



Chirality induction to carbon-based materials and foldamers using silica nanohelices

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Par Piyanan Pranee

**Induction de chiralité sur des matériaux carbonnés et des Foldamères
à l'aide de nano-hélices de silice**

Sous la direction de
Dr. Reiko Oda

Soutenue le: 9 Novembre, 2023

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Chirality induction to carbon-based materials and foldamers using silica nanohelices

In this thesis, nanometric silica helices were used to transfer the chirality information onto achiral carbon-based materials (graphenoid nanoparticles and polymer) and racemic oligoamide foldamers. The silica nanohelices (INHs) with helical morphology was organized via a sol-gel approach using organic self-assembly of surfactant molecules (achiral gemini-type surfactant) and chiral tartrate anion as a template. The handedness of silica nanostructures is controlled by the enantiomers of constituent molecules. In the first part of my thesis, chiral carbon dots (CDots) were synthesized by pyrolysis of hybrid silica nanohelices under a vacuum, which had an organic template and helical silica as a carbon source and chiral inducer, respectively. These CDots showed symmetrical Circular Dichroism (CD) signal in the wavelength range of 200-700 nm with the dissymmetric factor (g_{abs}) $\sim \pm 3.0 \times 10^{-4}$. We also used these INHs to induce the chiroptical properties to achiral polymer (PolyDHN-TMTA) synthesized by the polymerization of 2,6-dihydroxyanthracene (DHN) and 1,3,5-trimethyl-1,3,5-triazine (TMTA) through *ex-situ* and *in-situ* methods. In the case of *ex-situ* synthesis, PolyDHN-TMTA was synthesized in solution, then was drop-casted on a substrate made of a dried monolayer film of silica helices. This resulted in mirror-image CD and Circularly Polarized Luminescence (CPL) responses with $g_{\text{abs}} \sim \pm 2.0 \times 10^{-3}$ and $g_{\text{lum}} \sim \pm 1.0 \times 10^{-2}$. The *in-situ* approach was carried out by introducing the two components in contact with the nanohelical space of INHs and let polymerize directly, which resulted in the chiroptical properties of PolyDHN-TMTA with $g_{\text{abs}} \sim \pm 1.0 \times 10^{-3}$ and $g_{\text{lum}} \sim \pm 5.0 \times 10^{-3}$. Apart from chirality induction to achiral carbon materials, we studied the enantiomeric enrichment of racemic foldamers which are in an equilibrium between *M*- and *P*-enantiomers. After drop-casting racemic foldamers into a chiral environment of silica nanohelices, we could observe CD and CPL signals controlled by the handedness of helical silica. Interestingly, we could observe a clear cooperative effect between the molecular chirality of the foldamers and the helicity of the INHs when chiral foldamers (Q₄R and Q₄S) were drop-casted on INHs. This research gave significant insight and versatile design of chirality induction of achiral carbon based-materials and enantiomeric enrichment of racemic foldamers using INHs for further applications.

Keywords: Chirality induction, Carbon dots, Polymers, Foldamers

Induction de chiralité sur des matériaux carbonnés et des Foldamères à l'aide de nano-hélices de silice

Dans cette thèse, des hélices nanométriques de silice ont été utilisées pour transférer l'information de chiralité sur des matériaux carbonnés achiraux (nanoparticules graphénoïdes et polymère) et des Foldamères oligoamides racémiques. Les nanohélices de silice (INHs) à morphologie hélicoïdale ont été obtenues via une approche sol-gel utilisant auto-assemblage organique de molécules de tensioactif (tensioactif achiral de type gémini) et un anion tartrate chiral comme un moule. La direction du pas des nanostructures de silice est contrôlée par le choix de l'énantiomère des molécules de tartrate. Dans la première partie de ma thèse, des nanosphère de carbone chirales (CDots) ont été synthétisés par pyrolyse sous vide de nanohélices de silice hybride, contenant à la fois le surfactant organique et de la silice hélicoïdale servant respectivement de source de carbone et d'inducteur chiral. Des signaux de dichroïsme circulaire symétrique (CD) ont été observés dans la plage de longueurs d'onde de 200 à 700 nm avec le facteur dissymétrique $g_{\text{abs}} \sim \pm 3,0 \times 10^{-4}$ pour ces CDots. Nous avons également utilisé les INHs pour induire des propriétés chiroptiques au polymère achiral (PolyDHN-TMTA) synthétisé par la polymérisation du 2,6-dihydroxyanthracène (DHN) et du 1,3,5-triméthyl-1,3,5-triazinane (TMTA) par des méthodes *ex situ* et *in situ*. Dans le cas d'une synthèse *ex situ*, le PolyDHN-TMTA a été synthétisé en solution, puis déposé via une goutte de solution sur un substrat constitué d'un film monocouche séché d'hélices de silice. Une réponse CD en image miroir et de la luminescence à polarisation circulaire (CPL) ont été obtenues avec des $g_{\text{abs}} \sim \pm 2,0 \times 10^{-3}$ et des $g_{\text{lum}} \sim \pm 1,0 \times 10^{-2}$. L'approche *in situ* a été réalisée en introduisant les deux composants dans l'espace nanohélicoïdal des INHs et en les laissant polymériser directement, ce qui a donné des propriétés chiroptiques du PolyDHN-TMTA avec des $g_{\text{abs}} \sim \pm 1,0 \times 10^{-3}$ et des $g_{\text{lum}} \sim \pm 5,0 \times 10^{-3}$. Outre l'induction de la chiralité sur les matériaux carbonnés achiraux, l'enrichissement énantiomérique des Foldamères racémiques a été étudié. Ces Foldamères sont en équilibre entre les énantiomères *M*- et *P*- en solution. Après avoir déposé des Foldamères racémiques dans un environnement chiral de nanohélices de silice, des signaux de CD et de CPL ont été observés et contrôlés par la direction du pas de la silice hélicoïdale. Il est intéressant de noter qu'un effet coopératif clair entre la chiralité moléculaire des Foldamers et l'hélicité des INHs a été mis en évidence lorsque des Foldamères énantiomériquement purs ont été utilisés. Cette recherche a donné des informations significatives et une conception polyvalente de l'induction de la chiralité utilisant les INHs pour d'autres applications.

Mot clé: Induction de chiralité, Carbon dots, Polymères, Foldamères

List of Abbreviation

AuNPs	Gold nanoparticles
APTES	(3-aminopropyl)triethoxysilane
CD	Circular Dichroism
CDots	Carbon dots
CPL	Circularly Polarized Luminescence
CPs	Polymer dots
°C	degree Celsius
cm	centimeter
DRCD	Diffuse Reflectance Circular Dichroism
DMF	Dimethylformamide
DHN	2,6-dihydroxynaphthalene
DRIFT	Diffuse Reflectance Infrared Fourier Transform
EA	Elemental Analysis
FT-IR	Fourier Transform Infrared
GSH	Glutathione
hrs	hours
g_{abs}	Dissymmetry factor in absorption
$g_{\text{abs in TCD}}$	Dissymmetry factor in absorption (calculated from TCD spectra)
$g_{\text{abs in DRCD}}$	Dissymmetry factor in absorption (calculated from DRCD spectra)
g_{lum}	Dissymmetry factor in emission (calculated from CPL spectra)
LD	Linear Dichroism
LD_{TCD}	Linear Dichroism in TCD
LD_{DRCD}	Linear Dichroism in DRCD
LD_{CPL}	Linear Polarized Light
LH	Left handedness
HNHs	Hybrid nanohelices
INHs	Inorganic silica nanohelices

min	minute
M	Molar
mM	millimolar
nm	nanometer
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
RH	Right handedness
SEM	Scanning Electron Microscope
PAHs	Polycyclic aromatic hydrocarbon
PolyDHN-TMTA	Polymer after polymerization between DHN and TMTA
Q _n	Racemic oligoamide foldamers
Q ₄ R	Q ₄ (tetramers) functionalized with <i>R</i> -camphenyl group
Q ₄ S	Q ₄ (tetramers) functionalized with <i>S</i> -camphenyl group
QY	Quantum yield
TCD	Transmission Circular Dichroism
TEOS	Tetraethoxysilane
TEM	Transmission Electron microscopy
TMTA	1,3,5-trimethyl-1,3,5-triazinane
TPPS	<i>meso</i> -tetra-(4-sulfonatophenyl) porphyrin
VCD	Vibrational Circular Dichroism
μL	microliter
3D	Three dimensional
XPS	X-ray photoelectron spectroscopy
16-2-16	Gemini tartrate

Contents

Table of Contents	Page
Abstract	I
List of abbreviation	III
Contents	V
 Chapter 1 Introduction	 1
1.1 Introduction of chirality	1
1.2 Chirality characterization	6
1.3 Introduction of carbon-based materials	9
1.3.1 Carbon-based materials	9
1.3.2 Carbon dots	10
1.3.3 Chirality induction of carbon dots	13
1.4 Introduction of polymer	18
1.4.1 π -conjugated polymer	21
1.4.2 Chiral polymers	22
1.5 Introduction of foldamers	25
1.6 References	28
 Chapter 2 Research design	 35
2.1 Silica nanohelices	35
2.2 Previous studies in the group for chirality induction to various atoms, molecules and particles using silica nanohelices	36
2.2.1 Anionic dyes incorporated inside HNHs and induction of chirality	36
2.2.2 Chirality induction to monoatomic anions	37
2.2.3 GNPs helically grafted on INHs	38
2.2.4 Dyes helically grafted on INHs	39
2.2.5 QDs helically grafted on INHs	40
2.2.6 The growth of helical QDs inside INHs	41

2.3	Research design	41
2.4	Preparation of silica nanohelices	43
2.4.1	Synthesis of gemini tartrate (16-2-16)	43
2.4.2	Formation of organic gel of gemini tartrate and silica transcription	44
2.4.3	Fabrication of inorganic silica nanohelices (INHs)	45
2.4.4	Preparation of silica thin film by drop-casting method	45
2.5	References	46
Chapter 3 Chirality induction to carbon dots using silica nanohelices		48
3.1	Experimental section	48
3.1.1	Synthesis of gemini tartrate and preparation of HNHs	48
3.1.2	Preparation of doped HNHs	48
3.1.3	Synthesis of CDots	49
3.2	Results and discussion	50
3.3	Conclusion	70
3.3	References	71
Chapter 4 Chirality induction to achiral polymer using silica nanohelices		74
4.1	Experimental section	75
4.2.1	Synthesis of gemini tartrate and preparation of INHs	75
4.2.2	Preparation of silica thin film for chirality induction to achiral polymer	75
4.2.3	Preparation of achiral polymer (PolyDHN-TMTA)	76
4.2.4	<i>Ex-situ</i> synthesis of PolyDHN-TMTA/INHs	76
4.2.5	<i>In-situ</i> synthesis of olyDHN-TMTA/INHs	77
4.2	Results and discussion	78
4.2.1	<i>Ex-situ</i> synthesis of PolyDHN-TMTA/INHs	78
4.2.2	<i>In-situ</i> synthesis of PolyDHN-TMTA/INHs	92
4.4	Conclusion	100
4.5	References	100

Chapter 5	Enantiomeric enrichment of racemic foldamers using silica nanohelices	104
5.1	Experimental section	105
5.1.1	Preparation of inorganic silica nanohelices (INHs)	105
5.1.2	Drop casting of oligoamide foldamers (Q_n) on INHs	105
5.1.3	Study on solvent effect for drop-casting of Q_4 on INHs	106
5.1.4	Kinetic study for enantiomeric enrichment of Q_4 using INHs	106
5.1.5	Optimization of the ratio between Q_4 and INHs	106
5.1.6	Enantiomeric enrichment of foldamers with different lengths	106
5.2	Results and discussion	106
5.2.1	Solvent effect for drop-casting of Q_4 on INHs	106
5.2.2	Kinetic studies for enantiomeric enrichment Q_4 using INHs	110
5.2.3.	Optimization of the ratio between Q_4 and INHs	111
5.2.4	Enantiomeric enrichment of foldamers with different lengths	114
5.2.5	Surface variation of chiral silica nanohelices for enantiomeric enrichment of foldamers	119
5.2.6	Temperature effect on enantiomeric enrichment of foldamers	122
5.2.7	TEM characterization of Q_n /INHs	124
5.2.8	Chiral foldamers (Q_4R and Q_4S) in chiral environment of helical silica template	124
5.3	Conclusion	127
5.4	Appendix	127
5.5	References	130
Chapter 6	Conclusion and perspectives	133
	Publications and communication	138
	Acknowledgements	140

Chapter 1

Introduction

1.1 Introduction of chirality

Chirality is a fundamental geometric property of molecules, particles or macroscopic objects exhibiting a pair of “left-handed” and “right-handed” mirror images known as enantiomers that could not be superimposed on their mirror image by translation and rotation.¹ It is one of the basic character traits of the universe ranging from the subatomic level to the molecular level and macroscopic scales (Figure 1-1).² It plays an important role in nature, for instance, chiral molecules exist in living organisms as a single enantiomer which shows a crucial role in molecular recognition and replication processes. The two enantiomers show similar structures and physical properties but often present different activities when they are in interaction with other entities as observed in the biological, pharmaceutical, biotechnology and food industries.³ Homochirality is a fundamental feature of all known life in one specific chiral form.⁴ It also refers to enantiopure substances in which all the constituents are the same enantiomer. Sugars and amino acids are regarded as homochiral molecules because amino acids appear almost exclusively in the L-form and sugars represent in the D-form. Indeed, chiral building blocks in carbohydrates and amino acids are naturally used to produce chiral supramolecular structures of proteins, glycoproteins, glycolipids, and enzymes. The different enantiomers of these bioactive species have a different impact on the biological mechanisms process as it requires specific interaction with chiral molecules.⁵ Furthermore, the two different enantiomers of active pharmaceutical ingredients (APIs) often exhibit different therapeutic and pharmacokinetic profiles.⁶ For instance, S-(-)-secobarbital is more potent on anaesthetic effect.⁷ The (+) isoflurane is more effective than the (-) isomer for induction and maintenance of general anaesthesia.

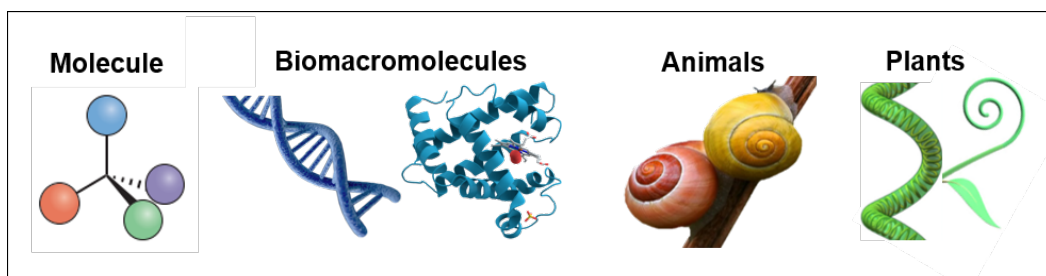


Figure 1-1 Chirality in various scales from molecular level to macroscopic scales.

At the molecular level, the most common definition of chiral molecules can be found through tetrahedral center with sp^3 hybridization of a carbon atom. This sp^3 hybridized center is asymmetric and the molecule is chiral when the four substituents are different, called as “point chirality”. In addition, a molecule can also possess geometrical chirality in the absence of a chiral center (Figure 1-2). For instance, helicenes are polycyclic compounds with nonplanar screw-shaped skeletons formed by *ortho*-fused benzene or other aromatic rings.⁸ Helicenes have a C_2 -symmetric axis which is perpendicular to the helical axis due to the steric hindrance.⁸ Meanwhile, propeller molecules have several molecular-scale blades attached at a certain pitch angle aligned along the rotational axis.

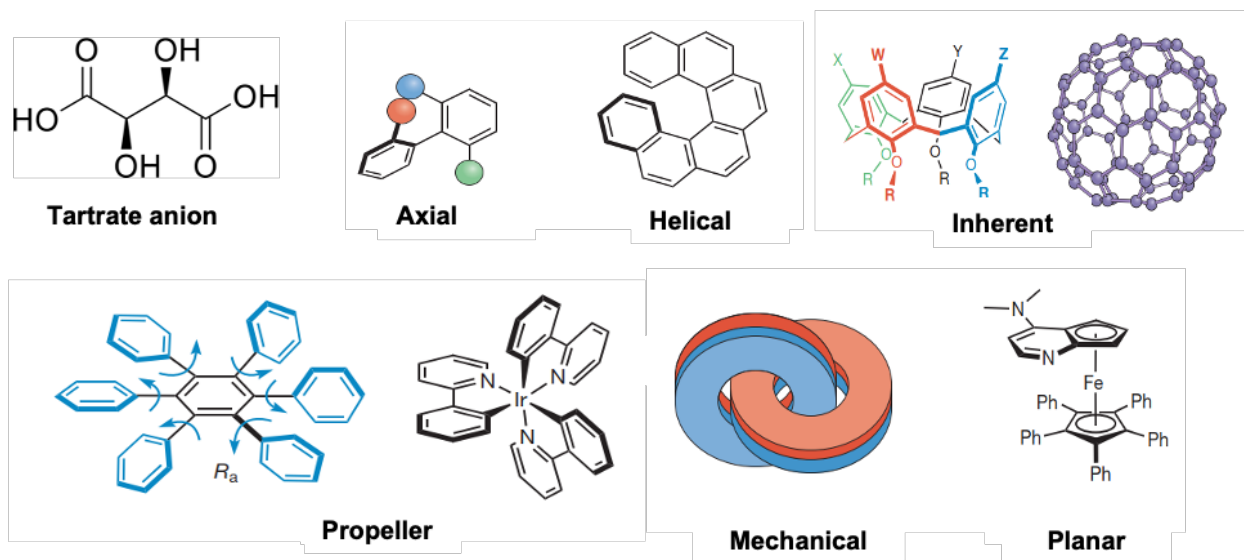


Figure 1-2 Examples of chiral molecules.¹

Besides molecular chirality, chirality could be found in nano-/micro-structures often artificially made. These artificial chiral materials are synthesized by various approaches such as top-down and bottom-up methods, and subsequently present outstanding optical properties for advanced applications; circular polarizers,⁹ biosensors,¹⁰ enantiomer separation,¹¹ and photoelectronic devices.¹¹ The key point to design chiral materials is asymmetric architectures in the three-dimensional chiral shape which includes helical, spiral, and pyramidal shapes (Figure 1-3).¹² This approach can be applied to either intrinsic shape of the materials themselves or the organization of achiral entities to these chiral shapes. In 2012, Kuzyk A., et. al.¹³ studied the self-

assembly of 10-nm gold nanoparticles (AuNPs) with DNA origami 24-helix bundles. AuNPs contain multiple thiol-modified DNA stands, which are able to complement this staple extension. The induced chirality was observed due to the helical arrangement of AuNPs on the self-assembly of DNA. Both left- and right-handed nanohelices showed a diameter of 34 nm and helical pitch of 57 nm forming by 9 AuNPs (Figure. 1-3a). Yan W., et. al.¹⁴ demonstrated the self-assembly of nanoparticles into a pyramidal arrangement with strong *R*-/*S*- optical activity in Figure. 1-3b. The pyramidal shape of nanoparticles (NPs) was prepared by DNA-driven self-organization from individual building blocks containing medium-size AuNPs (15 nm), and large-size AuNPs (25 nm). Silver nanoparticles (AgNPs, 10 nm) and CdSe@ZnS quantum dots (5 nm). The self-assembly of NPs displayed strong chirality in the range of 520-540 nm plasmonic region, which could be attributed to the high degree of asymmetric geometry.

