirradiation of a thin layer of the precursor through a photomask would polymerize the methylacrylate. An additional baking step and a washing with methanol removes the non-polymerized precursor and allowed to pattern pentacene after the thermolysis.^[116] A more recently reported thermally cleavable precursor is the adduct with diethylketomalonate. Its solubility was also in the range of 50 g.L⁻¹ in chlorinated solvents and acetone and smoothly reconverted to the pentacene upon heating.^[117]



R = H, -CHCH₂

Figure 1.29: Thermoresponsive precursors of pentacene.

Another example of thermoresponsive precursor is the monoketone adduct based on norbornadienone. The 7-norbornadienone itself and the 9,10-dihydro-9,10-methanoanthracen-11-one (anthracene derivative) undergo direct decarbonylation at room temperature. The rate constant of decarbonylation for 10-dihydro-9,10-methanoanthracen-11-one was determined to be $2.52 \times 10^{-5} \text{ s}^{-1}$ in 1,4-dioxane at 25°C .^[118] The tetracene and pentacene derivatives, on the other hand, are stable. Furthermore, the more extended norbordienones can also be converted by photoirradiation resulting in near quantitative conversions for the pentacene derivatives (Figure 1.30). The overall solubility on the other hand did not improve immensely (1.5 mg.mL⁻¹ versus 50 mg.mL⁻¹ for the previous mentioned adducts).^[119,120]



Figure 1.30: Photoactive/thermoactive precursors of pentacene.

In contrast to the dual conversion of the monoketone, the decarbonylation of the alphadiketone is a pure photochemical conversion. The pentacene precursor is stable up to temperatures around 200°C and in contrast to the monoketone derivatives has a clear n- π^* transition around 400- 520 nm. This allows direct irradiation of the carbonyl group with visible light. The reaction was first reported by Strating *et al.* who were investigating the expulsion of ethylene dione.^[121] Whereas the ethylene dione was never isolated, they did report a quantitative conversion of α -diketone-anthracene under irradiation. In 2005, Ono *et*

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al. adopted this method to facilitate the device fabrication with pentacene (Figure 1.31).^[122] As the previous mentioned reactive groups, it increases the solubility and inhibits the photo-oxidation by breaking the conjugation of the molecule.



Figure 1.31: Photoconversion of alpha-diketone-pentacene in toluene.

It is this photoactive moiety which inspired us to pursue the synthesis of photoactive selfassembling 2,3-dialkoxy acenes to obtain light induced control over the gelation mechanism and possible photopatterning. Further characteristics of this specific functional group will be given in Chapter 2.

1.7. Aim and outline of the thesis

In this thesis, we aim to combine molecular self-assembly with photochemistry to control the nucleation and direct the growth of the DDOA nanofibers with the aid of light. To that end, we aim to synthetically modify the DDOA by the addition of the photoactive α -diketone moiety, which should have a higher solubility in DMSO than DDOA and inhibit the molecular interactions which trigger the self-assembly. Most important, it is the chemical moiety which should convert DDOA into a phototriggerable low molecular weight gelator.

Chapters 2 and 3 will discuss an in-depth study of the photogelation of DDOA. In Chapter 2, we describe the synthetic modification of DDOA to obtain the alpha-diketone DDOA and study the photophysical properties of the dkDDOA in solution. Furthermore, the photocontrolled (irreversible) sol-gel transition will be evaluated and a comparative study will be performed to see if the gel made by photodecarbonylation (supersaturation) differs from the DDOA gels made by supercooling.

In **Chapter 3**, we use a scanning laser microscopy setup as a synthetic and analytic tool to perform and subsequently investigate the surface patterning of DDOA. Several factors will be discussed which influence the control over the nucleation density and subsequently the growth direction of the DDOA fibers to obtain anisotropic micropatterns. The investigated parameters are the water content of DMSO, the substrate, mono- or biphotonic excitation or the use of epi-illumination. To our knowledge, this is the first system which allows the photopatterning of an LMWG at the microscale from solution instead of a gel phase. Interesting anisotropic optical properties at the nano- and micro-scales result from this process.

Chapter 4, will discuss the general synthetic strategy adopted to synthesize different 2,3alkoylated anthracenes and tetracenes. These molecules were used for different purposes and studies and not all of them are treated in this thesis.

Chapter 5, resulted from a secondment at TU Delft and allowed to explore other methods exploiting photochemistry to influence gel properties. Several small studies evolved around the post-treatment of a functionalised cyclohexanetriscarboxamide hydrogelator. More precisely, the photochemical crosslinking of the supramolecular nanofibers with the thiol-ene or thiol-yne reaction was performed to influence the mechanical properties. Therefore, oscillatory rheology is the analysis technique of choice. The other small studies discuss the kinetic control of hydrogelation before crosslinking and the set-up of a protocol to determine the crosslink efficiency.

Afterwards a general conclusion will be given with perspectives of where to go from here followed by **Chapter 6**, the experimental section.

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2.1. Introduction

LMWGs which can be triggered by chemical stimuli are currently in increasing demand.^[1] Indeed, the stimulus provides a better control over the dynamics of the gelation i.e. the properties of the resulting gel^[2], as shown in Chapter 1. This can lead to self-healing of the LMWG^[3] or controlled release of drugs^[4]. In contrast, light-triggered self-assembly is a physical approach providing several advantages as compared to chemical stimuli. Light is a traceless reagent and can provide spatial control and temporal control over the self-assembly. In this work, the pro-gelator was meant to transform into the well-studied 2,3didecyloxyanthracene (DDOA) supergelator by a clean photochemical reaction, preferably triggered by visible light (see Scheme 2.1). Therefore, the specifically designed alphadiketone-2,3-didecyloxyanthracene (dkDDOA) was prepared by multi-step synthesis. The diketone moiety interrupts the π -conjugation and hinders the π - π stacking, preventing aggregation and subsequently increasing the solubility of the precursor in solution.^[5] Furthermore, the acene is protected from undesired photo-oxidation typically occurring on the central rings of *n*-acenes (see Introduction). For these particular reasons alpha-diketone acene derivatives have already been used for device fabrication^[6,7] and the synthesis of larger *n*-acenes^[8,9] (heptacene, nonacene). A promising feature of diketoanthracenes is the quantitative conversion described for some derivatives^[10–13], yielding as only side-product the gaseous carbon monoxide. The quantitative conversion for anthracene derivatives is favoured by the lack of spectral overlap of the generated anthracene with the n- π^* transition band of the 1,2-diketo precursor around 400- 520 nm (see paragraph 2.2.3.). This allows to selectively excite the 1.2-diketoanthracene derivative and avoid photobleaching of the resulting acene. In prospective, the spectral properties should also allow efficient energy transfer and subsequent autocatalysis of the photoconversion.^[12] In fine, since the conjugation is regained upon photoconversion of this type of derivatives, an irreversible fluorescence switch-on has been reported in several cases^[14,15]. The fluorescence activation, favoured by the low $\Phi_{\rm F}$ of the precursor diketo-compounds^[16], will be a very useful spectroscopic handle to investigate and analyse the photochemical mechanism.



Scheme 2.1: Photodecarbonylation of dkDDOA into DDOA upon irradiation.

This chapter will discuss the photo-chemical and -physical properties of dkDDOA in solution followed by the investigation of the photogelation process in DMSO. To better determine the efficiency of the process, the photogelation will be compared with the conventional supercooling of a DDOA gel. Furthermore, the interactions between DDOA and dkDDOA upon (photo)gelation will be analyzed. As last, dKG10 will be presented, a photoactivatable tetracene, and the energy transfer between DDOA and G10 upon photoconversion will be studied towards spatially controlled colour tuning.

2.2. Results and discussion

2.2.1. Synthesis of alpha-diketone-2,3-didecyloxyanthracene

The synthesis of the alpha-diketone moiety consists of three steps starting from DDOA and was realized adopting the procedure of Yamada and co-workers.^[5] The six-step synthesis of DDOA has been developed previously (see Chapter 4). The last three steps are shown in Scheme 2.2:



Scheme 2.2: Synthesis of alpha-diketone-2,3-didecyloxyanthracene (dkDDOA).

First, a Diels-Alder reaction between DDOA and vinylene carbonate is performed in xylene. The xylene was degassed prior to the reaction and the reaction flask protected from light to overcome possible photo-oxidation of the DDOA. The reaction has to be carried out in a sealed tube at 180°C for 3 days to reach completion. The slow reaction rate is due to vinylene carbonate, which is a rather neutral dienophile (LUMO is $-0.25 \text{ eV}^{[17]}$) and therefore the reaction needs to be carried out in a sealed tube under autogeneous pressure. The two resulting diastereoisomers collected by column chromatography gave a high yield of 85%. The subsequent hydrolysis was readily done in a mixture of 1,4-dioxane:NaOH (4 M) in two hours and gives the diol in 86% yield after neutralization. The obtained product is a viscous liquid which solidifies slowly over weeks at room temperature. The diketone moiety is obtained by oxidizing the diol with the Swern oxidation at -78° C. Trifluoroacetic acid was used as the dehydration agent instead of oxalyl chloride to overcome the formation of side-

products. Finally, diisopropylethylamine was used as base to obtain dkDDOA as an orange solid in a good yield of 77%.

2.2.2 Photophysical properties of dkDDOA in solution

In Figure 2.1, the solvent dependent absorption and emission spectra of dkDDOA are shown. All chosen solvents (cyclohexane, toluene, THF, acetontrile and DMSO) are either aprotic polar or non-polar solvents since the α -diketone moiety is sensitive towards protic solvents and moisture and can undergo a nucleophilic substitution reaction.^[18]



Figure 2.1: Solvent dependent absorption in M^{-1} cm⁻¹ and the corresponding emission spectra ($\lambda_{ex} = 470 \text{ nm}$) of a 0.1 mM dkDDOA solution.

The absorption spectra show three distinguishable peaks where the absorption in the UV (< 300 nm, partially visible) can be assigned to π - π * transition and the n- π * transition is the absorption band in the visible at 400-520 nm. These are the two characteristic peaks reported for other diketone derivatives. The absorption peak at 320-350 shows a clear solvent dependency and is attributed to an ICT state due to the push-pull effect on the asymmetric dkDDOA. Upon increasing the solvent polarity a bathochromic shift and decrease in the molar extinction coefficient are observed (Table 2.1). The other two transitions show only negligible solvent dependency and only have slight differences in the molar extinction coefficient and the absorption wavelength. Nevertheless, a bathochromic absorption tail appears above 500 nm in the polar solvents, in particular in DMSO.

Solvent	Polarity	$\lambda_{\rm Abs}{}^{\rm ICT}$	Epsilon	$\lambda_{\rm Abs}{}^{\rm n-\pi*}$	Epsilon	$\lambda_{\!\rm Em}{}^{\rm max}$
	index	(nm)	$(10^3{ m M}^{-1}{ m cm}^{-1})$	(nm)	$(10^3 { m ~M^{-1} \ cm^{-1}})$	(nm)
CyH	0.2	321	5.5	466	1.5	553
Toluene	2.4	339	4.0	468	1.2	574
THF	4.0	338	4.5	467	1.4	582
ACN	5.8	342	3.4	466	1.2	622
DMSO	7.2	349	3.7	470	1.4	622

 Table 2.1: Maximum absorption and emission wavelengths of dkDDOA according to solvent polarity.

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The n- π^* transition is emissive and the resulting emission spectra have very broad peaks and show a bathochromic shift with increasing solvent polarity. The quantum yield of fluorescence (Φ_F) of dkDDOA is however very small, in the range of 0.004 to 0.008^a over the range of all solvents. The value of 0.004 in toluene is in agreement with previously reported values.^[16] However, the bathochromic shift upon increase of solvent polarity suggest that the emission has a CT-character. This behaviour, combined to the absorption tail mentioned previously, suggests that two transition states with similar energies are present. Whereas in an apolar solvent, the n- π^* transition is emissive, in polar solvents the CT-state is more stable and becomes the emissive solvent-sensitive state.

2.2.3. Photoconversion of dkDDOA

DDOA is known to gelate a variety of solvents. The most efficient gelations are in most alcohols and DMSO. Alcohols however, were discarded since they can act as nucleophiles on dkDDOA, Therefore, DMSO was chosen as a solvent since it presents several advantages over the other possible solvents: (i) DDOA is a supergelator^[19] in DMSO; (ii) DDOA nanofibers formed in DMSO display polarized emission, due to a higher crystallinity confirmed by SAXS experiments^[20]; (iii) DMSO does not evaporate during microscopy studies and has been used extensively to study DDOA; (iv) solubility of CO is negligible^[21]. The solubility limit of dkDDOA in DMSO was found to be ~5.5 mg.mL⁻¹ (10 mM), whereas 0.5 mg.mL⁻¹ (1 mM) of DDOA already gels DMSO at room temperature. The higher solubility of dkDDOA as compared to DDOA can be exploited to find conditions in which the solution can be supersaturated and the gelation triggered.

The absorption and emission spectra of dkDDOA and DDOA in DMSO are shown in Figure 2.2 for comparison.



Figure 2.2: Absorption spectra of 1 mM of dkDDOA and DDOA in DMSO in M⁻¹ cm⁻¹ and the corresponding emission intensity ($\lambda_{ex} = 365$ nm for DDOA and 470 nm for dkDDOA) of 1 mM dkDDOA and DDOA in DMSO.

^a $\lambda ex = 450$ nm, reference is tetracene in cyclohexane (Q_F = 0.17)^[16]

As mentioned in paragraph 2.1, the lack of a spectral overlap in the blue region of the visible spectrum makes it possible to excite the dkDDOA without perturbation by an induced inner filter effect or photobleaching of DDOA. Furthermore, emission spectroscopy shows that DDOA is of higher intensity than dkDDOA making it possible to use fluorescence analysis to investigate the photogelation (Chapter 3). In Figure 2.3, the photoconversion of 1 mM dkDDOA in DMSO at room temperature is shown. Direct irradiation in the n- π^* band with a 450 ± 25 nm LED induces a gradual decrease at 470 nm and simultaneous appearance of the absorption peaks at 338, 347, 365 and 384 nm attributed to the characteristic vibronic structure of the S_0 - S_1 absorption in DDOA.^[22] Over the course of the photoconversion, two isosbestic points appear at 336 and 393 nm indicating a constant reaction stoichiometry and the absence of secondary reactions. Interestingly, the sudden increase in absorption at 384 nm towards the end of the conversion can be attributed to the gelation of DDOA. Furthermore, the isosbestic points are lost due to the aggregation of DDOA. The decrease in concentration of dkDDOA versus time showed a mono-exponential dependence ($\chi^2 = 0.99$) and quantitative conversion. In addition to the visual observation and the inverted test-tube test (ITT), this spectroscopic data proofs the efficient photogelation of DMSO by DDOA.^[22]



Figure 2.3: (a) Photoconversion of a degassed solution of 1 mM dkDDOA in DMSO. The irradiation source is a 450 ± 25 nm LED. The power at the front of the cuvette is 2.1 mW. Inner graph shows the mono-exponential dependence of the photoreaction at 470 nm. (b) dkDDOA 1 mM solution before and after photoirradiation visually proving the photogelation.

Nevertheless, the photoconversion followed by UV-vis spectroscopy does not exclude the formation of non-absorbing species. Therefore, the photoconversion was also followed by ¹H-NMR in solution (CDCl₃). Figure 2.4 shows the gradual decrease of the bridgehead hydrogen (Ha) at 4.85 ppm. Concomitantly, a peak appears at 8.16 ppm corresponding to the hydrogens at the 9,10-position (Hb) of the anthracene core. The reaction takes place without any detectable side-products in these measurements.


Figure 2.4: Photoconversion of 1,5 mg.mL⁻¹ of dkDDOA in $CDCl_3$ by ¹H-NMR. The irradiation source was a 450 ± 25 nm LED.

The quantum yield of the photoreaction ($\Phi_{\rm R}$) was determined in DMSO and toluene under irradiation at 468 nm by quantification of the initial change of the absorption at 471 nm of the reactant (Table 2.2). The reaction was studied in toluene because it is most commonly used in the literature to determine the $\Phi_{\rm R}$ of alpha-diketones. The $\Phi_{\rm R}$ in toluene is 14%, whereas the $\Phi_{\rm R}$ in DMSO is found to be 2%. In DMSO the quantum yield is not extremely high but sufficient to achieve gelation in the bulk also thanks to the complete lack of sidereactions. A steep decrease in the $\Phi_{\rm R}$ between highly polar and non-polar solvents, in this case by a factor of 7, has already been reported for diketone-pentacene and porphyrin derivatives.^[23,24] The increase in solvent polarity was reported to stabilize the charge separated excited states and hence increases the probability for decay by a competitive radiationless pathway.^[23] This interpretation is coherent with the solvent effect observed in fluorescence which seems to result from a CT-state in polar solvents.

Table 2.2: $\Phi_{\rm R}$ values of dkDDOA in toluene and DMSO at different wavelengths of irradiation.

Solvent	$\Phi_{ m R}$ at 468 nm*	$\Phi_{ m R}$ at 336 nm*
Toluene	0.14	0.22
DMSO	$0.020{\pm}0.002$	$0.045 {\pm} 0.004$

*= Reference for Φ_R determination was ferrioxalate. Method can be found in the Experimental Section.

The $\Phi_{\rm R}$ was also determined by irradiation in the UV, since in microscopy studies the UVlight used to induce the fluorescence of DDOA will simultaneously be absorbed by dkDDOA. This will induce the photodecarbonylation. In order to facilitate the determination of $\Phi_{\rm R}$, the solution of dkDDOA was irradiated at the wavelength of an isosbestic point between the two compounds in order to ensure a constant optical density of the solution. Surprisingly, the $\Phi_{\rm R}$ is higher at 336 nm than $\Phi_{\rm R}$ at 468 nm by a factor of ≈ 2 (Table 2.2). In order to explain this increased efficiency, a triplet sensitization, shown to occur in other systems^[16], could be proposed. Although, the exact energy of the T₁ state of DDOA and dkDDOA are not known, an estimation can be extrapolated using the reported values for anthracene and diketoanthracene. The triplet energy of diketoneanthracene is 54 kcal.mol^{-1[16]} whereas for anthracene the lowest lying triplet (T₁) is at 42 kcal.mol^{-1[25]}. In this case, triplet sensitization seems thus unlikely. Another mechanism could result from the overlap between the emission of DDOA and the absorption of dkDDOA, which would favour a possible energy transfer from DDOA to dkDDOA. This would increase the $\Phi_{\rm R}$ under UV irradiation since photons absorbed by DDOA could be involved in the photoconversion causing an autocatalytic effect^[12] and affect the measurement of $\Phi_{\rm R}$. However, the low concentration of 3.14 x 10⁻⁵ M in DMSO reduces the possibility of an energy transfer requiring diffusion in solution to minimal probability. Only a static energy transfer would be possible, which requires a strong association in the ground state. This again is highly improbable in particular at the beginning of the reaction when the concentration of DDOA is very low.



Figure 2.5: Excitation spectrum of dKDDOA. $\lambda_{em} = 605$ nm. Small peak at 520 nm is scattering of the lamp.

Finally, the excitation spectrum of dkDDOA was measured in DMSO to characterize the efficiency of the internal conversion processes by comparing the relative intensities of the bands with those of the absorption spectrum (see Figure 2.5). The spectra overlap quite well from 370-550 nm, taking also into account the experimental uncertainties due to a very weak emission. The internal conversion to the emissive excited state occurs with the same efficiency whether the higher energy state or the lower energy state is excited. This suggests in this spectral range the photophysical pathways leading to the population of the emissive lower energy singlet state are identical. However, at wavelengths lower than 370 nm, a decrease in the excitation spectrum intensity, also resulting in an apparent red-shift of the higher energy transition band, suggests that an alternative pathway is populated to some extent. This pathway could lead to a more efficient population of one of the reactive excited states, most probably a triplet state^[16]. In conclusion, the difference in yields can be

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explained by (i) an additional pathway upon 336 nm excitation leading more efficiently to a reactive triplet state than upon excitation in the visible; (ii) an incorrect actinometry, at one of the wavelengths.

2.2.4 Interaction of dkDDOA and DDOA during photogelation

The efficiency of the gelation of DDOA in DMSO by using the photoreactive dkDDOA as progelator has been established. The photoconversion is a quantitative reaction without any detectable side-products when excited in the blue region of the visible spectrum. However, the photoconversion experiments do not give any details on the interaction between DDOA and dkDDOA over the course of the photoirradation. It is imaginable that dkDDOA can have effects on the aggregation of DDOA and thereby inducing an alteration in the packing at the molecular or microscopic level. A change in molecular packing could alter the material properties and in our case the photophysical properties.^[26,27] Therefore, the fluorescence intensity, fluorescence lifetime and absorption were measured on a thermal induced and photoinduced gels of DDOA.

The absorption and emission spectra (all measured at 23° C) of the supercooled (see paragraph 1.3.1.) and photoinduced DDOA gels are shown in Figure 2.6. The absorption peak at 384 nm shows that the same amount of self-assembling DDOA is converted into a gel for both samples. The photoinduced gel only has a slight higher absorption in the UV. We excluded it from being the 2,3-didecyloxyanthraquinone, photodegradation product of DDOA, since the photogelation is performed at 450 ± 25 nm where DDOA does not absorb. Furthermore, the 2,3-didecyloxyanthraquinone has an absorption band at 400 nm, the region where the two samples have the same absorption. Therefore, this is thought to be due to the incomplete photoconversion. There is still $\pm 2\%$ of dkDDOA (0.985 mM converted instead of 1 mM) which remains in solution, even after extensive irradiation. Therefore, the spectral overlap in this region for DDOA and dkDDOA explains the higher absorbance.

In the emission spectra, neither a spectral shift nor new peaks are observed when comparing both spectra. Only the plots of the spectra on a logarithmic scale reveal that the fine structure of the photoinduced gelation is less apparent above 470 nm. This fine structure is related to the rigidity in the solid state and homogeneity of the chromophore environment, and is an indication for crystallinity, as previously evidenced by scattering techniques^[20]. Furthermore, the ratio of fluorescence intensity at 425-550 is higher for the DDOA gel made by the photogelation than the thermal gelation. The superposition of these two spectral features can be at the origin of the lack of observation of fine-structure at high wavelength.



Figure 2.6: Absorption spectra of a supercooled solution of 1 mM DDOA in DMSO (red) and the gel of DDOA from the photoconversion of 1 mM of dkDDOA in DMSO (black). Spectra were taken at 23°C. Emission spectra ($\lambda_{ex} = 375$ nm) of the same samples taken by CFLM. Spectra are also shown in the logarithmic scale (dotted lines) to visualize the fine structure.

The fluorescence lifetimes were measured to further elucidate the origin of the small differences between the gels. The average lifetimes (amplitude averaged) are obtained from FLIM images (Figure 2.7), which show that the fibers of the photoinduced gel clearly have a longer average lifetime than the thermally induced gel. These images are representative for the whole sample and once integrated yield an average lifetime for the photoinduced gel of 8 ns, that is larger than that of the thermally induced gel of 6 ns. The fluorescence decay curve of the photoinduced gel was fitted with a biexponential function with lifetimes of 11 ns (37.6%) and 4 ns (62.4%), whereas the thermally induced gel has a biexponential decay with lifetimes of 12 ns (7.8%) and 4.7 ns (92.2%). These lifetimes are thus identical in both samples, and only differ by their relative contribution.

These observations indicate that the broad emission component from 425 to 550 nm (Figure 2.6) and the longer emission lifetime are related. Previous studies on DDOA gels and recent studies on diphenylanthracene nano-ribbons clearly allow to attribute this to excimer-like emission from structural defects within the fiber. These defects can be attributed to anthracene pairs that pack in a J-aggregate geometry that favours a stronger transition dipole coupling, therefore emitting at higher wavelength with a longer fluorescence lifetime. The defects are not detectable by absorption, most probably due to their low concentration. Even very small amounts of structural defects can be clearly observed. Indeed, in DDOA fibers an efficient exciton hopping^[28] comes into play revealing the emissive defects that act as exciton traps. For example, 1 DDOT molecule can induce the quenching of up to 100 DDOA excitons.^[29] The formation of 2,3-didecyloxyanthraquinone is also excluded in this case since the lifetimes were measured at low power of 375 nm laser diode in absence of oxygen.



Figure 2.7: (a) FLIM images of the DDOA gel prepared by supecooling (thermally induced) and supersaturation (photoinduced). (b) Corresponding fluorescence lifetime decay curves. A 405 nm longpass filter was used.

In brief, the fluorescence properties show that the photoinduced gelation only induces a trivial amount more of structural defects than the supercooling technique which is visible only in emission due to the efficient exciton hopping. Nevertheless, we desired to more accurately understand the mechanism inducing the formation of these defects. Therefore, the influence of dkDDOA present in excess during the photoconversion, was examined. Concentration dependent measurements were performed in order to simulate the variation in concentration of DDOA occurring during irradiation. A series of temperature dependent absorption measurements and fluorescence quenching experiments were performed.

In the case of DDOA, the T_{gel} and T_{melt} (see paragraph 1.3.1) can be determined by temperature dependent absorption measurements due to the change of the absorption of the 0-0 transition at 384 nm upon aggregation. Initial DDOA solutions or gels were heated to 80°C and a subsequent cool cycle and heat cycle were performed at 1°C.min⁻¹ till 19°C. At the same time interval an absorption spectrum is taken to monitor the difference in absorbance at 384 nm versus temperature. The resulting curves are given in degree of aggregation^[30,31] (see experimental section).