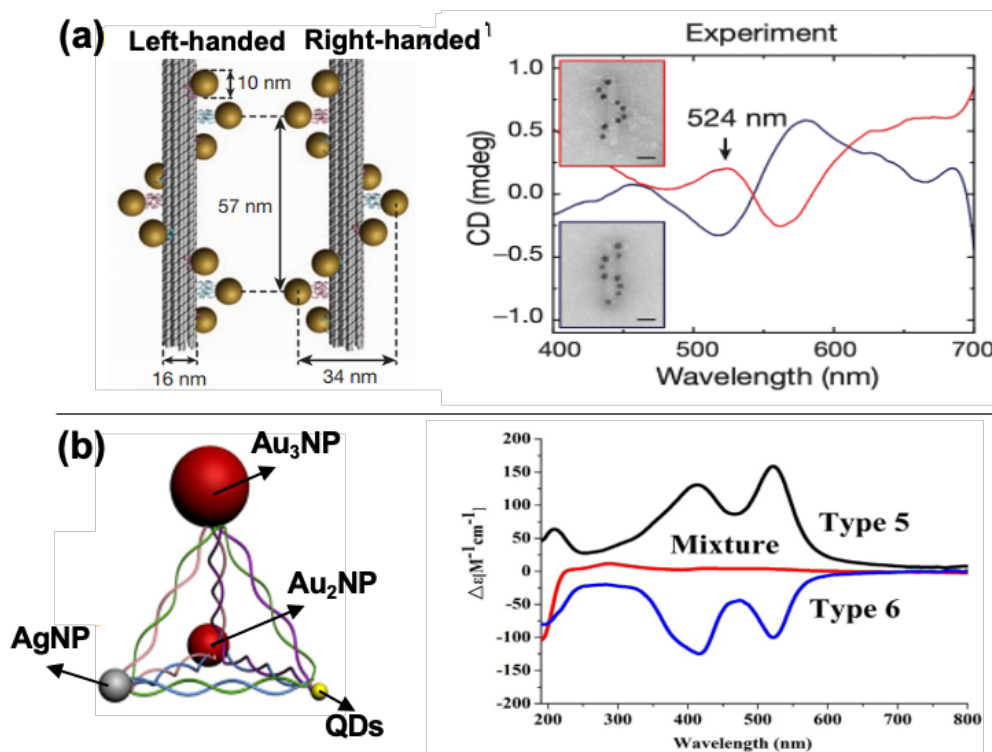


Figure 1-3 Artificial chiral materials in helical (a)¹³ and pyramidal shape.¹⁴

In the case of the two examples above, the chirality is induced by the chiral arrangement of achiral particles. In 2013, Andrew G. Mark, et. al.¹⁵ demonstrated the fabrication of helical gold nanostructure Figure 1-4, which was based on micellar nanolithography related to metafluidic approach with rapid wafer-scale fabrication demonstrating electric, magnetic, optical and

mechanical chiral properties. Au nanohelices with two turns with a pitch of 34 nm and a height of 100 ± 8 nm were observed. The normalized Circular Dichroism (CD) spectra were observed from 400 – 1,100 nm for both left-handed and right-handed helices. Moreover, they found that changes in shape and material composition within nanostructures could tune the CD response in the visible range.

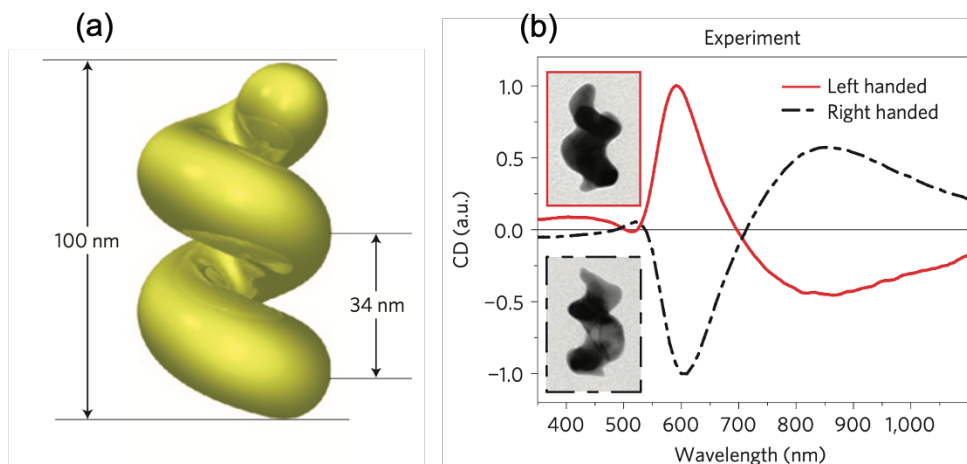


Figure 1-4 (a) Model two-turn gold nanohelix, and (b) Normalized Circular Dichroism (CD) spectra of left-handed and right-handed gold nanohelix. Inset: TEM images of right- and left-handed gold nanohelix.¹⁵

In 2020, Yan J., et. al¹⁶ fabricated chiral semiconductor helices with tunable optical activity. Semiconductor nanoparticles were assembled into helices demonstrating high chiroptical activity, enantiomer selectivity and structural uniformity. Chiral CdTe NPs containing L- or D-cysteine as surface ligands, served as the building blocks for the assembly of semiconductor helices. The coordination assembly of nanoparticles was achieved by mixing 2 mM Cd^{2+} and 5 mM L- and D-cysteine in a mixture of water and methanol (1:1). The pitch of these semiconductor helices was in a range of ~ 390 nm to ~ 940 nm. All the semiconductor helices showed a chiral property in a board spectral range from 300 to NIR with the maximum $g_{\text{abs}} \sim 0.06$. The geometry of these semiconductor helices could be controlled by adjusting pH, as well as the concentration of chiral surface ligand and Cd^{2+} .

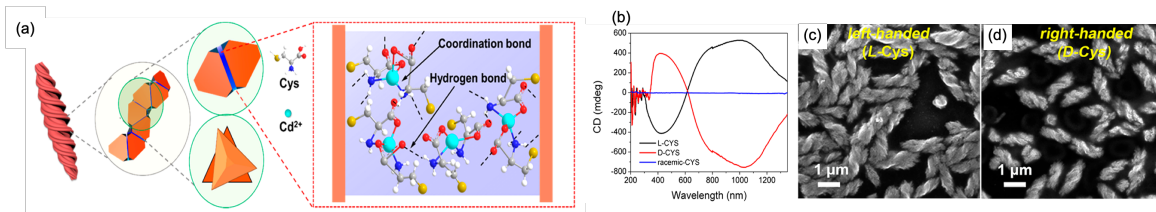


Figure 1-5 (a) Origin of enantiopurity in NPs assembly into helices. CdTe NPs pack into helices with chiral bias exerted by the chiral ligands at the interface, (b) CD spectra made with cysteine surface ligands, (c,d) SEM images of helices.¹⁶

In 2019, Kita T., et. al.¹⁷ reported chirality transcription from metal-organic framework (MOF) to polythiophene. The chiral MOF was successfully prepared by complexing Lanthanum (La^{3+}) and chiral phenylalanine. Subsequently, 1,3,5-benzenetrisbenzoate (BTB) was substituted with phenylalanine to obtain chiral MOF ($\text{La}(\text{BTB})_n$).¹⁸ The chirality of MOF was governed by a propeller-like twisted conformation of BTB ligand, which could be left-handed and right-handed depending on a pure enantiomer of phenylalanine. After synthesizing chiral MOF, terthiophene was encapsulated in the nano-channel of MOF by sublimation and followed by oxidative polymerization in order to obtain polythiophene in MOF, which resulted in a strong chirality in the UV-visible range.

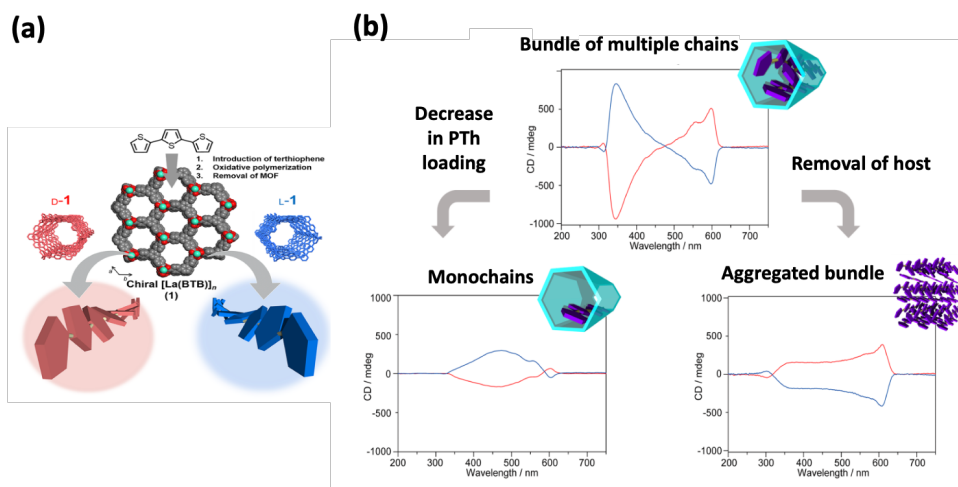


Figure 1-6 (a) Preparation of chiral polythiophene based on chiral MOF, (b) CD spectra of composites including bundles of polythiophene in chiral MOF, monochain of polythiophene in chiral MOF, aggregated bundle without chiral MOF.¹⁷

1.2 Chirality characterization

Circular Dichroism (CD) is an absorption spectroscopy representing the different absorption of left-handed and right-handed circularly polarized light. Chiral molecules with chromophores will preferentially absorb one of the circularly polarized light. This phenomenon can occur for all wavelengths resulting in electronic CD (ECD) in the ultraviolet and visible wavelength, and vibrational CD (VCD) in the infrared region. In general, electromagnetic radiation consists of electric and magnetic fields perpendicular to each other. The fields oscillate in all directions perpendicular to the direction of propagation. The circularly polarized light occurs when the electric field vector rotates around the propagation axis with a constant magnitude. In other words, circularly polarized light is a polarization of electromagnetic radiation where the vector of the magnetic field tends to execute a circle perpendicular to the light propagation. Circularly polarized light can be absorbed by a media. The circular dichroism corresponds to the difference in absorption between two directions of circularly polarized light. The primary observable of CD is the differential absorption in left- (A_L) and right- (A_R) circularly polarized light, as shown in the equation.

$$\Delta A = A_L - A_R$$

The anisotropic factor for polarization rotation is also known as the dissymmetric factor (g_{abs}). It is defined as a parameter expected to be independent of concentration. It could be calculated as the different absorbance between left-handed and right-handed circularly polarized light. Therefore, g_{abs} is calculated by a ratio of Circular Dichroism (CD) signal to absorption as;

$$g_{\text{abs}} = \Delta\epsilon/\epsilon = \Delta A/A = \theta(\text{mdeg})/(32980 \times A)$$

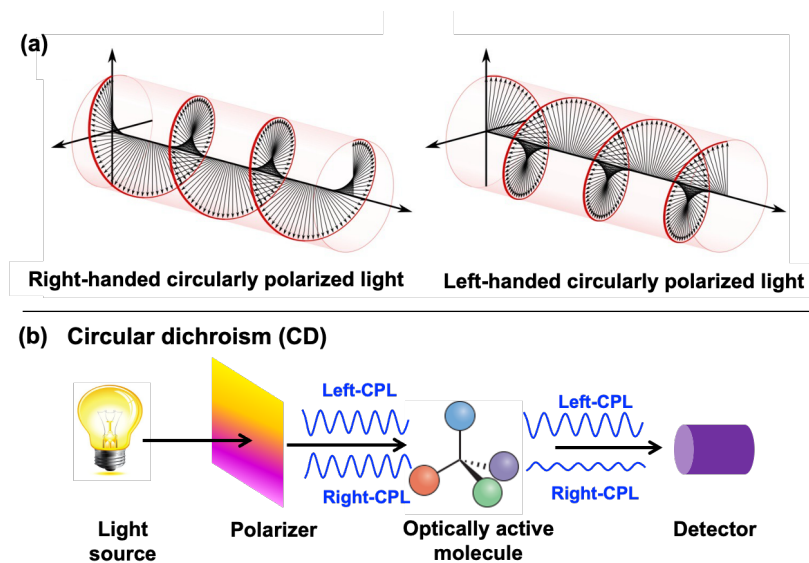


Figure 1-7 (a) Right-handed and left-handed circularly polarized light, (b) Schematic Circular Dichroism (CD) spectroscopy.

When measuring ECD in a solid state which tend to have scattering issues due to high refractive index, we could use not only Transmission CD (TCD) but also use Diffuse Reflectance Circular Dichroism (DRCD).¹⁹ In the case of TCD, the detector could detect the transmitted light, therefore CD signal is equal to absorption CD and backward/forward scattering (CD = absorbance CD + backward and forward scattering). Meanwhile, DRCD contains an integrating sphere for removing the scattering effect. The detector in DRCD detects the backward and forward scattering and transmitted light. Therefore, the DRCD signals are avoid of scattering contribution from the samples.

Another artefact to be considered is the Linear Dichroism (LD) and Linear Birefringence (LB). Typically, measured CD, CD_{tot} is made up of many contributions, as shown in an equation below.^{20, 21}

$$CD_{tot} \approx CD_{true} + 1/2(LD' \cdot LB + LD \cdot LB') + (LD \cdot \sin \alpha + LB) \cdot \cos 2\theta + \dots$$

The prime in $LD' \cdot LB$ and $LD \cdot LB'$ mean a $+45^\circ$ shift between LD and LB axes. θ angle relates to the sample rotation around the incident light direction, while α refers to the residual birefringence of the photoelastic modulator (PEM). Therefore, true Circular Dichroism (CD_{true}) is independent of sample orientation, while the LD spectrum is angular dependent.²²

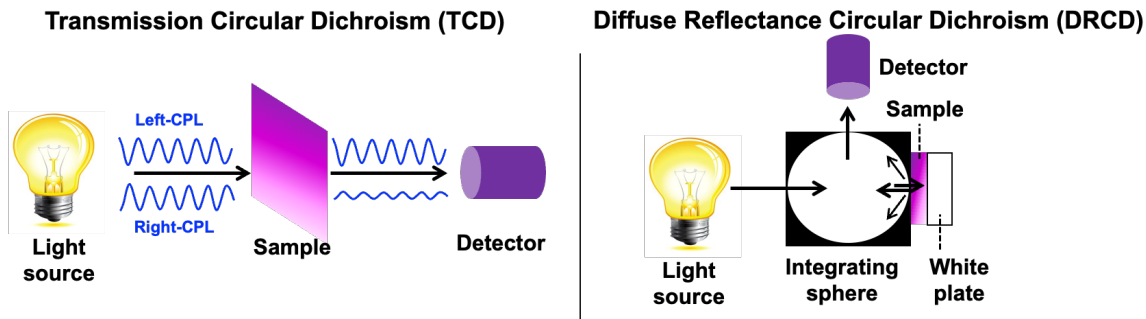


Figure 1-8 (a) Schematic Transmission Circular Dichroism (TCD) and Diffuse Reflectance Circular Dichroism (DRCD)

Circularly Polarized Luminescence (CPL)²³ An excited molecule relaxes to the ground state by emitting light, which is defined as luminescence. Luminescence is the transition from an excited state to a ground state. Instead of emission, there are several processes that could occur during transition such as relaxation, conformational change, and reorientation. CPL measures the different emissions of left-handed and right-handed circularly polarized light. To measure CPL signal, the excitation light source is generally unpolarized. The different emission intensity (ΔI) is defined as an equation below.

$$\Delta I = I_L - I_R$$

I_L and I_R refer to the intensity of left- and right-handed circularly polarized light, respectively. Similar to the dissymmetry factor for CD, the degree of dissymmetry of CPL is quantified by the luminescence dissymmetry factor (g_{lum}). The g_{lum} is calculated as

$$g_{lum} = 2(I_L - I_R)/(I_L + I_R)$$

The maximum value of $g_{lum} = \pm 2$ means an ideal left-handed and right-handed CPL, whereas $g_{lum} = 0$ means unpolarized luminescent light. Theoretically, g_{lum} is related to the electric (μ) and magnetic (m) dipole moment as known in an equation.

$$g_{lum} = 4(\mu^*m)/(|\mu|^2 + |m|^2)$$

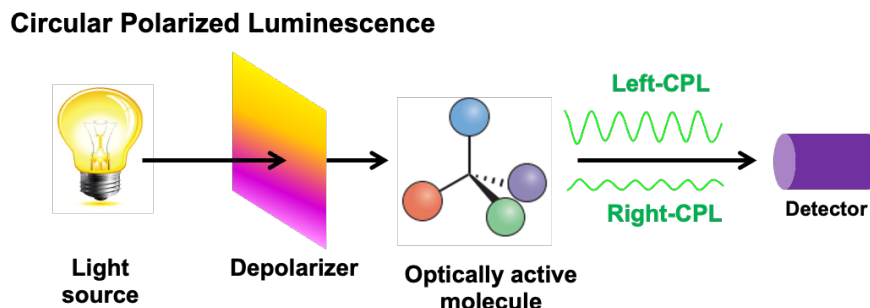


Figure 1-9 Circularly Polarized Luminescence (CPL) spectroscopy.

1.3 Introduction of carbon-based materials

1.3.1 Carbon-based materials

Carbon-based materials (CBMs) play an important role in the development of scientific research and industries ranging from traditional carbon-based materials (such as activated carbon) to new carbon nanomaterials (such as graphene and carbon nanotube). In nature, carbon occurs in different kinds of compounds such as amorphous carbon in organic molecules and biomacromolecules. The multiple forms of carbon including sp , sp^2 , sp^3 have different orientations of their orbitals, which initiate different structures with characteristic properties.²⁴ CBMs showed different forms such as carbon fibers, carbon nanotubes, fullerenes, fullerenes, carbon black, porous carbon, diamond and graphite/graphene. Therefore, CBMs are used for several applications due to their excellent properties such as high strength, high density and high hardness, high chemical stability, good electrical conductivity, and porosity.²⁴ For example, CBMs are utilized as:

- 1) Electrodes in electrochemistry for the degradation of organic pollutants and H_2 generation from water splitting.²⁵
- 2) Electrode materials for fast-charging lithium-ion batteries owing to their abundance, low cost, electrochemical diversity and nontoxicity in energy storage technology.
- 3) Adsorbents for inorganic and organic compounds in water treatment by absorbing dangerous and hazardous pollutants such as dyes, heavy metals, phenolic, and pharmaceutical compounds.²⁶
- 4) Stabilizers for the perovskite solar cells when incorporated in different functional layers of the devices including electro-selective layer, perovskite active layer, and hole selective layer, resulting in long-term stability for scaling and commercialization in solar cell technology.²⁷

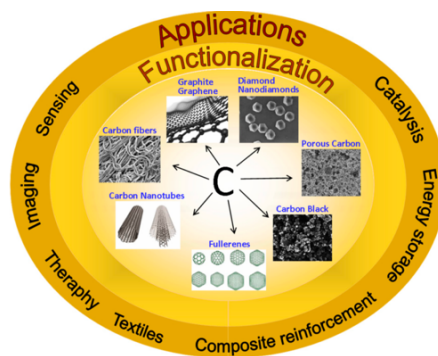


Figure 1-10 Different forms and applications of carbon-based materials.²⁴

1.3.2 Carbon dots (CDots)

Carbon dots (CDots) are new rising stars in carbon-based nanomaterials which have attracted attention due to their excellent and tunable photoluminescence, biocompatibility and low toxicity. CDots could be defined as quasi-0D carbon-based materials with a size below 10 nm with their intrinsic luminescent properties. CDots are mainly categorized into graphene quantum dots (GQDs), carbon dots (CDots), and carbonized polymer dots (CPDs) corresponding to their different formation mechanisms.²⁸ GQDs could have one- or multiple- graphite layers containing chemical functional groups on the surface or edge or in interlayer defect. GQDs are normally synthesized by top-down method, which is related to cutting layer bulk carbon materials such as carbon rods, carbon black and graphene sheets. Meanwhile, CQDs and CPDs were synthesized by assembling or polymerization, cross-linking, and carbonization of small organic molecules, biomass and polymers. This method is known as a bottom-up method via combustion and thermal treatment.²⁹⁻³¹ The fluorescence of CDots is based on the quantum confinement effect,^{32a} which occurs when the size of the particle is small compared to the wavelength of the electron. The absorption of CDots occurs when the energy of the light is equal to or larger than its bandgaps, promoting electron transition from the valence band (VB) to the conduction band (CB) resulting in a hole in the valence band and then generating an exciton. The characteristic length scale of an exciton is related to the exciton Bohr radius (α_0) ~ 2 to 50. When the size of CDots is smaller than the Bohr radius, the exciton wave function is affected by spatial confinement. Therefore, the discrete energy corresponding to energy bandgap between the valence band and the conduction band can be controlled by the size and shape of nanoparticles. This quantum confinement of electrons in all three directions as in the CDots strongly influences their optical properties.