A series of pristine DDOA gels and a mix with 3 mM of dkDDOA were measured. The concentration of DDOA ranges from 0.5 to 2 mM in DMSO. The measured T_{gel} and T_{melt} do not give any insight on the mechanical properties of the gel, but are related to the thermodynamic properties of a gel with a specific composition. Therefore, the values do give an insight if the same amount of energy is needed to reach supersaturation to form a gel.

For the samples with 3 mM dkDDOA the T_{gel} was determined from the absorption spectra (Figure 2.8b). The overlap in absorption between DDOA and dkDDOA which changes over time makes it unfeasible to accurately determine the extinction coefficient to plot the degree of aggregation. Furthermore, there is a change in absorption and light diffusion when gel is formed. The measured values are shown in Figure 2.8d. The T_{gel} for the sample with 0.5 mM DDOA/3 mM dkDDOA was not determined since no gel was formed at 19°C and further cooling would solidify the DMSO.

The addition of 3 mM dkDDOA clearly affects the gelation temperature and systematic difference of 3 ± 1 °C is observed. This gives a direct indication that the dkDDOA interferes with the gelation process to some extent and dkDDOA may be integrated in the DDOA fibers during gelation. In contrast, the temperature of the melt is unaffected. This suggests that the final fibrous structure of DDOA is not strongly affected by the presence of dkDDOA.



Figure 2.8: (a) Shift in absorption upon gelation of a 1 mM DDOA in DMSO. It shows the increase at the 0-0 transition band at 384 nm. (b) Evolution of the absorbance for a 2 mM + 3 mM dkDDOA in DMSO. The degree of aggregation not determined due to the overlap in absorbance. (c) Example of a cooling and heating curve (2 mM DDOA in DMSO) of the pristine DDOA gel. It shows nicely the hysteresis of 10°C. (d) T_{gel} and T_{melt} values of pristine DDOA gels in DMSO and the corresponding mix with 3 mM dkDDOA added.

In Figure 2.9, the Stern-Volmer plot of the average fluorescence lifetime (τ_0/τ) and steadystate fluorescence (I_{436}^0/I_{436}) of a 1 mM gel of DDOA with different amounts of dkDDOA is shown. The fluorescence intensities at 436 nm were corrected with equation 6.7, see Experimental section, to compensate for the inner filter effect due to dkDDOA. The fluorescence of DDOA shows a quadratic dependence upon addition of dkDDOA. This means that DDOA is quenched by dynamic (diffusion dependent quenching) and static quenching (formation of a ground state complex between a donor and acceptor). At lower concentrations of dkDDOA, the I⁰/I and τ_0/τ have the same values indicating a pure dynamic quenching of the fluorescence of DDOA. At higher concentrations of dkDDOA

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(> 0.4 mM), the static quenching is proposed to be related to the incorporation of dkDDOA in the DDOA fibers favoured by the increased relative concentration of dkDDOA. Indeed, the spectral overlap between DDOA emission and dkDDOA absorption is favourable for a photo-induced energy transfer. This results in a quenching of DDOA emission and may enhance the fluorescence of dkDDOA. The latter is however weak and not detected when DDOA is present.



Figure 2.9: Corrected Stern-Volmer plot of the average of the steady state fluorescence (black square, $\lambda_{ex} = 365 \text{ nm}$, $\lambda_{em} = 436 \text{ nm}$) and the time resolved fluorescence quenching (blue squares, $\lambda_{ex} = 371 \text{ nm}$, $\lambda_{em} = 436 \text{ nm}$) of DDOA upon the addition of dkDDOA.

These results suggest that in the case of the photoconversion of dkDDOA into DDOA, dkDDOA molecules get entrapped in the DDOA aggregate and integrate within the fibers. DDOA forms rigid fibers without any clear evidence of occurring dynamics, which could support restructuration or rearrangement and thereby supporting the idea of entrapment. A co-assembly seems less likely due to the large difference in electron density and dipole moment between the two molecules (see Figure 2.10). It also explains why the incorporation occurs with larger amounts of dkDDOA in solution.



Figure 2.10: Electron density map and dipole moment of DDOA and dkDDOA calculated with Gaussian 03. Calculations were provided by Dr. L. Gartzia-Rivero.

The enclosed dkDDOA molecules convert into DDOA due to direct excitation or photosensitization by DDOA in the fiber. The incorporated dkDDOA does however, not necessarily pack the same way as the DDOA molecules, and after photoconversion they could induce the defects detected by FLIM. The effect of the release of CO would further contribute to local structural defects.

The inclusion of dkDDOA into DDOA is further supported by preliminary results obtained by confocal microscopy. In these experiments, photoconversion was induced by a focused 473 nm laser beam and emission recorded simultaneously (note that DDOA emission is not induced at 473 nm). The nucleation of DDOA within the focal point of the laser could be identified indirectly by a sudden increase of the dkDDOA emission intensity and a hypsochromic shift (Figure 2.11). We already established that dkDDOA is very sensitive towards its environment (paragraph 2.2.2) showing fluorescence at lower wavelengths and intensity increase in solvents of lower polarity. Therefore, the change in emission suggests the incorporation of dkDDOA in the photoinduced nucleus since the polarity of the environment is expected to be lower when entrapped by DDOA than solvated in DMSO.



Figure 2.11: Hypsochromic shift and subsequent intensity increase of the emission of dkDDOA upon nucleation/aggregation in the vicinity of the focal point of the focused laser ($\lambda_{ex} = 473$ nm). A 405 nm longpass and 473 nm notch filter were used.

In conclusion, the DDOA gel obtained by photodecarbonylation is similar to the thermally induced gel. Only a trivial amount of additional structural defects is introduced in the fibers by the incorporation of dkDDOA during the photo-induced self-assembly process and subsequent conversion of the latter. Again, it is due the efficient exciton hopping that a low amount of defects can be detected.

2.2.5. Towards spatially controlled energy transfer

A key characteristic of DDOA fibers is their light-harvesting efficiency and the tuning of emission colour by the incorporation of a suitable energy acceptor. The addition of only 1-2 mol% of acceptor can induce sufficient quenching of the blue donor emission and a subsequent appearance of the acceptor emission through efficient Förster resonance energy transfer processes. In previous studies, DDOT^[29] and G16^[32] were used as green emitting acceptors. The energy transfer efficiency is larger between DDOA and DDOT due to a better dispersion of DDOT. However, G16 displays a similar acceptor efficiency, whereas it has a higher $\Phi_{\rm F}$ and is less prone to oxidization. Previous reports show that a very similar behaviour should be obtained using a new related compound 5,12-diphenyl-2,3didecyloxytetracene (G10), see Figure 2.12.^[33]



Figure 2.12: Molecular structure of G10.

The efficiency of the energy transfer is favoured by a good incorporation of G10 into the DDOA nanofiber, a large spectral overlap (same for G10 and G16), aligned dipoles and a favourable distance and angle between the donor and acceptor. Therefore, we calculated the overlap integral ($J_{DDOA/G10}$) between the emission of the DDOA and the absorption of G10 as follows.

The overlap integral is defined by:

$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda)d\lambda}$$
(2.1)

 $F_D(\lambda)$ is the emission spectrum of the donor and is dimensionless, ε_A is the absorption spectrum of the acceptor expressed in M⁻¹.cm⁻¹ (molar extinction coefficient). The value of the overlap integral J was calculated to be 6.3.10¹² M⁻¹.cm⁻¹.nm⁴ and thereby the distance between the donor and acceptor to have an energy transfer efficiency of 50% is 1.04 nm. This was calculated by using equation (2.2.

$$R_0 = 0.211 \left[\frac{\kappa^2 \Phi_D J(\lambda)}{n^4} \right]^{1/6}$$
(2.2)

 $\Phi_{\rm D}$ is the donor fluorescence quantum yield, κ^2 , the orientation factor and n the refractive index. The orientation factor (κ^2) between the donor and the acceptor is ¹/₄ and was previously estimated^[32] based on the perfect replacement of a DDOA molecule by a G16

molecule in the fiber. The DDOA molecules are packed in a coaxial triad, where the emission dipoles along the small axis of the molecule are arranged with a relative angle of 60° (Annex B).

The aim of the following work was to photo-induce the formation of green emitting gels, thus a blend of DDOA including a small amount of G10 acting as an energy acceptor. In particular, G10 was introduced in the solution by photo-converting the diketone precursor dKG10 into G10. Having similar photo-cleavable functions, the simultaneous photogeneration of DDOA and G10 could be attempted.

The synthesis of dKG10 follows the same procedure as for dkDDOA also resulting in moderate to high yields. Experience tells that the decyl chain, rather than a hexadecyl chain, facilitates the synthesis and purification. The high yields are also favoured by the steric hindrance on the 5,12-position which allows to specifically functionalize the 6,11-ring with the photocleavable alpha-diketone moiety and avoids formation of isomers. The resulting dKG10 did not form a solid, but a rather viscous orange oil. The reaction scheme is shown in Scheme 2.3.



Scheme 2.3: Synthesis of $6,11-\alpha$ -diketone-5,12-diphenyl-2,3-didecyloxytetracene (dKG10).

For comparison, the photophysical properties of dkDDOA, dkG10, G10 and DDOA are given in Table 2.3.

Photoinduced gelation of DDOA

	$\lambda_{\rm Abs}{}^{\rm max}$	Epsilon	$\lambda_{\!\rm Em}{}^{\rm max}$	$\Phi_{ m F}$	τ
	(nm)	$(10^3 { m ~M}^{-1} { m ~cm}^{-1})$	(nm)		(ns)
DDOA	365	6.7	412	0.24^{a}	6^{b}
G10	493	17.0	505	0.76°	17.3
dkDDOA	350, 470	3.7, 1.4	622	0.004	d
dKG10	350, 470	4.4, 0.95	е	e	d

Table 2.3: Photophysical properties of a 1 mM DDOA gel in DMSO, a 10⁻⁴ M G10 solution in deoxygenated cyclohexane, 1 mM dkDDOA and 10⁻⁴ M dKG10 in DMSO.

^a Measured in an integrating sphere^[28]. ^b Average lifetime of a multiexponential decay. ^c The used reference is fluorescein in 0.1 M NaOH ($\Phi_F = 0.95$) ^d Lifetimes of dkDDOA and dKG10 were not measured. Diketone derivatives were reported to have lifetimes in the picosecond range^[16]. ^e Not measurable due to the spectral overlap of dKG10 with G10.

In Figure 2.13, the absorption spectra of dKG10 and dkDDOA in DMSO are shown for comparison. The spectra are quite similar considering the difference in the molecular structure. At the wavelength of excitation $(450\pm25 \text{ nm})$, the ratio between the molar extinction coefficient of the diketones is 1.5. This demonstrates that the absorption of the two compounds is in the same range.



Figure 2.13: Absorption spectra of dkDDOA and dKG10 in DMSO.

Before any energy transfer experiments, the photoconversion of a 10^{-4} M solution of dKG10 in DMSO was measured over time (Figure 2.14) to verify the occurrence of the photodecarbonylation reaction. The direct irradiation of the n- π^* band with a 450±25 nm LED shows a gradual decrease at 470 nm which is subsequently followed by the appearance of absorption peaks at 493, 462, 435, 410 and 387 nm attributed to G10.^[32] The photoconversion yields stoichiometric proportions of reactant and product up to 38 min, as indicated by the isosbestic point at 396 nm. Thereafter, it shifts to 403 nm indicating the occurrence of second underlaying reaction. The second reaction is attributed to the photooxidation of G10.^[34] dKG10 and G10 absorb in the same region and therefore the two molecules are simultaneously excited during the photoconversion. The photoconversion however, is still quantitative, meaning all dkG10 is converted. G10 is however, not the only obtained photoproduct. The exact percentage of conversion cannot be determined due to the spectral overlap and the photoconversion in ¹H-NMR was not performed.



Figure 2.14: Photoconversion of 10^{-4} M of dKG10 in DMSO. The irradiation source was a 450 ± 25 nm LED. The power at the front of the cuvette was 2.1 mW.

The $\Phi_{\rm R}$ of dKG10 at 468 nm was not measured due to the spectral overlap between reactant and product. However, the trend can be deduced from the literature. Quinton *et al.* reported that the $\Phi_{\rm R}$ decreases with the increase in length of the *n*-acene.^[11] Therefore the dkDDOA should convert faster than the dKG10. In addition, only a few mol% of acceptor is necessary for efficient energy transfer in a millimolar gel. Therefore, a difference in the kinetics of the conversion of dkDDOA and dKG10 irradiated simultaneously is inevitable. This could be an issue, meaning that the DDOA will already have self-assembled into nanofibers before the inclusion of the G10. A way to circumvent this is to adjust the concentration of dKG10. However, G10 will aggregate in DMSO if the concentration is too high. Therefore, in a first attempt to colour pattern, the concentration of dKG10 is kept at 2 mol% (4.10⁻⁵ M) in a 2 mM dkDDOA solution. These are the same optimized concentrations as used in previous reported experiments and a good starting point.

In Figure 2.15, it is clear that despite the above mentioned obstacles, dKG10 actually photoconverts and the corresponding tetracene incorporates into the DDOA fibers over the course of the photoirradiation. There is a clear increase in the emission from 500- 600 nm, with the characteristic bands of the tetracene and a clear difference in the emission colour of a 2 mM DDOA gel with and without 2 mol% of photoconverted dKG10. Furthermore, we see a quenching in the lifetime of the photoconverted gel ($\lambda_{ex} = 371$ nm, $\lambda_{em} = 436$ nm). Indirect excitation of the G10 ($\lambda_{ex} = 371$ nm, $\lambda_{em} = 502$ nm) induces an emission decay with a mono-exponential lifetime of 17.4 ns which corresponds to the lifetime of the G10 in

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solution. This mono-exponential character of the decay proofs that the distribution of G10 in the gel is homogeneous and G10 is well dispersed (Figure 2.15c).

The results shown in Figure 2.15 were quite original. Thanks to the photo-controlled gelation, the evolution of the incorporation of an acceptor into the DDOA fibers has been followed for the first time. The increase in the concentration of DDOA can be fitted with a mono-exponential fit (Figure 2.15b) proving once again the quantitative conversion of dkDDOA into DDOA without side-products. The point of gelation can be deduced indirectly from the kinetic trace at 505 nm. Here, the emission of the G10 only starts to be detectable after 14 min. After that, the increase in the emission of the G10 more or less follows the dependence of the DDOA emission until it starts photobleaching. The photobleaching can be due to an overexposure to the 450 ± 25 nm LED or an excessive photosensitization in the fluorimeter ($\lambda_{ex} = 365$ nm).

The incorporation of the converted dKG10 in the DDOA fibers can occur through two different mechanisms: (i) both diketones are simultaneously converted and at the point of gelation the DDOA and G10 co-assemble; (ii) the DDOA gel forms upon irradiation and dKG10 is incorporated and subsequently converted into the tetracene upon photosensitization by DDOA. The photosensitization by energy transfer is possible due to a favourable spectral overlap of DDOA emission and dkG10 absorption. Taking this into account, but also the slower reaction rate of dkG10, a combination of the two mechanisms may reflect the situation at best. Confocal Laser Scanning Microscopy experiments are momentarily in progress to repeat the same experiment in single fibers and attempt two colour photopatterning.



Figure 2.15: (a) Evolution of the emission spectra of a 2 mM dkDDOA solution in DMSO with 2 mol% dKG10 over the course of the photoirradiation showing an increase in intensity for both spectra. The converted G10 again showed photobleaching after 50 min. (b) Kinetic traces of the emission intensity of DDOA (412 nm) and G10 (505 nm). (c) Fluorescence decay curves of a 2 mM DDOA gel in DMSO (black) ($\lambda_{ex} = 371$ nm, $\lambda_{em} = 420$ nm), a photoconverted 2 mM dkDDOA and 2 mol% dKG10 gel in DMSO ($\lambda_{ex} = 371$ nm, $\lambda_{em} = 436$ nm) (red), a 4x10⁻⁵ M photoconverted dkG10 ($\lambda_{ex} = 371$ nm, $\lambda_{em} = 502$ nm) (blue). (d) Absorption spectra of the photoinduced gel after the photoconversion. (e) Emission colour of a 2 mM DDOA gel in DMSO ($\lambda_{ex} = 365$ nm). (f) Emission colour of the photoconverted 2 mM dkDDOA and 2 mol% dKG10 solution in DMSO ($\lambda_{ex} = 365$ nm). The power at the front of the cuvette was 2.1 mW.

2.3. Conclusion and perspectives

In conclusion, a new molecule was presented, π -diketone-2,3-didecyloxyanthracene, which can be turned into a DDOA gel in DMSO upon an external light-trigger. The quantitative photodecarbonylation of the progelator under 450±25 nm converts dkDDOA into DDOA by liberation of two CO molecules inducing the gelation at supersaturation. The efficiency of the photoconversion is proven to be lower in the highly polar DMSO than toluene due to an increase in the nonradiative pathways and the $\Phi_{\rm R}$ was seen to be more efficient in the UV (336 nm) than in the blue (468 nm).

A more in depth study on the photogelation showed that the photoinduced gels are very similar to the thermally prepared DDOA gels, but present a slight increase in structural defects. FLIM and time resolved fluorescence lifetimes showed that the average lifetime of the photoinduced gel is 2 ns longer than the thermally prepared gel indicating possible dipolar coupling. Temperature dependent absorption measurements and fluorescence quenching experiments verified this hypothesis and showed that the defects are caused by the incorporation of dkDDOA into the DDOA fibers upon self-assembly. The incorporation is especially seen at higher concentrations of dkDDOA which increases the static quenching of the DDOA emission at 436 nm. Another possibility to verify the increase in excimer-like emission would be by performing hyperspectral imaging. This technique could give more information about the packing due to the potential to obtain an emission spectrum for each pixel. It provides the possibility to study the possible contributions of different emitters within in one fiber or an ensemble of fibers and hence the identification of defects packed within the supramolecular structure. Unfortunately, the relative high powers needed for this technique are not compatible with DDOA, since it is too sensitive to photobleaching.

Despite the spectral overlap of dKG10 with the excitation wavelength and the subsequent photo-oxidation, the incorporation of 2 mol% of the photoactivatible tetracene, dKG10 did induce efficient energy transfer. This shows the potential to perform colour patterning through the photodecarbonylation of matching diketones. One could imagine two-colour patterning in single fibers or micropatterning with a focused laser. However, to overcome the photo-oxidation of the tetracene a constant nitrogen/argon flow or an oxygen scavenger might be needed to maintain an inert atmosphere during microscopy experiments.

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3

Control over the self-assembly at nanoand microscales: photopatterning of DDOA nanofibers

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In Chapter 2, we have shown that the bulk gelation of DDOA can be efficiently controlled by photochemically converting a DMSO solution of the progelator dkDDOA. Here, a new method is described to photopattern defined nano-objects of DDOA by changing the blue divergent LED for focused laser illumination. The control over the self-assembly on the surface with focused laser light provided *spatiotemporal control* and *anisotropic alignment*.

3.1. State of the art alignment techniques of self-assembling materials

In this paragraph, the anisotropic alignment of three classes of self-assembling materials are described. This will provide a small overview of the techniques developed in different research areas to control self-assembly in creating patterns and/or anisotropic materials.

The first technique presented is the patterning and alignment of *n*-acenes single crystals for field-effect transistors. It describes the anisotropic crystallization of conjugated molecules and nicely highlights the parameters to control in order to better govern the nucleation and growth. These are the same parameters which control the fiber formation of DDOA. The second example concerns the photopatterning of liquid crystals and demonstrates how light can aid in the alignment. Finally, an overview will be given of the vast amounts of methods already used to align LMWGs and DDOA in particular. During the discussion, important parameters to efficiently govern nucleation and growth (i.e. the mechanism that governs the gelation of DDOA) will be highlighted.

3.1.1. Alignment of single crystals for organic field effect transistors

As for many LMWGs, single crystals grown for organic field effect transistors are controlled through nucleation and growth. Single crystal based transistors became of high interest, because of the low content of defects which is thought to guarantee a better charge mobility than their thin film counterparts. However experimentally, the crystallization has to be controlled in a scrutinous manner to obtain high performing devices. Indeed, any defects at the molecular scale such as grain boundaries would be detrimental for the electronic properties of a macroscopic device.^[1] Therefore, a good understanding of the necessary experimental parameters to govern the fabrication of anisotropic materials can be found in this field.

Briseno *et al.* were the first to report full spatial control over the growth of several *n*-acenes based single crystals (rubrene, pentacene, tetracene or anthracene) through a surface pretreatment^[2,3]. The growth of vapour deposited crystals was restricted to microcontact-printed film domains of octadecyltriethyloxysilane (OTS) on a Si/SiO₂ surface. More importantly, by tuning the size of the OTS film domain, the nucleation density could be controlled to one crystal per area. Thereby, the stochastic nature of nucleation can be overcome and surface selectivity is demonstrated. In addition, this technique provides a breakthrough in device

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fabrication since the direct crystallization on the substrate replaces tedious hand-picking of previously sublimated fragile single crystals.

Other pioneering methods, based on solution-processing, were also developed in the group of Bao and co-workers. The easier processing from solution allows direct crystallization over larger substrates and is better suitable for industrialization. The techniques discussed below are droplet-pinned crystallization^[4] (DPC) and solution shearing^[5,6]. These methods do not only allow to cover larger surfaces, but do so in a directional manner.

In DPC, the solution is 'pinned' with a piece of silicon wafer on a divinyltetramethylsiloxane bis(benzylcyclobutene) coated Si/SiO₂ surface. During the controlled heating, the drop gradually evaporates creating aligned crystals according to the receding direction (Figure 3.1). The directionality in DPC depends on two requirements: a high nucleation density and a steady receding of the droplet. Supersaturation, the critical concentration to evoke a nucleation event, is achieved at the contact line through the mentioned solvent evaporation. The technique was proven to be successful with fullerene-C₆₀ and TIPS-pentacene. Furthermore, the morphology of crystals was shown to be dependent on the solvent, since mxylene solutions of C₆₀ yielded needles whereas carbon tetrachloride solutions of C₆₀ gave ribbons.



Figure 3.1^[4]: Schematic illustration of the DPC method. (Image is a reprint from ref 4).

Solution shearing concerns the homogeneous spreading of a solution of organic semiconducting material over a heated surface with a drag plate. The drag plate provides the necessary directionality of the crystallization upon solvent evaporation. This adds another variable where the morphology depends on the shearing rate. At slow shearing rates (0.4-2.8 mm.s⁻¹) the solution of TIPS-pentacene forms crystal rods according to the shearing direction, whereas at higher rates (4-8 mm.s⁻¹) the directionality disappears which results in an isotropic coverage of the surface (Figure 3.2a). The shearing plate and bottom substrate were pre-treated with OTS (hydrophobic crystalline layer) and phenyltrichlorosilane (PTS) (good wetting ability for the TIPS-pentacene solution) respectively.



Figure $3.2^{[6,7]}$: (a) Schematic illustration of the solution shearing of TIPS pentacene and the dependence of the morphology on the shearing rate at 1.6 and 8 mm.s⁻¹. (b) Patterned Si/SiO₂ surface to better direct the anisotropy of the crystallization. The triangles temporarily 'pin down' the drag plate to induce nucleation. The pattern provides surface selectivity and overcomes grain boundaries. Birefringence of the made crystals is shown with crossed polarizers proving the unidirectionality during the crystal growth. (Images are a reprint form ref 6 and 7).

Recently, the solution shearing method was improved by pre-patterning the surface of the device and including microgrooves on the shearing plate to allow better mass transport. The pattern is shown in Figure 3.2b, where the triangles and following bands are consisting of grafted PTS. The triangles temporarily 'pin down' the shearing plate to induce a nucleation event and the continuing stripes prevent any undesired crystal growth to minimize grain boundaries. The resulting anisotropic bands of single crystals are shown in Figure 3.2b under crossed polarizers.

In summary, the previously described examples show that surface selectivity can aid in obtaining spatial nucleation and influences its density. A better affinity of the molecules for the surface increases the probability for the material to nucleate and overcome the stochastic behaviour of nucleation by decreasing the energy barrier needed to initiate a nucleation event. Directionality is achieved by a combination of surface selectivity (nucleation density) and a guiding mechanical force (the shearing or receding solvent droplet upon solvent evaporation).

3.1.2. Photoalignment of liquid crystals

A recent example of aligning a self-assembling material with light can be found in the field of liquid crystals (LCs). The importance of this process is illustrated by its commercialization for the production of LC displays.^[8] LCs or mesogens are a state of matter, which is an intermediate between a crystalline solid and an isotropic liquid, *i.e.* structured liquids. Therefore, they possess the mechanical properties of a liquid such as high fluidity and

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droplet coalescence, but also exhibit anisotropy in their optical, electric and magnetic properties. This is induced by the anisotropic shape and aspect ratio of the LC and provides a long-range orientation order in the material due to interactions (see paragraph 1.2) between the liquids crystalline molecules and align as an ensemble. The different shapes of LC mesogens are categorized into rod-like (calamatic), disk-like (discotic), board-like (sandic) or bent-shaped mesogens. The corresponding temperature dependent phases and two examples of liquid crystalline molecules are shown in Figure 3.3.^[9]



Figure 3.3^[9]: The different anisotropic shapes of liquid crystals and their mesophases depending on the temperature. Below an example of a rodlike and discotic liquid crystalline molecule is shown. (mesophases diagram is a reprint from ref 9).

In order to efficiently exploit the anisotropic physical properties in rod like liquid crystalline molecules, the long axis, better known as the director (n) (see Figure 3.3), of the molecules has to be aligned along the preferred direction. Uniform alignment can be achieved by applying an external field which is either electric^[10] or magnetic^[11]. The induced or permanent electric dipole of the molecule, depending if the LC is a polar or non-polar molecule, will interact with the applied field and align accordingly.

Besides applying an external field, the LC can also be aligned by interfacial interactions with a solid substrate. The LC molecules at the interface will experience a different environment than the bulk LC due to different molecular interactions at the surface. However, the bulk LC adapts itself according to the interfacial LC and hence aligns the whole film without applying an external field. It is the long-range orientational order, non-covalent interactions, among the LCs, which provides the driving force for these cooperative effects. The alignment of nematic LCs can be surface-mediated by using anisotropic substrates.^[12]

The most conventional method to create an anisotropic substrate, or *alignment layer*, is by mechanical rubbing. The simple unidirectional rubbing of a polyimide coated glass surface aligns the polymer chains by frictional heating and creates parallel laying grooves. The LCs close to the rubbed polyimide layer will lay parallel to the rubbing direction to minimize the surface energy and will extend the order into the LC bulk on a macroscopic scale.^[13] Although the technique is simple and allows to treat large surfaces, the generation of dust and electrical charges introduces defects. In addition, the rubbing technique only allows a uniform alignment and no spatial control can be obtained. Therefore, ideally, the surface alignment would be achieved by a non-contact technique.

In order to achieve this, a photoalignment method was developed. The photoalignment effect is created by angular irradiation of a pre-treated surface with a thin film of photoresponsive material with linearly polarized light. The linearly polarized light induces an anisotropic response of the photoactive material, hence aligning on the substrate and subsequently transferring the anisotropy to the LCs at the interface and subsequently the bulk. A much used mechanism introduced by Ichimura and co-workers is the E/Z photoisomerization of an azobenzene monolayer grafted on quartz used to reversibly align a nematic LC.^[14]

Azobenzene is a well-known 'photochromic' molecule (see also paragraph 1.5).^[15] It is particularly interesting due to the large change in conformation and dipole moment. The *trans*-configuration has a length of 9 Å and a dipole moment of 0 Debye, whereas the *cis*configuration has a length of 5.5 Å and a corresponding dipole moment of around 3 Debye.^[16] The reversible conformational change and the ease to synthesize modified azobenzenes makes it a very well studied molecule used to induce geometrical changes^[17] or translational motion as shown by Ishow *et al*^[18].



Scheme 3.1: (a) The photoalignment of azobenzene with linear polarized light. The *cis-trans* isomerisation reorientates the molecule along the long axis perpendicular to the polarization of the UV light source. (b) Representation of the photoalignment of azobenzene on a solid surface.

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By exciting the azobenzene with, in this example, vertically polarized UV light the azobenzene will undergo a series of E/Z isomerisation reactions until it is perpendicular to the light source and does not absorb anymore. Then it will relax back thermally to the rod like trans conformation. Over time, all grafted molecules will reorientate perpendicular to the light source resulting in an anisotropic aligned surface (Scheme 3.1).

Ever since the discovery of Ichimura different azobenzene containing materials have been investigated such as azo-dye containing polymers^[19] and diazo laser dyes^{[20][21]}. In the case of the diazo dyes, the E/Z isomerisation has never been proven to be the working mechanism for the alignment in contrast to the other azobenzene based materials.^[21]

A recent new method reported by Seki and co-workers aligns a LC polymer without the use of a pre-treated surface. By blending a LC polymer with another photoresponsive LC polymer (azobenzene block polymer) a photoresponsive 'command skin layer' (alignment layer lays on top) is created through phase segregation upon annealing the mixture. Applying the command skin layer by inkjet printing allowed spatial control and patterning after irradiating the device with UV light. Soaking in cyclohexane removed the skin layer without dissolving the LC polymer nor changing its alignment (Figure 3.4).^[22,23]



Figure 3.4^[22]: (a) Inkjet printing of the skin command layer onto a perpendicular aligned LC polymer followed by a annealing step and the irradiation with polarized light at 80 °C to align the made pattern parallel with the solid surface. (b) An example of a made pattern under crossed polarisers showing the directionality. (Images are a reprint of ref 22).

Other reported methods are the anisotropic photodegradation of polyimide thin films or the [2+2] cycloaddition of coumarin and cinnamates.^[24-26]

Polymer chains parallel to the UV polarized light source will absorb a maximum of photons and undergo a (retro) [2+2] cycloaddition changing the length distribution of the polymer chains in one direction allowing anisotropic alignment (Figure 3.5)



Figure 3.5: Photodegradation reaction of polyimide with linear polarized light.

Besides the surface-mediated alignment of nematic LCs there is also a technique reported which uses direct irradiation of the discotic triphenylene (see Figure 3.3) with infrared light. An alignment was observed by exciting the aromatic C-C stretching vibration at 1516 cm⁻¹ of the triphenylene.^[27,28]

3.1.3. Anisotropic alignment of LMWGs

In the field of LMWGs also extensive research has been done to obtain more control over the growth direction of the nanofibers. In contrast to crystals, the 1D growth in LMWGs already provides directionality. Therefore, aligned fibers can be an interesting alternative to the above mentioned classes of self-assembling materials. Normally, isotropic networks are obtained, but aligned fibers or a certain degree of alignment can be induced by several external stimuli. For example, flow^[29] and shear forces^[30], electrical^[31–33] and magnetic fields^[34,35], gradual cooling or chemical gradients^[36]. Other techniques include liquid crystal assisted alignment^[37] (see paragraph 3.1.2.), rigid macrocycles^[38,39] or Langmuir-Blodgett films^[40]. The similarity in all mentioned techniques is that the external stimulus provides the necessary directionality.

DDOA has also been subjected to several alignment studies using some of the abovementioned techniques. A major interest in aligning DDOA nanofibers resides in the resulting organization of the anthracene chromophores at multiple scales, from nano- to milli-scales. Therefore, an aligned network of chromophores gives rise to polarized emission and birefringence.

Our group studied the alignment under mild constant shear forces^[41] and a high magnetic field^[42] at high concentration in DMF and *n*-butanol, respectively. The procedure contains the similar feature, where a heated solution of DDOA is gelated by controlled cooling under the influence of the external force.

The alignment under shear forces produced birefringent macrofibers 0.5 mm thick and several centimetres long by immersing the tip of a heated syringe (75°C) into a rotating polymer solution. Fibers are formed at the end of the needle due to a cooling effect and small shear rates. Figure 3.6 shows the dependence of the transmitted light versus the angle of the long axis macrofiber and the main axis of the polarisers.



Figure 3.6^[41,42]: (a) Shear-aligned DDOA and the fluorescence intensity upon angle. (b) Magnetic aligned DDOA and the fluorescence spectrum perpendicular and parallel to the fiber. B gives the direction of the magnetic field. (Images are a reprint of ref 41 and 42).

The susceptibility of DDOA to applied external magnetic fields comes from its diamagnetism. The diamagnetism of a single molecule, however, is too weak to overcome random thermal motion (Brownian motion). In contrast, an ensemble of ~ 60000 aggregated DDOA molecules acts as a unique microstructure with increased magnetic susceptibility that aligns along the external field. As a result, all fibers orient perpendicular to the magnetic field. Within these fibres, the anthracene core was found to be oriented in average at an angle below 45° relative to the very high magnetic field (20 T). This results in measurable birefringence and polarized emission (see Figure 3.6).

Kato and co-workers took another approach by gelating DDOA in the liquid crystalline 4cyano-4'-pentylbiphenyl (5CB) or 4-cyano-4'-octylbiphenyl (8CB). Anisotropic LC gels were obtained by dissolving 9,1 mol% of DDOA in 8CB at 80°C and letting it cool down in a parallel rubbed cell (paragraph 3.1.2. Photoalignment of liquid crystals). The phase transition of 8CB from isotropic to smectic A (mesophases are shown in Figure 3.3) aligns the DDOA molecules/aggregates at a higher temperature (42°C) before the sol-gel transition of DDOA is reached. The alignment was proven to be solely due to the LC alignment and not surface induced, because no anisotropy was observed from cooling down a hot *n*-butanol solution of DDOA in a parallel rubbed cell. They also found the fibers were aligning perpendicular to the long axis of the LC.^[43]

In this chapter, we go a step further by patterning micrometre sized anisotropic nano-objects on isotropic surfaces in contrast to epitaxy^[44,45]. The patterns were made by spatially controlling the nucleation density of DDOA through the photoconversion of dkDDOA in solution at room temperature. The patterning and analysis were done by using a confocal laser scanning microscope as a writing and analytic tool. Therefore, a brief introduction will be given on the principles of confocal microscopy before discussing any results.

3.2. Principles of confocal laser scanning microscopy

Scheme 3.2 gives the used set-up throughout all experiments and allows to explain the principles of confocal laser scanning microscopy (CLSM).



Scheme 3.2: Schematic overview of the Confocal Laser Scanning Microscope and its working principle. In this setup, the sample is scanned in x-y and the objective is scanned in z (vertical), thereby determining the position in z of the fixed focal point.

The laser (375, 473 or 770 nm) is sent though an optical fiber to deliver a Gaussian shaped beam. The combinations 375/770 or 375/473 nm are used separately by using a flip mirror (FM1). The selected laser beam is then reflected by the dichroic mirror (DM) and focused (in a diffraction limited spot) by the 100x objective onto the sample which is positioned in the focal plane of the objective. The portion of the sample exposed to the laser waist is excited, more intensely at the focal point, and emits fluorescence in all directions. Part of the light emitted from the sample along with scattered excitation light is collected back through the same objective and is transmitted by the dichroic mirror which reflects most of the backscattering of the laser beam. Residual scattering intensities are removed by an additional blocking filter (BF). The transmitted light is imaged by a tube-lens (TL) onto a pinhole aperture before it reaches a detector. The image focused on the pinhole corresponds exactly to the excitation spot in the sample, that is why the pinhole and the laser spot are said to be "confocal" (cyan dots). Any fluorescence light originating from another plane than

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the confocal point (depicted as the red dots) is doubly discriminated by the laser waist geometry and the mismatch with the pinhole. Therefore, the addition of a pinhole results in sharper images than with conventional fluorescence microscopy, especially in dense 3D samples such as gels. The image is then formed by scanning of the excitation volume in a plane. Furthermore, it allows to obtain virtual optical slices enabling 3D-reconstruction. After passing the pinhole, the focus is replicated at infinity by a collimating lens (CL) thus creating an infinity space. The beam passes through a 50/50 beam splitter (BS) that dispatches the signal on two time resolved photon counters. The SPAD (Single Photon Avalanche Diode) detector, in combination with a pulsed excitation laser, allows to measure the fluorescence decay by the TCSPC technique (Time Correlated Single Photon Counting) for each pixel of an image, generating a FLIM image.

For this study, the same setup could also be switched to widefield illumination where the fluorescence of the sample is transmitted onto a sCMOS camera, see Scheme 3.3:



Scheme 3.3: Set-up for epi-illumination.

In this mode, the sample is illuminated evenly on the field of view with a LED (375 nm, epiillumination), by imaging the LED on the back focal plane (BFP) of the objective. The fluorescence passes through the same dichroic mirror and blocking filter as in CLSM mode, but is then diverted in a second pathway where it is imaged by a tube-lens (L2) on a sCMOS camera.

The resolution in optical microscopy is limited by the diffraction of emitted light. The lateral resolution (d_{min}) and axial resolution (Z_{min}) are defined as:

$$d_{min} = \frac{0.61\lambda}{NA} \qquad \qquad Z_{min} = \frac{1.44\lambda}{NA^2}n \qquad (4.1)$$

Where λ stands for the emission wavelength, NA is the numerical aperture of the objective lens and n is the refractive index of the medium. The emission of DDOA in DMSO is around 411 nm ($\lambda^{\text{em}}_{\text{max}}$) and the NA of the 100x objective lens is 1.4 limiting the theoretical lateral and axial resolution to 176 and 447 nm, respectively.

As mentioned before, the confocal laser scanning microscope could also be used to locally induce photoreactions, thus function as a photolithography tool. Photopatterning is achievable in all directions with high accuracy of positioning (\pm 10 nm) due to the sensitive piezo stage allowing spatiotemporal control. For the patterning of the DDOA nano-objects, the excitation wavelength is 473 nm (continuous, monophotonic) or 770 nm (150 femtosecond pulse, biphotonic, 13kW.cm⁻²). The analysis and imaging of the created patterns were done with a 375 nm LED in wide field illumination in combination with the sCMOS or a 375 nm laser diode in confocal mode by the excitation of DDOA. All ecperiments are performed under N₂ atmosphere.

It is important to mention again that dkDDOA also absorbs at 375 nm (π - π^* band at 350 nm in DMSO). Therefore, imaging under wide field illumination with the 375 LED promotes further growth after photopatterning. This feature has been exploited for directing fiber growth and will be explained in more detail in paragraph 3.3.2. Effects of water addition on the photoconversion The same is however, not observed for the 375 laser diode. This is probably due to the low powers used in confocal mode.

3.3. Results and discussion

3.3.1. Preliminary results

The experimental conditions used in Chapter 2 (1 mM dkDDOA solution in DMSO) were directly translated to initiate the study of photopatterning of DDOA under the microscope. Unfortunately, apart from the fiber formation being induced in vicinity of the focal point of the laser, experiments were irreproducible and uncontrollable. Fibers even redissolved in the dark. Therefore, actual spatial and temporal control were not achievable and prevented an in-depth study of the new photoactive system. Since the uncontrolled contribution of humidity became an obvious reason for the irreproducibility, photopatterning was performed with a controlled amount of H_2O .

3.3.2. Effects of water addition on the photoconversion

A simple photopatterning experiment consists of irradiating with a focused laser beam a dkDDOA/DMSO solution *above* the cgc of DDOA at the glass-solvent interface. Repetitive linear scans ("line scans") are used in the aim to produce a "linear" pattern, either "blindly" *i.e.* without simultaneous observation, or by monitoring the light scattered by the sample. The surface was imaged by epi-fluorescence microscopy after the irradiation process in order to analyze the fluorescent aggregates formed at the irradiated spots and around.

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In a first experiment, the aggregation was induced with a 473 nm continuous laser diode. The amount of H_2O in solution was gradually increased, in vol%, while keeping all other parameters constant: the power is 2.2 W.cm², the overall concentration of dkDDOA 2 mM and the sample volume is 100 µL. The evolution of the photopatterning was followed during irradiation by the diffraction of the laser and irradiation was stopped when the scattering became intense.

The confocal images in Figure 3.7 show that fibers are formed around the irradiated line. In addition, the origin of the fibers can be attributed to nucleation sites, which are confined in the irradiated line (0-5 vol% H₂O). Interestingly, the density of nuclei increases with the amount of water. In addition, with the increase in nuclei there is also a visual decrease in the length of the fibers. The average length was, however, difficult to estimate for the whole series, because the fibers tend to grow out of plane for samples with 0 or 1 vol% of H₂O.



Figure 3.7: Line of nuclei made by repetitively scanning a 473 nm diode laser (2.2 W/cm²) across 70 μ m on a borosilicate glass surface. The concentration is 2 mM dkDDOA in DMSO with 0-10 vol% of H₂O. The total volume is 100 μ L. Scan was stopped when objects were detected by laser diffraction. The images were taken by exciting the made DDOA at 375 nm by wide field illumination. Scale bar is 10 μ m.

In a second experiment, the average time of appearance of nuclei was probed by detecting the laser diffraction at the glass/sample interface during a stationary irradiation with the 473 nm laser diode. Figure 3.8 shows that the time of appearance decreases exponentially with the addition of H_2O . Furthermore, the nucleation time is highly irreproducible at a low concentration of water emphasizing the importance to control the amount of H_2O present in the hygroscopic DMSO. However, this improves gradually with the addition of H_2O , which favours the nucleation of DDOA upon photoconversion and induces a reduction of the nucleation time.



Figure 3.8: Average nucleation time vs. the amount of H_2O with a concentration of 2 mM dkDDOA at 473 nm (2.2 W/cm²). The total volume is 100 µL. The exponential is a guide to the eye.

In order to clarify whether the effects previously described results occur only on the surface or also in the bulk, a solution of dkDDOA was irradiated using wide field illumination (Figure 3.9). As mentioned in paragraph 3.2., the illumination at 375 nm excites dkDDOA and DDOA simultaneously enabling real time analysis. The images were taken at 15 μ m from the glass interface. They reveal the formation of "star-shaped" aggregates with fibers growing away from dense nucleation sites (Figure 3.9). The length of the branched fibers visibly decreases with the increase of water concentration. At the same time, the amount of objects increases significantly. This confirms that water favours nucleation and inhibits lengthening of fibers. A large excess of water results in the formation of confined fluorescent particles, reminiscent of previously studied DDOA nanoparticles obtained by reprecipitation in H₂O.^[46]



Figure 3.9: Irradiation of a 2 mM dkDDOA in DMSO with 0 to 50 vol% of H_2O in the volume with a 375 LED. The total volume is 100 μ L. Scale bar is 10 μ m.

The formation of nuclei at the glass/solvent interface while varying the concentration of dkDDOA and not the water content also reveals an increase in nucleation density while

increasing the concentration of dkDDOA from 0.5 to 3.0 mM (see Annex A). Here, the amount of H₂O and the sample volume are constant at 5 vol% and 100 μ L, respectively. The fiber length also showed a modest decrease. The average fiber length for the solution of 0.5 mM is 13.2±1.6 μ m whereas for the solution of 3 mM the average length is 5.7±0.8 μ m.

In contrast, in the volume a different tendency was observed. No clear visual difference in number of nuclei was observed and the fibers have the same appearance in length (see Annex A). These results indicate that the nuclei density is related to the added amount of H_2O and results in shorter fibers and even particles at large excess.

Besides the nucleation density and the length of the fibers, we also measured the influence of H_2O on the actual growth speed. Indeed, after the formation of the nuclei with the 473 nm laser diode, the growth can be analyzed real-time with the epi-illumination at 375 nm. Therefore, after imaging the outcome of the line irradiation in Figure 3.7 the illumination with 375 nm was continued on the same samples to estimate the growth speed. This is the first time such an analysis has been attempted for DDOA. The preliminary results are shown in Figure 3.10.



Figure 3.10: Growth speed distribution of DDOA fibers versus the amount of H_2O (0 to 5 vol%) under the 375 nm widefield illumination (0.65 μ W). Total volume was 100 μ L. Analysis was done with MTrack (https://imagescience.org/meijering/software/mtrackj/).

The graphs for 0 and 1 vol% have been obtained on a shorter timescale than the others, because after the nucleation with the 473 nm laser there were already short fibers present under wide field illumination. Furthermore, since the fibers eventually grow out of plane, the final length given in Figure 3.10 does not correspond with the actual length of the fibers. Nevertheless, certain trends can be deduced: (i) the increase in nuclei density and the growth speed are correlated to the addition of H_2O . The fibers with 0 to 1 vol% H_2O grow faster than the ones of 2, 3 and 5 vol% H_2O ; (ii) the samples with higher water content reveal an induction period in the beginning; (iii) the growth speed is not uniform, especially at higher concentration of H_2O .

Point i and iii are related to the increase in nuclei, since the increasing amount of nuclei creates a subsequent increase in growing fibers while the concentration of available DDOA stays roughly the same through the series of experiments. Therefore, looking at a single fiber, the growth is limited if the nuclei density increases. Furthermore, the increase of number of fibers on the dense line of nuclei also increases the chance of steric hindrance or bundling thereby affecting the growth speed.

Overall, H₂O also has a clear influence on the growth speed and for the first time in the study of DDOA, a mechanism has been presented which allows to more accurately determine the growth speed. The average speed at 0.65 μ W is in the range of μ m.s⁻¹. Further experiments however are needed to confirm these preliminary results.

3.3.3. Effects of H₂O on DDOA

In order to better understand the overall effect of H_2O on the system, additional spectroscopic studies on macroscopic gels of DDOA were combined with microscopy analysis (FLIM). T_{gel} and T_{melt} of DDOA gels were measured by monitoring the change in absorption of the 0-0 transition at 384 nm upon temperature (see Chapter 2). In the presence of 0 to 5 vol% of H_2O for a concentration of 1 mM of DDOA, the gelation temperature increases from 28°C to 40°C respectively. The melting temperature also increases with the addition of H_2O and ranges from 38 to 49°C (see Figure 3.11). The hysteresis (typical in LMWGs) is constant with the same difference of $10\pm1°C$ between the melting and gelation temperatures, as reported by previous experiments.^[47]



Figure 3.11: (a) Cooling curve of 1 mM DDOA in DMSO/H₂O. (b) Heating curve of 1 mM DDOA in DMSO/H₂O. (c) Corresponding T_{gel} and T_{melt} at 0, 1, 2.5 and 5 vol% H₂O. The temperature range was 293 to 353 K, 1 K/min. Curves are obtained by plotting the absorbance at 384 nm and recalculate it to the degree of aggregation.

Although the absorption allows to analyse DDOA aggregation in the bulk, the higher sensitivity of fluorescence in the aggregated state can be exploited to unravel more details on what can induce such a difference in T_{gel} and T_{melt} . Indeed, the fluorescence intensities and lifetimes even reveal small changes in environment as proven in Chapter 2. Previous studies

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on DDOA, already shown the aggregation is induced by the addition of antisolvents, as is the common trend for a large variety of fluorophores.^[48,49]

The average fluorescence intensity of DDOA measured in solution during photoconversion is shown in Figure 3.12 (375 nm LED illumination 0.65 μ W, wide-field detection by sCMOS camera) and decreases with the addition of H₂O. The fluorescence decrease can be related to lower concentrations of DDOA in solution or a quenching process. The latter was further investigated with FLIM images and bulk gel lifetime measurements.



Figure 3.12: Mean greyscale intensity of DDOA vs. the amount of H_2O just before the appearance of nano-objects on the surface monitored by the SCMOS camera. Photoconversion performed with 375 LED at 0.65 μ W.

Figure 3.13a shows the FLIM images of gels obtained by thermal cooling of DDOA solution with and without addition of water. The average fluorescence lifetimes of DDOA in the fibers decreases with the addition of water. DDOA in the dry DMSO gel emits with an average lifetime of 6 ns (biexponential decay, Chapter 2), whereas the emission of the gel self-assembled in DMSO/H₂O (5 vol%) decays according to a three exponential function with fitted lifetimes of 12.6 ns (3.3 %), 4.1 ns (84 %) and 1.5 ns (12.7 %) resulting in an average lifetime of 4.9 ns. The fluorescence decay measurements in the bulk gels (Figure 3.13b) also show that the lifetime decreases with the addition of H₂O.

Previous studies on DDOA gels in DMSO have demonstrated that a decrease in fluorescence lifetime of the excited DDOA in the gel state can be related to the presence of non-emissive exciton-traps, which can be small amounts of impurities or structural defects. Therefore, the decrease of the fluorescence intensity and lifetimes of DDOA upon addition of H₂O can be related to the presence of few percent of less ordered sites within the fibers acting as excitontraps, as in the case of dkDDOA inclusion (Chapter 3). The amount of defects appears to increase with the addition of H₂O, although the actual percentage of traps remains low. By comparison, remember that the addition of 1 % of a tetracene derivative can totally quench DDOA emission^[50] due to energy transfer processes combined to exciton hopping. A mechanism involving diffusional quenching of DDOA emission by water could not be evaluated due to the complete absence of knowledge of the photophysical properties of DDOA in water in which the molecule is insoluble.



Figure 3.13: (a) FLIM image of a 1 mM DDOA gel made by dropcasting a hot solution of DMSO or $DMSO/H_2O$. (b) Fluorescence decays of a 1 mM DDOA gel in DMSO with variable vol% of H_2O .

At first sight, the fluorescence data and the thermodynamic data (gel formation/melting temperatures) are contradictive. The defects responsible for the decrease in average lifetime should lead to a destabilization of the DDOA assembly and a resulting decrease of the T_{gel} and T_{melt}. However, the latter temperatures reflect not only the stability of the assembly, but also the solubility of DDOA. The solubility of DDOA in water is negligible, and the addition of water to DMSO strongly decreases the solubility of DDOA in the mixture. This explains the increased thermodynamic driving force towards DDOA aggregation and subsequent increase in T_{gel}. The lower solubility of DDOA with the addition of H₂O induces a fast supercooling and increases the crystallographic mismatch nucleation^[51]. In other words, the lower solubility enhances the nucleation and the degree of defects in the resulting fibers inducing branching. Therefore, the corresponding values of the T_{melt} are higher with the addition of H_2O , because the fiber branching creates more junction points or entanglements in the gel. Both the primary nucleation and the supersaturation are related to the solubility of the LMWG. The same effect can be obtained with the addition of additives, like surfactants or polymers.^[52,53] The FLIM images in (Figure 3.13a) emphasize the change in gel morphology with the concentration of H_2O , and in particular the number of nucleation sites per unit volume increases with water content.