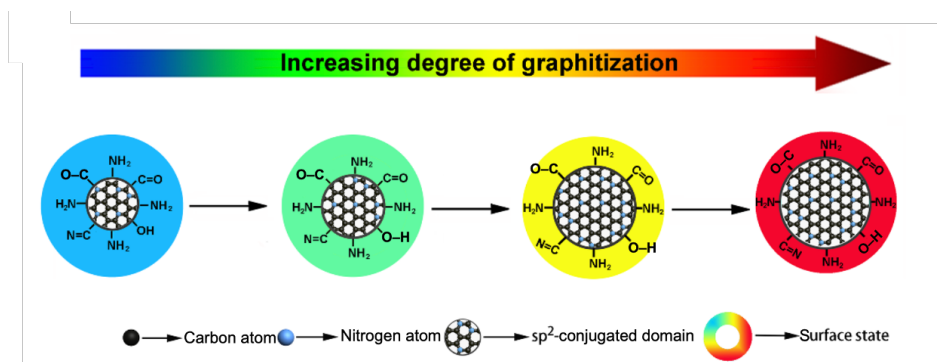


Figure 1-11 Scheme illustration of CDots with tunable PL emission.^{32b}

CDots generally contain a conjugated π -domain carbon core and functional groups on the surface,^{33,34} and the relationship between the two can be used to tune their photoluminescence. The fluorescent mechanism refers to the electrons directly transiting from the conduction band to an empty hole of the valence band. In general, the conjugated sp^2 carbon cluster of CDots is dispersed in sp^3 carbon structure, therefore the fluorescence is mainly related to the radiation transition (π - π^*) of the electron-hole pairs in the sp^2 carbon core. The conjugated π -domain size could be adjusted by various parameters such as reaction solvents, precursors, reaction time and reaction temperature. The larger size of CDots exhibits the smaller electronic band gap transition resulting in more red-shift fluorescent emission.^{35, 36}

One of the important parameters that affect electronic band gap transition is the surface defect states, which refer to a boundary region containing surface functional groups and chemical groups from sp^2 and sp^3 carbons. The fluorescence mechanism of surface defect states originates from the electron transition from the conduction band to the valence band when the oxidative state acts as a capture center for exciton. The different functional groups have different energy levels related to their ability to supply electrons, therefore generating a series of emission traps. Consequently, the higher the degree of surface oxidation of CDots, the more surface defects they have, resulting in red-shift fluorescent emission. The surface functional groups of CDots play a crucial role in combination with quantum confinement for controlling their optical properties.³⁴

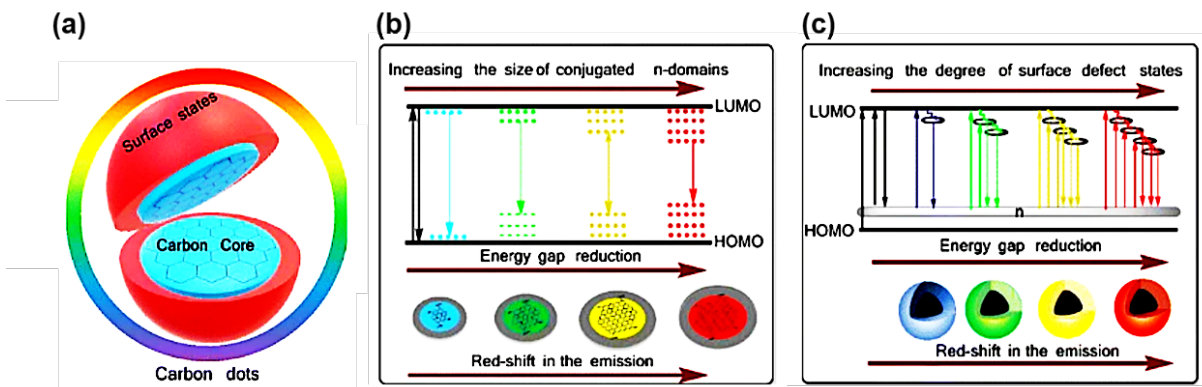


Figure 1-12 (a) two main parts of CDots (a), the effect of size (b) and surface defects on emission.³³

The fluorescent molecules or fluorophores derived in the structure of CDots also have an impact on the luminescent properties of CDots. These fluorescent molecules are connected to the carbon backbone of CDots and can exhibit fluorescent emission directly. These fluorescent molecules have a large effect on the fluorescent bandgap corresponding to colour-emitting of CDots. CDots containing only carbon and oxygen elements usually show blue fluorescence with low quantum yield (QY). To improve QY, elemental doping such as nitrogen, sulfur, phosphorus, and metal ions) can increase electron local density and turn the energy band gap of CDots resulting in a shift in emission, additionally, elemental doping also develops the photoluminescent decay and lifetime. Nitrogen is one of important elemental dopants as its radius is similar to that of a carbon atom, consequently nitrogen atom is incorporated easily into the carbon-core structure of CDots. The nitrogen dopant could generate a new energy level, therefore the fluorescence exhibits a red-shift wavelength. For instance, it was reported that the band gap energy decreased from 2.01 to 0.64 eV after introducing nitrogen into CDots.³⁷ Furthermore, nitrogen dopant can serve as electron-donating groups which could improve the degree of conjugated π -domain system, therefore it can increase QY of CDots.³⁴ Nitrogen dopant of CDots generally exists in three different structures including pyridinic, graphitic and pyrrolic. Sulfur has also been reported as a hetero atom dopant of CDots usually embedded in the carbon core of CDots in the form of a thiol, thioether and sulfonic group. Sulfur atom in CDots acts as a catalyst for oxidation-reduction reaction,³⁸ resulting in an increase in passivated surface defect of CDots. Therefore, the sulfur dopant could increase the probability of electronic transition and then generate a change in the energy gap and improve QY of CDots.³⁹

CDots could be synthesized using either top-down or bottom-up methods.⁴⁰⁻⁴² Top-down methods refer to the synthesis approach of cutting down macroscale materials to produce carbon-based nanoparticles. The precursors for the top-down synthesis of CDots can be graphene sheets or carbon nanotubes with various cutting methods, such as chemical oxidation, laser treatment, and hydrothermal or electrochemical methods. Meanwhile, bottom-up methods could transfer the organic molecules to CDots by hydrothermal reaction,^{43, 44} pyrolysis⁴⁵ and reflux.⁴⁶ The transformation of organic molecules to CDots will occur among the condensation of functional groups and carbonization during synthesizing.⁴⁷

1.3.3 Chirality induction of carbon dots (CDots)

The chiral CDots have been previously reported, and usually three different approaches are used for their synthesis, 1) Incomplete carbonization of chiral molecules, 2) Covalent grafting of chiral molecules and 3) Incorporation within chiral supramolecular self-assembly.

1. Incomplete carbonization

In this case, chiral CDots are synthesized from chiral precursors via incomplete carbonization. The temperature during the synthesis can retain the asymmetric carbon from chiral precursors, therefore this carbon embeds in the carbon core structure and then induces the chiral property to CDots. For instance, Deka M. J., et al.⁴⁸ reported chiral CDots which were synthesized via the incomplete-carbonization method without attaching or doping with other moieties. The chiral organic molecules including D-methionine, L-methionine, D-glucose, L-aspartic acid, L-alanine and D-glucosamine act as chiral precursors to synthesize chiral CDots. The size of CDots was characterized by Dynamic Light Scattering (DLS) representing a size of 2-5 nm with a uniform and spherical morphology. Additionally, Zeta Potential Analysis suggested the negative surface charge of CDots corresponding to the presence of functional groups (-OH, -NH₂ and -COOH). Meanwhile, CDots represented the chiral properties relating to the enantiomer precursors. CDots synthesized from D-methionine show a CD peak at 210 nm with a positive response, while CDots from L-methionine exhibit a negative CD response at 210 nm. Subsequently, it was suggested that the different configurations of D- and L- methionine precursors generated the difference in their polarized light rotation of CDots. This research proposed that asymmetric carbon in D-/L-

methionine could retain after thermal treatment at 280 °C and subsequently perform as a chiral inducer to endow the chiral property of CDots.

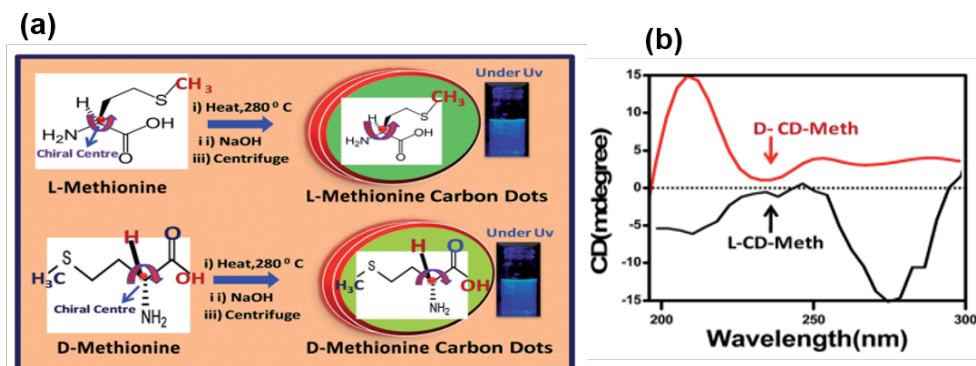


Figure 1-13 (a) Scheme of the synthesis and (b) CD spectra of D- and L-CDots synthesized from D- and L-methionine.⁴⁸

2. Covalent grafting of chiral molecules

For this method, chiral molecules are covalently grafted on achiral CDots. For instance, Suzuki, et al.⁴⁹ attached chiral D- or L-cysteine on achiral CDots via amide covalent grafting using N-ethyl-N'-(dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxy succinimide (NHS). The sizes of CDots before and after functionalizing chiral cysteine molecules are in the range of 2-7 nm. XRD spectrum evidenced a peak at $2\theta=25^\circ$ which corresponds to 022 carbon-to-carbon spacing of 3.7 Å. The chiroptical property of L-/ D-CDots could be observed with a characteristic CD spectrum of chiral cysteine, interestingly, the new CD signal could be observed at around 250-265 nm influenced by the out-of-plane buckling of graphene sheet via intramolecular interactions of chiral surface ligands. L-CDots displayed a right-handed helicity in the conformation, meanwhile D-CDots expressed a left handedness with $g_{\text{abs}} (\sim 1 \times 10^{-4})$. These CDots did not represent CPL signal. These chiral CDots also showed good biocompatibility in liver cells with low cytotoxicity, their atomistic simulation indicated that chiral CDots strongly bind to the lipid bilayer of the cells.

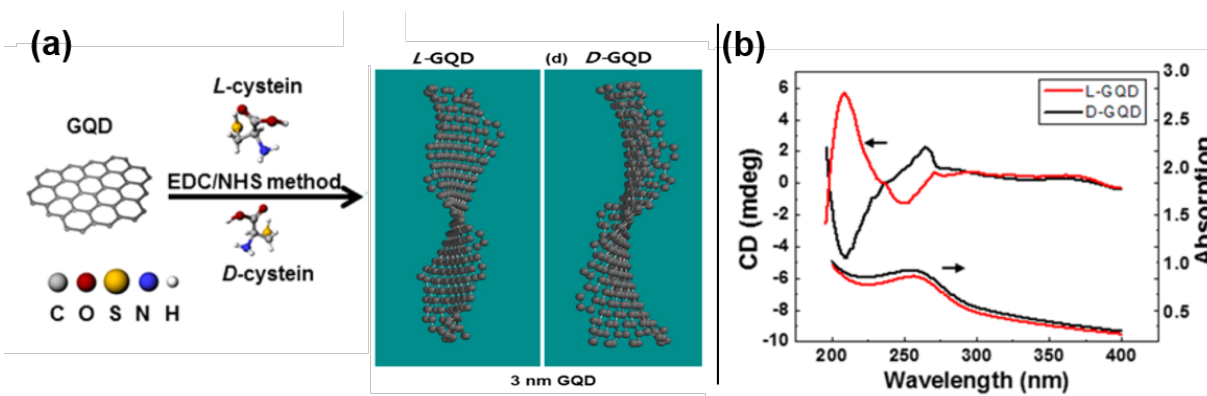


Figure 1-14 (a) Scheme of the chirality induction of CDots by covalently attaching D-/L-cysteine, (b) CD-absorption spectra of chiral CDots.⁴⁹

3. Incorporating with chiral supramolecular self-assembly

Supramolecular co-assembly is used as a powerful platform to transfer the chirality onto achiral CDots via non-covalent interaction. Li A., et al.⁵⁰ studied the chirality induction to CDot based on supramolecular self-assembly of a sol-gel system, which was organized by a chiral gelator composed of L- or D-glutamic acid. Achiral carbon dots with a size range of 1-3 nm have been prepared by citric acid and ammonium hydroxide. Meanwhile, the self-assembly of gelator was prepared in a mixture of ethanol and water to organize tubular nanostructures. This self-assembled chiral gelator showed a cotton effect at 213 nm in CD spectra. Subsequently, achiral CDots showed induced CD signal when incorporated in the self-assembly of chiral tubular gelator, which relied on the intermolecular hydrogen bonding between the carboxylic functional groups of CDots and amino groups from the gelator. Interestingly, these chiral CDots with chiral assembly gel not only showed a CD signal but also exhibited a CPL signal.

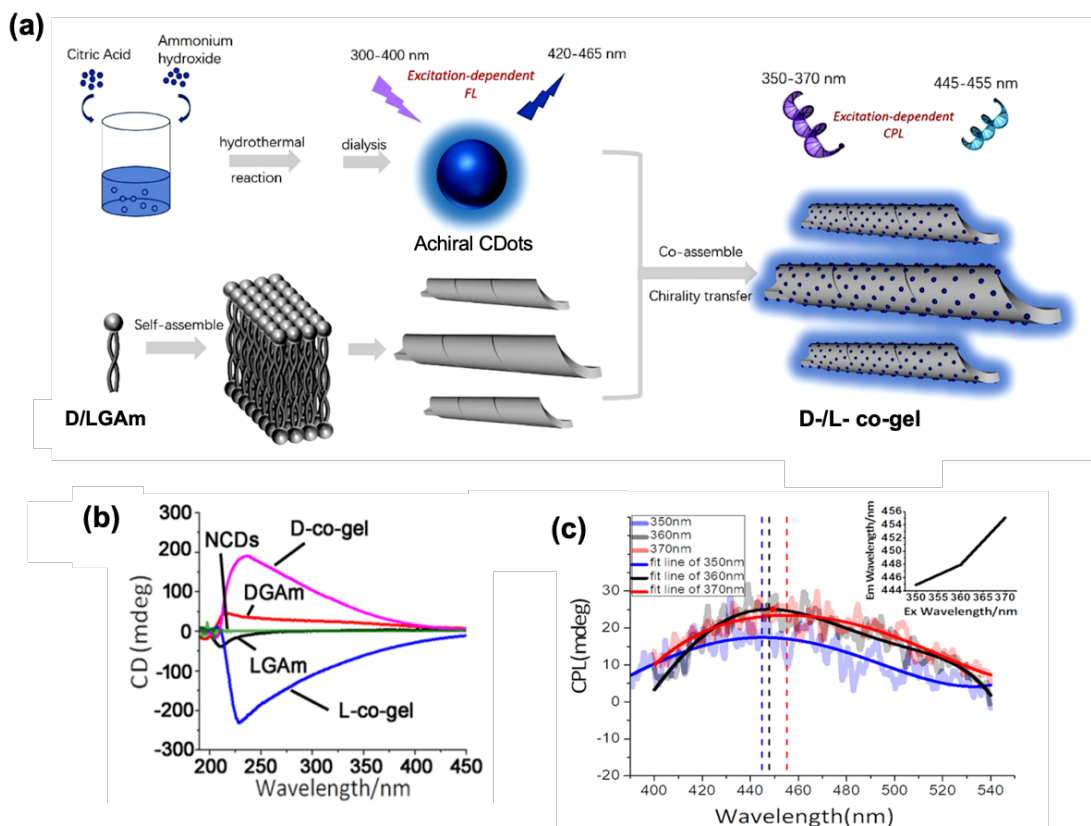


Figure 1-15 (a) Scheme of the chirality induction of CDots via supramolecular self-assembly of chiral gelator, CD (b) and CPL (c) spectra for chiral CDots.⁵⁰

In 2021, Ru Y., et. al.⁵¹ synthesized one kind of CDots called polymer dots (CPDs) with multicolour emission. The CPDs are defined as a novel kind of luminescent materials combining the optical and electronic properties of semiconductor quantum dots. The CPDs were synthesized from precursors including *O*-phenylenediamine and chiral L-/D-tryptophane by solvothermal approach. The solvothermal reaction was carried out at 160 °C for 7 hrs in different solvents including H₂O, HCl/ethanol (1:10), H₂SO₄/H₂O (1:20). Tryptophane has a melting point at 281 °C, therefore the original chirality of asymmetric carbon is preserved when the synthesized temperature (160 °C) is below the melting point of the chiral precursor. Three different sets of CPDs were purified and dispersed in ethanol, they showed different colours in emission with blue, yellow and red (emission peak at 441, 546 and 604 nm, respectively, under excitation at 365 nm). The multicolour emission of the CPDs was influenced by their different sizes, it was observed by TEM image that the sizes of blue-, yellow- and red-emitting CPDs were 2.5 ± 0.5 , 3.0 ± 0.4 , and 4.6 ± 0.6 nm, respectively. The absorption spectrum illustrated the absorption peaks at 215 and 280

relating to the π - π^* transition of C=C and C=N bonds, respectively. The chiral CDPs with yellow or red emission showed a significant increase in 280-nm absorption due to the enhancement in nitrogen-doped aromatic in CPDs. The L-/D-Tryptophane showed the symmetrical CD signal at a range of 200-246 nm, meanwhile the CD signal of CPDs after carbonization and polymerization expressed a new CD response at 245-300 nm. However, these chiral CDots showed chirality in absorption with no CPL signals. To endow the chirality in emission, chiral CDots were incorporated with chiral organogel lipid N,N-bis(octadecyl)-D-glutamic diamide (DGAm) and N,N-bis(octadecyl)-L-glutamic diamide (LGAm). It was observed that chiral CPDs are aggregated on the surface of the nanotube of self-assembly DGAm/LGAm through electrostatic interaction. After incorporating CDots in chiral organogel, it was observed symmetrical CD spectra with mirror-image CPL signals at 450, 550 and 610 nm ($g_{lum} \pm 10^{-2}$). The research elucidated the chirality induction of CDots materials by using incomplete carbonization of chiral precursors and incorporating with chiral supramolecular self-assembly.

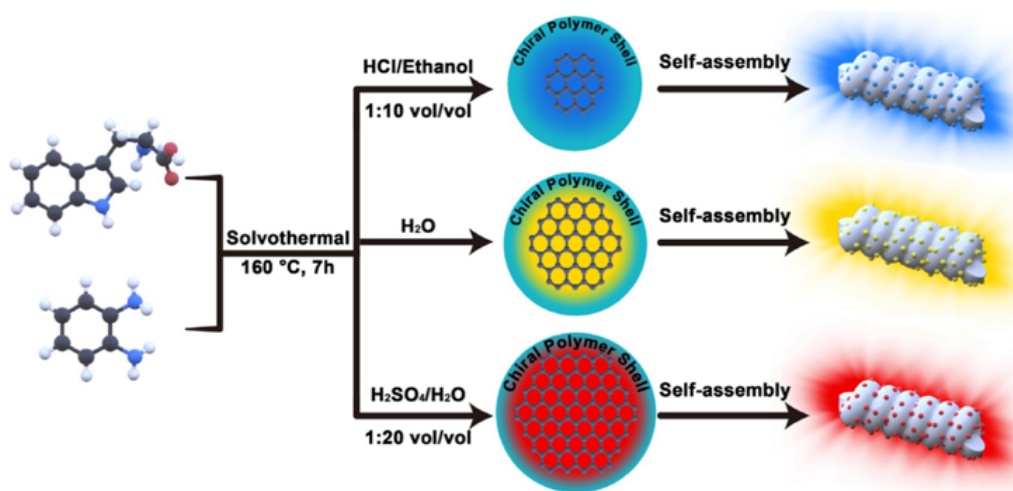


Figure 1-16 Preparation procedure of multicolour-emitting CPDs with CPL signal.⁵¹

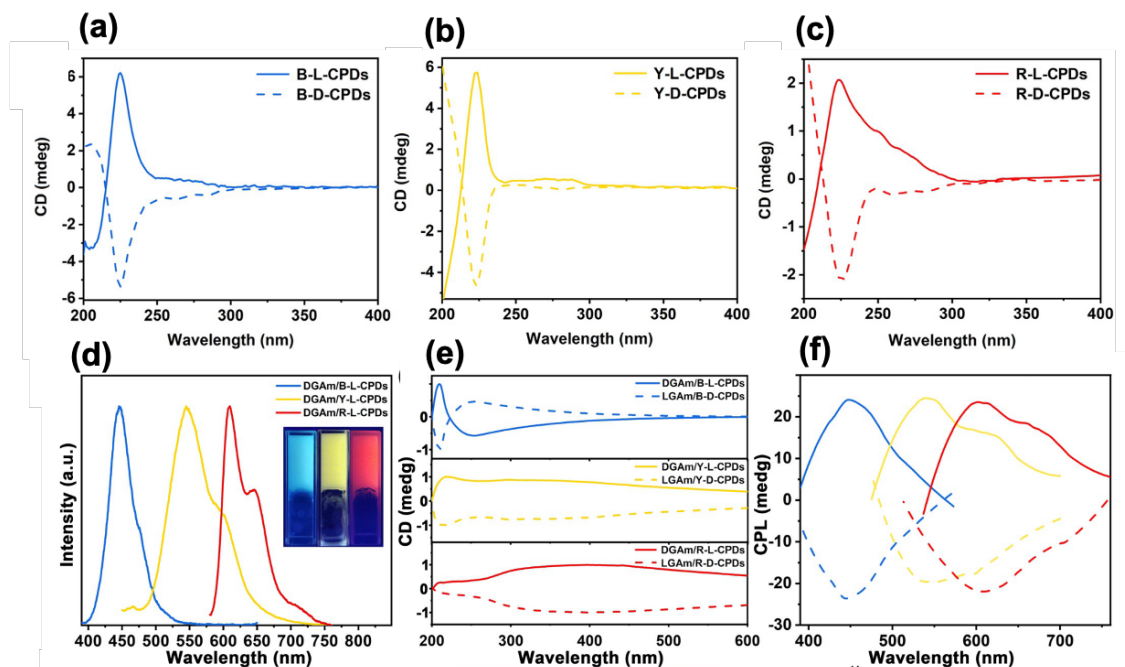


Figure 1-17 CD spectra of CPDs with blue- (a), yellow-(b) and red-(c) emitting CPDs, luminescent spectra of CPDs (d), (e) CD and (f) CPL spectra of CDPs after incorporating into self-assembly organogel.⁵¹

1.4 Introduction of polymer

Polymer is defined as a substance or material composed of repeating units of small molecules called monomers. One can find polymers from different sources including nature (silk, cotton, wool) and synthetic processes (PET filter, PET bottle, PVA package). The polymer chain structure is divided into two categories including homopolymers and copolymers. Homopolymers are linked by only one type of monomer, whereas copolymers contain different types of monomeric units in alternating sequences. Block copolymers are made from a linear arrangement of blocks of copolymers. A block is a portion of a polymer molecule in which the monomer has one constitutional feature.⁵² A random copolymer is one in which the monomer residues are located randomly in the polymer chain, in other words, it is composed of two or more different monomers with a completely random sequence of repeating units. In the case of graft polymer, it is a copolymer consisting of a linear backbone and randomly distributed branches as side chains. In order to synthesize polymers, the monomeric units need to be linked via polymerization reactions including addition polymerization and condensation polymerization. The addition polymerization

occurs if monomers link together through initiation, propagation and termination,⁵³ for instance, polystyrene is a versatile plastic in various consumer products, and it is generally synthesized by using styrene as a monomer via addition polymerization.⁵⁴ Another type of polymerization is a condensation reaction,⁵⁵ is derived from two monomers containing reactive functional groups such as carboxylic acid and amine. These functional groups will react with each other to form the polymer chains containing amide bond.