In addition to the altered aggregation of DDOA, the behaviour and the contribution of dkDDOA has also to be considered. In fact, increasing the concentration of dkDDOA in DMSO/H₂O (5 vol%) to 4 mM or higher resulted in the formation of obvious crystals on the glass surface. The crystallization of dkDDOA with the addition of H₂O resembles a similar procedure which is highly exploited in the pharmaceutical industry named antisolvent crystallization^[54]. It corresponds to the continuous addition of an 'antisolvent', in most cases H₂O, into a miscible solvent to reach supersaturation without any heating or cooling cycles
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to induce the crystallization of temperature sensitive molecules. The technique is also known to influence the selection of crystalline polymorphs.

The application of this method in the bulk on dkDDOA yielded crystals that were large enough for X-ray crystal structure analysis. Flat orange crystals are obtained from a solution of 5 mM dkDDOA in DMSO in a humid environment to induce the diffusion of water vapour in the dkDDOA solution. In Figure 3.14 the crystal structure shows that dkDDOA packs in a monoclinic Pc space group with a carbonyl dihedral angle (O=C-C=O) of 6.5° revealing a slight torsion in the molecule. The corresponding n- π^* absorption maximum of 468 nm is in correlation with a previous study showing the absorbance maximum of the n- π^* transition is related to the intercarbonyl dihedral angle. Studies on the correlation between the carbonyl dihedral angle and the absorption maximum of the n- π^* transition shows a gradual decreases when the angle varies from 0 to 90°.^[55]



Figure 3.14: Crystal packing of dkDDOA in $DMSO/H_2O$ along all axes from X-ray diffraction. Space group = monoclinic Pc. The carbon atoms of the alky chains are grey, the diketone bridgehead orange and the benzene rings green for more clarity in the packing. Oxygen is depicted in red.

More interesting, the crystals consist of pure dkDDOA, revealing that there is no inclusion of the hydrolysed form. This shows that in supersaturated conditions the diketone moiety does not hydrolyse, while it is known to be sensitive towards nucleophiles. This contrasts with the hydrolysis observed at lower concentrations of dkDDOA (0.5 mM), which was observed on a longer timescale (a day). The lack of hydrolysis is also confirmed by the preservation of the photoreactivity as shown on these crystals. Indeed, a 473 nm irradiation yields a change of the emission colour from orange to blue and even results in the formation of fibers on the crystalline surface. Since, the photoconversion of the hydrolysed form has been reported to not generate the corresponding n-acene.^[56]

At the same time, we also observed partial disassembly of the crystals upon irradiation. The disassembly is most likely due to the disappearance of the 1,2-diketone bridge, crucial for the crystallization of dkDDOA (see Figure 3.14), as gaseous carbon monoxide. The same was

reported by Masuo *et al.* for the photoconversion of crystals of 1,2-diketonepentacene.^[57] They clearly observed the photoconversion taking place within the crystal with a maximum penetration depth around 2 μ m ($\lambda_{ex} = 488$ nm), which induced the destruction of the single crystal through rearrangement or CO expulsion.

More quantitative values on the possible hydrolysis, such as reaction rate constants and equilibrium constants in the supersaturated conditions were not obtained due to the aggregation of dkDDOA. The crystallization of dkDDOA at 4 mM upon addition of H_2O can be extrapolated to lower concentrations, albeit no aggregates were observed by optical microscopy techniques. Nevertheless, from the presented results we can deduce that the direct addition of H_2O induces to some extent the formation of dkDDOA aggregates in supersaturated conditions, which upon irradiation progressively convert into DDOA aggregates. This mechanism is supported by the increase in DDOA nuclei upon photoconversion with a gradual increase in water content leading to an eventual aggregation/crystallization of dkDDOA in solution. Furthermore, the faster nucleation seen in Figure 3.8 indicates a higher local concentration of DDOA upon photoconversion, which strengthens the interpretation of the existence of pre-aggregates of dkDDOA. The resulting shorter fiber length (Figure 3.7) and induction period in the initial part of the growth (Figure 3.10) indicate a fast supersaturation which reduces the thermodynamic driving force due to the depletion of the local region of available DDOA after the fast nucleation. This results in the growth of smaller, thinner fibers and induced branching. The increase in branching is proven by the higher T_{gel} and T_{melt} for DDOA, as explained previously. Furthermore, the enhancement in primary nucleation increases the amount of exciton traps and thereby decreases in fluorescence- intensity and lifetime. In brief, water induces the local concentration in the form of pre-aggregates of dkDDOA and favours a fast supersaturation of DDOA upon photoconversion.

3.3.4. Surface selectivity

Surface interactions can also influence the self-assembly, as described in paragraph 3.1. ^[58] The gelation of DDOA is no exception and has already been proven to be sensitive towards solvent and nature of the surface.^[59] The surface can influence the nucleation process, and the resulting nucleation density, but also the fiber/surface interactions.^[60,61] Three surfaces differing in hydrophobicity/hydrophilicity have been chosen to study these effects: polysiloxane-coated glass, borosilicate glass and piranha-etched glass. All the surfaces are available or obtained as transparent coverslips to be able to perform microscopy. The water contact angles (WCA) measurements yielded a value of $101.5^{\circ}\pm 0.5$ for the polysiloxane and 61 ± 2 for the commercial borosilicate surface. It has to be noticed that the commercial borosilicate glass most likely have an unknown surface treatment that slightly increases its hydrophobicity as compared to non-treated glass. Untreated borosilicate glass normally has a WCA around 45°. The polysiloxane coating is compatible with DMSO and H₂O, since it does

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not swell in these solvents.^[62] Furthermore, it also has an excellent UV resistance. These are commercially available hydrophobic coverslips, but the exact nature of the surface modification was not provided by the manufacturer. In the case of the piranha-etched glass surface, the WCA was not measurable. This means that water perfectly wets the highly hydrophilic surface and has a contact angle of $< 10^{\circ}$ (the images are depicted in the experimental section).

The influence of the nature of surface on the photopatterning is shown below for a 3 mM solution of dkDDOA in DMSO with 5 vol% H_2O irradiated by a focused laser (770 nm, biphotonic) or by wide field illumination (375 nm).



Figure 3.15: Lines of DDOA fibers obtained by repetitive line scans over 70 μ m with a focused laser on (a) Piranha-etched borosilicate glass, (b). Borosilicate glass and (c) polysiloxane-coated glass. Scale bar is 10 μ m.

In Figure 3.15, the line scans reveal a clear relation between the surface hydrophobicity and both the density of nuclei and fiber morphology. The conversion of dkDDOA on the piranhaetched surface produces nuclei and fiber growth in vicinity of the scanned area, but the confinement of DDOA nuclei is not achieved. The hydrophilicity makes that the formed DDOA nuclei/fibers do not adhere to the surface and diffuse into the solution instead. The result is a random distribution of fibers as seen in Figure 3.15a. In contrast, DDOA has a noticeable better surface affinity for the polysiloxane-coated surface. A dense line of nucleation sites is formed precisely in the irradiated area by the focused laser beam and the resulting fibers are attached to the surface. These even form bundles of fibers, unlike on the other surfaces (see Figure 3.15c). Interestingly, the fibers grow essentially perpendicularly to the scanning direction of the laser. This particular feature will be explored in more details in the next paragraph. In addition, the fibers seem to be less wide. Further investigation of the fiber thickness and width by AFM was however hindered by the presence of residual DMSO even after drying the patterned surfaces. The remaining solvent residues after extensive vacuum drying pollute the AFM tip and impede high-resolution imaging. The option of washing with large volumes of H_2O was discarded due to the precipitation of DDOA under these conditions and a subsequent collapse of the gel fibers.

The untreated glass surface induces an intermediate behaviour. The irradiated line displays packed nucleation sites attached to the surface, but the fibers grow straighter and are less numerous than on the polysiloxane surface. Therefore, the bundling is also negligible. These experiments demonstrate that the spatial control of fiber-patterning is related to the created nucleation density and governed by a combination of factors such as the localization of focused laser illumination, tuning of critical aggregation concentration by the addition of H₂O and tuning of the aggregate/surface interaction by surface hydrophobicity modification. Surprisingly, no clear effect of the laser power could yet be demonstrated. The efficiency of the photoreaction is however most probably another important factor, since a clear difference has been seen in the $\Phi_{\rm R}$ of the photodecarbonylation in different solvents (Chapter 2). However, it was not possible to demonstrate the dependence of solvent polarity on the photopatterning, because no other solvent with all the necessary characteristics was found.

Under widefield illumination, the dkDDOA to DDOA photoconversion also yields different surface coverage of the three different surfaces (see Figure 3.16). When the most hydrophobic surface is used, the DDOA fibers densely cover the surface due to a favourable interaction between DDOA and the hydrophobic polysiloxane surface. Moreover, DDOA fibers form coils maximizing the configurational entropy on the surface.^[63] The nucleation sites are not clearly distinguishable and it can be supposed that the nucleation density is therefore high. In contrast, the coverage of borosilicate glass is less dense and only straight fibers are formed. The nucleation sites are randomly distributed and clearly distinguishable, yielding fiber branches that display preferable angles in spite of being adsorbed to the surface. The preferred angles observed between two branches are around 60, 90, 120, 160 and 180 °, coinciding with the proposed hexagonal packing of DDOA. The molecular structure of the DDOA fibers is proposed to consist of triads with an angle of 60° along the short axis of the aromatic plane within in a triad, whereas the hexagonal unit cell consists of 90° and 120° angles (for clarity the proposed structure is given in Annex B).^[64] The packing was extrapolated from a hexyl chain derivative and indicates that the branching relates to the proposed packing of the DDOA fiber and underlines the previously mentioned crystallographic mismatch nucleation. This special case of heterogeneous nucleation takes place on the crystal layer of the parent crystal and the mismatch growth is reported to not deviate much from the crystallographic orientation of the parent crystals.^[51]

Both types of experiments clearly demonstrate that a link exists between the nucleation density and affinity of DDOA for the surface. This can be exploited to control the surface coverage even further (see next paragraph).



Figure 3.16: Surface coverage of DDOA obtained by wide field ($80x80 \ \mu m$) photoconversion at 375 nm. (a) Polysiloxane-coated glass. (b) Untreated borosilicate glass and (c) the measured angles of the branches. Scale bar is 10 μm .

3.3.5. Anisotropic photopatterning of nanofibers

With a better insight on the parameters that influence the DDOA photopatterning, we attempted to control the distribution of the nanofibers of DDOA on the surface at the microscale. As mentioned in paragraph 3.2. Principles of confocal laser scanning microscopy, a femtosecond pulsed 770 nm laser is used for biphotonic excitation of the dkDDOA to localize exclusively the photoreaction at the surface and limit the photoconversion occurring without control in the volume of the liquid. The solution for photopatterning consists of a 3 mM dkDDOA solution DMSO/H₂O (5 vol%) in order to achieve a high nucleation density on the surface. As shown in Figure 3.17, the combination of these conditions and a tight raster on the surface with successive lines allows to successfully cover a 15x20 micron sized surface with a dense mat of fibers. Clear contours of the surface are obtained at this scale. In identical conditions, a repetitive drawing of a 60x60 micron sized cross also clearly demonstrates the localization of the nucleation and a growth of fibers. The patterns were drawn with an average power of 13 kW/cm².



Figure 3.17: Representation of the photopatterning of micron sized squares. The separation between the raster lines is 125 nm. The average power is 13 kW/cm². Scale bar is 10 μ m.

Interestingly, in contrast to what is well-known in the field of photopolymerisation in photoresins,^[65] the resolution in this dkDDOA/DDOA system is governed by the selfassembly process and not limited by the beam size (and propagation of radicals). At this stage, the smallest well-resolved squares obtained are 5 µm wide and the lines of nuclei around 1 µm. The emission spectrum of the patterned fibers is given in Figure 3.18. It shows that the spectrum has an underlying additional broad band when compared with the emission spectrum of a macroscopic gel of DDOA (orange spectrum). The formation of the corresponding anthraquinone can be excluded (blue spectrum) since the broad peak at 530 nm does not appear. Furthermore, the sample was degassed before patterning. However, "excimer-like" emissions at lower wavelengths have been proposed in previous studies. Correlating this result with the increase in supersaturation upon H_2O addition, the expected reason is again the enhanced detection of structural "excimer-like" emissive defects in the DDOA fiber. This is supported by the study done on 2,3-alkoxylated diphenylanthracene nano-ribbons by Dr. P. Schäfer, where it was shown that faster kinetics of assembly induce some disorder resulting in an additional broad cyan emission band in the overall spectrum. (unpublished results)



Figure 3.18: (a) Emission spectrum of fibers growing from the photoinduced nuclei. (b) Emission spectrum of a macroscopic DDOA gel in DMSO (orange), same as a (black) and the corresponding anthraquinone (blue), respectively.

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A closer look at the patterns made on the surface reveals that the fibers essentially grow perpendicular to the direction of the laser writing, as mentioned in paragraph 3.3.4. To the best of our knowledge, this is the first time such a phenomenon has been seen in the photopatterning of supramolecular fibers. Only one similar case, to our knowledge, has been reported by Reymann *et al.* on the control of the growth of actin fibers by microcontact printing domains with a nucleation-promoting factor (pWA). When the surface is submerged in an actin polymerization mix, the nucleation will only start from the pWA treated areas. Thereby, the nucleation geometry and subsequent fiber growth could be controlled separately.^[66]

In contrast to the actin fibers, DDOA fibers display the particular property to emit polarized light, as mentioned in paragraph 3.1.3. The collective anisotropic arrangement of nanofibers on the surface is particularly well-suited to exploit this anisotropic optical property. Indeed, such an organized pattern should yield polarized emission at the micro-scale, rather than only at the nanoscale. In order to determine if the orientation of the fibers can be controlled, two $20x20 \ \mu m$ squares where patterned with different writing directions, XY (see Figure 3.17a) and YX (90° turn). The degree of anisotropy of the patterned surface can be determined by polarization microscopy. An explanation on polarization microscopy and its principles can be found in the Experimental Section.

As a control experiment, the polarization of the emission of DDOA at the nanoscale is determined on an isotropic sample. In other words, dkDDOA was photoconverted with wide field illumination to obtain fibers in all random directions (no confinement in nucleation). The polar plot representing the polarization as a function of the orientation of fragments of isolated fibers is shown in Figure 3.19.



Figure 3.19: Fitted polar plot of an isotropic sample of photoconverted DDOA on a borosilicate glass surface (left) and the corresponding image (right). Polarization value is given in false colour scale.

The plot demonstrates that the emission is polarized perpendicular to the long axis of the DDOA fibers with a maximum amplitude of 0.16, which is similar to values published previously for DDOA fibers obtained by cooling of DDOA/DMSO solutions^[59]. These previous data have contributed to elucidate the packing of the LMWG within the fiber, by combination with a series of other studies.^[43,64,67-69] In the case of the photopatterning, the polarization of the emission of highly aligned DDOA fibers should have values between 0.2 (fibers perpendicular to the laser source) and -0.2 (fibers parallel to the laser source). In a first experiment, the patterning was performed on borosilicate glass. The distributions of the polarization of both squares are shown in Figure 3.20 in comparison with that of the isotropic DDOA sample of Figure 3.19. The fitting of the distributions shows that average values of -0.05 and 0.1 are reached. The wide distribution and maximum values close to the isotropic sample proof that the fiber direction on the borosilicate surface is more random than expected and the alignment is less enhanced as anticipated by the naked eye observation.



Figure 3.20: (a) Polarization image of an YX scanned square of DDOA on a borosilicate glass surface. (b) Polarization histograms of square a (orange) and c (blue) and the isotropic distribution of Figure 3.19 (black). (c) Polarization image of an XY scanned square of DDOA on a borosilicate glass surface. Polarization value is given in false colour scale.

However, as mentioned in paragraph 3.1.1. for the DPC method, a high nucleation density is necessary to induce crystal alignment. Therefore, we tried the polysiloxane-coated glass since it facilitates the heterogeneous nucleation by a decrease of the necessary energy to initiate a nucleus and therefore induces a higher nucleation density. Photopatterning on the polysiloxane surface was clearly successful. A high anisotropy of the DDOA fibers is observed with more narrow distributions of polarization values and average values of -0.2 and 0.15. Both values reach almost the limit of 0.2 and -0.2 observed on single objects obtained by isotropic growth.



Figure 3.21: (a) Polarization image of an YX scanned square of DDOA on a polysiloxane-coated glass surface. (b) Polarization histograms of square a (orange) and c (blue) and the isotropic distribution (black). (c) Polarization image of an XY scanned square of DDOA on a polysiloxane-coated glass surface. Polarization value is given in false colour scale.

The anisotropy on the polysiloxane surface emphasizes the need of a high nucleation density and surface affinity in combination with spatial confinement. In contrast to existing techniques requiring surface pre-treatment in combination with a receding or shearing force (paragraph 3.1.1.), in this case the spatial confinement and directionality results from the focused laser illumination. The confinement of the laser and the strong(er) interactions of DDOA with the hydrophobic surface keep the fibers growing in one main direction. In other words, the high density of fibers attached to the surface hinders the growth of fibers, which tend to deviate out of the main "collective" direction following the concentration gradient created by the laser. This can be seen in Figure 3.21, since in both squares the growth is initially more isotropic (left of Fig. 3.21a, top of Fig. 3.21c), whereas it becomes more unidirectional over time (right of Fig. 3.21c, bottom of Fig. 3.21c). This results in highly anisotropic patterns. A major advantage of this method as compared to the already existing alignment techniques (paragraph 3.1) consists in the fact that alignment and patterning can be controlled independently on the same completely isotropic surface just by sequentially changing the laser localisation and scanning direction. In contrast, nowadays most techniques only allow to obtain a single direction for the whole surface. Furthermore, no extensive surface treatments were necessary to achieve these results, like micro contact printing or other lithography techniques such as those used for the crystallization of single crystals. Instead, the coverslips are commercially available and a laser is necessary to provide the confinement and directionality.

Finally, the control over the self-assembly of DDOA at multiple scales should allow the anisotropic coverage of the surface at the microscale. Indeed, Figure 3.22 shows the 'checkered ensemble' of several squares on a polysiloxane surface with their respective anisotropy. The values are as high as -0.2 and 0.17, as can be deduced from the polarization histogram. This proofs this method is reproducible and can deliver anisotropic micropatterned surfaces. The value of 0.17 is higher than observed for Figure 3.21, because

the fibers immediately grow in a unidirectional sense, as is not the case in the beginning of the squares in Figure 3.21.



Figure 3.22: (a) Polarization histogram and (b) the corresponding patterned reactangles (16 x 20 μ m) in YX (blue squares) and XY (red squares). Substrate is a polysiloxane coated glass substrate. Scale bar is 10 μ m. Polarization value is given in false colour scale.

3.4 Conclusion and perspectives

The self-assembly of DDOA on and at the vicinity of a surface was controlled using a photoconvertible precursor and allowed to create micropatterns, including high anisotropy. In a self-assembly process governed by a nucleation-growth mechanism, the critical process resulted to be the nucleation. The latter is influenced by several parameters, including light, the nature of the precursor, but more unexpectedly the fine-tuning of assembly processes by addition of water. Indeed, water reduces both the solubility of dkDDOA and DDOA in DMSO. Thereby, in a first step, water induces the aggregation of dkDDOA into small aggregates that can still diffuse in solution. In a second step, the supersaturation of DDOA obtained by photoconversion of dkDDOA is reached at a lower concentration, resulting in an increased thermodynamic driving force for self-assembly. This results in a quite fast nucleation creating a high density of nuclei. These nuclei are at the origin of the growth of fibers. The length and direction of the growth of the fibers depends strongly on the density of these nuclei. The fibers that are grown by this photoinduced method are very similar to the ones obtained by thermal treatment. However, an increase in defects can be observed and is related also to the presence of water and the increase in the crystallographic mismatch nucleation (branching) induced by the fast self-assembly process. The presence of defects is demonstrated by a change in the photophysical properties and the observation of branching angles coinciding with the proposed hexagonal molecular packing in DDOA fibers. Another reason for additional defects can be due to entrapment of dkDDOA in DDOA aggregates

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upon fast nucleation as mentioned in Chapter 2. An additional effect results from the nature of the surface. Indeed, the polysiloxane coated coverslips promote the efficient attachment of the aggregates on the surface due to the higher affinity of DDOA for the hydrophobic surface. This decreases the energy barrier for DDOA to perform a nucleation. The control of nucleation could also be accompanied by the control of the growth. Indeed, the growth of fibers can be supported by irradiation intensities that do not lead to nuclei formation and only "feed" the growth of fibers by supplying DDOA. This compensates for the local decay of DDOA concentration by diffusion or due to the self-assembly. The control of nucleation and growth resulted in the achievement of highly unusual patterning. Anisotropic patterns are obtained by combining spatial confinement of the biphotonic excitation, creation of dense areas of nuclei, and anisotropic growth exploiting steric hindrance between fibers and the DDOA concentration gradient. The polysiloxane surface ensures the local attachment of fibers instead of out-of-plane growth.

In perspective, additional experiments could further support the aforementioned mechanism. Rheology measurements would be useful to determine the effect of H_2O addition on the mechanical properties of DDOA. More branching means a more dense and entangled fiber network, which should increase the mechanical strength of the gel. Furthermore, DLS or TEM measurements should be performed to confirm the pre-aggregates of dkDDOA formed in solution at lower concentrations than 4 a 5 mM dkDDDOA. It would also give information about the possible dispersion in size of the formed pre-aggregates.

An alternative to the addition of H_2O would be to tune the laser power to control the nucleation density. In our case, however, we found that the system was better controllable by adding H_2O than tuning the laser power. In the absence of water addition, the appearance of any nano-objects by changing the laser power was inconsistent and unpredictable, as mentioned in the beginning of this chapter. Fast photoconversion by increasing the laser power resulted in a loss of spatial control at 473 nm due to the increased photoconversion in the laser waist. At 770 nm, the high powers needed to start the photoconversion are already at the reasonable limits of our setup. A fine-tuning of the combination of water addition and laser power control will be attempted.

At last, further growth studies should be performed. The unique ability to further grow and simultaneously analyse a confined line of nuclei under widefield illumination at 375 nm allows to determine the evolution of the fiber growth and the speed. This ability should be exploited more to gain more information about the growth mechanism. Preliminary studies on glass were difficult due to the out of plane growth of the fibers. Exchanging the borosilicate glass surface for the polysiloxane-coated surface might be an option. However, the coiling and bundling observed so far on that surface would induce further complications. In the preliminary studies, the speed of growth of a fiber was determined to be in the range of μ m.s⁻¹ in the conditions used.

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4

Synthetic strategy for selfassembling *n*-acenes

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4.1. Introduction

This chapter discusses the synthesis of the 2,3-alkoxylated anthracenes and tetracenes realized during this thesis and describes the synthetic strategy adopted to change the optical properties^[1] of acenes while still keeping their ability to self-assemble.

The synthesis can be divided into three parts, starting with the synthesis of the 2,3dimethoxy protected anthraquinone or tetraquinone. The second part is the introduction of the desired alkoxy chains through a simple deprotection and subsequent alkylation.^[2,3] It is the length of the alkoxy chains which influences the 1-dimensional assembly. The last part consists of the reduction of the quinone to obtain the parent acene or extend the conjugation by performing a Grignard reaction. The extension of the acene backbone provides a lowering of the energy in the S₀-S₁ transition inducing a bathochromic shift in the absorption and fluorescence spectra (or maximum wavelengths) and simultaneously increasing the radiative constant (see paragraph 1.6).



Scheme 4.1: Retro synthetic scheme of the synthesis of 2,3-dialkoxy acenes.

Every paragraph will finish with a small discussion on the photophysical properties in solution to show the versatility this synthetic strategy can provide.

4.2. Synthesis of anthracene derivatives

The synthesis was performed according to an optimized procedure of Dr. Jens Reichwagen developed in Braunschweig and Bordeaux.

4.2.1. 2,3-dimethoxyanthraquinone

The synthesis of the 2,3-dimethoxyanthraquinone consists of three steps. The first step is the formation of the highly reactive 7 from the acetal of 2,3-butadiene. The acetal is formed in methanol under acidic conditions. The equilibrium reaction is shifted towards the acetal formation by adding a large excess of methylorthoformiate. The orthoformiate acts as a water scavenger removing it from the reaction mixture and forming methyl formate and methanol instead to ensure a constant excess of alcohol. The acid catalyst, H_2SO_4 , was added after bringing the mixture of the diketone, methanol and dimethylorthoformiate to reflux, rather than in the initial mixture. The following distillation serves a double purpose: the elimination/deprotonation reaction of the acetal by the addition of ammonium dihydrogen

Synthetic strategy for self-assembling n-acenes

phosphate and the removal of the alcohol to shift the equilibrium reaction towards the formation of the diene. In order to avoid the self-polymerization of the activated diene, hydroquinone is added as inhibitor. The next step is the formation of **8** through a Diels-Alder reaction with 1,4-naphthoquinone under reflux. The diene is added in excess in a 4:1 molar ratio to ensure the addition reaction. The unstable adduct is then converted to the anthraquinone by aerative oxidation in the presence of KOH. The yield of the reaction is low, around 15%. This is due to polymerization of 2,3-dimethoxy-2,3-butadiene as it is in excess under reasonable high temperatures. This complicates the [4+2]-cycloaddition and the work up. The pure product was obtained by column chromatography followed by a recrystallisation in EtOAc.