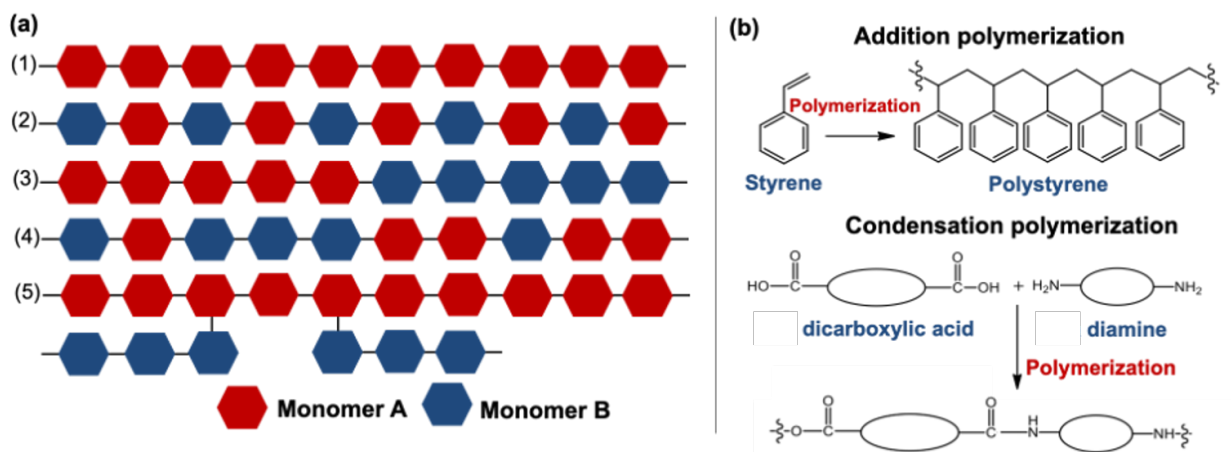


Figure 1-18 (a) (1) homopolymers, (2) copolymers, (3) block copolymer, (4) random copolymers, (5) graft polymer, (b) addition polymerization and condensation polymerization.

The functional polymer materials promise a great potential in a variety of renewable energies, medical diagnostics, environmental protection, and water treatment.⁵⁶ Therefore, the development of synthetic and natural polymers has been investigated in order to improve their impact and stability. For instance, conducting polymer or electroactive polymers have been studied to improve their ability to conduct electricity in energy-assembly applications such as solar cells, batteries, photocatalysis materials and electrochromic devices. For instance, polymers could be used as platinum-free counter electrodes, pore- and film-forming agents for photoanode films in dye-sensitized solar cells, meanwhile polymers were used as the additive to control the nucleation and crystallization in perovskite solar cells.⁵⁷ In 2021, Huiting Fu, et. al.⁵⁸ developed a novel polymer as a narrow-band gap acceptor by incorporating a benzothiadiazole-core fused ring, which resulted in an enhancement in current density and open-circuit voltage. Importantly, the regioregularity induced the polymer acceptor to have more extended and intense absorption, as well as superior backbone ordering. The porous polymeric membrane has gained a lot of attention

to enhance porosity and hydrophilicity in water treatment. The properties of the polymer can be managed by controlling chemical- and physical- parameters. The polymeric membrane was classified into four types of separation; microfiltration, ultrafiltration, nano-filtration and osmosis.⁵⁹ Meanwhile, polymers and functionalized polymers have been applied for biomedical applications to potentially enhance the performance of medical diagnostics. Biomedical polymers have been developed for smart drug delivery, disease detection, disease treatment and regenerative medicine.⁶⁰ For example, Quan Zaou, et. al.⁶¹ studied a γ -glutamyl transpeptidase-responsive polymer that could actively infiltrate throughout the tumour tissue, which exhibited potent antitumor activity in mouse models for eradication of small-size tumour ($\sim 100 \text{ mm}^3$) and regression of large-size tumor ($\sim 500 \text{ mm}^3$). In addition, the hydrophobicity of polymers is a promising property which has a huge impact on interactions with lipid membranes and proteins. Therefore, the incorporation of hydrophobic parts into polymers could influence their properties in biomedical applications.⁶² Hydrogel-based natural polymers, such as gelatin, agarose, and collagen) are utilized as bio-inks in the preparation of 3D cell-laden structures and chemotherapeutic drug screening.⁵⁶

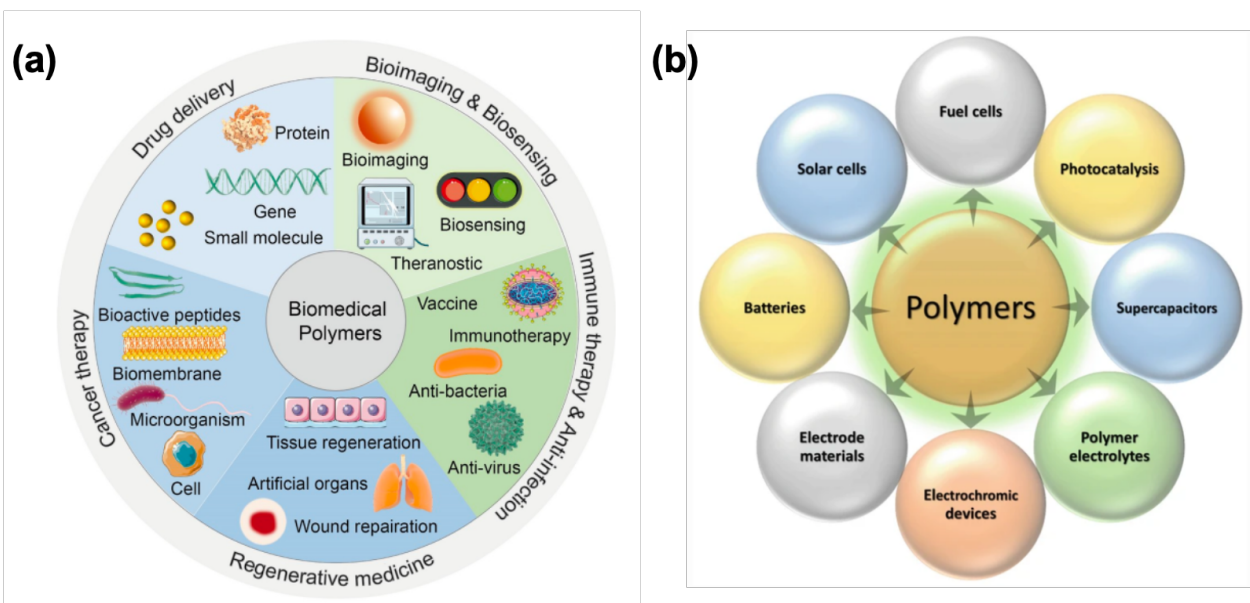


Figure 1-19 Polymers in biomedical⁶⁰ (a) and energy⁶³ (b) applications.

1.4.1 π -conjugated polymer

π -conjugated polymer is one of the interesting polymers for numerous applications in biomedical imaging, organic electronics and energy storage.⁵⁷ The π -conjugated polymers show their extraordinary properties such as structural versatility, light weight and environmentally friendly. Conjugated polymers such as polythiophene, polyfluorene and polyacetylene, have semiconducting properties as their band gap is commensurate to the visible light, photons could be absorbed and emitted the exciton. Therefore, their optoelectronic properties are potentially useful for organic photovoltaics, light-emitting diodes and field-effect transistors. Furthermore, the π -conjugated polymers contain the delocalized π -systems resulting in stacking interaction and the formation of the crystalline phase of polymers, thus it is extremely beneficial for charge carriers. One of the conjugated polymers⁶⁴ is conjugated conducting polymers containing a long π -conjugated system in the skeleton which generates delocalization of free electrons. The movement of free electrons in the conjugated system was improved by reducing the energy band gap between full and empty bands. The conducting polymer with conductive properties is widely utilized in organic field effect transistor, sensors and organic solar cell. Conjugated polymers could be synthesized by various approaches such as electrochemical and chemical oxidation reactions, palladium-catalysis Suzuki-Miyaura coupling polymerization, and Grignard metathesis. Besides applications of aromatic polymers, the usage in bio-medication has gained attention dramatically to improve diagnosis and medical treatment for various diseases. The aromatic polymers are generally used in blood and tissue interaction medical devices, as well as drug delivery systems. These conjugated polymers need to be non-toxic, biocompatible, and biodegradable because they will be directly in contact with the human body's system. The required properties of aromatic polymer for medical applications are self-healing adhesion and superhydrophobicity to avoid any disaster for the human body. In addition, polymeric-based materials should be able to treat and heal any size of a material defect, and have excellent stability in mechanical and thermal performance.⁵⁷ Conjugated polymer could be used as precursors to synthesize conjugated-polymer nanoparticles (CPNPs) for electronic bioimaging, photothermal and photodynamic therapies. In order to prepare CPNPs, there are several methods such as nanoprecipitation, mini-emulsion polymerization, and crystallization-driven self-assembly of amphiphilic block copolymers (CDSA).⁶⁵ Furthermore, conjugated polymers are regarded as a potential platform for electrochemical and biomedical applications. Conjugated polymers have a fundamental unit as a

conjugated backbone, which facilitates high stability and biocompatibility.⁶⁶ Conjugated polymer backbone could be synthesized from an electron donor and acceptor group, therefore their properties could be tuned by controlling the length of conjugation, adjacent groups of monomer and molecular interaction. Their sensing application using conjugated polymer relies on energy transfer, complexation and charge transfer, meanwhile electrochemical applications by conjugated polymer are corresponding to an efficient charge transfer group between the analyte and conjugated polymer chain.⁶⁶

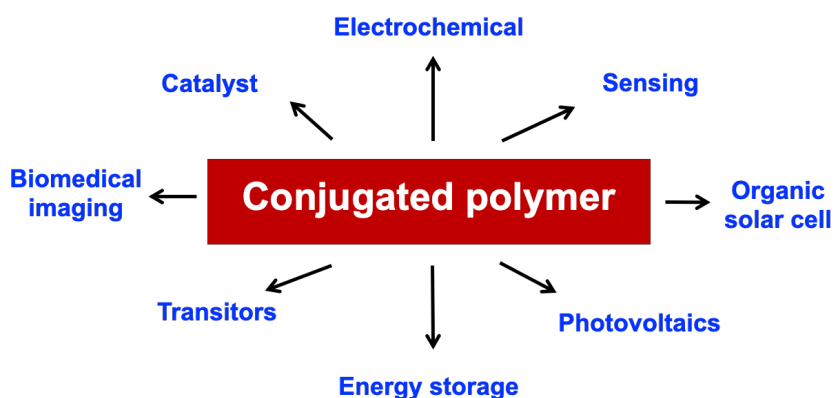


Figure 1-20 Applications of conjugated polymer.

1.4.2 Chiral polymer

Optically active polymers are synthesized by the introduction of chiral substituents to the repeat units of the polymer via covalent bonding. Hiromasa G.⁶⁷ synthesized chiral polymer by attaching the chiral molecule onto an aniline monomer, subsequently this chiral monomer was used as a precursor to synthesize polymer with the chiroptical property. The CD response showed a quasi-mirror image cotton effect corresponding to the chiral R-P3 or S-P3 molecule with positive and negative signals, respectively. Meanwhile, Huajun H., et. al.⁶⁸ prepared chiral polymeric spheres consisting of helical substituted polyacetylene. These chiral microspheres were synthesized by precipitation using M1S or M1R as chiral monomers (Figure 1-21). Then, this chiral monomer reacted with 1,4-diethylbenzene as a crosslinker in the presence of Rh catalysts. The variation of solvent for synthesis was studied by turning the butanone/n-heptane ratio. It was observed that polymeric spheres using M1S showed a positive CD signal, meanwhile polymeric

spheres from M1R expressed a negative CD response. This chiral phenomenon suggested that chiral polymer spheres consist of helical polymer with opposite helical handedness corresponding to chiral monomer. In addition, the CD signal could be turned in the following solvents (CHCl_3 , THF, and N,N -dimethylacetamide), which suggested that the helical structures of the polymer were disturbed by hydrogen bonding in a polymer chain in different solvents.

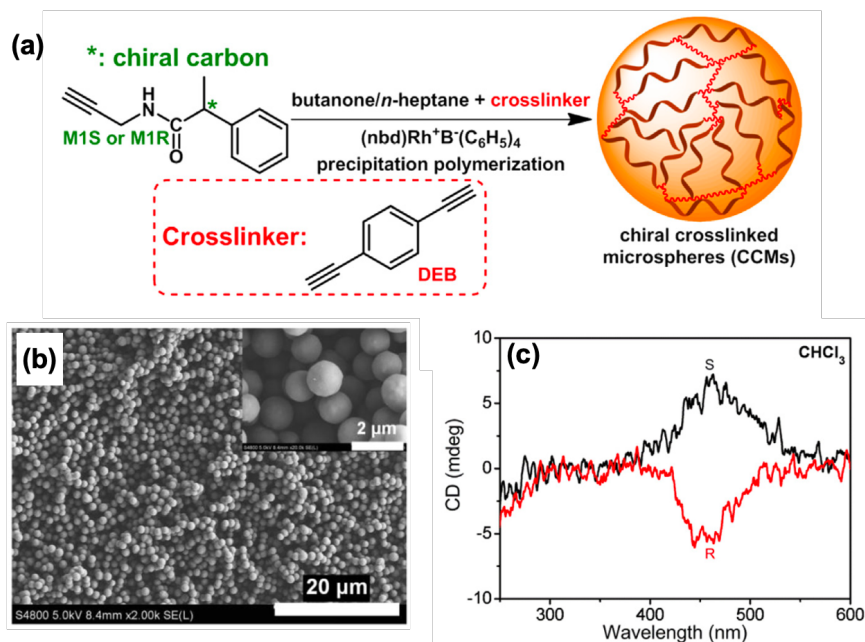


Figure 1-21 (a) Preparation of chiral crosslinked microsphere by precipitation polymerization, SEM images (b) and CD spectra (c) of chiral crosslinked microsphere from M1R using 0.03 g of crosslinker in (2.5/3.5) butanone/*n*-heptane.⁶⁸

In 2021, Hong J., et. al.⁶⁹ synthesized chiral polymer hosts showing CPL signals by free-radical polymerization of 3-vinyl carbazole with a chiral *N*-alkyl unit. These chiral polymers possess chiral repeating units to form helical half-sandwich conformers with preferred *P*-helicity, which suggests the chirality transfer from a chiral monomer to a polymer chain. The absorption spectra of polymers showed three main bands at 352, 308 and 265 nm, which were assigned the short- and long-axis electronic transitions relating to absorbance peaks at 352 and 308 nm, respectively. In addition, the chiral polymer diastereoselectively interacts with enantiomers of phosphorescent *R*- and *S*-dopants. It was noted that g_{abs} of *P*-helically polymer with *R* dopants was higher than that of polymer with *S*-dopant, meanwhile the g_{lum} of chiral polymer film with *R*-dopant was around 10^{-3} . Interestingly, the chiral polymer exhibited energy transfer to the

phosphorescent dopants than the achiral polymer host. Practically, polymer electroluminescence devices employing chiral polymer hosts were fabricated for further application in electroluminescent fields.

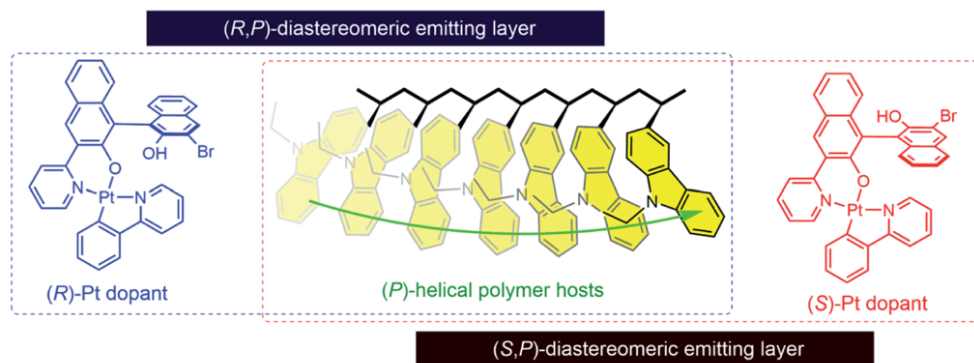


Figure 1-22 Diastereomeric interaction between dopants and polymer hosts with enriched helical sense.⁶⁹

In 2021, Toya M., et. al.⁷⁰ developed the novel helically-folded poly(arylene diethynylene)s by the light-induced topochemical polymerization of diacetylene moieties. They reported three types of Poly-NaphDE, Poly-ArDE and Poly-PyDE consisting of naphthaleneimide, pyrene and pyridine. The monomer unit has three parts including a diacetylene linker, a centre aromatic chain and a chiral side chain. The diacetylene linker generates the structural transformations, while a central aromatic unit contributes to the helical folding. Therefore, the poly-ArDE with naphthalene, pyrene and pyridine performed as a central aryl group. Poly-NaphDE was expected to expand the cavity of a helical structure due to hydrogen bonding. Poly-PyrDE was expected to exhibit photophysical properties based on pyrene moiety. While Poly-PyDE was expected for the coordination of molecules and metals by the pyridine. In addition, these polymers were influenced by solvent resulting in a change in UV-Vis absorption, fluorescence and CD spectra.

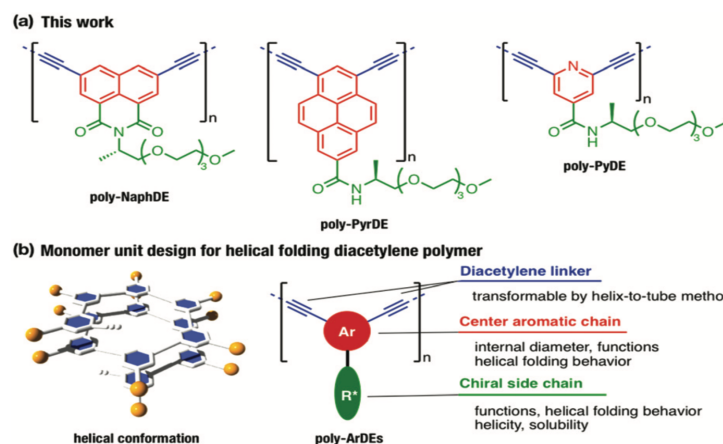


Figure 1-23 Designed and synthesized poly-ArDEs. (b) Monomer design for helical folding poly-ArDE.⁷⁰

1.5 Introduction of foldamers

Foldamers are oligomers with specific sequences with well-defined three-dimensional structures. J.S. Moor, et al. described foldamers as “any oligomer that folds into a conformationally ordered state in solution, the structures of which are stabilized by a collection of non-covalent interactions between nonadjacent monomer units”⁷¹ There are various examples of foldamers including helices, oligonaphthalenes, polyisocyanate and polyaldehydes. The folding reaction and dynamic conformation are important for oligomers to be existing in foldamers. Foldamers are structurally stabilized by non-covalent interactions between monomers within a molecular chain. The single-stranded foldamers mainly rely on intra-chain interaction for folding of structure, meanwhile multiple-strand foldamers also need to associate through inter-chain interaction.