Scheme 4.2: Synthesis of 2,3-dimethoxyanthraquinone (8).

8 serves as a basic skeleton which can be further functionalized by changing the chain length on the 2,3-position, whereas the 9,10-dione provides a reactive function to modify the acene core. The advantages of this precursor are its high stability under ambient conditions and the possibility to synthesize it in gram scale.

4.2.2. 2,3-dialkoxyanthraquinone

The substitution of the 2,3-dimethoxy with another chain length starts with a demethylation. The demethylation of **8** in the original publication of Bouas-Laurent and coworkers^[4] was done by using BBr₃ in CH₂Cl₂ as reagent. The more mild combination of strong Brønsted acid, 48% HBr and glacial acetic acid^[5], was however used in this work. The deprotection is a S_N type reaction where the hydrobromic acid protonate the ether oxygen and the acetic acid functions as a nucleophile. The good stability of **9** in the described conditions ensures a high yield of 92%. The subsequent alkylation of **9** follows a classical Williamson ether synthesis. The phenol is deprotonated with K₂CO₃ and the desired 1bromoalkane is added to the solution. The reaction mixture is then heated till 135°C to facilitate the reaction and solubility of the anthraquinone.

In our case we used the 1-bromodecane or 1-bromohexadecane to obtain 10 and 11 in a high yield (94 and 90%, respectively) after the evaporation of DMF and column chromatography.



Scheme 4.3: Synthesis of 2,3-didecyloxyanthracene (10) and 2,3-dihexadecyloxyanthracene (11).

4.2.3. Functionalisation of the acene core

As a last step, the fluorescent anthracene is synthesized by reducing the 2,3alkoxyanthraquinone or performing a Grignard reaction to extend its conjugation.

The reduction is done using the Meerwein-Ponndorf-Verley reduction.^[6] The reduction make use of an alkoxide aluminium catalyst to reduce ketones to their corresponding alcohols. The used aluminium catalyst is cyclohexyl aluminium alkoxide and was prepared *in situ* under an inert atmosphere by refluxing cyclohexanol and aluminium powder in combination with traces of mercury(II)chloride and carbon tetrachloride. The mercury(II)chloride and carbon tetrachloride catalyse the aluminium alkoxyde formation forming the more reactive amalgam.^[7] The reaction is performed at high temperature, ~170°C to favour a direct dehydration after the reduction giving the parent anthracene in high yields (92%). Despite the high yield, the work up can be cumbersome due to the high boiling point of cyclohexanol (162°C) and the ability of **12** (DDOA) to gel alcohols.



Scheme 4.4: Meerwein-Ponndorf-Verley reduction of 2,3-didecyloxyanthraquinone to obtain 12.

A Grignard reaction with phenylacetylene at -78° C in THF followed by a reduction with SnCl₂ (10% HCl solution) in Et₂O gave **13** in 45% yield. During the reduction **13** precipitates directly out of solution. A filtration followed by a recrystallization from DCM/MeOH gave the pure compound. In this case, **11** was used since the diphenylethynylanthracene of **10** forms transient gels.^[8] In the solid state, **13** gave wide twisting fibers which from a translucent gel at 4 mM in *n*-butanol.



Scheme 4.5: Grignard reaction to extend the conjugation on the anthracene backbone (13).

4.2.4. Photophysical properties in solution

In Figure 4.1 and Table 4.1, the photophysical properties of 12 and 13 in tetrahydrofuran (THF) are given. It shows that extending the conjugation of the S_0 - S_1 transition has the exact effect as expected: a bathochromic shift in absorbance and emission, an increase in fluorescence quantum yield (0.24 vs 0.93) and radiative constant. The lower lifetime for 13 compared to 12 is expected to come from the higher molecular extension coefficient (higher oscillator strength) and better overlap in the Morse potential. Therefore, the fluorescence decays relatively faster for the extended anthracene. The large increase in the radiative rate constant can be attributed to lowering of the S_1 of 13 making the efficient ISC to the T_2 state seen in anthracene less probable.^[9]

Table 4.1: Photophysical properties of 12 and 13 in THF. The concentration is 10^{-5} M.

	$\lambda_{ m Abs}{}^{ m max}$ $(m nm)$	${ m Epsilon} \ (10^4 \ { m M}^{-1} \ { m cm}^{-1})$	$\lambda_{ m Em}{}^{ m max} \ (m nm)$	$\Phi_{ m F}$	τ (ns)	${ m k_r}\ (10^8~{ m s}^{-1})$
12	358	0.7	409	0.24^{a}	6.6	0.36
13	462	3.8	475	$0.93^{ m b}$	3.4	2.7

References were diphenylanthracene in CyH ($\Phi_F = 0.93$)^a, Perylene in CyH ($\Phi_F = 0.94$)^b.



Figure 4.1: Absorption and emission spectra of 12 ($\lambda_{ex} = 365 \text{ nm}$) and 13 ($\lambda_{ex} = 436 \text{ nm}$) in THF. The concentration is 10⁻⁵ M.

4.3. Synthesis of tetracene derivatives

The synthesis of the tetraquinone core (18) was performed according to the optimized procedure of Dr. Jens Reichwagen.^[10]

4.3.1. 2,3-dimethoxy-5,12-tetracenedione

The synthesis of 16 is similar to that of 8 starting with the synthesis of 14 by a Diels-Alder reaction between 7 and benzoquinone. A threefold excess of benzoquinone is added in respect to the diene to avoid the double addition on the symmetric dienophile (this would form 2,3,6,7-tetramethoxyanthraquinone). Furthermore, the excess of benzoquinone provides an *in situ* oxidation of the adduct. The yield was 49% after column chromatography. The reduction of 14 was carried out using Zn in acetic acid under ultrasounds. The best results were obtained when Zn was added in portions over the course of two hours. The yield was never established since the crude is directly used for the following aldol condensation with phthalaldehyde to avoid the possible re-oxidation under ambient conditions. The aldol reaction was performed in 2,2,2-trifluoroethanol under basic conditions. The sodium carbonate deprotonates 14 and attacks the pthtalaldehyde as nucleophile. The dehydration is again performed *in situ* providing 16 in 30% yield. The lower yield is expected to be due to the fluctuating quality of the dimethoxynaphthalene due to the already mentioned re-oxidation.



Scheme 4.6: Synthesis of 2,3-dimethoxytetracene-5,12-quinone (16).

4.3.2. 2,3-dialkoxy-5,12-tetracenedione

The demethylation and alkylation to obtain the 2,3-dialkoxytetracene-5,12-quinone were performed according to the methods described for the synthesis of the 2,3-alkoxyanthraquinone. The only difference are the lower yields, 84% and 32% respectively, due to the insolubility of the tetracenequinone.



Scheme 4.7: Alkylation of the 2,3-dimethoxytetracene-5,12-dione (18).

4.3.3. Functionalisation of the acene core

As mentioned for the anthracenes, the photophysical properties can be altered by extending the conjugation at the 5,12-position with conjugating substituents. Here, the extension with phenyl and phenylethynyl groups is described.

19 was synthesized through a lithiation reaction of the alkylated teraquinone with PhLi at 0°C. The reaction was performed at 0°C, because of the precipitation of the tetraquinone at lower temperatures. Ambient temperatures are unthinkable, due to the high reactivity of the lithium reagent which deprotonates the hydrogens on the 6,11-position of 18 and degrades the reagent. The diol-adduct was dehydrated with 57% hydroiodic acid in Et₂O under reflux to give the substituted tetracene in 57% yield. The solid tetracene is obtained by recrystallisation from DCM/MeOH.



Scheme 4.8: The synthesis of 2,3-didecyloxy-5,12-diphenyltetracene (19).

For the synthesis of **20**, the tetracene quinone was substituted by a Grignard reagent. The lithiumphenylacetylide was formed *in situ* at -78°C in dry THF. Afterwards a solution of **18** in dry THF was added. Due to the low solubility of the tetracene quinone, the reaction is left to come to room temperature after 45 min at -78°C. After the dehydration reaction with $SnCl_2$ in 10% HCl solution, **20** is obtained with a 20% yield.



Scheme 4.9: Synthesis of 2,3-didecyloxy-5,12-diphenylethynyltetracene (20).

An explanation for the lower yield as compared to the phenylation reaction can be related to the lower stability of the lithium phenylacetylide compared to phenyllithium. The solvent, THF, is a good hydrogen donor at higher temperatures^[11] and might inactivate a part of the lithium reagent. A solution to this problem would be to change the solvent for Et₂O. Et₂O is also a directing solvent, but less susceptible to deprotonation than THF. The option of the alkoxy chain acting as a direct metalation group seems less likely since the lithium phenylacetylide has a pKa ~ 26 and the phenyllithium a pKa of ~44. The directed metalation reaction is known to work typically with only strong alkyllithium bases (pKa ~52).^[12]



Figure 4.2: Reaction mechanism of directed ortho metalation. DMG = directing metalation group and E = electrophile.

Substituting all peripheral hydrogens on the tetracene to obtain a highly rigid red emitting tetracene required an adaptation to the synthetic route as presented till now.

4.3.4. Synthesis of RG10



Scheme 4.10: Synthesis of 2,3-bis(decyloxy)-6,11-diphenyl-5,12-bis(phenylethynyl)tetracene (23).

The synthesis of **23** is given in Scheme 4.10. As a first step, **21** is formed through a [4+2]cycloaddition reaction between the commercially available 1,3-diphenylisobenzofuran and **14** at room temperature in CH₂Cl₂ followed by a subsequent dehydration with BBr₃ in 63% yield.^[13] Instead of the mixture of 48% HBr/AcOH, we choose to perform the demethylation in BBr₃/CH₂Cl₂ due to solubility issues. The demethylation of **21** was directly followed with the alkylation of the diol with 1-bromodeacane and K₂CO₃ in DMF at 135°C. The yield was rather low 35%. For the substitution on the 5,12-position, the Grignard reagent was again prepared *in situ* by the lithiation of phenylacetylene at -78°C. Afterwards the tetraquinone was added and the reaction left to come to room temperature after 45 min. After a subsequent dehydration reaction with SnCl₂ (10% HCl solution) in Et₂O **23** was obtained in low yield, 18%. Possible reasons for the low yields are the photo-oxidation of **23** in solution during the work-up and the use of THF at 0°C.

Further studies of 23 in the solid state can be found in the thesis of Dr. P. Schäfer.

4.3.5. Photophysical properties in solution

In Table 4.2 and Figure 4.3, the photophysical properties of **19**, **20** and **23** in cyclohexane are given. Again, the effect of extending the conjugation of the S_0 - S_1 transition has a clear effect on the photophysical properties of the tetracenes *i.e.* the same tendency can be seen as for the anthracenes. On the other hand, for **23** all values stay more or less the same compared to **20** besides a bathochromic shift in the absorption and emission. This is because the phenyl rings are out of plane with the acene core.^[14,15] Therefore the phenyl groups do not (fully) participate to the excited state. In the absorption and emission spectra the transitions of **23** are also broader than **20**.

	$\lambda_{\rm Abs}{}^{\rm max}$	Epsilon	$\lambda_{\!\rm Em}{}^{\rm max}$	$\mathbf{\Phi}_{ ext{F}}$	τ	$\mathbf{k}_{\mathbf{r}}$
	(nm)	$(10^4 { m M}^{-1} { m cm}^{-1})$	(nm)		(ns)	$(10^8 { m s}^{1})$
19	493	1.7	505	0.76^{a}	17.3	0.44
20	543	2.9	555	$0.85^{ m b}$	8.3	1.0
23	567	2.7	599	0.76°	9.2	0.83

Table 4.2: Photophysical properties of 19, 20 and 23 in degassed cyclohexane. The concentration is 10^{-5} M.

References were Fluorescein in 0.1 M NaOH ($\Phi_F = 0.95$)^a, Rhodamine 6G in EtOH ($\Phi_F = 0.94$)^b and Sulforhodamine 101 in EtOH ($\Phi_F = 0.95$)^c.



Figure 4.3: Absorption and emission spectra of 19 ($\lambda_{ex} = 462 \text{ nm}$), 20 ($\lambda_{ex} = 475 \text{ nm}$) and 23 ($\lambda_{ex} = 528 \text{ nm}$) in cyclohexane. The concentration is 10⁻⁵ M.

4.4. Conclusion

The presented results show that with the adopted synthetic strategy a series of functional self-assembling 2,3-dialkoxy acenes can be realized with custom photophysical properties. This is due to the remarkable specific interaction of the 2,3-dialkoxy chains which induce a 1-dimensional assembly in all cases. Nevertheless, the self-assembly of the 2,3-dialkoxyacenes is still not completely understood. For example, the non-substituted 2,3-alkoxylated anthracene, tetracene and pentacene have been characterized as efficient molecular gelators. This is however, less evident for their substituted derivatives. It is thought that the substituents induce a higher crystalline order since most of the above mentioned structures (13, 19, 20 and 23) form nanoribbons.

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5

Photochemical cross-linking of self-assembled fibers

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This work was performed at the Delft University of Technology in the Advanced Soft Matter group in collaboration with Vincent A. A. Le Sage under the supervision of Jan H. van Esch. The more significant results obtained during those two months are presented in this Chapter.

5.1. Introduction

Bulk mechanical properties in (supramolecular) gels are governed by several factors: average thickness of the fibers, the degree of branching, the density of entanglements (also called junction points) and the distribution of the fibers along the whole gel.^[1,2] Supramolecular gels from LMWGs normally break at relatively low strain compared to covalently bonded polymer gels due to weak interactions governing the junction points. More importantly, the mechanical strength tends to fluctuate from sample to sample due to the sensitive nature of the self-assembly which governs the previously mentioned factors. The reproducibility of the mechanical strength in polymer gels, on the other hand, is better regulated by carefully controlling the degree of (chemical) cross-links.^[3,4] Nowadays several methods exist to make more robust low molecular weight gels. A first method consists in combining the LMWG with (covalent) polymer gels or polymer solutions to form hybrid materials with enhanced bulk mechanical properties.^[5] Another method is to introduce crosslinkable moieties on the molecular gelator. Post-treatment by chemical crosslinking after the self-assembled gel has been formed would permit to further strengthen the gel by increasing the amount of crosslinks and the mechanical resistance (strain).

A number of methods have already been reported on the post-modification of supramolecular gel fibers through chemical cross-linking and several similarities can be found in these methods:^[6-10]

- The use of a photoreaction or photoinitiation to perform the chemical crosslinking.
- An initial increase of the viscoelastic properties followed by a collapse of the gel and subsequent precipitation if a certain threshold of crosslinks is exceeded. This is due to the fine balance in LMW gels between solubility and precipitation.
- Intrafibrillar covalent bonding. A consequence of using reactive groups which lack orthogonality and as a consequence even negates the reversibility.

Several methods have been explored to overcome some of the aforementioned problems. Khalify *et al.*^[11] used dynamic covalent cross-linking avoiding the collapse of the gel. By adding glutaraldehyde to their peptide amphiphile, dynamic imine bonds were formed between the two compounds thereby significantly increasing the storage modulus and critical strain amplitude of the bulk gel. However, they still suspected the (dynamic) covalent bonding within the fiber to be the major contribution (see Figure 5.1).



Figure 5.1^[11]: Schematic representation of the dynamic crosslinking with glutaraldhyde (a) and the peptide amphiphile based hydrogelator (b). (Figure is a reprint of ref 11)

In an attempt to introduce more orthogonality and suppress the intrafibrillar cross-linking, Diaz Diaz *et al.* investigated the use of the Huisgen 1,3-dipolar cycloaddition^[12] and the photo-initiated thiol-ene 'click reaction'^[13]. For the latter, they mixed the hydrogelator dibenzoyl-l-cystine (DBC) with a small fraction (10%) of alkene functionalized DBC in H₂O:DMSO (0.5 wt%) to homogenize the whole mixture and tested several short polyvalent thiol cross-linkers. The increase in the moduli and critical strain amplitude were modest, but the reversibility of the gel was maintained as proven by the sol-gel transition at T_{gel} . Therefore, the use of the orthogonal thiol-ene reaction appears to be a promising approach to obtain stronger gels and preserve the thermoreversibility indicating interfibrillar crosslinking.



Figure 5.2^[13]: Dibenzoyl-l-cystine and the crosslinkable alkene derivative.

In this study, we aim to set up a protocol to better regulate the mechanical properties of the 'OG2'^[14] hydrogelator (Figure 5.3) through photoinitiated crosslinking. The envisioned reactions are the mentioned *thiol-ene* and the *thiol-yne* reaction. The orthogonality and spatial temporal control of the reaction serve to obtain gel networks with on-demand mechanical properties. Rheology is used to analyse the mechanical properties and follow the dynamics. In addition, a feasibility study was performed to determine if the Ellman reagent can serve as an indicator to determine the crosslink efficiency.



Figure 5.3: Molecular structure of the hydrogelator OG2 based on the 1,3,5-cyclohexanetricarboxamide core.

5.1.1. Thiol-ene and thiol-yne reaction

The thiol-ene and thiol-yne reaction are the radical initiated conjugation of a thiol with an alkene or alkyne, respectively. Both reactions are also referred to as "click reactions". This definition was introduced by Sharpless in 2001 and describes organic synthetic reactions which are wide in scope, high yielding, orthogonal, insensitive to oxygen and water and stereospecific with a high atom efficiency. Both reactions apply to these criteria. Therefore photoinitiated thiol-ene and thiol-yne are used in many research domains such as polymer chemistry^[15,16], nanoparticle functionalization^[17], glycochemistry^[18,19] or surface chemistry^[20].

The reaction mechanisms are described as follows: both reactions are initiated through the formation of a thiyl radical via hydrogen abstraction of a thiol-functionalized molecule. The initiation is either performed by a thermal or photo-activated radical initiator. Then, the thiyl radical readily reacts with an alkene or alkyne on the least substituted side (anti-Markovnikov) in a step growth like manner. In the last step the radical adduct abstracts a hydrogen from another available thiol, resulting in the reaction product and the regeneration of a thiyl radical (see Figure 5.4).

The thiol-yne reaction can perform the cycle two times depending on the amount of thiol. If two equivalents or an excess of thiol are added the second addition will take place due to the higher reactivity of the vinylthioether compared to the alkyne.



Figure 5.4: Reaction mechanism of the thiol-ene: (1) Addition of the thiyl radical to the alkene. (2) Hydrogen abstraction by the radical adduct leading to the alkyl thiol and another thiyl radical (left). Thiol-yne reaction: (1) Alkyne addition. (2) Hydrogen abstraction by the radical adduct and a thiyl radical. (3) Addition of the thiovinylether. (4) Second hydrogen abstraction by the radical adduct leading to the disubstituted product and thiyl radical (right).

The insensitivity to oxygen comes from the reversible reaction of the thiyl radical with oxygen. The equilibrium constant of oxygen addition and fragmentation has been demonstrated to be almost unity in oxygen saturated solvents allowing the thiol-ene and thiol-yne to occur efficiently in aerobic conditions.^[21] Nevertheless, side reactions can still occur. Secondary reactions consist in disulfide coupling, homopolymerization and head-tohead coupling of a carbon centred radical (Figure 5.5). These secondary reactions depend on the reactivity between the third radical and the alkene or alkyne.



Figure 5.5: Possible secondary reactions during the radical thiol-ene reactions. Disulfide formation, homopropagation or radical combination.

Hoyle *et al.* reported the general trend of the alkene-reactivity of three classes of thiols (alkyl-3-mercaptopropionates, alkyl thioglycolates and alkylthiols) under radical conditions as follows (Figure 5.6)^[22]:



Figure 5.6^[22]: Order of 'ene'-reactivity towards thiols. Norbornene (1), vinylsilane (2), allylether (3), vinylether (4), dimethylfumarate (5), propene (6), maleimide (7), methylacrylate (8), methylcrotonate (9), styrene (10), acrylonitrile (11), butadiene (12). (Figure is a reprint of ref 22).

The increased reactivity for the norbornene is a rather special case and comes from the loss in ring strain upon reaction. The reactivity of the other alkenes, except styrene, acrylonitrile and conjugated dienes, depend solely on the electron density. The weak reactivity of the last three alkenes is a result of the efficient radical stabilisation (resonance effects). The stabilisation induces a chain growth process instead of a step growth process and subsequently the mentioned side reactions. Electron rich alkenes do not have these stabilizing effects and therefore do not suffer from homopolymerization nor chain transfer.

5.2. Results and discussion

*All synthetic work has been performed by Vincent A. A. Le Sage (TUD, Delft, NL).

5.2.1. Towards kinetically controlled gelation by imine hydrolysis

The gelation of the OG2 hydrogelator can be triggered by pH using the 6-aminoquinoline moiety (see Figure 5.3). The pKa value of the quinoline is $5.6^{[23]}$ and makes the gelator soluble in acidic conditions. Gelation can be induced upon deprotonation by the addition of equimolar amounts of NaOH. However, as mentioned in paragraph 1.3.2.1, the physical properties of the resulting gel can be very sensitive to the rate of addition^[24], which can limit the reproducibility and the quantitative study of the effect upon post-treatment. Therefore, base releasing agents consisting of a conjugated imine were synthesized* and added to kinetically control the gelation of OG2. The low pH of the solution assists the hydrolysis of the base precursor, inducing the release of a basic amine in solution and the increase of pH over time. A dosed amount of base precursor can thereby neutralize the initially acidic solution and trigger the self-assembly. The synthesized imines consist of different hydroxylated benzaldehydes coupled to primary amines such as ethanolamine (pKa = 9.5 at 25°C) or tris(hydroxymethyl)aminomethane (TRIS, pKa = 8.07 at 25°C). All structures are shown in Annex E and Figure 5.7 shows an example of the reaction.



Figure 5.7: Example of imine hydrolysis under acidic conditions.

In order to compare the average outcome of this method on the gel formation, multiple time sweeps were performed by rheology using two of the synthesized imines and NaOH. The storage moduli of the gel in Figure 5.8a show that the release of TRIS over time provides stronger gels than the direct neutralization using NaOH. Furthermore, the two imines neutralize the solution at a different rate and induce different gel strengths. The gel strength obtained using 2,3,4-trihydroxybenzene-TRIS-imine reaches a plateau after 180min with a G' of 1450 Pa, whereas for 2,3-dihydroxybenzene-TRIS-imine G' stagnates at 2700 Pa after 60min. These values are related to the gel morphology using confocal fluorescence microscopy (Figure 5.8b). The OG2 solution neutralized with 2,3-dihydroxybenzene-TRIS yields a gel with homogenous fiber distribution, whereas the other two gels display an irregular fiber density. In particular, the solution neutralized with NaOH consists mostly aggregates than a distinguishable fiber network. This coincides nicely with the factors governing bulk mechanical properties discussed in paragraph 5.1. Introduction The difference in entanglements and the distribution of fibers over the whole sample clearly affect the mechanical properties. In brief, the rate at which the pH changes over time has a distinctive effect on the gel morphology and subsequently the strength of the gel network. The controlled release of a base provides a better reproducibility as reported for the hydrolysis of glucono- δ -lactone by Adams *et al.*^[24] (paragraph 1.3.2.1).

The storage modulus of the gels triggered y 2,3-dihydroxybenzene-TRIS-imine has an error margin of roughly 11%, whereas for the gels made with NaOH the storage modulus varies within a margin of almost 40%. Therefore, the 2,3-dihydroxybenzene TRIS-imine was used as pH trigger to assure a regularity in the formation of the gel allowing to perform a quantitative study on the post-modification by photochemical cross-linking.



Figure 5.8: (a) Average of multiple time sweep of OG2 with 2,3-dihydroxybenzene-TRIS-imine (red + error bar), 2,3,4-trihydroxybenzene-TRIS-imine (orange) and NaOH (blue + error bar). (b) Confocal images of corresponding gels with show the difference in morphology. OG2 was grafted with rhodamine B.

5.2.2. Photochemical cross-linking of self-assembled gels

Two derivatives of the OG2 gelator were synthesized to perform the post-modification by the thiol-ene or thiol-yne reaction. The OG2 is either functionalized with 5-norbornene-2-carboxylic acid (OG2-norbornene) or 4-pentynoic acid (OG2-alkyne)* forming a statistical mixture. Every molecule of the OG2-norbornene is (at least) mono-functionalized whereas for the OG2-alkyne only 1 on 2 is mono-functionalized due to the higher yield of the former reaction. The commercially available trimethylolpropane tris(3-mercaptopropionate) (trivalent SH) was used as a cross-linker and the photoinitiator was lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP)^[25] (Scheme 5.1).



Scheme 5.1: Illustration of the pH triggered molecular self-assembly followed by the postmodification through the radical thiol-yne or thiol-ene reaction.

The mixture of OG2:OG2-alkyne (1 to 5 mol% of OG2-alkyne) was dissolved in an acidic solution (pH = 1) followed by gentle heating, as confirmed by a naked eye observation. Unfortunately, the same conditions resulted in a colour change for the OG2-norbornene indicating possible ester hydrolysis in the high temperature acidic conditions. Therefore, experiments with the OG2-norbornene were discarded and only the OG2-alkyne was further tested.

Blank experiments excluded any side reactions under irradiation of the created radicals with the non-functionalized gelator or imine. Indeed, no alternation was observed by rheology (results not shown). Surprisingly, irradiating a OG2 gel with all necessary components (5 mol% OG-alkyne, LAP, imine and crosslinker) did not show any increase in the storage modulus (G'). In contrast, the storage modulus decreases upon irradiation at times t = 80, 90, 100 min, and returns within minutes to the initial value when the irradiation is stopped (Figure 5. 9).


Figure 5. 9: Time sweep of OG2:OG2-alkyne (5 mol%, 4 mg.mL⁻¹), TRIS imine (3.8 mg), trivalent thiol cross-linker (1.85 mg, excess) and LAP (0.25 mg). Strain was 0.2%. Inner graph shows the dip in G' under irradiation. Illumination source was white light ($400 < \lambda < 800$ nm).

This behaviour could tentatively be attributed to direct heating of the sample, since the same behaviour is seen when performing temperature-dependent experiments. Here, the storage modulus follows exactly the temperature cycle: G' decreases with an increase in temperature and vice versa (see Annex E). However, turning on the lamp without irradiating the sample showed the same decrease during a time sweep measurement. This indicates that the irradiation source may cause other additional disturbances during the measurements. Another possible explanation is an inner filter effect caused by the imine (bright yellow in solution) or the gelator OG2 (absorbing quinoline moiety). LAP has a very low molar extinction coefficient and the other two compounds are present in much higher concentrations (see Figure 5. 9).

Replacing the imine and the associated inner filter effect with a neutralization with NaOH resulted in a successful thiol-yne cross-linking. Indeed, an increase of the storage modulus is observed upon irradiation a gel without imine at times t = 80, 90 and 100 min (Figure 5.10). Even with a OG2-alkyne proportion as low as 1 mol%, a strengthening of the gel can be measured. In these successful experiments, an excess amount of trivalent SH is used whereas no effect is observed when using equimolar amounts of thiol crosslinker. The use of NaOH, on the other hand, is not ideal as discussed in paragraph 5.2.1. Towards kinetically controlled gelation by imine hydrolysis The storage modulus would however still decrease upon illumination due to the incompatibility of the light source with the rheometer.



Figure 5.10: Increase in storage and loss moduli of an OG2:OG2-alkyne gel (4 mg.mL⁻¹) under irradiation at t = 80, 90, 100 min. Illumination source was white light($400 < \lambda < 800$ nm). The amount of OG2-alkyne was 2.5 mol% (black) or 1 mol% (red). The cross-linker was trivalent thiol (1.85 mg, excess) and the photoinitiator LAP (0.25 mg). Strain was 0.1%.

5.2.3. Absorbance of the imines and their hydrolysed products

In order to get a better insight on the inner filter effect, absorption spectra of the OG2 gelator and the imine in solution were taken at 10^{-4} M. Whereas the gel only absorbs in the deep UV (< 300 nm, not shown), the imine has clear absorption bands at 295 and 414 nm with a molar extinction coefficient of 14000 and 4000 M⁻¹.cm⁻¹, respectively. These bands partially overlap with the absorption of the photoinitator. The extinction coefficient at 365 nm of the imine is 1840 M⁻¹.cm⁻¹ whereas the reported extinction coefficient of LAP is only 218 M⁻¹.cm⁻¹.^[25] At 365 nm, 92% of the light is absorbed by the imine (sample thickness of 384 µm), clearly masking the LAP. In addition, the overlap even becomes more pronounced over time. Indeed, upon hydrolysis the absorption of the imine blue-shifts by 74 nm without significant decrease in absorbance (Figure 5.11).



Figure 5.11: Absorbance of the 2,3-dihydroxybenzene-TRIS-imine in H₂O. Concentration is 10^{-4} M (a). Absorbance of lithium phenyl-2,4,6-trimethylbenzoylphosphinate in H₂O (solid line) and the cleavage products (dashed line) (graph was taken from ref 25) (b). Evolution of the absorbance of 2,3-dihydroxybenzene-TRIS-imine during hydrolysis over 24 hours. Concentration is 10^{-4} M (c).

Almost all the available imines show a significant higher molecular extinction coefficient at 365 nm as compared to that of LAP. Even the corresponding aldehydes, formed after hydrolysis, have a higher absorption at 365 nm ($\varepsilon = 3000$ to 10000 M⁻¹.cm⁻¹, see annex D for spectra). The higher absorbance of the imines and corresponding aldehydes can be explained by the resonance- and push-pull effects caused by the conjugation of strongly donating and withdrawing substituents which can induce large red shifts and masking LAP by the high absorbance of the imines during irradiation.

The only exception to the previously described problem is provided by the precursor 2,4-dihydroxybenzaldehyde. Indeed, this aldehyde absorbs only till 350 nm and, after full hydrolysis of the imine, its absorption should not overlap with that of LAP. The change in absorption upon hydrolysis can be seen in Figure 5.12 where the shoulder of the spectrum is shown. The post-modification of the supramolecular gel should be possible by irradiation at the standard wavelength of 365 nm. However, the kinetics of gelation are expected to differ from the ones using 2,3-dihydroxy imine and the amount of LAP needs to be increased (for former measurements 0.25 mg was used). Therefore, further experiments on this are still ongoing.



Figure 5.12: (a) Normalized spectrum of 2,4-dihydroxybenzene-TRIS-imine (black) and 2,4-dihydroxybenzaldehyde (red). (b) Hydrolysis followed over time by absorbance of an acidic 1 mM solution in MilliQ water (pH =3). The interval is 30min.

5.2.4. Thiol content determination with the Ellman reagent

In order to fully characterize the photochemical post-modification of the gels, a protocol was set up to verify the thiol content after chemical cross-linking and provide a more quantitative analysis. The thiol concentration is determined by using the Ellman reagent^[26] (5,5'-dithio-bis-[2-nitrobenzoic acid]) and will allow the calculate the percentage of non-reacted crosslinker. The Ellman reagent has a disulfide bond which reacts rapidly and stoichiometrically with free thiols under basic conditions (pH = 8.2) in solution, thereby cleaving the 2-nitro-5-benzoate which ionizes to the dianion (see Figure 5. 13). The dianion is highly absorbent at 412 nm ($\varepsilon = 14150 \text{ M}^{-1}.\text{cm}^{-1}$) and thereby is a much used indicator.



Figure 5. 13: Reaction mechanism of Ellman which gives the absorbing 2-nitro-5-benzoate dianion.

Initially, a calibration curve was made from a dilution series of cysteamine hydrochloride, chosen as reference compound. The application of the calibration curve was tested using several concentrations of different cross-linkers: the trivalent trimethylolpropane tris(3-mercaptopropionate) (trivalent SH), Thiocure[®] ETTMP 700 and Thiocure[®] ETTMP 1300.



Figure 5.14: Calibration curve made with cysteamine hydrochloride (black dots) and the corresponding determined concentrations of cross-linker. (a) Thiocure 1300 and (b) trivalent SH and Thiocure 700.

Thiocure 1300 agreed nicely with the calibration curve and concentrations as low as 0,01 mmol (absorbance = 0.016 at 412 nm) could be measured. In contrast, for the other two cross-linkers the concentration of thiol is underestimated due to their partial dissolution in water. In order to improve this method for those latter cases, the addition of DMSO would be necessary to solubilise the cross-linkers. However, the molecular extinction coefficient of the thiolate of the Ellman reagent would need to be revaluated.

5.3. Conclusion and perspectives

In conclusion, the timed release of a base (amine) through imine hydrolysis is proven to have a positive effect on the gelation and gave stronger gels than the direct addition of NaOH. By comparing the effect of two imines and NaOH, a clear link is observed between the rate of pH change and the impact this rate has on the gel morphology and resulting strength. The main aim to develop a working protocol for the photo-chemical cross-linking of OG2 self-assembled fibers by the thiol-yne or thiol-ene reaction was partially met. The high absorbance of the dosed base releasing agents hampered the photoinitiation reaction with LAP through an inner filter effect and the illumination source interfered with the rheology. Nevertheless, by using the less controlled direct neutralization with NaOH in combination with the photochemical reaction certain qualitative results were obtained:

- The thiol-yne reaction only works when all necessary compounds are in solution
- No effect was observed on the mechanical properties when equimolar amounts of thiol cross-linker were used.
- The ratio of OG2-alkyne:OG2 can be as low as 1:99 to induce an increase in the mechanical strength.
- Spectroscopic measurements suggest that the incompatibility of the base releasing imine and the photoinitiator LAP can possibly be overcome. Upon full hydrolysis, the absorption spectrum of some hydrolysing agents can decrease enough for the activation of the photo-initiator to be possible. As an example, the 2,4-dihydroxybenzaldehyde does not absorb above 350 nm. However, changes in kinetics have to be taken into account.

With an established protocol, a more in depth study can be performed on this particular gel system by trying to visualize the cross-links using, ideally, two colour super-resolution microscopy. This technique could provide more insights on what the actual role of the cross-links are on the mechanical properties. Until today, it is still not completely clear what effect the cross-links have on the gel morphology.

The current ongoing research on this system consists in realizing the imaging of the chemical cross-links with super-resolution microscopy and testing the possibility of super-resolving solely the OG2 gelator. Therefore, the OG2 will be functionalized with a fluorescent dye, Cy5 or Cy3. The necessary microscopy set-up and software to be able to perform super resolution microscopy are currently being installed. The proposed functionalization of the OG2 is presented in Figure 5.15:



Figure 5.15: Functionalisation of the OG2 gelator to couple with Cy3 or Cy5 for super-resolution microscopy.

The primary amine will allow to couple the commercially available NHS ester of the Cy3 or Cy5 to the gelator.^[27] Primary fluorescence imaging with a different dye proved the fibers dimensions are suitable for super-resolution microscopy.

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General conclusion

The main aim of this thesis was to spatially and temporally control the self-assembly of a blue fluorescent rodlike molecule into anisotropic nanostructures. The chosen method to achieve this goal was to induce a photochemical reaction and directly convert a reactive precursor into the gelator 2,3-didecyloxyanthracene (DDOA), known to form nanofibers which emit polarized light. This method has allowed to control separately the nucleation and the growth of the nanofibers obtained upon self-assembly with the aid of light under microscopy.

To meet this goal, new photo-reactive 2,3-alkoxylated acenes, the precursor of anthracene dkDDOA and of tetracene dkG10, were synthesized by addition of the photocleavable α -diketone moiety in three high yield synthetic steps.

dkDDOA proved to quantitatively convert under irradiation by visible light (450 ± 25 nm) thereby gelating DMSO at concentrations as low as 1 mM at room temperature. A more indepth study on the influence of dkDDOA on the gelation of DDOA showed a small impact of dkDDOA on the T_{gel} and a minor increase in structural defects within the DDOA fibers. This was mainly due to the entrapment/inclusion of dkDDOA during the gelation.

The control over the nucleation and growth using focused laser illumination was successful, and shown to depend on the precise composition of the solvent and the affinity of the gelator for the surface of the substrate. The addition of 5 vol% of H₂O contributed to achieve fast supersaturation at the microscopic scale by lowering the solubility of dkDDOA and DDOA in solution. Surprisingly, the moisture sensitive 1,2-diketone was not affected by the addition of H₂O under supersaturating conditions. The crystal of dkDDOA did not have any hydrolysed form included into the unit cell and still showed photoconversion and subsequent blue fluorescence when excited. The addition of D₂O might be a possible alternative for H₂O since the reaction with the 1,2-diketone is slower due to the isotope effect. This was confirmed by preliminary measurements (Annex D).

The combination of the aforementioned parameters with a hydrophobic polysiloxane coated substrate also increased the nucleation density at the surface, an important factor to induce alignment at the microscale. The confinement of the photoreaction at the surface by a biphotonic 770 nm excitation allowed to photopattern highly anisotropic micropatterns. The growth directions of the fibers in the patterns was entirely controlled by the direction of the scanning of the laser. This was confirmed by polarization microscopy showing polarization values ranging from -0.17 to 0.17 for an entire surface, whereas the extreme values reported for single nanofibers of DDOA do not surpass -0.2 and 0.2. Interestingly, this photopatterning method seems not to be limited by the optical diffraction limit, but by the

General conclusion

dimension of the supramolecular fiber. The molecular packing and bundling of the DDOA fibrils induces fiber width of 80 nm to 1 micron (mostly 100-200 nm). In perspective, changing DDOA for other (photoactive) molecular gelators which yield smaller fibers by self-assembly could allow to deposit smaller anisotropic nano-objects. It would also be of interest to extrapolate the method to water based molecular gelators since they can be applied in other fields, for example biology. Nevertheless, the new system would have to be optimized again, because only the general design rules given here would be applicable.

In perspective, it would also be interesting to exploit the tuneable emission property of these nanofiber systems. Initial work performed on macroscopic gels have demonstrated that colour of the emission of the gel can be changed from blue to green by addition of 2 mol% of dkG10 to dkDDOA. This allowed to obtain, by simultaneous photoconversion, a homogeneous mixed gel in which the tetracene is sensitized upon excitation of the anthracene. Further experiments are needed to proof that the co-assembly can be performed under microscope. This would allow multi-color patterning at the submicron scale. So far, preliminary experiments under the confocal microscope with dkG10 were not successful and the incorporation of other available acceptors is being attempted.

In summary, we have presented a new photoactive gelator, which efficiently gels DMSO without the formation of side-products and for the first time, to our knowledge, highly anisotropic micropatterns were made by controlling the self-assembly of an LMWG at multiple length scales.

In the second part of the thesis it was shown that the synthetic strategy allows to synthesize a versatile group of self-assembling 2,3-alkoxylated acenes. By following the design rules given in the Chapter 4, the length of the aromatic core on the long and short axis of the acene can be altered to achieve custom photophysical properties while maintaining the 1dimensional self-assembly property. However, one disadvantage of these series of 2,3alkoxylated acenes, is their lowered stability towards dioxygen. The increase in electron density makes the 2,3-substituted acene more susceptible to oxygen than the corresponding parent acene. The addition of more electron withdrawing groups such as fluorine or cyano groups would be appropriate to increase the stability. Furthermore, the introduction of these groups is easily accessible with the existing synthetic protocols. Nevertheless, the electron withdrawing groups might also alter the molecular packing as seen for 2,3-dichloro-6,7didecyloxyanthracene (Cl_2DDOA) in comparison with DDOA. Here, the crystallinity seen for DDOA fibers was proven to be lesser in Cl_2DDOA , but the obtained fibers were smaller in width.

In fine, the use of the orthogonal thiol-yne reaction has been proven to be a valid method to increase the mechanical properties of the OG2 hydrogelator. Nevertheless, the large amount of compounds necessary to control the gelation and post-treatment introduces a large amount of parameters to control. Some hurdles to overcome were the inadequate light source, the highly absorbing imines masking the photoinitiator through an inner filter effect and the partial insolubility of the crosslinker used. However, from a fundamental point of view the system is very interesting since in combination with super-resolution microscopy it can provide more insight on the actual role crosslinks have on the mechanical properties. This part on the research of gelators still lacks knowledge. The super-resolution imaging of the hydrogel is still an ongoing project.

Changing the used crosslinks for more water soluble /biocompatible crosslinks as thiolated hyaluronic acid could also increase the applicability of the system for applications such as cell culture due to the biocompatibility of hyaluronic acid compared to PEG. The posttreatment would allow to alter mechanical properties to appropriate properties suitable for cell culture.

6

Experimental section

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6.1. Materials

All reagents and chemicals were purchased at Sigma-Aldrich, Acros Organics, ABCR Chemicals or TCI Europe and used as received unless otherwise stated. Anhydrous THF, toluene or DCM were obtained by distilling it over sodium/benzophenone or sodium, respectively, whereas DCM was distilled over CaH₂. Anhydrous DMSO, MeOH and DMF were purchased from Acros Chemicals containing an AcroSeal[®] and 4 Å molecular sieves.

For all water sensitive reactions, the used glassware was dried in the oven overnight prior to the reaction. Diisopropylethylamine was stirred with CaH_2 under argon for 12 hours, distilled and stored over 4 Å molecular sieves. K_2CO_3 and Na_2CO_3 were stored in the oven.

6.2. Methods

Column chromatography was performed on Sigma Aldrich Silica 40 (230-400 mesh size or 40- 63μ m) as stationary phase. Thin layer chromatography was performed on TLC Silica gel 60 F254 coated aluminium plates from Merck.

¹H-NMR- en ¹³C-NMR-spectra were recorded on a Bruker Avance III 200 (¹H: 200 MHz, ¹³C: 50 MHz), Bruker Avance I 300 (¹H: 300 MHz, ¹³C: 75 MHz) or a Bruker Avance III 600 (¹H: 600 MHz, ¹³C: 150 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (¹H) or the internal solvent signal (¹³C). Coupling constants were reported in Hz. The multiplicity of the shifts are given as s = singlet, d = doublet, t = triplet, q = quintet or m = multiplet.

Mass spectra are measured by the Centre d'Etude Structurale et d'Analyse des Molecules Organique (CESAMO) at the University of Bordeaux. The measurements were ran using a ESI-QTOF mass spectra (including all HRMS) performed on a QStar mass spectrometer of Applied Biosystems equipped with an ESI source and spectra were recorded in the positive mode. Electrospray mass spectra were recorded with a spectrometer Varian Saturn-4D were the electron spray needle was maintained at 5000 V and operated at room temperature. Samples were introduced by injection through a 20 μ L sample loop into a 4500 μ L.min⁻¹ flow of methanol from the LC pump. ESI-MS experiments were performed on an ion trap spectrometer equipped with an electrospray ion source (ESI). Field desorption (FD) spectra were recorded on a TOF mass spectrometer using an FD emitter with an emitter voltage of 10 kV.

UV-vis spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer with a Peltier $1 \ge 1$ Cell Holder for temperature dependent UV-vis measurements. Fluorescence spectra were recorded on a Horiba Scientific FluoroMax 4 spectrofluorometer. Lifetimes were recorded on a Horiba Jobin-Yvon spectrofluorometer by time-correlated single photon counting, exciting with a NanoLED N-375L 371±10 nm driven by a FluoroHub A+. The

detector used is a HAMAMATSU 928P PMT in single photon counting mode. Photophysical properties were recorded in degassed HPLC grade solvents.

Irradiation experiments were performed with a Powerstar LED "Deep Blue 450 nm" from Osram for the photocarbonylation reactions and the LED power was measured with a Lm htd thermal power sensor from Coherent. Irradiations to estimate the quantum yield of the reaction (Φ_R) were performed with a home-build optical bench using a high pressure mercury lamp and a monochromator.

Theoretical calculations were performed with Gaussian at the DFT (B3LYP) level. The optimization of the geometry in the ground state was carried out by the DFT method using 6-31G^{*} basis set and the default options to converge (calculations were performed by Dr. L. Gartzia-Rivero).

Rheological experiments at the TU Delft were performed using a rheometer (AR G2, TA instruments) with a steel bottom plate and a homemade glass top plate. The experiments were done in a strain controlled mode equipped with plate-and-plate geometry of 40 mm in diameter at 25 ± 0.2 °C. Sample volume was kept at 1 mL providing an approximate plate-to-plate distance of 300-400 µm. The actual composition of the sample was 0.1 mL HCl with 0.4 mL of MilliQ water and the OG2, 0.4 mL MilliQ water with the photoinitiator and crosslinker and 0.1 mL 1 M NaOH. The NaOH solution was mixed with the photoinitiator and directly brought onto the bottom plate. The light irradiation was performed using the APEX optical fiber illuminator over the top glass plate.

6.2.1. Fluorescence quantum yield^[1]

The fluorescence quantum yield gives the efficiency of emitted photons vs the absorbed photons upon excitation. The fluorescence quantum yields were determined in dilute solution (A < 0.1) by comparing it with a reference of known fluorescence quantum yield using equation (6.1).

$$\Phi_F = \frac{I * A_R * n^2}{I_R * A * n_R^2} \Phi_F^R$$
(6.1)

Where, $\Phi_{\rm F}$ is the fluorescence quantum yield of the sample in absolute percentage, I the integrated fluorescence (area under the spectrum) intensity of the sample and I_R is the integrated fluorescence intensity of the reference. A and A_R are the absorbance of the sample and reference (A \approx (1-10^{-A})/ln10 for A \approx 0) at the wavelength of excitation, respectively. The absorbance is always < 0.1 for every measurement. n and n_R are the refractive index of the sample and reference respectively.

Different reference compounds have been used for several compounds and the most important is that the measured sample and reference have a similar absorbance at the wavelength of excitation (< 0.1) and emit in around the same spectral region.

6.2.2. Photochemical quantum yield (actinometry)^[2,3]

The photochemical quantum yield has been determined according to a standard method using potassium ferrioxalate as reference at two different wavelengths (336 and 468 nm) in two different concentrations (0.012 and 0.15 M).

A solution of ferrioxalate (0.012 or 0.15 M) in 0.05 M H_2SO_4 and a phenanthroline (0.1%) solution in 0.5 M buffered with sodium acetate (225 g.L⁻¹) were prepared. The photochemical quantum yield was measured according to the Fischer method, a "microversion" of the Hatchard and Parker method. Upon irradiation the ferrioxalate decomposes according to the following rate equations:

$$Fe(C_2O_4)_3^{3-} \xrightarrow{hv} Fe^{2+} + C_2O_4^{*-} + 2C_2O_4^{2-}$$
(6.2)
$$Fe(C_2O_4)_3^{3-} + C_2O_4^{*-} \xrightarrow{\Delta} Fe^{2+} + 2CO_2 + 3C_2O_4^{2-}$$

After irradiating a solution of ferrioxalate (3 mL) for a certain time, 0.5 mL of the phenanthroline solution is added to form the tris-phenanthroline complex with the Fe²⁺ ions ($\varepsilon = 11100 \text{ M}^{-1} \text{ cm}^{-1}$ at 510 nm). The absorbance is measured according to a reference solution of ferrioxalate with phenanthroline kept in the dark and the difference between the two solutions is used to calculate the concentrations of Fe²⁺ with the equation

$$mol \, Fe^{2+} = \frac{V * \Delta A(510 \, nm)}{l * \varepsilon_{510 \, nm}} \tag{6.3}$$

where, V is the volume of the sample (3.5 mL), ΔA is the difference in absorbance, l is the optical path length (1 cm) and ε_{510nm} is the molar extinction coefficient of the trisphenanthroline complex with Fe²⁺. This gives the photons absorbed by the irradiated solution:

$$N(\frac{hv}{t}) = \frac{mol \ Fe^{2+}}{\Phi_R * t * F}$$
(6.4)

where, $\Phi_{\rm R}$ is the is the photochemical quantum yield of the decomposition of ferrioxalate at 336 nm (1.21) or 468 nm (0.93), t is time in seconds and F is the absorbance of the ferrioxalate solution at the wavelength of excitation (1-10^{-A}). If the ferrioxalate solution is sufficiently concentrated F (=~1) can be omitted. It should also be taken into account to not surpass 10% of photoconversion to obtain a reliable value for the photochemical quantum yield. The concentration of converted dkDDOA into DDOA can be calculated as follows:

$$C_i = \frac{\Delta A}{\varepsilon_{\infty} - \varepsilon_{t=0}} \tag{6.5}$$

Where C_i is the change in concentration upon irradiation, ΔA is the difference in absorbance, $\boldsymbol{\epsilon}_{\infty}$ is the molar extinction coefficient if all of the dkDDOA was photoconverted and $\boldsymbol{\epsilon}_{t=0}$ is the molar extinction coefficient of dkDDOA at t=0. The quantum yield of the reaction can then by calculated according to equation (6.6).

$$Q_R = \frac{C_i * V}{\left[\frac{Nh\nu}{t}\right] * t}$$
(6.6)

Where Φ_R is the quantum yield of the photoreaction, V is the irradiated sample volume and t is the time of irradiation in seconds.

6.2.3. Correction for competitive absorption in emission spectra

Fluorescence measurements of a mixture of absorbing molecules (dkDDOA in a gel of DDOA) needs to be corrected for the competitive absorption or reabsorption of the added dkDDOA if it absorbs at the excitation wavelength and/or emission wavelength of the emitting molecule (DDOA). The used correction factor is as follows^[4,5]:

$$F_{corr} = F\left(\frac{1 - e^{-\varepsilon_{ex(a)}c_{ex(a)}}l_{ex}}{\varepsilon_{ex(a)}c_{ex(a)}}\right) \left(\frac{\varepsilon_{ex(a)}c_{ex(a)} + \varepsilon_{ex(b)}c_{ex(b)}}{1 - e^{-(\varepsilon_{ex(a)}c_{ex(a)} + \varepsilon_{ex(b)}c_{ex(b)})l_{ex}}}\right) \left(\frac{\varepsilon_{em(b)}c_{em(b)}l_{em}}{1 - e^{-(\varepsilon_{em(b)}c_{em(b)})l_{em}}}\right)$$
(6.7)

where F_{corr} is the corrected fluorescence intensity, F is the measured fluorescence intensity and $\varepsilon_{ex(a)}$, $c_{ex(a)}$ and $\varepsilon_{ex(b)}$, $c_{ex(b)}$ are the molar extinction coefficients and concentrations of DDOA (a, $\varepsilon_{365 \text{ nm}} = 6666 \text{ M}^{-1} \text{.cm}^{-1}$) and dkDDOA (b, $\varepsilon_{365 \text{ nm}} = 3185 \text{ M}^{-1} \text{.cm}^{-1}$) at the excitation wavelength (excitation = 365 nm), respectively. $\varepsilon_{em(b)}$, $c_{em(b)}$ are the molecular extinction coefficient and concentration of dkDDOA at the emission wavelength (436 nm for the Stern Volmer plot, $\varepsilon_{436} = 790 \text{ M}^{-1} \text{.cm}^{-1}$). Finally, l_{ex} and l_{em} are the excitation and emission path lengths, which were estimated to be 0.03 cm.