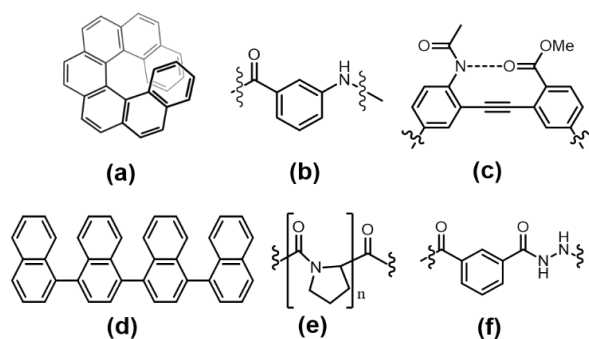


Figure 1-24 Examples of foldamers (a) helicene, (b) polyacrylamide, (c) polyphenyl ethynylene, (d) oligonaphthalenes, (e) polyprolines, (f) polyprolines.

Typical secondary structures observed with foldamers are helices which can be used to mimic the biopolymers. The thermodynamic and kinetic parameters involved in the helical folding of foldamers, implies the reduction of entropy while gaining in enthalpy thus leading to their stabilization. One of the families of foldamers is those with aromatic amides that are stabilized by intramolecular hydrogen bonding. The rotation around the amide C-N bond is restricted as it has the rotational energy around 65-90 kJ/mol as a barrier which depends on the environment and connected group. In the case of aromatic amide foldamers, the (Ar)C-CO(NHAr) and (Ar)CNH(COAr) bond will freely rotate if the ortho position of the amide bond has no substituents, resulting in two partially coplanar conformations. The intermolecular bonding between oxygen/nitrogen acceptors and aromatic amide hydrogen atoms is strong for the construction of compact structures. There are two patterns of intra-molecular hydrogen bonding in aromatic foldamers, those with the hydrogen bonds between the amide hydrogen and acceptors in the aromatic unit attached to the amide nitrogen atom, and another between the amide proton and acceptors in or on the aromatic ring attached to the amide carbon atom. These intramolecular hydrogen bonds could be formed in 4-, 5-, and 6-membered rings.⁷²

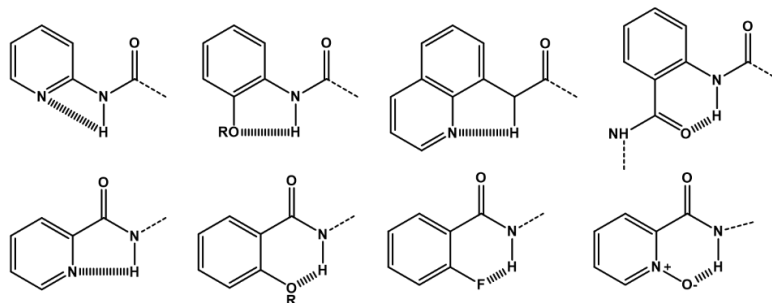


Figure 1-25 Representative intramolecular hydrogen-bonding patterns of aromatic amide foldamers including the aromatic unit attached to the amide nitrogen atom and the aromatic unit attached to the carbonyl carbon atom.⁷²

The strength of intramolecular hydrogen bonds between hydrogen atoms and acceptors at the *ortho*-position of connected aromatic rings is mainly influenced by the geometry of foldamers and the nature of the acceptors. Furthermore, the electrostatic interaction between amide hydrogen and electronegative interaction as well as the repulsive interaction between the carbonyl oxygen atom and nitrogen atom in pyridine ring also affects the stabilized conformation of aromatic amide

foldamers. Due to the electrostatic repulsion between the two electronegative atoms, while the pyridine ring and amide bond force them to be formed in coplanar, they form anti-conformation (*cis*-conformation). The energy between *cis*- and *trans*-conformation indicated the *trans-trans* conformation is more stable than *syn-syn* and *trans-syn* conformations. One of the most common secondary structures in polypeptide is β -sheet, therefore mimicking this structure plays a crucial role in representing functions in discrete areas by the construction of well-defined artificial architectures. Aromatic amide oligomers can adopt similar conformation of secondary structures by intra-molecular hydrogen bonding of amide units linking to aromatic parts in the backbone of oligomers.

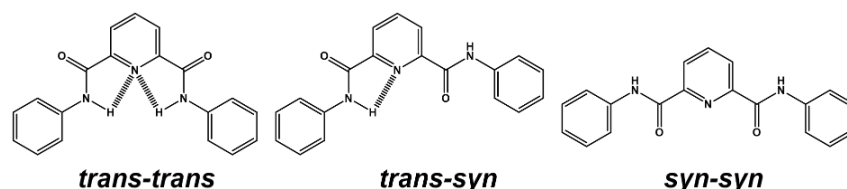


Figure 1-26 Structures of aromatic amide foldamer in *trans-trans*, *trans-syn* and *syn-syn* conformation.⁷²

In 2003,⁷³ oligoamide foldamers were reported by using quinoline molecule as a monomer. The hydrogen bonds between the amide hydrogen and adjacent nitrogen from quinoline could generate a bent shape and give rise to form a helix. It was reported that a stronger shielding of aromatic, amide, and ester protons was influenced by an increasing strand length with a tight contact between aromatic rings. The octamers of foldamers were characterized by single-crystal X-ray diffraction as shown in. Figure 1-27. The pitch of 8 is representative of the pitch of other helical foldamers and corresponds to the thickness of one aromatic ring (3.4 Å) with 5 units in two helical turns.

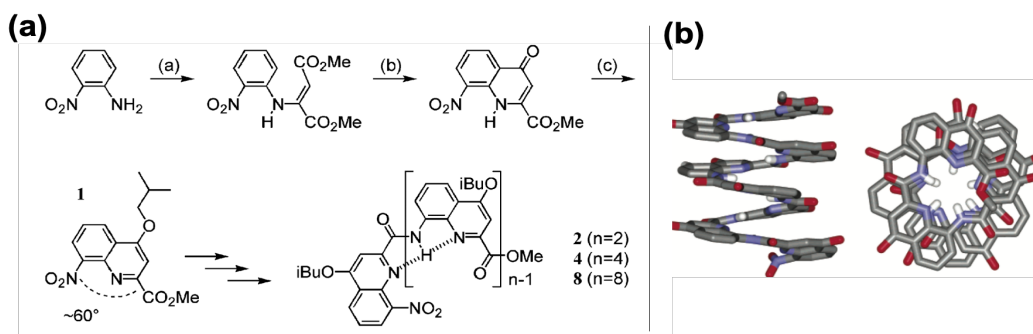


Figure 1-27 (a) Synthesis of oligoamide foldamers, (b) Side view and top views of the structure

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Chapter 2

Research design

2.1 Silica nanohelices

In this chapter, the research design for the projects of my PhD thesis, which develop carbon dots, polymers, and oligoamide foldamers with tunable chiroptical properties using silica nanohelices as chiral scaffold is introduced. These chiral nanostructures with helical morphology are expected to serve as chiral inducers to induce chiral property to achiral entities. The chiral silica nanohelices which are since many years, developed in the group, were prepared by using self-assembly of an organic molecule called “gemini tartrate 16-2-16 (*N'**N'*-dihexadecyl-*N, N, N', N'*-tetramethylethylene diammonium)” composed of gemini surfactant and tartrate anion.^{1, 2} The handedness of nanometric helices could be controlled by the stereochemistry of tartrate anion. The morphology of organic nano-template depends on the ageing time, concentration, pH and enantiomer excess of tartrate molecule. The organic gel needs to be incubated at 20 °C for 3-4 days in order to obtain helical morphology via inter-intramolecular hydrogen bond, van der waals forces and hydrophobic interaction. The assemblies of these 16-2-16 showed a wide diversity of morphologies that exhibit the chirality of tartrate ions at the nano- and micro-scale. Subsequently, the robust system was organized by using helical organic nanohelices as a soft template to be transcribed into silica nanostructure via sol-gel polycondensation of tetraethoxysilane (TEOS). After silica transcription, our chiral nanomaterial will consist self-assembly of gemini tartrate as an organic part and helical silica as an inorganic part, thereby these chiral materials could be defined as hybrid nanohelices (HNHs).³

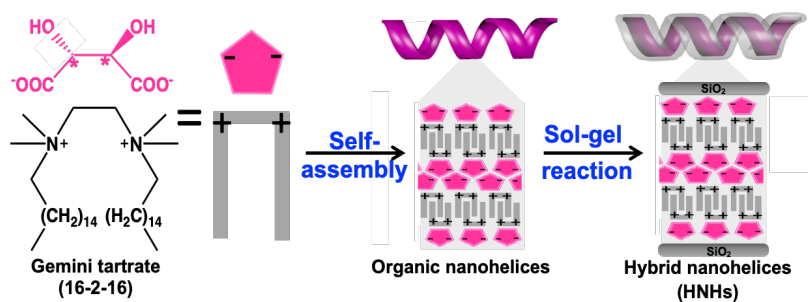


Figure 2-1 Preparation of hybrid nanohelices (HNHs).

2.2 Previous studies in the group for chirality induction to various atoms, molecules and particles using silica nanohelices.

2.2.1 Anionic dyes incorporated inside HNHs and induction of chirality.

Ryo N., et. al.⁴ studied the chiral arrangement of self-assembled gemini tartrate surfactant by using an achiral dye molecule called methyl orange (MO) in Figure 2-2. HNHs were prepared by silicification of bilayer organic nanostructure. The tartrate anion performing as a chiral source in HNHs was firstly replaced by achiral bromide and followed by washing with cold water to remove excess Br⁻ at 4 °C. Subsequently, achiral MO was introduced into the chiral system by ion-exchanging method and then resulted in the CD signal. It suggested that the chiral arrangement of self-assembly 16-2-16 could be memorized in silica even though the tartrate anion was replaced by achiral MO. The absorption peak of MO in water at pH 5.0 and pH 3.0 showed a peak at 465 nm and 505 nm, respectively. After the introduction of MO in HNHs, the absorption peak at 505 nm decreased and a new peak at 373 nm appeared. In addition, the spit cotton effect appeared related to R-chiral (right-handed) H-aggregates of MO due to exciton chirality theory. The interaction between gemini surfactant and MO was regarded as the electrostatic interaction, thus the chiral arrangement of gemini in helical silica nanostructure induces H-aggregation of MO molecule. Additionally, the pH effect on the chirality of MO molecule in a chiral environment of self-assembled gemini surfactant was studied. The results showed the chiral H-aggregated MO presented at pH 10, but the cotton effect is smaller than at pH 3 because of the electrostatic repulsion between MO and negative charge on silica surface at basic condition.

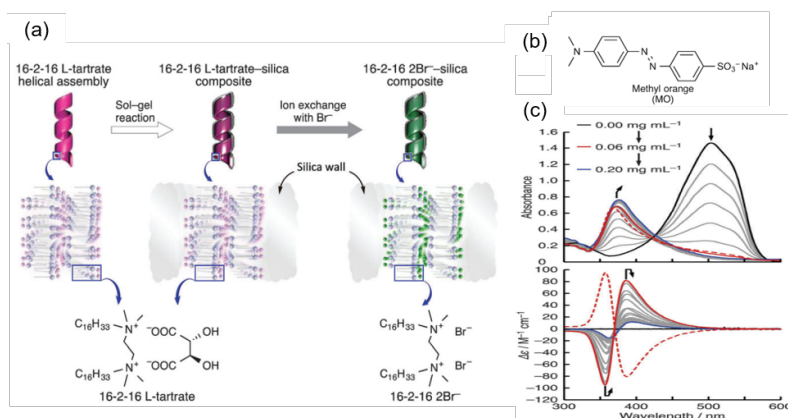


Figure 2-2 (a) Schematic illustration of HNHs prepared from gemini surfactant and the ion-exchange method with Br⁻, (b) Chemical structure of methyl orange (MO), (c) UV-vis absorption and CD spectra of MO (0.04 mM) in the presence of various concentrations of HNHs with Br⁻.⁴

2.2.2 Chirality induction to monoatomic anions

Okazaki Y., et. al.⁵ investigated the chirality induction of monoatomic anion. Gemini tartrate surfactant (16-2-16) surfactant presents the chiral molecular arrangement of double bilayer nanostructure in hybrid silica nanohelices in Figure 2-3. These HNHs with tartrate anion were washed with 100 mM KX (X=I, Br, Cl, F) in order to replace tartrate counterion by X⁻. The cation-anion interaction corresponds to Hofmeister effect, which is related to the hydration free energy of the anions, N-F < N-tart < N-Cl < N-Br < N-I. In general, HNHs with tartrate anion shows the Cotton effect at the absorbance below 240 nm. After washing by X⁻, hybrid nanohelices with F⁻, Br⁻ and I⁻ present CD signal for both left- and right-handed nanohelices, whereas HNHs with Cl⁻ show no CD cotton effect above 200 nm because CTTs bands of Cl⁻ are at the lower wavelength. These results of CD signal of X⁻ could confirm the chirality induction from a chiral arrangement of 16-2-16 surfactant, which possibly originates from two mechanisms; 1. Symmetry breaking of the electron orbitals of monomeric halide ions. 2. Exciton coupling from the chiral organization of halide ions. In addition, HNHs with I⁻ have a chiral environment to act as chiral nano-reactor through the formation of CuI and I₂. The HNHs with CuI/I₂ showed CD and CPL signals with g_{abs} ~5 x 10⁻⁴ (207 nm) and ~5 x 10⁻⁴ (318 nm), respectively.

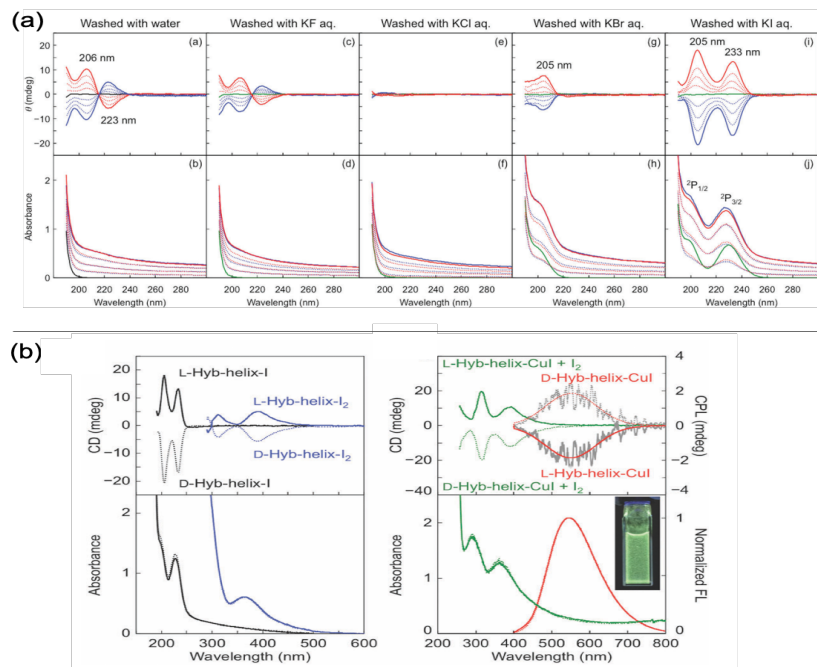


Figure 2-3 (a) Preparation of organic nanohelices (Org-helix-tart), hybrid nanohelices with tartrate (Hyb-helix-tart), hybrid nanohelices with halide ions (Hyb-helix-X), (b) CD and absorption spectra of hybrid nanohelices after washing with water and solution of halide ions.⁵

2.2.3 GNPs helically grafted on INHs.

Cheng J., et al.⁶ studied a templated-assisted approach to organize gold nanoparticles (GNPs) on the surface of functionalized silica nanostructure (Figure 2-4). Silica nanohelices were fabricated by supramolecular self-assembly of gemini surfactant (16-2-16) through sol-gel condensation, subsequently the surface was functionalized by 3-aminopropyltriethoxysilane (APTES). The GNPs were synthesized by using HAuCl_4 as a precursor with a variation of reducing agents and stabilizers, such as trisodium citrate, tannic acid, and sodium borohydride. After that, achiral GNPs were arranged onto the surface of silica nanohelices resulting in CD induction representing plasmonic coupling with $g_{\text{abs}} \sim 1 \times 10^{-4}$. The interaction between GNPs and silica surface was influenced by the ability of amino/thiol modified surface to replace the stabilizer of GNPs. The interaction strength corresponds to the chemical bond strength; S-Au interaction > N-Au interaction > carboxylate-Au interaction. GNPs were synthesized in a size range of 5-10 nm. The results indicated that 4-nm AuNPs showed useful optical properties, whereas smaller GNPs could not generate surface plasmon resonance. Therefore, the surface plasmon resonance of GNPs on helical silica increased with particle size, however, too large GNPs (size > 10 nm) lead to inhomogeneous adsorption of GNPs on silica surface. To obtain a high CD signal, there are four important parameters to consider for grafting GNPs on functionalized helical silica surface; GNPs size, grating interparticle distance, UV-visible shift and absence of random GNPs aggregates. This research showed a novel approach for designing a chiral system with photonic applications using a 3D network of nanohelices.

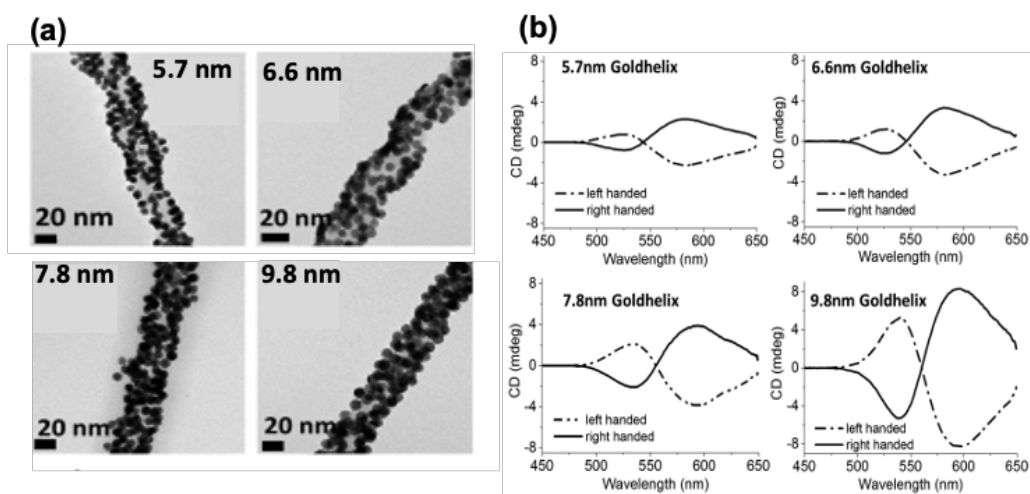


Figure 2-4 (a) TEM images, and (b) CD spectra of GNPs on the surface of silica nanohelices in different sizes.⁶

2.2.4 Dyes helically grafted on INHs

Scalable A., et al. studied chirality induction from macroscopic objects to achiral molecular chromophores in Figure 2-5.⁷ The surface of INHs was functionalized by (3-aminopropyl) triethoxysilane (APTES), and their amino groups were supposed to react with the carboxylic group of achiral PCA, DPBI and PAA via electrostatic interaction. The results indicated that the absorption and emission spectra of all four chromophores shift upon grafting on silica nanohelices. The absorption shift could be implied to excitonic effects due to intermolecular interaction resulting from the H-aggregate of packing molecules on the silica surface, while the emission showed a broad peak at 475 nm relating to excimer. Interestingly, achiral chromophores grating on chiral silica nanohelices showed the induced chirality with g_{abs} around 1×10^{-4} (280 nm). Furthermore, the results suggested that the dissymmetry factor (g_{abs}) is strongly correlated to the density of the grafted chromophores. The g_{abs} remains below 10^{-4} when the grafting densities of ca. ~ 0.13 PAA/nm² (Relating to a molecular surface area of ca. 6.5 nm² per PAA molecule). Meanwhile, the g_{abs} reached 5×10^{-4} at grafting densities of ca. ~ 0.27 PAA/nm². At higher grafting density, the fluorescent emission was generated almost from excimers due to loosing of a monolayer-packed chromophore. Furthermore, the higher grafting density could lead to a shift in absorption resulting in a broadening of the peaks. It implied that the environment of the chromophores and electronic interaction was turned because of the high-packed density. This research showed us the chirality induction of achiral dye through the electrostatic interaction of silica surface and carboxylic group of dye, corresponding to aggregation of dye on the silica surface.