Using the correction factor the emission at 436 nm was corrected to plot the Stern-Volmer of a mixture of DDOA and dkDDOA.

6.2.4. Temperature dependent absorption measurements

All used test tubes were dried in the oven prior to the sample preparation. The needed amount of DDOA was weighted on a XP6 Microbalance from Mettler Toledo and put in a dried test tube charged with argon, sealed tight with a septum and wrapped in aluminum foil. Anhydrous DMSO is added through a syringe and the sample is heated to 90°C in an oil bath until dissolution. Afterwards the solution is degassed by bubbling argon through the solution for an additional 5 min at 100°C. The solution is kept at 100°C, transferred into a 1 mm cuvette and put in the preheated 1 x 1 Peltier cell holder with a 9 mm copper spacer at 80°C. After 10 min at 80°C, a cool cycle (from 80°C to 19°C) and a heat cycle (19°C to 80°C) were performed with a speed of 1°C.min⁻¹. A spectrum was taken every minute between 300 and 550 nm. DMSO was used as a reference.

The degree of aggregation (α) was calculated from:

$$\alpha(T) = \frac{\varepsilon(T) - \varepsilon_M}{\varepsilon_A - \varepsilon_M} \tag{6.8}$$

where $\boldsymbol{\epsilon}(T)$ is the extinction coefficient at temperature T; $\boldsymbol{\epsilon}_M$ and $\boldsymbol{\epsilon}_A$ are the extinction coefficients of the monomer in solution and the fully aggregated state, respectively. The latter two values were determined from the data.

6.2.5. Sample preparation of the alphadiketone-2,3-decyloxyanthracene for photopatterning

The test tubes were dried in the oven prior to the sample preparation. A 4 mM solution of alpha-diketone-2,3-decyloxyanthracene is prepared by weighing the needed amount of alphadiketone-2,3-decylocyanthracene (± 4 mg for 2 mL) on a XP6 Microbalance from Mettler Toledo. The compound is put in a dried test tube charged with argon, sealed tight with a rubber septum and wrapped in aluminum foil. The weighing was performed under orange light. Anhydrous DMSO is added through a syringe and the sample is heated to 90 °C in an oil bath until dissolution. Afterwards, the solution is degassed by bubbling argon through the solution for 5min at 90°C. The solution is left to cool down to room temperature and the sample is kept under argon pressure (argon balloon) during the whole experimental session. The addition of the solvent, dissolution and argon bubbling were performed under red light.

Additional test tubes were charged with argon and used to dilute the 4 mM stock solution to the desired concentration. 100 uL of the stock solution is diluted by adding the necessary amount of anhydrous DMSO. In the case where H_2O was added, at the very last moment in the amount of H2O is added in volume percentage (vol%). The overall volume used for microscopy is always 100 µL

6.2.6. Confocal laser scanning microscopy

The confocal laser scanning microscope is a PicoQuant Microtime 200 based on an inverted IX 71 inverted microscope from Olympus. Two-photon excitation was provided by the laser chain consisting of a tuneable (700-1000 nm) convertible (picosecond/femtosecond) Ti:Sa laser (Coherent MIRA900) and a pulse picker affording pulses of (6 ps/150 fs) at single shot to 4.75 MHz repetition rate. It is pumped by a Coherent VERDI G10, a continuous 10 W 532 nm laser. For mono-photonic excitation at lower wavelengths, the laser output (700-1000 nm) is frequency doubled by a LBO crystal (to 350-500 nm) after the pulse picker. The polarization state is then controlled by a Babinet-Soleil compensator.

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Mono-photonic irradiation was provided in some experiments by a 473 nm continuous laser (CNI MBL-F-473-300 mW) from Changchun New Industries Optoelectronics Technology Co., Ltd.

Alternatively, a PicoQuant 375 nm laser diode was used as excitation source to do fluorescence imaging. It provides pulses of \sim 70 ps (power dependent) at set repetition rates (typically 5 MHz).

These lasers are coupled into a polarization maintaining fiber and sent to the objective of the microscope. The objective is a 100 x oil immersion objective from Olympus (UPLSAPO) with a numerical aperture of 1.4. The sCMOS is an ORCA-Flash4.0 V3 Digital CMOS camera (C13440-20CU) from Hamamatsu.

All experiments were done at constant room temperature of 23°C controlled by air conditioning. The setups were given in Chapter 4.

6.2.7. Polarization microscopy and determination of the G-factor

The mean arrangement of (intrinsic) fluorescent molecules within the fibers can be estimated by detecting the fluorescence polarization after excitation. To realize these measurements, the following setup is used:



Scheme 6.1: Emission pathway to measure fluorescence polarization.

Molecules are excited by selectively absorbing linearly polarized laser light when their dipole orientation contains a sufficiently large component along the axis of the excitation beam. The emission beam is sent through a polarizing beam splitter which separates the beam according to two orthogonal polarizations (90° angle). The two polarizers in front of the detectors clean up any residual orthogonal component to assure that the light detected is as linearly polarized as possible. The emission parallel or perpendicular to the polarization of the excitation are denoted as I_{II} and I_{\perp} . These intensity values are used to calculate the anisotropy (r) or polarization (P).

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$$P = \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}} \qquad r = \frac{I_{//} - I_{\perp}}{I_{//} + 2I_{\perp}}$$
(6.9)

The polarization can theoretically vary from -1 to 1, and -0.5 to 1 for the anisotropy.

The spectral sensitivity of the two detectors are never exactly the same due to several reasons. For instance, there can be a variation in their tolerance (reflection, transmission etc). Therefore, a correcting G factor has to be determined. In our case the G factor is determined by one of these two methods. (i) A sample that does not display any measurable polarization, typically a diluted solution, is measured, and the G factor is similar to the one of the sample of interest, and when the emission spectrum of the solution is similar to the one of the sample of interest, and when the dissolved molecules show very fast fluorescence depolarization (through rotation of molecules after photo-selection) compared to their intrinsic decay of fluorescence. (ii) When the required conditions cannot be assured in a solution, the sample itself is imaged and a first set of I_{II} and I_{\perp} are measured, from a Region of Interest (ROI) easily retrievable later on. Then the sample is rotated by 90° as well as the polarization of the laser (using the Babinet-Soleil compensator), and a second set of I_{II} and I_{\perp} is obtained from the same ROI, rotated. The following equation is then used to determine G:

$$G = \sqrt{\left(\frac{I_{//}}{I_{\perp}}\right)_{1} \left(\frac{I_{//}}{I_{\perp}}\right)_{2}} \tag{6.10}$$

Then polarization and anisotropy are written as:

$$P = \frac{I_{//} - GI_{\perp}}{I_{//} + GI_{\perp}} \qquad r = \frac{I_{//} - GI_{\perp}}{I_{//} + 2GI_{\perp}}$$
(6.11)

The polarization and the anisotropy are bound through,

$$r = \frac{2P}{3 - P} \tag{6.12}$$

The self-assembling 2,3-alkoxy access take in a certain molecular order i.e. the self-assembled structure restricts the free rotational and translational motion of the molecules. Therefore, polarization microscopy makes it possible to image the degree of organization of the ensemble of molecules within the nanofiber. For the analysis, the fluorescence polarization emitted by the nanofibers is shown in an image with a false colours map. Red indicates the parallel polarization (P=+1) and blue indicates perpendicular polarization (P=-1) in respect to the excitation source. Green (P=0) is indicative of either a purely linear polarization oriented exactly at 45° angle either of non-polarized light, expected for disordered assemblies (see Figure 6.1). All situation are possible, including partially linearly polarized light oriented at 45° giving P=0, so that a single measurement is in general not conclusive,

and the dependence of the fluorescence polarization with the angular orientation of the objects must be measured through a customized Labview program.



Figure 6.1: (a) False colour scheme for the analysis of polarization images and the corresponding orientation. (b). The transition dipole of DDOA in the excited state.

6.2.8. Contact angle measurement

Contact angles were measured with a Drop Shape Analyzer Krüss DSA 100. For each sample, a 3 μ l of MilliQ water droplet was deposited onto the treated surface (polysiloxane coated, commercial borosilicate and piranha etched) using a microsyringe. A snapshot of the deposited drop was taken within 10 sec to exclude solvent evaporation. The static contact angle of a sessile drop was measured using a goniometer. This was repeated 3 times per sample.

The borosilicate glass slides are commercially available at CarlRoth, polysolixane coated slides were donated by Marienfeld and the piranha etched slides were first washed with acetone, isopropanol and MilliQ water. Afterwards, the cleaned slides were etched for 10 min in Piranha (3:7, H_2O_2 : H_2SO_4) and rinsed with MilliQ water before blow drying with dry air.



Figure 6.2: Water contact angles (WCA) depicted from hydrophobic to hydrophilic (from left to right). A. polysiloxane coated surface (101.5°±0.5), commercial borosilicate surface (61°±2.1) and the piranha etched borosilicate surface (< 10°, not measurable).

6.2.9. Protocol free thiol content determination using the Ellman reagent First the needed buffers are prepared. For the PBS buffer (pH = 7.4), the salts and EDTA are dissolved in MilliQ in 4/5 of the used volume (in a volumetric flask). Afterwards, the pH is readjusted to 7.4 and the remaining volume is filled with MilliQ water and the pH is verified afterwards

Salt	Concentration	Concentration
	$(mmol.L^{-1})$	$(g.L^{-1})$
NaCl	137	8.0
${f Na_2HPO_4}$	10	1.42
$\mathrm{KH}_{2}\mathrm{PO}_{4}$	1.8	0.24
EDTA	1	0.29

 Table 6.1: Concentration of salts for preparation of saline phosphate buffer with EDTA:

For the boric acid buffer (pH = 8.2-8.3), boric acid and EDTA are dissolved in MilliQ in 4/5 of the used volume (in a volumetric flask) and the pH is afterwards adjusted to 8.2-8.3 with NaOH. The remaining volume is filled with MilliQ and the pH is verified afterwards.

 Table 6.2: Concentration of salts for the preparation of a boric acid buffer

Compound	Concentration	Concentration
	$({ m mmol.L}^{-1})$	$(g.L^{-1})$
Boric acid	100	6.18
EDTA	0.2	0.058

Both buffers and MilliQ were degassed for 20 min with nitrogen. Next, a 5 mM solution of DTNB (Ellman reagent) is prepared from the PBS buffer.^[6] To dissolve all the DTNB, the stock solution is sonicated for 2 a 3 min at 30°. Afterwards, the sample to measure by UV-vis can be prepared and has the following composition: 700 μ L of boric buffer, 200 μ L of Ellman reagent in PBS and 100 μ L of the thiol in aqueous solution (MilliQ). The final pH is 8.2 and the total volume 1 mL. For the reference sample the same composition is used, but the thiol is replaced by MilliQ. Both samples are vortexed at 1000 rpm for 5 min before the measurement. On the UV-VIS spectrometer the baseline is taken with the reference sample and a solution of the same composition in both sample holders followed by measuring the absorbance of the reference and the sample containing the free thiol. Everything was measured in a 1 mm cuvette. The reference and the sample are preferably measured in the same cuvette. The measured range is 280- 800 nm.

To calculate the concentration of free thiol the absorbance spectra of the reference and sample were corrected to 0 at 600 nm and concentration of thiol in the sample was calculated through the following simple equation at 412 nm. The epsilon value of TNB^{2-} anion is 14150 cm⁻¹.M⁻¹ at a pH > 7.3 at 412 nm.

$$conc SH(M) = \frac{Abs_{sample} - Abs_{ref}}{14150 * 0.1}$$
6. 13

6.3. Synthesis

The procedures to synthesize 2,3-dimethoxyanthraquinone and 2,3-dimetoxytetraquinone can be found in the literature and the experimental procedures will not be discussed here.^[7,8]

6.3.1. General procedure for the demethylation of 2,3 dimethoxyacenequinone

A suspension of the 2,3-dimethoxyacenequinone in HBr 48% aq. (7 ml.mmol⁻¹) was refluxed for 24h at 135°C. The suspension was allowed to come to room temperature and glacial acetic acid (7 ml.mmol⁻¹) was added. The reflux was continued for another 24h at 135°C. The suspension was allowed to cool to room temperature and water (15 ml.mmol⁻¹) was added.

2,3-bis(hydroxyl)anthracene-9,10-dione



The 2,3-dihdroxy-anthraquinone was washed with additional H_2O and filtered. The residue was washed with MeOH and Et₂O and dried under high vacuum. The crude product was used in the next step. (yield = -92%).

¹H-NMR (200 MHz, DMSO-d₆): δ 10.59 (s, 2H, OH), 8.14-8.10 (m_c, N = 9 Hz, 2H, ArH), 7.87-7.82 (m_c, N = 9 Hz, 2H, ArH), 7.52 (s, 2H, ArH).

2,3-bis(hydroxyl)tetracene-5,12-dione



The 2,3-dihydroxy-tetraquinone was washed with water and filtered. The residue was washed with acetone and diethyl ether and dried under high vacuum. The crude product was used in the next step. (yield = 84%)

¹H-NMR (200 MHz, DMSO): δ : 10.68 (s, 2 H, OH), 8.68 (s, 2H, ArH), 8.21 (m_c, N = 9.4 Hz, 2H, ArH), 7.73 (m_c, N = 9.5 Hz, 2H, ArH), 7.57 (s, 2H, ArH).

6.3.2. General procedure for the alkylation of the 2,3-dihydroxyacenequinone

The hydroxyacenequinone was dissolved in dry DMF (17 ml.mmol⁻¹) and deprotonated over 45min with K_2CO_3 (5 eq.) under argon at room temperature. The alkylbromide was added (5 eq.) and the reaction mixture was refluxed for another 15 hours at 135°C. After reaction completion the mixture was allowed to cool down to room temperature. The solvent was evaporated *in vacuo* and the product was purified by column chromatography using dichloromethane/petroleum ether as eluent.

2,3-bis(decyloxy)anthracene-9,10-dione



2,3-Dihydroxyanthracene-9,10-quinone (1 g, 4.16 mmol), K_2CO_3 (2.9 g, 20.8 mmol), $C_{16}H_{33}Br$ (2.18 mL, 10.5 mmol), DMF (70 ml). Purification by column chromatography (1:4 CH_2Cl_2 :petroleum ether) gave a waxy yellow solid (1.9 g, 3.65 mmol, 88%).

NMR (300 MHz, CDCl₃): δ =8.28 (m_c, N = 9 Hz, 2H, ArH), 7.76 (m_c, N = 9.1 Hz, 2H, ArH), 7.68 (s, 2H, ArH), 4.19 (t. ³J = 6.6 Hz, 4H, OCH₂), 1.94-1.85 (q, 4H, OCH₂C<u>H₂</u>), 1.6-1.2 (m, 28H, CH₂), 0.88 (t, ³J = 6.9 Hz, 6H, CH₃).

2,3-bis(decyloxy)tetracene-5,12-dione



2,3-Dihydroxytetracene-5,12-quinone (0.31 g, 1.07 mmol), K_2CO_3 (0.74 g, 5.35 mmol), $C_{16}H_{33}Br$ (1.11 mL, 5.35 mmol), DMF (20 ml). Purification by column chromatography (1:1 CH₂Cl₂:petroleum ether) gave a waxy yellow solid (0.35 g, 0.61 mmol, 57%).

¹H NMR (300 MHz, CDCl₃): $\delta = 8.82$ (s, 2 H, ArH), 8.11 (m_c, N = 9.5 Hz, 2 H, ArH), 7.78 (s, 2 H, ArH), 7.71 (m_c. N = 9.5 Hz, 2 H, ArH), 4.25 (t, ³J = 6.6 Hz, 4 H, OCH₂), 2.00-1.90 (q, 4 H, OCH₂CH₂), 1.60-1.24 (m, 28 H, CH₂), 0.93 (t, ³J = 6.8 Hz, 6 H, CH₃)

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2, 3-bis (hexadecyloxy)-anthracene-9, 10-dione



2,3-Dihydroxyanthracene-9,10-quinone (0.25 g, 1.04 mmol), K_2CO_3 (0.72 g, 5.2 mmol), $C_{16}H_{33}Br$ (0.8 mL, 2.6 mmol), DMF (18 ml). Purification by column chromatography (1:1 CH₂Cl₂:petroleum ether) gave a waxy yellow solid (0.65 g, 0.94 mmol, 90%).

¹H-NMR (300 MHz, CDCl₃): 8.27-8.24 (m_c, N = 9 Hz, 2H, ArH), 7.75-7.72 (m_c, N = 9 Hz, 2H, ArH), 7.67 (s, 2H, ArH), 4.18 (t, ${}^{3}J = 6.6$ Hz, 4H, OCH₂), 1.89 (q, 4H, OCH₂C<u>H₂</u>), 1.57-1.44 (m, 4H, CH2), 1.43-1.15 (m, 48H, CH₂), 0.87 (t, ${}^{3}J = 6.3$ Hz, 6H, CH₃)

 $^{13}\mathrm{C}\text{-NMR}$ (75 MHz, CDCl₃): 182.78, 153.88, 133.79, 133.73, 128.24, 127.06, 109.44, 69.53, 32.08, 29.87, 29.82, 29.76, 29.52, 29.06, 26.09, 22.85, 14.28

2, 3-bis (decyloxy) - 9, 10, 11, 15-tetrahydro-9, 10-[4,5] epidioxoloanthracen-13-one



A solution of 2,3-didecyloxyanthracene (DDOA) (1 g, 2.04 mmol) and vinylene carbonate (1.3 mL, 20.4 mmol) in deoxygenated xylene (30 mL) was heated at 180°C in a sealed flask for 3 days. After removal of the solvent *in vacuo*, the residue was purified by column chromatography. At 35:65 petroleum ether: CH_2Cl_2 a transparent liquid (0.45 g, 0.78 mmol, 88%) was obtained. (collected both the diastereomers)

MS [FD]: m/z 576.4

HRMS (FD+) calcd for $C_{37}H_{52}O_5$ 576.3815, found m/z = 576.3792

IR [KBr] = 1753, 1734, 3056 cm⁻¹

¹H-NMR (200 MHz, CDCl₃, mix of diastereomers): 7.31-7.39 (m, 4H, ArH), 7.18-7.26 (m, 4H, ArH), 6.92 (s, 4H, ArH), 4.86 (t, ${}^{3}J = 1.6$ Hz, 2H) 4.83 (t, ${}^{3}J = 1.7$ Hz, 2H), 4.57 (s, 4H), 3.88-4.05 (m, 8H, OCH₂), 1.72-1.85 (q, 8H, OCH₂C<u>H₂</u>), 1.38-1.51 (m, 8H, CH₂), 1.18-1.37 (m, 48H, CH₂), 0.88 (t, ${}^{3}J = 6.9$ Hz, 12H, CH₃).

¹³C-NMR (100 MHz, CDCl₃, mix of diastereomers): 153.3, 148.8, 138.4, 136.9, 136.8, 136.7, 130.0, 128.6, 127.8, 127.7, 126.5, 125.5, 112.9, 112.1, 76.5, 76.4, 69.9, 69.7, 47.6, 47.5, 32.1, 29.7, 29.5, 26.2, 22.8, 14.3.

2, 3- bis (decyloxy) - 9, 10- dihydro-9, 10- ethano anthracene - 11, 12- diol



To a solution of 2,3-bis(decyloxy)-9,10,11,15-tetrahydro-9,10-[4,5]epidioxoloanthracen-13-one (0.94 g, 1.63 mmol) in 1,4-dioxane (7 mL), 4M NaOH (aq, 6 mL) was added under argon. After 2 hr of reflux (117°C), the mixture was cooled to room temperature and neutralized with 1 M HCl. After the addition of H₂O, the mixture was extracted with CH₂Cl₂. The combined organic fractions were washed with H₂O (1x), brine (2x), dried over Na₂SO₄. The filtered solution was concentrated *in vacuo* obtaining a beige viscous liquid (0.9 g, 1.63 mmol, quantitative).

IR (KBr) = 2852, 2922, 3421

MS (FD+): m/z 573.392, 1123.79 [M+]

HRMS (FD+) calcd for $C_{36}H_{54}O_4Na$ 573.3914, found m/z = 573.3919

¹H-NMR (200 MHz, CDCl₃, mix of diastereomers): 7.25-7.4 (m, 4H, ArH), 7.09-7.23 (m, 4H, ArH), 6.95 (s, 2H, ArH), 6.88 (s, 2H, ArH), 4.3 (s, 4H), 3.87-4.07 (m, 12H, OCH₂ + bridgehead), 1.88 (s, 4H, OH), 1.67-1.85 (q, 8H, OCH₂CH₂), 1.15-1.52 (m, 52H, CH₂), 0.88 (t, J = 6.4 Hz, 12H, CH₃).

¹³C-NMR (100 MHz, CDCl₃, mix of diastereomers): 148.0, 140.5, 139.2, 132.4, 130.9, 126.7, 124.6, 113.5, 111.8, 69.9, 69.8, 68.5, 68.3, 51.1, 51.1, 32.1, 29.8, 29.7, 29.6, 29.5, 26.2, 22.8, 14.2

2, 3-bis (decyloxy) - 9, 10-dihydro-9, 10-ethanoanthracene-11, 12-dione



To a mixture of dry DMSO (1.8 mL, 25.4 mmol) and dry CH₂Cl₂ (25 mL), TFAA (3.25 mL, 23.4 mmol) was added dropwise at -78°C under argon. After 10 min a solution of 2,3bis(decyloxy)-9,10-dihydro-9,10-ethanoanthracene-11,12-diol (0.4 g, 0.73 mmol) in dry CH₂Cl₂ (50 mL) was added dropwise at -78°C. After stirring for 2 hours, DIPEA (14.2 mL, 79.6 mmol) was added dropwise and stirring was continued for an additional 1.5 hour at - 78°C. Afterwards the reaction was left to come to room temperature. 1 M HCl was added and the organic layer was separated. The aqueous layer was washed with CH₂Cl₂ (2x). The combined organic fractions were washed subsequently with H₂O (2x) and brine (1X), dried over Na₂SO₄, filtered and concentrated *in vacuo* while protecting it from light. The foul smelling red paste was purified by column chromatography in a dark room with 60:40 CH₂Cl₂:petroleum ether to give an orange solid (0.31 g, 0.56 mmol, 77%) after drying under high vacuum.

MS [CI]: m/z 547.4

HRMS (CI) calcd for $[C_{36}H_{51}O_4]^+$ 547.38051, found m/z = 547.37873

¹H-NMR (400 MHz, CDCl₃): 7.42-7.48 (m, 2H, ArH), 7.34-7.39 (m, 2H, ArH), 6.97 (s, 2H, ArH), 4.85 (s, 2H), 3.99 (t, ${}^{3}J = 6.6$ Hz, 4H, OCH₂), 1.76-1.86 (q, 4H, OCH₂C<u>H₂</u>), 1.41-1.5 (q, 4H, CH₂), 1.16-1.41 (m, 24H, CH₂), 0.88 (t, J = 7.04 Hz, 6H, CH₃).

 $^{13}\text{C-NMR}$ (100 MHz, CDCl₃): 183.6, 150.75, 135.4, 129.3, 126.9, 126.3, 111.5, 69.7, 59.4, 32.1, 29.8, 29.7, 29.5, 29.3, 26.2, 22.8, 14.3.

2, 3- bis (hexadecyloxy) - 9, 10- bis (phenylethynyl) anthracene



To a solution of phenylacetylene (0.08 mL, 0.73 mmol) in dry THF (5 mL) n-BuLi (0.44 mL, 1.6 M in hexanes) was added dropwise while stirring vigorously at -78°C under argon. 2,3bis(hexadecyloxy)-anthraquinone (100 mg, 0.145 mmol) was dissolved in dry THF (8 mL) and after 30 min dropwise added to the reaction mixture at -78°C. After an additional 30 min at -78°C, the reaction was allowed to come to room temperature and stirred overnight. The solution was quenched with a saturated NH₄Cl solution and extracted with Et_2O . The collected organic fractions were washed with H_2O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. The crude was dissolved in Et_2O (20 mL) followed by $SnCl_2$ (83 mg, 0.44 mmol) in 10% HCl solution (5 mL) under argon. The reaction was allowed to cool down to room temperature. The reaction was given in H_2O and the precipitate was filtered off and subsequently washed with MeOH. The residue was recrystallized in DCM/MeOH to give a bright yellow solid (56 mg, 0.065 mmol, 45%)

MS [EI]: m/z 858.6, 1718.35

HRMS (EI) calcd for $[C_{62}H_{82}O_2]$ 858.63148 found m/z = 858.6319

¹H-NMR (300 MHz, CDCl₃): 8.6 (m_c, N = 9.9 Hz, 2H, ArH), 7.87 (s, 2H, ArH), 7.75 (dd, 4H, 1J = 8 Hz, ²J = 1.8 Hz, ArH), 7.58 (m_c, N = 9.9 Hz, 2H, ArH), 7.51-7.38 (m, 6H, ArH), 4.28 (t, ³J = 6.6 Hz, 4H, OCH₂), 1.99 (q, 4H, OCH₂<u>CH₂</u>), 1.62-1.26 (m, 52H, CH₂), 0.88 (t, ³J = 6.3 Hz, 6H, CH₃).