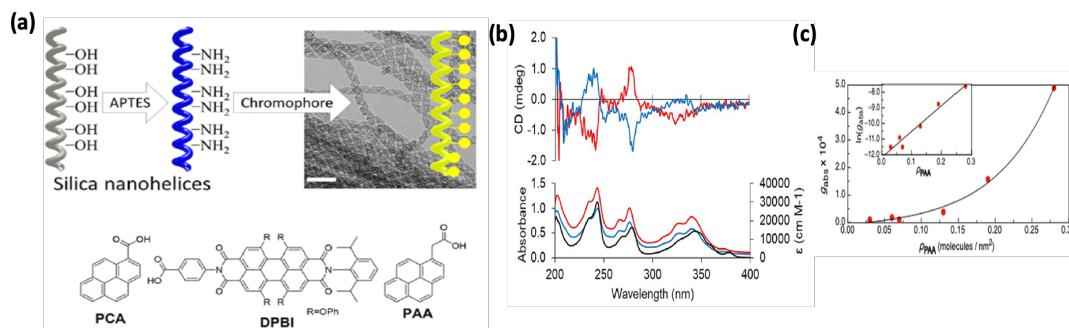


Figure 2-5 (a) Preparation of grafting silica nanohelices (above) and achiral chromophore (bottom), (b) CD and absorption spectra of PCA after grafting on silica nanohelices. (c) the correlation of g_{abs} (at 358 nm) with the density of PAA on the surface of silica nanostructures.⁷

2.2.5 QDs helically grafted on INHs

Liu P., et al.⁸ investigated the chiral perovskite CsPbBr₃ nanocrystals (PNCs) based on helical arrangement on INHs. The silica surface was functionalized by APTES molecule before grafting achiral perovskite CsPbBr₃ nanocrystals by a ligand-exchange approach. The preparation of CsPbBr₃ nanocrystal was similar to the previous report.⁹ The perovskite CsPbBr₃ was stabilized by two ligands including oleic acid and oleylamine. Oleic acid bounds to cations of Cesium or Lead meanwhile oleylamine bounds to halide anions. It was observed a cubic shape with average size of 9.5 nm. After grafting PNCs onto aminated silica nanohelices, it showed no CD and CPL signals in toluene. However, the chiroptical properties could be observed strongly when the suspension of CsPbBr₃ was drop-casted on a substrate to obtain a thin film with $g_{\text{abs}} \sim 6.2 \times 10^{-3}$ and -6.4×10^{-3} (at 367.5 nm) for LH- and RH-silica nanohelices, respectively. In addition, the thin film of CsPbBr₃ on aminated silica nanohelices showed symmetrical CPL signals with $g_{\text{lum}} \sim 6.9 \times 10^{-3}$ and -5.7×10^{-3} for LH- and RH-silica nanohelices, respectively. In the cryo-EM image, the grafted CsPbBr₃ of dried samples were closer to the surface of inorganic helical silica and led to show a helical arrangement of the PNCs along the helical silica nanostructure. It could be suggested the stronger local interaction and organization resulting from ligands collapse and chiral rearrangement during toluene evaporation. It is explained that PNCs on thin film have stronger interaction and organization on silica surface.

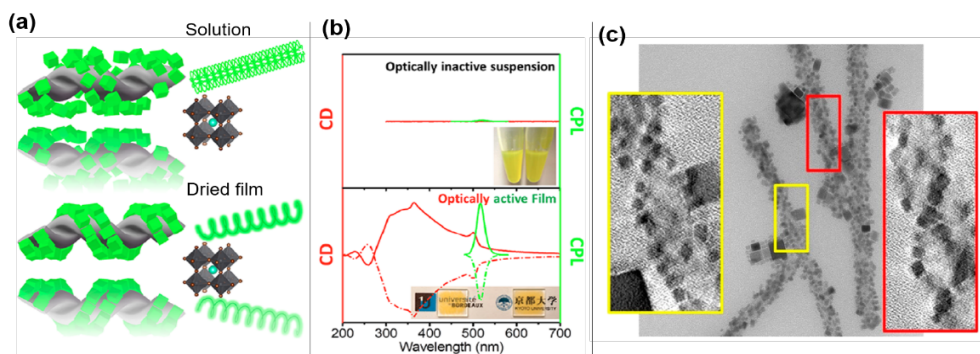


Figure 2-6 (a) Scheme representation, (b) CD and CPL spectra of CsPbBr₃ grafting on silica nanohelices in solution (above) and in dried film (bottom), (c) TEM images of nanohelices@PNCs and the cross sections with the tomography 3D (framed in red and yellow) for a dried film.⁸

2.2.6 The growth of helical QD inside INHs

Helical perovskite nanocrystal was grown inside helical silica nanohelices.¹⁰ The INHs was drop-casted on a substrate and dried at room temperature. After that, the mixture of ion precursors including Cs^+ , Pb^{2+} , Br^- was dropped on INHs thin film and dry at room temperature. It was observed these dark domains of crystalline perovskite structure inside the pore of silica helices by HR-TEM. The electron diffraction (SAED) pattern relating 4.1 and $3.3 \text{ \AA}^\circ$, suggested to the (200) plane and (113), (202), and/or (022) plans of the orthorhombic phase of the CsPbBr_3 . Meanwhile, the ion precursor solution in DMF and the suspension of INHs can be mixed prior to the drop-casting on a substrate. It was observed CD and CPL signals with slightly lower g_{abs} and g_{lum} .

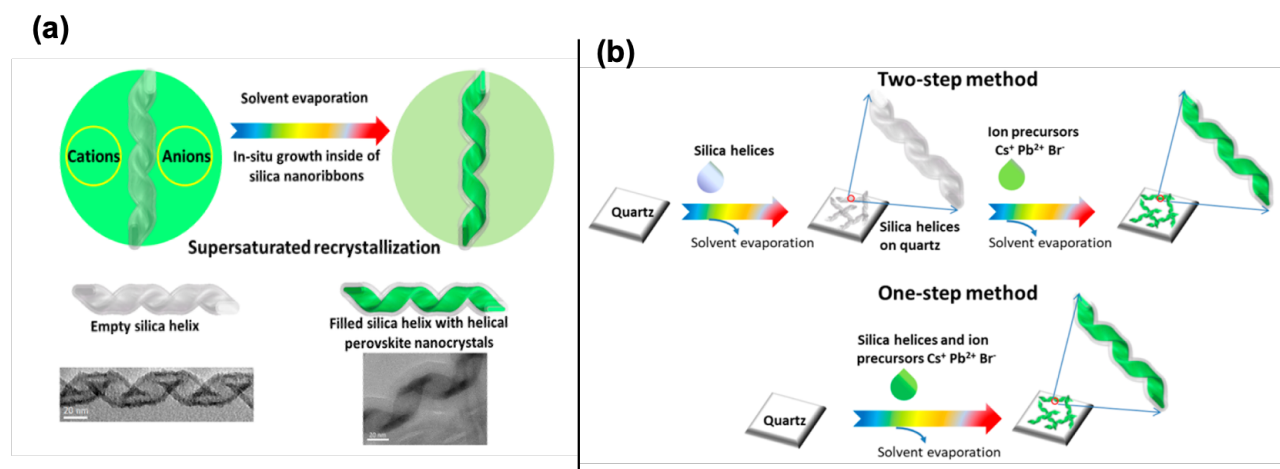


Figure 2-7 (a) Scheme representation of perovskite nanocrystal growth inside helical silica nanohelices and TEM image, (b) one-step and two-step methods based on drop-casting method.¹⁰

2.3 Research design

In the first part of my thesis, we are interested in the design of chiral carbon dots (CDots) using silica nanohelices. The self-assembly gemini tartrate in HNHs acts as a carbon source for preparation of CDots via pyrolysis at $600 \text{ }^\circ\text{C}$ under vacuum, while helical silica nanohelices perform as a chiral inducer to induce chiral property to CDots. The organic self-assembly of 16-2-16 was *in-situ* transformed to CDots resulting in symmetrical CD signals in the UV-visible range (200-700 nm). Furthermore, we also studied chiral doped-CDots by replacing tartrate ions with achiral other molecules or heteroatoms into HNHs before pyrolysis at the same condition.

In the second part, we aimed to induce the chiroptical properties to achiral polymer by using inorganic silica nanohelices. The achiral polymer was prepared by the polymerization of DHN monomer and TMTA crosslinker. We then expanded the conception of “chiralisation” of achiral polymer to racemic helical oligomer (oligoamide foldamers¹¹) which is in an equilibrium between *P*- and *M*-conformation to see if we could use the silica nanohelices to favor one of the enantiomers and/or induce the chiroptical signals from them.

In both cases, polymers and foldamers were put in contact with silica nano helices via drop-cast method¹⁰ as developed previously in the laboratory. The organic template of HNHs was removed to obtain chiral silica with chiral nanospace, it is called inorganic silica nanohelices (INHs).¹⁰ Then, INHs were drop-casted on a substrate, to which successively, the solution of polymers or foldamers drop-casted. The optimal condition of the drop-casting method has been studied including temperature, solvent, concentration and surface polarity.¹²

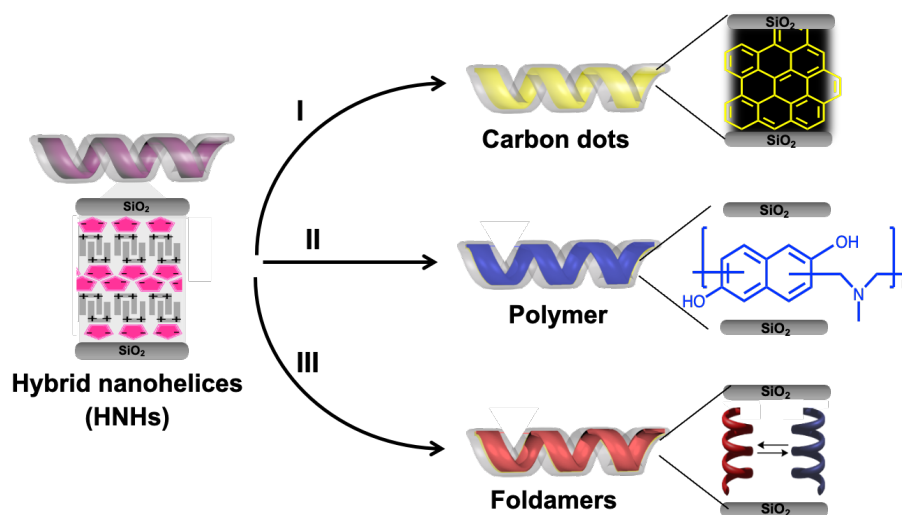


Figure 2-8 Scheme of chirality induction of achiral carbon dots and achiral polymers, and enantiomeric enrichment of racemic foldamers using silica nanohelices.

2.4 Preparation of silica nanohelices

2.4.1 Synthesis of gemini tartrate (16-2-16)

Gemini tartrate (16-2-16) was synthesized in three steps.¹³

1. Synthesis of 16-2-16 gemini bromide.

N,N,N',N'-tetramethylethylenediamine (TMEDA) is mixed with alkyl bromide of 1-bromohexadecane in a ratio of (1:3) in 50 mL acetonitrile. The synthesis reaction is set up at 80 °C for 48 hrs under refluxing. After the reaction is complete, the reaction is cooled down at room temperature and then the white powder will precipitate. Subsequently, the final product is purified by washing with acetone 3 times to remove by-products such as alkyl bromide and the monoalkylated compound, and then dried under vacuum overnight. Then, the product really needs to be recrystallized by methanol as a solvent.

2. Counterion exchange from bromide to acetate.

Gemini bromide synthesized as described above (1 equivalent) is dissolved in 50 mL methanol at 50 °C, then 3 equivalents of silver acetate are added into the solution and then continue the reaction for 24 hrs under reflux in a flask covered with aluminium foil. After cooling down the reaction, the suspension was filtrated on Celite to remove the black powder of silver bromide (AgBr). After that, the filtrated solution will be evaporated to remove methanol to obtain yellow oil. Then, acetone is added until the white solid precipitate and then washed with acetone 3 times. Finally, the product is dried under a vacuum overnight.

3. Counterion exchange from acetate to tartrate.

The 16-2-16 gemini acetate and tartaric acid are dissolved separately in methanol/acetone (1:9). Then, 1 molar equivalent of gemini acetate is added dropwise to the solution of tartaric acid (2 molar equivalents) by using a dropping funnel. The reaction continues for 2.5 hrs at room temperature. The white precipitant will be purified by washing it with methanol/acetone (2 times), cold water (4 times), and acetone (3 times). The final product will be dried under a vacuum overnight.

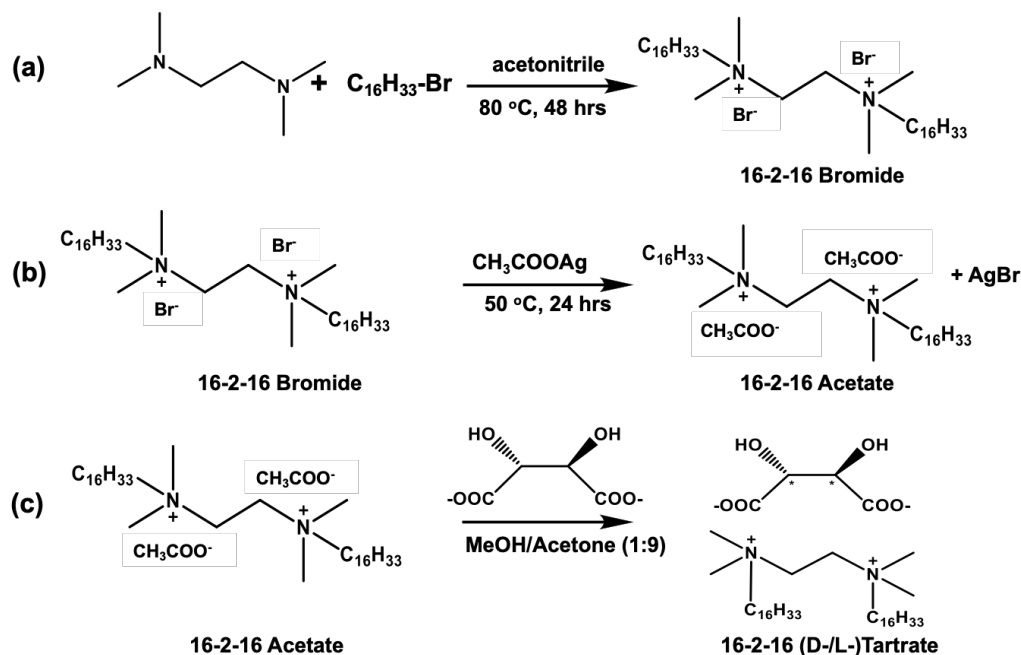


Figure 2-9 Three main steps for synthesis of gemini (D-/L-) tartrate; (a) synthesis of 16-2-16 gemini bromide, (b) synthesis of 16-2-16 gemini acetate, (c) synthesis of 16-2-16 gemini tartrate.

2.4.2 Formation of organic gel of gemini tartrate and silica transcription.¹⁴

Gemini tartrate (16-2-16) is mixed with water at the concentration of 1 mM and then heated up to 70 °C (the Kraft temperature: 43 °C @10 mM). After the white solid of 16-2-16 is dissolved completely at 1 mM (5 mL), the solution in the 15-mL tube is put on a roller mixer for 15 min at 20 °C and then let still horizontally for 4 days to obtain the helical morphology of self-assembly organic nanostructures. The morphology of nanostructures is time dependent: it forms twisted nanoribbons if it ages for 2 hrs, meanwhile they transform to helical ribbons and nanotubes after aging for 4 days and 7 days, respectively (Figure 2-10). The handedness of helical structure is dependent on the stereochemistry of tartrate counter ion, left-handed helices are observed with D-tartrate meanwhile right-handed helices are observed with L-tartrate. The organization of organic self-assembly relies on the weak interaction of hydrogen bond, hydrophobic interaction and Van der Waal force, so it could be easily disrupted by pH, temperature and additives. Consequently, a robust shell is needed to stabilize their helical nanostructures. To do so, organic nanohelices are transcribed to silica nanohelices via sol-gel polycondensation of TEOS. The TEOS is pre-hydrolyzed by mixing of 0.5 mL of ($\geq 99.0\%$)TEOS with 1.0×10^{-4} mM D-/L- tartaric acid for 7 hrs at 20 °C. After that, the pre-hydrolyzed TEOS (5 mL) is then introduced to the organic template

(1 mM, 5 mL) in the volume ratio (1:1) and then allow the transcription reaction for 12 hrs at 20 °C. The final material is purified by washing with cold water 3 times to remove excess TEOS, the obtained material is called hybrid nanohelices (HNHs).

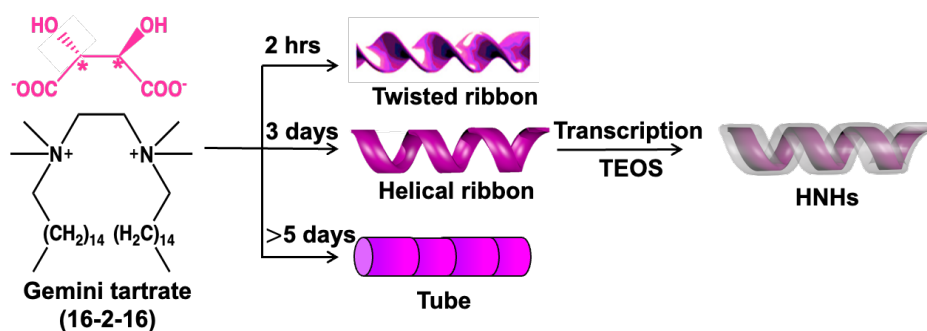


Figure 2-10 Scheme of self-assembling forming twisted ribbon, helical ribbon and nanotube at different aging times to fabricate hybrid silica nanohelices (HNHs).

2.4.3 Fabrication of inorganic silica nanohelices (INHs).

The self-assembly gemini tartrate (16-2-16) in hybrid nanohelices (HNHs) is washed away with methanol at 65-70 °C for 3 times and then dispersed in 5 mL of ethanol/2-propanol (1:1).

2.4.4 Preparation of silica thin film by a drop-casting method.¹⁰

The suspension of INHs is submitted to tip sonication in order to obtain shorter and individualized helices¹⁵. The sonication is done by putting the tip at 3 different positions; top, middle, and bottom of a 15-mL tube using the following condition; sonication time 5 min, power 100%, pulse off 1 sec, pulse on 1 sec. During using the tip sonication, the 15-mL tube containing INHs should be in ice to protect the over-heated situation. After cutting, INHs suspension in 15-mL tube is centrifuged at 4 °C, 10 min, and 4500 rpm to remove uncut and entangled INHs (precipitated at the bottom of the tube). The supernatant containing cut INHs was transferred to another tube and was subsequently quantified the amount by weighting mass. In the case of preparation INHs thin film on a substrate, the cut INHs were dropped on a quartz slide in the concentration of 200 µg/2x2 cm² and let the solvent evaporate at room temperature. The drop-casting approach could create a thin film on a substrate under variables such as substrate, evaporation rate, and capillary force associated with the drying step.

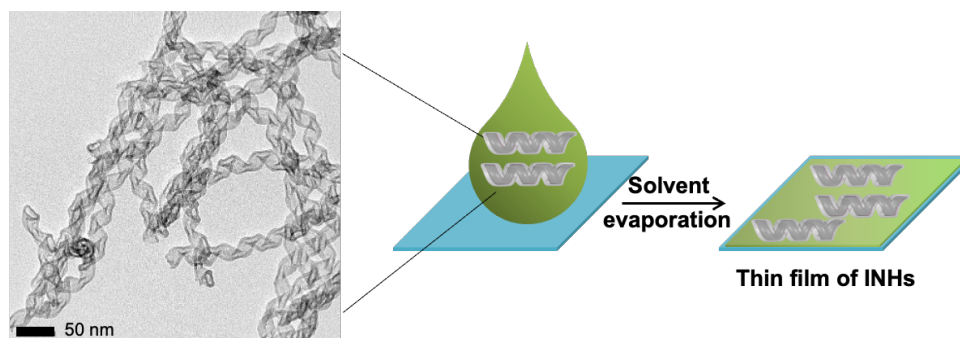


Figure 2-11 Preparation of chiral silica thin film by drop-casting method.

2.5 References

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Chapter 3

Chirality induction to carbon dots using silica nanohelices

In this chapter, we described how chiral CDots were obtained using hybrid nanohelices (HNHs). HNHs are synthesized as described in Chapter 2. The organic templates of 16-2-16 inside HNHs is used as carbon source meanwhile the helical silica nanostructures act as a chiral inducer. The HNHs suspension is lyophilized, then pyrolyzed at 600°C under vacuum as shown in Figure 3.1. This transformed the organic template in the chiral nanospace of HNHs to CDots@INHs. The original counterion tartrate can be replaced by other anions (heteroatoms, aromatic, metal-complex) before the pyrolysis, which can lead to doped-CDots@INHs. The CDots@INHs were characterized using several techniques such as X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Transmission Electron Microscopy (TEM) and Elemental Analysis (EA).

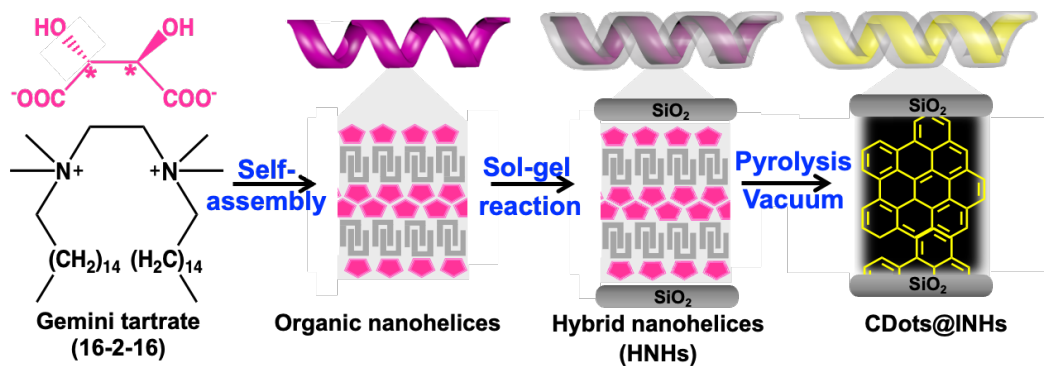


Figure. 3-1 Preparation of CDots@INHs.

3.1 Experimental section

3.1.1 Synthesis of gemini tartrate and preparation of HNHs

The synthesis of gemini tartrate (16-2-16) and the preparation of HNHs are described in Chapter 2.¹

3.1.2 Preparation of doped-HNHs

N-doped HNHs were prepared by ion exchanging using NaN_3 (100 mM) for 3 times at 4 °C to obtain azide (N)-doped HNHs. Then, these N-doped HNHs were washed by cold water 3 times to remove excess azide ion using centrifugation.

To prepare polymer-doped HNHs, tartrate anion in HNHs system was replaced by ion-exchanging with 100 mM KCl solution (5 times) at 4 °C. Then, the excess Cl⁻ anion was washed away by cold water at 4 °C for 3 times. This process assures the replacement of tartrate by Cl⁻ ion in HNHs system. After that, the suspension was washed by DHN 1 mM solution at 4 °C and to replace Cl⁻, then the excess DHN was washed by water (3 times) to remove excess DHN. Subsequently, TMTA (1 mM) was added to induce polymerization at DHN:TMTA ratio (1:1). Finally, the samples were washed by cold water 3 times to obtain polymer-doped HNHs.

The metal-doped HNHs including Zn(II)TPPS-doped HNHs, Mn(II)TPPS-doped HNHs and Eu(III)EDTA-doped HNHs were prepared by exchanging the counterion of HNHs tartrate by Cl⁻. Then, Zn(II)TPPS complex, Mn(II)TPPS complex or Eu(III)EDTA complex (100 mM, 10 mL) were introduced at 4 °C and subsequently washed with cold water (3 times). The amount of Zn(II)TPPS complex, Mn(II)TPPS complex or Eu(III)EDTA complex in HNHs was calculated following absorbance of supernatant after centrifugation.

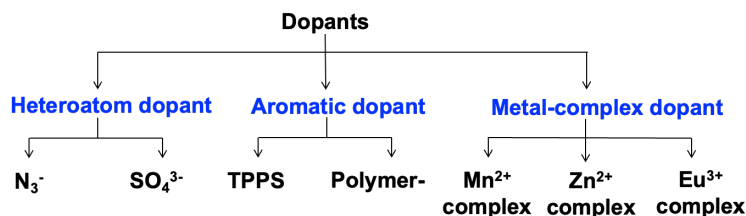


Figure. 3-2 Three groups of dopant.

3.1.3 Synthesis of CDots

The HNHs or doped-HNHs (~1.0 mg) are first kept in NMR tubes and then freeze-dried with liquid nitrogen. The frozen HNHs were kept under a lyophilizer for 24 hrs to remove water. After that, NMR tubes containing HNHs were sealed under a high vacuum (~10⁻⁴ mbar) to remove the oxygen gas before pyrolyzing at 600 °C for 5 hrs (rate 2 °C/min) in Figure. 3-3. After cooling down, the CDots@INHs were dispersed in a solvent.

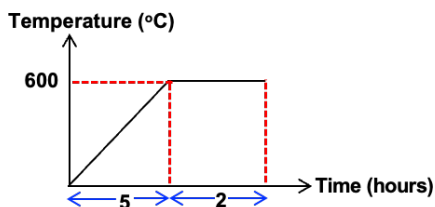


Figure. 3-3 Condition for synthesis of CDots@INHs by pyrolysis of HNHs at 600 °C.

3.2 Results and discussion

The CDots synthesized as described above, and dispersed in H₂O exhibit two absorption peaks at 223 and 247 nm, which correspond to π - π^* transition for C=C bond and n- π^* transition of C=O bond or surface defects of CDots, respectively.^{2,3} Broad absorbance which tails out to 700 nm observed with CDots@INHs is a typical signature of CDots-like structures with the coexistence of various domain sizes. Surprisingly, CDots clearly displayed symmetric CD spectra in the 200-700 nm with positive and negative signals for RH- and LH-INHs, respectively (Figure. 3-4b). The CD signal above 250 nm indicated the transformation of a new structure after pyrolysis with g_{abs} at 570 nm of -3.0×10^{-4} (LH) and 3.0×10^{-4} (RH), ($g_{\text{abs}} = \Delta\epsilon/\epsilon = \theta(\text{mdeg})/(32980A)$). The TEM images of CDots@INHs showed helical morphology is maintained even after the pyrolysis (Figure. 3-4d), which did not show significant modification compared to HNHs (Figure. 3-4c). All these results indicate self-assembly organic 16-2-16 was *in-situ* transformed to CDots confined in the chiral nano-space of INHs.

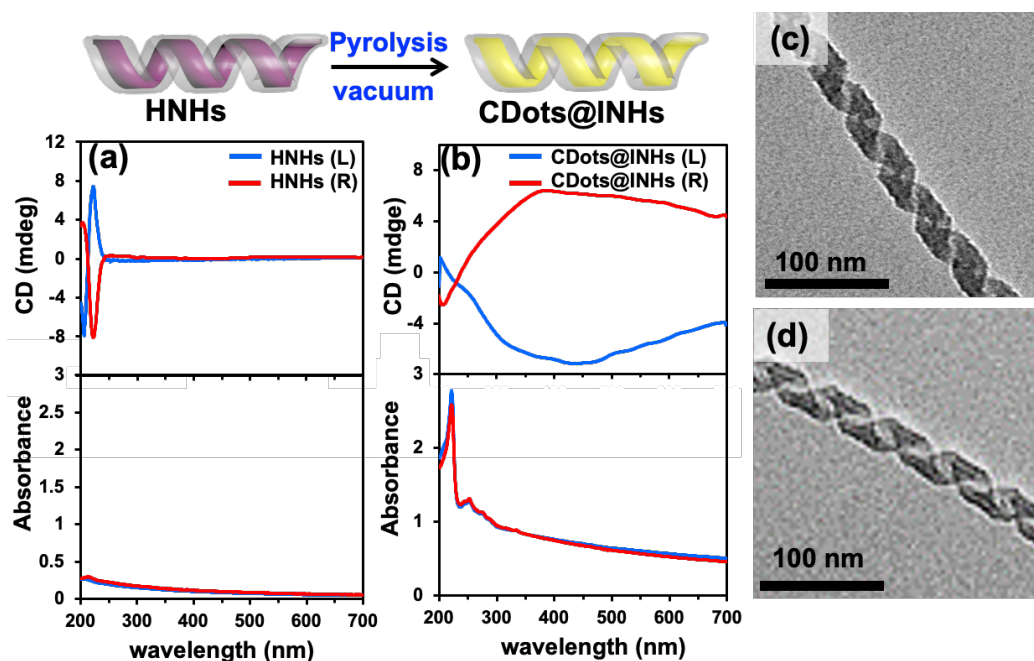


Figure. 3-4 CD and absorption spectra of LH-/RH-HNHs (a) and LH-/RH-CDots@INHs (b) dispersing in H₂O (~1 mg/mL), TEM images of LH-HNHs (c) and LH-CDots@INHs (d).

To study if these CD signals result from incomplete carbonization of chiral tartrate, the control experiment was set up by pyrolyzing 16-2-16 tartrate without a silica template under the same condition (600 °C, vacuum). The obtained CDots showed strong blue emission under UV light (λ_{ex} 365 nm) with no detectable CD signal (Figure. 3-5). This suggested that the helical silica nanohelices are crucial in chirality induction of CDots.

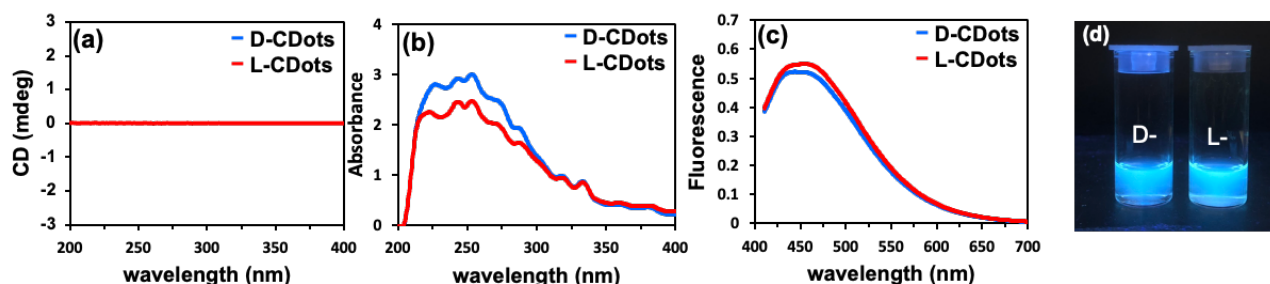


Figure. 3-5 CD (a), absorption (b), and fluorescent, λ_{ex} 365 nm (c) spectra of D-/L-CDots (~ 1.5 mg/mL), Photograph of D-/L-CDots dispersing in diethyl ether under UV light.,

For the mechanism of formation of CDots using 16-2-16 tartrate as a precursor, both ammonium headgroups and aliphatic chains are transformed to CDots. The ammonium part in 16-2-16 could be directly polymerized and carbonized at their functional groups during the pyrolysis. Meanwhile, the aliphatic carbon chain of 16-2-16 could be broken to form olefins (such as ethylene and propylene) and then generate aromatic moieties via cyclization and oligomerization.⁴ Additionally, it was previously reported that the alkyl chain could decompose to form alkyl radicals, and then alkane radicals can form macromolecule alkyl chains.⁵ After that, alkyl chain will be carbonized to form CDots.

To confirm that chiral properties did not come from asymmetric carbon of tartrate anion, the helical silica framework of CDots@INHS was removed by 6.0 M NaOH at 60 °C and washed by water 3 times. Then, oleic acid was used to introduce as a stabilizer to avoid aggregation. The obtained CDots showed no CD signal with an average size of 4.1 nm in TEM images (Figures. 3-6a to 3-6c).

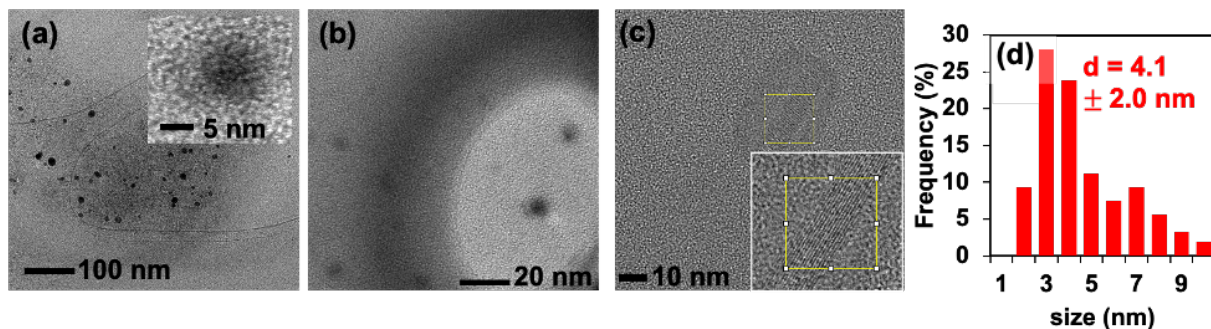


Figure. 3-6 HR-TEM images (a,b,c), and size distribution (d).

The elemental contents were investigated by elemental analysis (EA) on HNHs before and after pyrolysis, as shown in Table. 1. HNHs before pyrolysis contained C (20.9%), N (1.1%) and H (4.4%), it also has N/C ratio of 0.05 corresponding to the structure of gemini tartrate. After pyrolysis of CDots@SHNs, the elemental contents of C (8.12%), N (0.27%) and H (0.65%), respectively, with N/C ratio of 0.3. These results indicated that the pyrolysis step could decrease the elemental contents of the atoms with a higher loss of nitrogen than carbon.⁶ This might be because the nitrogen content was transformed into volatile molecules (NO_x species), NH_3 , HCN and N_2 during the pyrolysis of bio-mass.⁷⁻⁹ In addition, X-ray photoelectron spectroscopy (XPS) was used to study the chemical compositions and structure of CDots@INHs (Figure. 3-7a). XPS spectra reveal four main peaks including 9.24% (carbon, C1s), 0.21% (nitrogen, N1s), 57.53% (oxygen, O1s), and 32.66% (silicon, Si2p). The XPS high resolution showed a deconvolution of C1s peak in Figure. 3-7c, it showed the major peak at 283.8 eV with 58.34% relating to sp^2 graphitic structure in CDots@INHs. It also showed other peaks at 285.1 eV (28.42%), 286.6 eV (8.11%) and 288.9 eV (5.13%) correspond to C-C, C=O and O=C-OH, respectively. In case of the high-resolution N1s spectrum (Figure. 3-7d), there are three peaks at 379.5 eV, 399.8 eV and 402.3 eV attributed to pyridine N (24.2 %), pyrrolic N (54.82 %), and graphitic N (20.97 %), respectively.

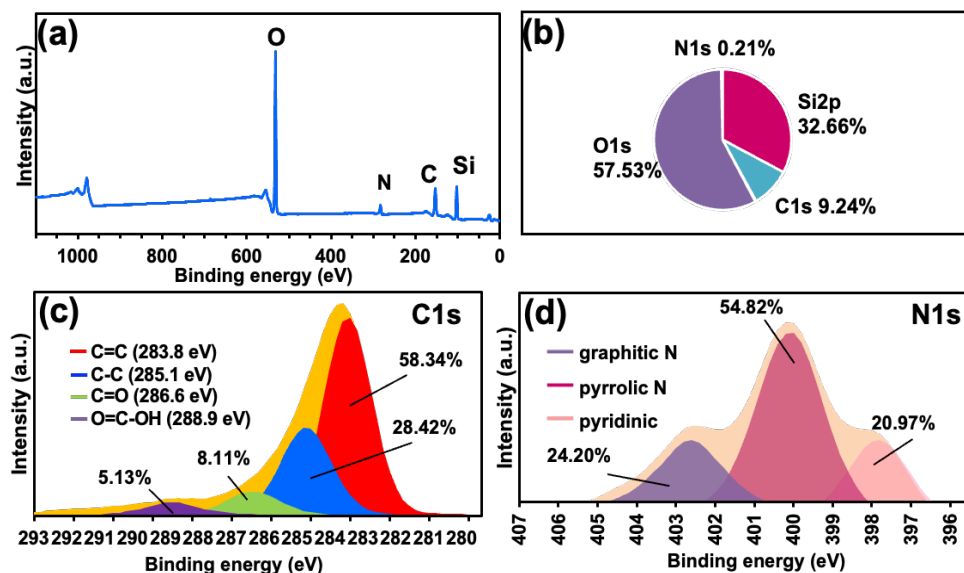


Figure. 3-7 XPS spectra (a), elemental contents (b), HR-XPS of C1s (c) and N1s (d) of CDots@INHs.

Therefore, pyrrolic N performed as the major state of nitrogen, which is generally located in defect areas or the edge of a graphitized structure. The Raman spectrum (recorded under excitation of 633 nm) in Figure. 3-8, it showed two peaks of D and G bands at ~ 1330 and ~ 1590 cm^{-1} , respectively. The G band is related to the E_{2g} mode of the graphite and the vibration of sp^2 -bond carbon atoms in hexagonal lattices, while the D band originates from the vibrations of carbon atoms in disordered graphite.^{10, 11} Therefore, both Raman spectrum and XPS data confirm that our CDots are composed of sp^2 carbon with sp^3 carbon defect. The I_D/I_G ratio of chiral CDots was ~ 1 which could provide the disorder and crystallite size of graphitic layers in CDots.¹²

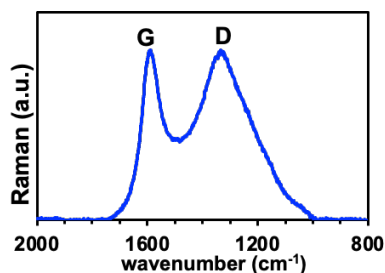


Figure. 3-8 Raman spectra of CDots@INHs (λ_{ex} 633 nm).

One of the outstanding properties of CDots@INHs is their luminescence, the fluorescent emission of CDots@INHs in water was measured by excitation at different wavelengths as shown in 2D fluorescent spectra (Figures. 3-9b and 3-9c). It indicated that the wavelength for maximum emission is 325 nm under the excitation wavelength of 270 nm (Figure. 3-9a). The variation in emission intensity at different excitation wavelengths relates to the different energy levels, therefore the fluorescence originated from quantum confinement.¹³

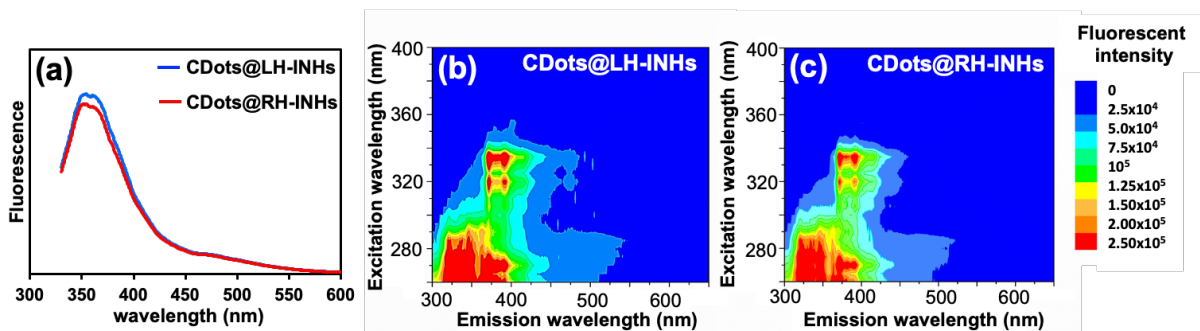


Figure. 3-9 Fluorescent spectra (a, λ_{ex} 270 nm), 2D fluorescent spectra of CDots@INHs (~ 1 mg/mL) in H_2O (b,c).

Furthermore, the luminescent property of CDots@INHs was influenced by solvent. The 2D fluorescent spectra of CDots@INHs in dimethylformamide (DMF) showed an emission wavelength of 425 nm, which is dramatically shifted compared to CDots@INHs in water, as shown in Figure. 3-10.