¹³C-NMR (75 MHz, CDCl₃): 151.18, 131.69, 131.11, 129.57, 128.72, 128.62, 126.89, 125.97, 123.85, 123.34, 115.85, 105.44, 101.75, 87.19, 68.91, 32.09, 29.89, 29.65, 29.54, 29.09, 26.33, 22.86, 14.29.

2,3-bis(decyloxy)-5,12-diphenyltetracene



To a solution of 2,3-bis(decyloxy)tetracene-5,12-dione (0.38 g, 0.66 mmol) in dry THF (23 mL) PhLi (0.86 mL, 1.9 M in *n*-dibutyl ether) was added dropwise while stirring vigorously at 0°C under argon. The reaction was stirred at 0°C for 1 hour and afterwards allowed to come to room temperature while stirring for another 24 hours. The solution was quenched with a saturated NH₄Cl solution and extracted with Et₂O. The collected organic fractions were washed with H₂O (1x), brine (2x), dried over MgSO₄ and concentrated *in vacuo*. The residue was dissolved in Et₂O (15 mL), protected from light and heated until reflux (60 °C). HI (57% in H₂O, 11 mL) was added dropwise and the mixture was stirred for another 30 min under reflux. Afterwards, the reaction was allowed to cool down to room temperature, given in a Na₂S₂O₃ solution (10% in H₂O) and extracted with Et₂O. The organic fractions were collected and washed subsequently with H₂O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. Purification by column chromatography using CH₂Cl₂:petroleum ether (1:4) and recrystallization from DCM/MeOH gave a yellow solid (260 mg, 0.38 mmol, 57%).

MS [EI] m/z: 715.5 [M+], 1407.9 [M+]

HRMS: m/z calcd for $\mathrm{C}_{50}\mathrm{H}_{60}\mathrm{O}_{2}\mathrm{Na}$ 715.4485 found 715.4509

¹H-NMR (600 MHz, CDCl₃): 8.20 (s, 2H, ArH), 7.77-7.76 (m_c, N = 9.7 Hz, 2H, ArH), 7.69-7.64 (m, 4H, ArH), 7.60-7.58 (m, 2H, ArH), 7.57-7.54 (m, 4H, ArH), 7.27-7.25 (m_c, N = 9.7 Hz, 2H, ArH), 6.81 (s, 2H, ArH), 3.86 (t, ${}^{3}J = 6.6$ Hz, 4H, OCH₂), 1.77 (q, 4H, CH₂), 1.38 (q, 4H, OCH₂<u>CH₂</u>), 1.34-1.22 (m, 28H, CH₂), 0.89 (t, ${}^{3}J = 6.9$ Hz, 6H, CH₃)

¹³C-NMR (150 MHz, CDCl₃): 149.64, 139.99, 134.21, 131.57, 130.54, 128.78, 128.71, 128.45, 127.58, 127.12, 124.99, 124.78, 104.52, 68.51, 31.08, 29.78, 29.72, 29.55, 29.51, 28.85, 26.15, 22.85, 14.27.

Experimental Section

8,9-bis(decyloxy)-6,11-diphenyl-5,12,13,17-tetrahydro-5,12-[4,5]epidioxolotetracen-15-one



To a solution of 2,3-bisdecyloxy-5,12-diphenyltetracene (0.1 g, 0.144 mmol) in deoxygenated xylene (5 mL), vinylene carbonate (0.1 mL, 1.44 mmol) was added and heated to 180°C in a sealed flask for 3 days. After removal of the solvent, the residue was purified by column chromatography. At 1:2 petroleum ether: CH_2Cl_2 a yellowish viscous liquid (32 mg, 0.0411 mmol, 57%) was obtained (collected both the diastereomers).

¹H-NMR (300 MHz, CDCl₃, mix of diastereomers): 7.70-7.51 (m, 8H, ArH), 7.49-7.43 (m, 1H, ArH), 7.37-7.30 (m, 2H, ArH), 7.23 (s, 2H, ArH), 7.19 (s, 2H, ArH), 7.24-7.19 (m, 2H, ArH), 6.84 (s, 1H, ArH), 6.82 (s, 1H, ArH), 4.9 (dd, ${}^{3}J = 2.1$ Hz, ${}^{4}J = 1.6$ Hz), 4.8 (dd, ${}^{3}J = 2.1$ Hz, ${}^{4}J = 1.6$ Hz), 4.64 (dd, ${}^{3}J = 2.1$ Hz, ${}^{4}J = 1.6$ Hz), 4.64 (dd, ${}^{3}J = 2.1$ Hz, ${}^{4}J = 1.6$ Hz), 4.64 (dd, ${}^{3}J = 2.1$ Hz, ${}^{4}J = 1.6$ Hz), 4.62 dd, ${}^{3}J = 2.1$ Hz, ${}^{4}J = 1.6$ Hz), 3.8 (t, ${}^{3}J = 6.6$ Hz, 4H, OCH₂), 1.75-1.66 (q, 4H, OCH₂<u>CH₂</u>), 1.44-1.18 (m, 28H, CH₂), 0.88 (t, {}^{3}J = 6.9 Hz, 6H, CH₃).

¹³C-NMR (75 MHz, CDCl₃, mix of diastereomers): 154.68, 154.17, 149.52, 149.29, 138.56, 138.26, 138.11, 136.93, 136.01, 135.17, 131.35, 131.05, 130.59, 130.25, 130.09, 130.04, 129.29, 129.03, 128.95, 128.41, 128.07, 127.85, 127.81, 127.66, 127.64, 127.50, 126.56, 125.67, 107.69, 107.51, 45.26, 45.05, 32.06, 29.75, 29.73, 29.70, 29.53, 29.48, 28.94, 26.08, 22.83, 14.27.

8, 9-bis (decyloxy)-6, 11-diphenyl-5, 12-dihydro-5, 12-ethanotetra cene-13, 14-diological action of the second statement of



To a solution of 8,9-bis(decyloxy)-6,11-diphenyl-5,12,13,17-tetrahydro-5,12-[4,5]epidioxolotetracen-15-one (0.11 g, 0.14 mmol) in 1,4-dioxane (3 mL), 4M NaOH (aq, 0.3 mL) was added under argon. After 2 hr of reflux (117°C), the mixture was cooled to room temperature and neutralized with 1M HCl. After the addition of H₂O, the mixture was extracted with CH₂Cl₂. The combined organic fractions were washed with H₂O (1x), brine (2x), dried over Na₂SO₄. The filtered solution was concentrated *in vacuo* obtaining a beige viscous liquid (0.084 g, 0.11 mmol, 80%).

8, 9-bis (decyloxy)-6, 11-diphenyl-5, 12-dihydro-5, 12-ethanotetra cene-13, 14-dione



To a mixture of dry DMSO (0.28 mL, 3.95 mmol) and dry CH₂Cl₂ (3 mL), TFAA (0.5 mL, 3.61 mmol) was added dropwise at -78 °C under argon. After 10 min a solution of 8,9bis(decyloxy)-6,11-diphenyl-5,12-dihydro-5,12-ethanotetracene-13,14-diol (0.085 g, 0.11 mmol) in dry CH₂Cl₂ (10 mL) was added dropwise at -78 °C. After stirring for 2 hours, DIPEA (1.4 mL, 8.03 mmol) was added dropwise and stirring was continued for an additional 1.5 hour at -78°C. Afterwards the reaction was left to come to room temperature. 1 M HCl was added and the organic layer was separated. The aqueous layer was washed with CH₂Cl₂ (3x). The combined organic fractions were washed subsequently with H₂O (2x) and brine (1x), dried over Na₂SO₄ and concentrated *in vacuo* while protecting it from light. The foul smelling red paste was purified by column chromatography in a dark room with 80:20 CH₂Cl₂:petroleum ether to give an orange viscous liquid (48 mg, 0.064 mmol, 58%) after drying under high vacuum.

¹H-NMR (600 MHz, CDCl₃): 7.65-7.63 (m, 2H, ArH), 7.60-7.54 (m, 4H, ArH), 7.43-7.42 (m, 2H, ArH), 7.33-7.27 (m, 6H, ArH), 7.27 (s, 2H, ArH), 4.98 (s, 2H), 3.81 (t = 6.6 Hz, 4H, OCH₂), 1.71 (q, 4H, CH₂), 1.35 (q, 4H, CH₂), 1.31-1.20 (m, 28H, CH₂), 0.87 (t = 7.2 Hz, 6H, CH₃).

¹³C-NMR (150 MHz, CDCl₃): 185.64, 149.85, 137.46, 136.06, 135.90, 130.78, 130.17, 129.32, 129.26, 128.81, 128.77, 128.20, 127.91, 126.26, 107.34, 68.80, 57.98, 32.05, 29.73, 29.69, 29.51, 29.48, 28.90, 26.07, 22.83, 14.26.

2,3-bis(decyloxy)-5,12-bis(phenylethynyl)tetracene



To a solution of phenylacetylene (0.048 mL, 0.44 mmol) in dry THF (5 mL) *n*-BuLi (0.27 mL, 1.6 M in hexanes) was added dropwise while stirring vigorously at-78°C under argon. 2,3-bis(decyloxy)-6,11-diphenyltetracene-5,12-dione (100 mg, 0.14 mmol) was dissolved in dry THF (5 mL) and after 30 min dropwise added to the reaction mixture at - 78°C. After an additional 30 min the acetone bath was removed and the reaction was allowed to reach room temperature overnight. The solution was quenched with a saturated NH₄Cl solution and extracted in DCM. The collected organic fractions were washed with H₂O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. The crude was dissolved in Et₂O (9 mL) followed by SnCl₂ (100 mg, 0.53 mmol) in 10% HCl solution (6 mL) under argon. The reaction was protected from light and refluxed at 60°C for 30 min. Afterwards the reaction was allowed to cool down to room temperature for 3 hour. The reaction was given in H₂O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. The crude was dissolved was given in H₂O and extracted with DCM. The organic fractions were collected and washed with H₂O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. The reaction was given in H₂O and extracted with DCM. The organic fractions were collected and washed with H₂O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by column chromatography using CH₂Cl₂:petroleum ether (1:4) and recrystallized from DCM/MeOH to give a dark red solid (27 mg, 0.036 mmol, 20%)

MS [FD] m/z: 740.46, 1481.97

HRMS: m/z calcd for $C_{54}H_{60}O_2$ 740.45933 found 740.46089

¹H-NMR (600 MHz, CDCl₃): 9.12 (s, 2H, ArH), 8.03-8.10 (m_c, N = 9.7 Hz, 2H, ArH), 7.85-7.83 (m, 4H, ArH), 7.82 (s, 2H, ArH), 7.56-7.47 (m, 8H, ArH), 4.25 (t, ${}^{3}J = 6.7$ Hz, 4H, -OCH₂), 1.98 (q, 4H, OCH₂<u>CH₂</u>), 1.57 (q, 4H, CH₂), 1.43 (q, 4H, -CH₂), 1.38-1.25 (m, 16H, CH₂), 0.89 (t, ${}^{3}J = 6.9$ Hz, 6H, CH₃).

¹³C-NMR (150 MHz, CDCl₃): 151.36, 131.75, 131.68, 130.30, 129.26, 128.77, 128.63, 125.56, 125.539, 124.01, 115.22, 104.91, 102.47, 87.80, 68.88, 53.57, 32.09, 29.86, 29.77, 29.66, 29.54, 29.08, 26.33, 22.86, 14.28.

2, 3- bis (decyloxy)-6, 11- diphenyltetracene-5, 12- dione



To a solution of 2,3-dimethoxy-6,11-diphenyltetracene-5,12-dione (300 mg, 0.65 mmol) in dry CH₂Cl₂ (20 mL) BBr₃ (1 M in CH₂Cl₂, 1.56 mL) was added dropwise while stirring vigorously at 0°C under argon. After 30 min, the ice bad was removed and the reaction was left to come to room temperature. After 2 hours, the reaction was refluxed (60 °C) for 1 hour.

The reaction was cooled down to room temperature and given in H_2O with a bit of HCl and extracted with Et_2O (3x). The collected organic fractions were washed subsequently with H_2O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*.

The crude product was dissolved in dry DMF (20 mL) under argon and K_2CO_3 (392 mg) as added to the solution and stirred at room temperature. After 45 min, 1-bromodecane (0.38 mL) was added and the reaction was heated till 135 °C overnight. Solvents were evaporated *in vacuo*. Purification by column chromatography using CH₂Cl₂: petroleum ether (2:3) and recrystallization with DCM/MeOH gave a yellow solid (170 mg, 0.24 mmol, 36%)

MS [FD+]: m/z 754.42, 1467.85 [M+]

HRMS [FD+]: m/z calcd for $C_{50}H_{58}O_4Na$ 745.4227 found 745.4215.

¹H-NMR (300 MHz, CDCl₃): 7.64-7.42 (m, 12H, ArH), 7.34-7.28 (m, 4H, ArH), 4.04 (t, ${}^{3}J = 6.7$ Hz, 4H, OCH₂), 1.82 (q, 4H, OCH₂<u>CH₂</u>), 1.5-1.15 (m, 28, CH₂), 0.88 (t, ${}^{3}J = 6.9$ Hz, 6H, CH₃).

 $^{13}\text{C-NMR} \ (75 \ \text{MHz}, \ \text{CDCl}_3): \quad 183.38; \ 153.72; \ 143.84; \ 140.93; \ 135.76; \ 129.57; \ 128.85; \ 128.76; \\ 128.64; \ 128.47; \ 127.62; \ 127.06; \ 109.07; \ 69.45; \ 32.04; \ 29.69; \ 29.47; \ 28.98; \ 25.98; \ 22.82; \ 14.27.$



2, 3-bis (decyloxy)-6, 11-diphenyl-5, 12-bis (phenylethynyl) tetracene

To a solution of phenylacetylene (0.08 mL, 0.69 mmol) in dry THF (5 mL), n-BuLi (0.42 mL, 1.6 M in hexanes) was added dropwise at -78 °C under argon while stirring vigorously. 2,3-bis(decyloxy)-6,11-diphenyltetracene-5,12-dione (100 mg, 0.14 mmol) was dissolved in dry THF (5 mL) and after 30 min added dropwise to the reaction mixture at - 78°C. After an additional 45 min the aceton bath was removed and the reaction was allowed to reach room temperature. After 4 hours, the solution was quenched with a saturated NH₄Cl solution and extracted in Et₂O. The collected organic fractions were washed with H2O (2x) and brine (1x), dried over MgSO₄ and concentrated *in vacuo*. The crude product was dissolved in Et₂O (7 mL) followed by SnCl₂ (80 mg, 0.639 mmol) in 10% HCl solution (aq, 5 mL) under argon. The reaction was protected from light and refluxed at 60°C for 30min. After one hour at room temperature the reaction was given in H₂O and extracted with Et₂O (3x). The organic fractions were collected and washed with H₂O (2x) and brine (1x), dried occentrated *in vacuo*. The crude product was purified by column chromatography using CH₂Cl₂:petroleum ether (25:75) and recrystallized from DCM/MeOH to give a purple solid (20 mg, 0.02 mmol, 18%)

MS [EI] m/z: 859.52; 1786.2

HRMS: m/z calcd for $C_{66}H_{68}O_2$ 892.52193 found 892.5253

¹H-NMR (400 MHz, CDCl₃): 7.83 (s, 2H, ArH), 7.61-7.57 (m, 4H, ArH), 7.57-7.54 (m_c, N = 10 Hz, 2H, ArH), 7.5 (t, ${}^{3}J = 7.4$ Hz, 4H, ArH), 7.38-7.32 (m, 2H, ArH), 7.28 (s, 10H, ArH), 7.25-7.21 (m_c, N = 10 Hz, 2H, ArH), 4.14 (t, ${}^{3}J = 6.8$ Hz, 4H, OCH₂), 1.89 (q, 4H, OCH₂<u>CH₂</u>), 1.45 (m, 4H, CH₂), 1.35-1.2 (m, 28H, CH₂), 0.88 (t, ${}^{3}J = 6.8$ Hz, 6H, CH₃).

¹³C-NMR (100 MHz, CDCl₃): 151.47, 141.56, 137.18, 132.79, 132.31, 131.63, 130.65, 128.14, 128.00, 127.83, 127.59, 127.01, 125.21, 124.38, 115.96, 107.68, 105.20, 90.37, 68.92, 32.07, 29.78, 29.71, 29.51, 28.92, 26.14, 22.85, 14.28.
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Annex

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A. dKDDOA concentration dependency of photopatterning

dKDDOA at different concentrations in DMSO with 5 vol% H₂O. Discussion of the results can be found in Chapter 4.



Figure A.1: Line of nuclei made by repetitively scanning a 473 nm laser (2.2 W/cm^2) across 70 µm on a borosilicate glass surface. The concentration is ranging between 0.5 to 3 mM dKDDOA in DMSO with 5 vol% of H₂O. Scan was stopped when objects were detected by back-scattering of the laser. The images were taken by exciting DDOA at 375 nm by wide field illumination. Scale bar is 10 µm.



Figure A.2: Irradiation of a dKDDOA with a concentration ranging from 0.5 to 3 mM in DMSO with 5 vol% of H_2O in the volume with the 375 LED. Scale bar is 10 μ m.

B. DDOA molecular packing

The series of 2,3-dialkoxyanthracene have been characterized to have a "odd-even" effect for the crystallization starting from butyl chains, where an even amount of carbon induces a $P\bar{3}$ trigonal packing and odd amount of carbons on the alkyl chain induces a packing with the space group R $\bar{3}$. Crystallization of these series of molecules was only successful till n = 7. Therefore, by extrapolation a trigonal packing is expected for DDOA. This coincides with the SANS and IR studies done on areogels of DDOA.^[1,2] The obstruction to crystallize is thought to come from the increased length of the alkoxy chains, which create an incompatibility between the length of the acene core and the alkoxy chains.



Figure B.1: Crystal packing of 2,3-dihexyloxyanthracene $(dHxOA)^{[3]}$. (a) Arrangement along the baxis (short axis) of the crystal showing 60° angle. (b) Arrangement along the c-axis showing the formation of triads showing a 120° angle. (c) One triad and the angle between the aromatic planes of the anthracene showing the 60° angle. Proposed packing of DDOA along the short axis (d)^[1]. (Image B.1d is a reprint of ref 1).

C. Patterns

Figure A.3 shows other obtained patterns by controlling the nucleation geometry of DDOA through the confined photoconversion of dKDDOA.



Figure B.2: Different patterns obtained by controlling the nucleation geometry. (a) Crossed lines obtained by repetitive scanning over 70 μ m. (b) Points irradiation creating a raster of nucleation points. Both were patterned with the 473 nm laser (2.2 W/cm²). (c) Rectangular patterns obtained by dense raster of lines of 100 nm apart with 770 nm pulsed laser at 13 kW/cm². Numbers are the size in micron. The scale bar is 10 μ m.

D. Hydrolysis kinetics of dKAnth with H_2O or D_2O

The hydrolysis was followed by ¹H-NMR with 1,3,5-trimethoxy benzene as internal standard (singlets at 6.1 and 3.7 ppm.)

Table 4.1: Rate constants of the forward (k_f) and backwards (k_b) reaction, the equilibrium constant (K) and the equilibrium constant of the reverse direction of the hydrolysis of dKAnth in DMSO-d6/H₂O or DMSO-d6/D₂O. H₂O/D₂O content is 5 vol%. The concentration of dKAnth is 8 mM.

	$k_{\rm f}({\rm s}^{\text{-}1})$	$\mathrm{k}_{\mathrm{b}}\left(\mathrm{s}^{\text{-1}}\right)$	Κ	К'	
H_2O	$2.83\mathrm{x}10^{-5}$	$5.78 \mathrm{x} 10^{-7}$	48	0.02	
D_2O	$2.15\mathrm{x}10^{-5}$	$2.45 \mathrm{x10^{-6}}$	8.4	0.11	

Preliminary measurement of the hydrolysis of dKAnth showing that the hydrolysis of the diketone is slower in D_2O due to the isotope effect. Indicating that a proton transfer is the rate limiting step.



Figure D. 1: Hydrolysis of dKAnth in DMSO with 5 vol% of H₂O followed by 1H-NMR with 1,3,5-trimethoxybenzene as internal standard (peak at 6.1 ppm).



Figure D.2: Hydrolysis of dKAnth in DMSO with 5 vol% of D_2O followed by 1H-NMR with 1,3,5-trimethoxybenzene as internal standard (peak at 6.1 ppm).



Figure D.3: Change in concentration of dKanth in $DMSO-d6/D_2O$ over time. b. Corresponding linear dependence of the hydrolysis of dKAnth in $DMSO-d6/D_2O$. c. Change in concentration of

dKanth in DMSO-d6/H₂O over time. d. Corresponding linear dependence of the hydrolysis of dKAnth in DMSO-d6/H₂O. H₂O/D₂O content is 5 vol%. The concentration of dKAnth is 8 mM.



E. Absorption spectra of imine base releasing agents



Figure E.1: Absorption spectra of all the different hydroxybenzaldehydes used for the synthesis of the base releasing imines.

Annex



Figure E.2: Absorption spectra of the corresponding imines with tris(hydroxymethyl)aminomethane as the released base.

Figure E.3: Absorption spectra o the corresponding imines with ethanolamine as released base.

F. Temperature dependence of the storage modulus of OG2

Figure E.1 shows the temperature dependence of the storage and loss modulus of 2 mg.mL⁻¹ OG2 during a series of temperature ramps between 5 and 45 °C. From the figure it is clear that the gel strength is temperature dependent and that heating of the sample would have an effect on the moduli.



Figure F.1: Series of temperature dependence of OG2 (2 mg.mL⁻¹) between 5 and 45 °C.

Auto-assemblage d'un anthracène fluorescent aux échelles nano- et micrométriques par photoréaction contrôlée.

Résumé : Le contrôle spatial et temporel de l'auto-assemblage de molécules fluorescentes en nano-objets organisés et en matériaux mous a été réalisé par photochimie. La photodécarbonylation quantitative du progélifiant dkDDOA sous irradiation génère le supergélifiant 2,3-didécyloxyanthracène (DDOA) à température ambiante et simultanément gélifie le DMSO. DkDDOA est réactif sous excitation avec de la lumière bleue en raison de la fonction alpha-dicétone sensible à la lumière qui est ajoutée au noyau aromatique. De plus, l'ajustement de la couleur de l'émission du gel du bleu au vert a été obtenu en ajoutant un dérivé 1,2-dicétone-5,12-diphényltétracène photoréactif qui donne un 5,12-diphényltétracène émissif vert sensibilisé par un transfert d'énergie efficace.

Sous un microscope, l'irradiation laser focalisée permet la structuration de nanofibres émissives sur une surface de verre. Bien que la surface de verre soit non traitée, on peut obtenir des micropattern de nanofibres de DDOA hautement alignées. Ces surfaces émettent une lumière bleue polarisée linéairement, comme le prouve la microscopie de polarisation. L'anisotropie élevée et l'orientation des fibres ont été obtenues en contrôlant la densité de nucléation et la direction de balayage du laser focalisé. Des micropattern orientés perpendiculairement peuvent ainsi être juxtaposés sur la même surface.

Mots clés : auto-assemblage, nano-fibres, nucléation et croissance, anthracène, tetracène, fluorescence, alpha-dicétone, photopatterning, densité de nuclei, anisotropie.

Photocontrolled self-assembly of a fluorescent anthracene at nanoand microscales.

Abstract : The spatial and temporal control of the self-assembly of fluorescent molecules into organized nano-objects and into soft materials was achieved by photochemistry. The quantitative photodecarbonylation of the progelator dkDDOA under irradiation generates the supergelator 2,3-didecyloxyanthracene (DDOA) at room temperature and simultaneously gelates DMSO. dkDDOA is reactive under excitation with blue light due to the light sensitive alpha-diketone moiety that is added to the aromatic core. Additional colour-tuning from blue to green emission from the gel was achieved by adding a similar photoreactive 1,2-diketone-5,12-diphenyltetracene that yields a green emissive 5,12-diphenyltetracene sensitized through an efficient energy transfer.

Under a microscope, focused laser irradiation enables the patterning of blue-emissive nanofibers onto a glass surface. Although the surface is non-treated, micropatterns of highly aligned DDOA nanofibers can be obtained. These surfaces emit linearly polarized blue light, as proven with polarization microscopy. The high anisotropy and the orientation of the fibers was achieved by controlling the nucleation density and the direction of scanning of the focused laser. Perpendicularly oriented micropatterns can thereby be juxtaposed on the same surface.

Keywords : self-assembly, nanofibres, nucleation and growth, anthracene, tetracene, fluorescence, alpha-diketone, photopatterning, nucleation density, anisotropy.

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