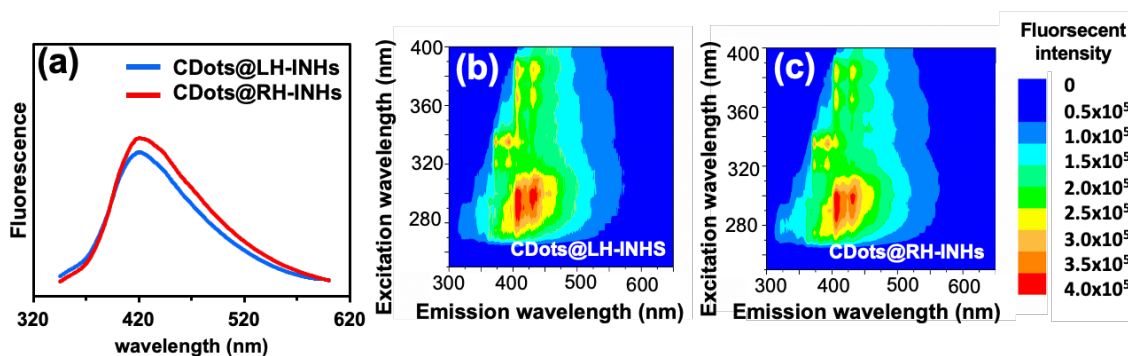


Figure. 3-10 Fluorescent spectra (b, λ_{ex} 290 nm), and 2D fluorescent spectra of CDots@INHs (~ 1 mg/mL) in DMF (c,d).

These results suggested the solvent-dependent emission of CDots@INHs. The shift in fluorescent emission of CDots@INHs is possibly related to the effect of solvent polarity and ground/excited state dipole moment.¹⁴ The stability of chiral CDots@INHs has been studied by measuring the fluorescent emission throughout five days. The emission of CDots@INHs in water (Figure. 3-11a) decreased dramatically by ~40% compared to CDots@INHs in DMF, we believed that this fluorescent decrease originated from quenching by water¹⁵ and chromophore-solvent hydrogen bonding.¹⁶

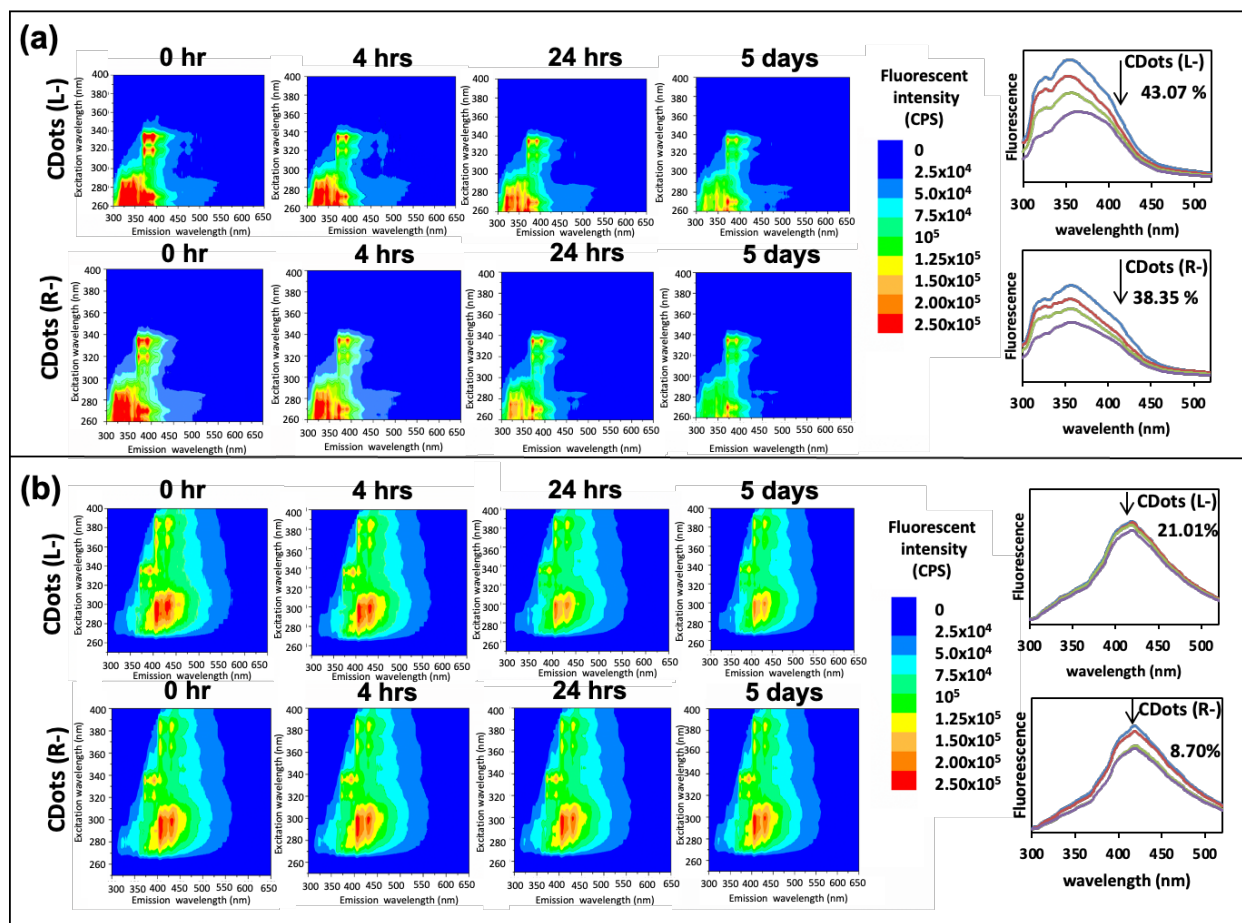


Figure. 3-11 2D fluorescent spectra of CDots@INHs and fluorescent spectra of CDots@INHs (~1 mg/mL) dispersing in water, λ_{ex} 270 (a) and in DMF, λ_{ex} 290 (b) for 5 days.

Meanwhile, the fluorescence of CDots@INHs in DMF was much more stable. The CD signal and absorption of CDots@INHs in water showed good stability for 5 days as shown in Figure. 3-11b, therefore it could suggest that the decrease in fluorescence in 5 days did not come from the change in the organization of CDots confined in silica nanospace.

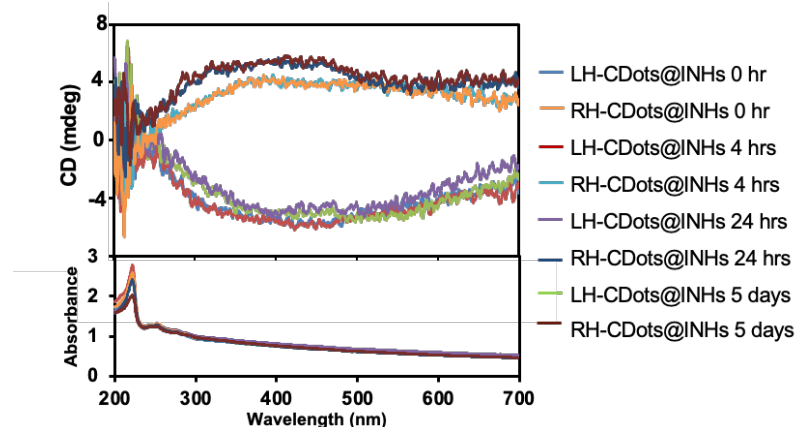


Figure. 3-12 Evolution of CD-absorption spectra of CDots@INHs (~1 mg/mL) in H₂O during 5 days.

The self-assembled 16-2-16 acted as a carbon source for the synthesis of chiral CDots via pyrolysis, therefore carbon is the main elemental content of CDots@INHs. To improve the luminescent property of CDots@INHs, we investigated the effect of doping these CDots by other heteroatom or metal ions. Doped CDots@INHs were prepared by introducing dopants into HNHs before doing pyrolysis at 600 °C under a vacuum. There are three different groups of dopants including hetero-atom dopants, aromatic dopants, and metal-complex dopants in Figure. 3-13. Tartrate anion in HNHs was replaced by dopants via electrostatic interaction between dopants and cationic gemini surfactant. This approach for replacing tartrate anion with other molecules is refined as an ion-exchanging method,¹⁷ which was previously reported for chirality induction of monoatomic anion (F⁻, Cl⁻, I⁻, Br⁻)¹⁷ and achiral dye molecules.¹⁸

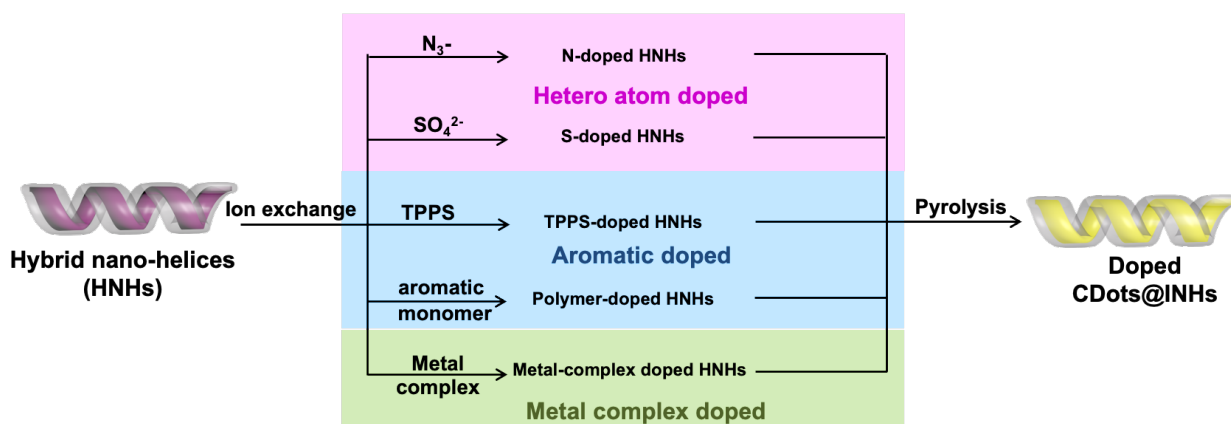


Figure. 3-13 Three types of dopants for the synthesis of doped CDots@INHs.

Table. 3-1 Elemental contents of HNHs and CDots@INHs by elemental analysis (EA)

		Experiment							Structure				
		Found				Ratio			N	C	H	S	N/C
		N%	C%	H%	S%	N/C	H/C	S/C					
gemini tartrate	HNHs	1.1	20.9	4.4	0.03	0.05	0.21	0.001	2	42	86	-	0.0476
	CDots	0.27	8.12	0.65	0.06	0.03	0.080	0.008					
TPPS doped	HNHs	2.01	28.7	4.74	2.26	0.07	0.165	0.079	10	158	276	4	0.0633
	CDots	0.83	18.6	0.46	0.53	0.05	0.024	0.029					
S doped	HNHs	1.14	21.4	4.54	1.48	0.05	0.212	0.069	2	38	82	1	0.0526
	CDots	0.19	7.7	0.19	8.42	0.03	0.024	1.100					
N doped	HNHs	-	-	-	-	-	-	-	5	38	82		0.1316
	CDots	0.38	13.4	0.55	0.14	0.03	0.041	0.010					

In the case of heteroatom dopants, azide (N_3^-) or sulfate ion (SO_4^{2-}) are expected to increase the elemental content of nitrogen and sulfur, respectively, for enhancing the luminescent property of CDots. Element doping (such as nitrogen and sulfur) could control the energy band gap and electron density of CDots resulting in improving their quantum yield¹⁹ and a shift in fluorescent emission.²⁰ The tartrate anion in HNHs was replaced by azide ion or sulfate ion by ion-exchange method in excess concentration (100 mM) of NaN_3 or Na_2SO_4 solution at 4 °C (3-4 times) to obtain N-doped HNHs and S-doped HNHs, respectively. The azide ion and sulfate ion do not absorb in the UV-visible signal, therefore the disappearance of CD signal suggests the complete replacement of tartrate ion by azide or sulfate ion in Figures. 3-14a and 3-14b. N-doped HNHs and S-doped HNHs were pyrolyzed at 600 °C under a vacuum to obtain N-doped CDots@INHs (N-CDots@INHs) and S-doped CDots@INHs (S-CDots@INHs), respectively. N-CDots@INHs and S-CDots@INHs also represented symmetrical CD signals as shown in Figure. 3-14c. The 2D fluorescent spectra of N-CDots@INHs and S-CDots@INHs were detected in Figure. 3-15, which were similar to CDots@INHs. The final percentages of N/Si and C/Si of N-CDots@INHs were higher than CDots@INHs (1.2% instead of 0.6% and 60% instead of 28% respectively) in Figure. 3-26c and 26d. While the N/C ratio of N-doped HNHs calculated from EA is much higher (0.13) than that of HNHs (0.05 both measured by EA or XPS), once pyrolyzed, N/C ratios both of CDots@INHs and N-CDots@INHs were similar ~ 0.03 (Table. 3-1). It possibly indicated the sublimation of organic matter in the form of gas during the pyrolysis step.²¹

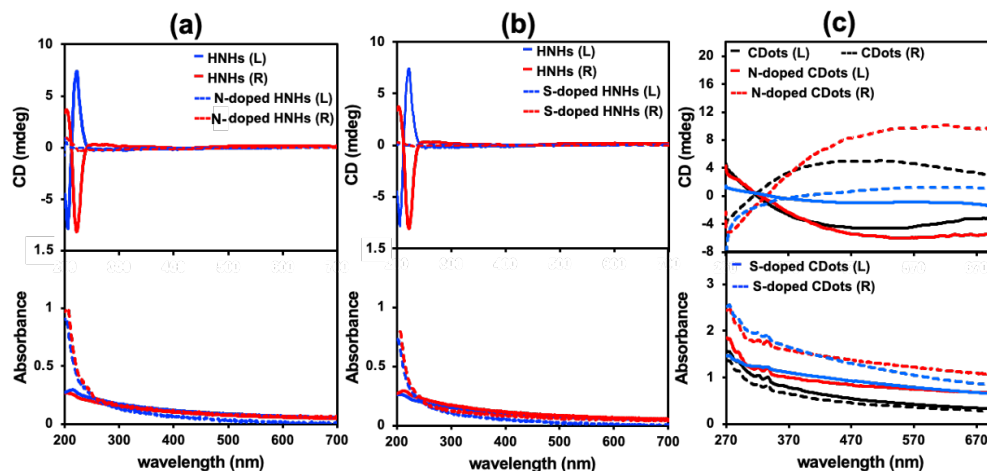


Figure. 3-14 CD and absorption spectra of HNHs, N-doped HNHs (a) and S-doped HNHs (b), CDots, N-doped CDots and S-doped CDots (c), (~ 1 mg/mL).

The S/C ratio of S-CDots@INHs was ~ 1.1 , which is much higher than CDot@INHs from gemini tartrate (~ 0.008) which does not have any source of S. However, surprisingly, it did not cause any change in 2D fluorescent spectra (Figure. 3-15b). Therefore, it implied that doping heteroatoms (nitrogen and sulfur) in HNHs system could not significantly change an emissive property of CDots in the range of the proportions. Meanwhile, g_{abs} of N-doped and S-doped CDots@INHs were around $\pm 2.5 \times 10^{-4}$ and $\pm 4.0 \times 10^{-5}$, respectively.

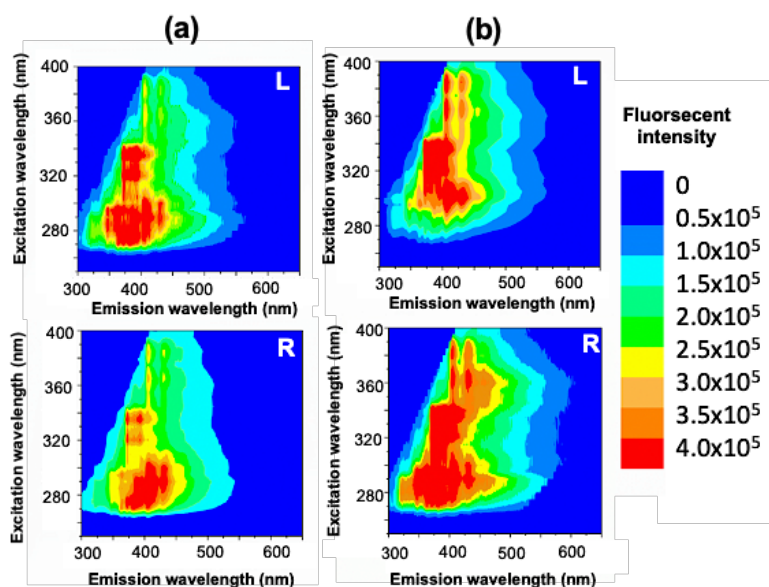


Figure. 3-15 2D fluorescent spectra of N-doped CDots (a) and S-doped CDots (b) in DMF, (~ 1 mg/mL).

One of the interesting dopants is aromatic moiety because aromatic precursors with sp^2 carbon core are supposed to easily form CDots than aliphatic precursors during synthesis. Therefore, we were interested in doping aromatic precursors such as *tetra*-phenyl porphyrin tetra-sulfonic acid (TPPS) and polymer containing aromatics into HNHs system via ion-exchanging method before pyrolysis at the same condition. To prepare aromatic-doped HNHs, tartrate anion needed to be replaced by Cl^- due to the strong interaction between carboxylate groups of tartrate and positive charges of gemini surfactant. After that, TPPS molecule was introduced into HNHs- Cl^- by ion-exchange method. Interestingly, the TPPS-doped HNHs showed a strong symmetrical CD signal of TPPS molecule at 400-450 nm with cotton effect, as shown in Figure 3-16a, with g_{abs} of -7.1×10^{-4} (L-) and 7.3×10^{-4} (R-) in agreement with our previous study.¹⁸ In Figures. 3-16b and 3-16c, the amount of TPPS in HNHs was calculated by plotting the standard calibration curve, the difference in absorbance between soaking solution and supernatant suggested the amounts of TPPS in HNHs systems. Then, the ratio between gemini- Cl_2 ; TPPS was calculated as 3 (LH) and 3 (RH) in Table. 3-2.

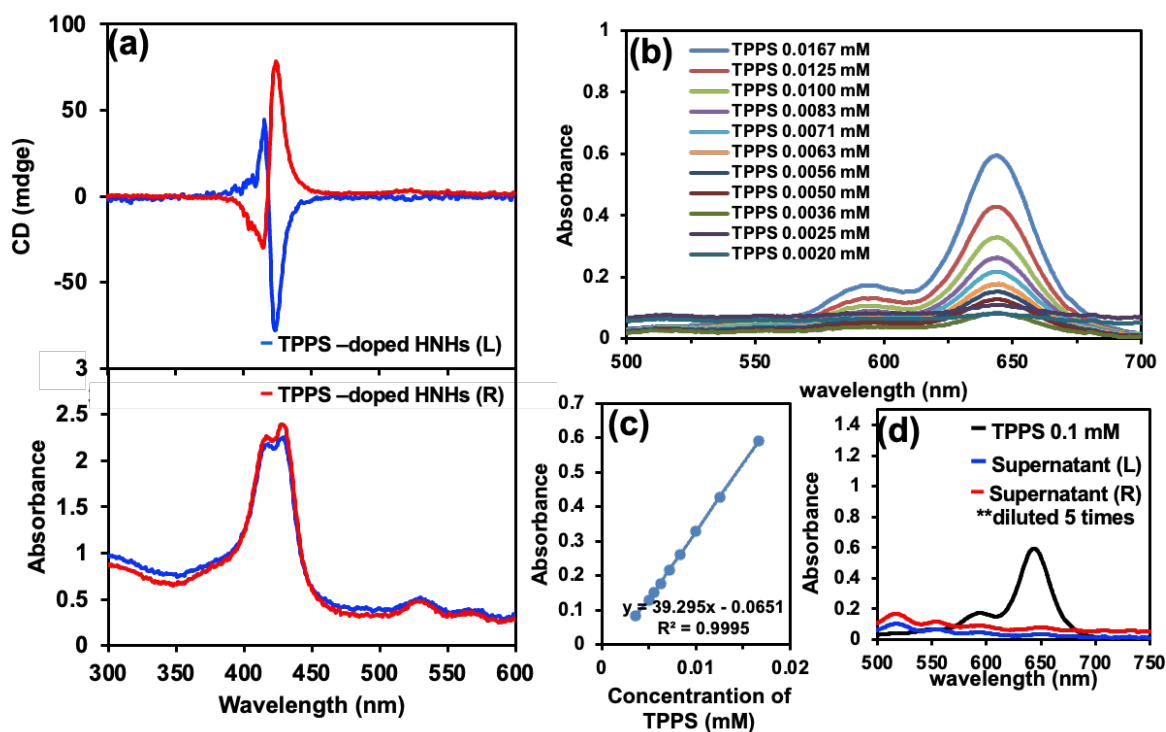


Figure. 3-16 (a) CD-absorption spectra of TPPS-doped HNHs, (b-c) standard calibration curves of TPPS as a function of concentration (0.0020-0.0167 mM), (d) absorption spectra of TPPS solution (0.1 mM) and supernatants after ion-exchange.

Subsequently, TPPS-doped HNHs were pyrolyzed for the synthesis of TPPS-CDots@INHs resulting in mirror-image CD signal with $g_{\text{abs}} \sim -1.5 \times 10^{-4}$ (LH) and 1.3×10^{-4} (RH) in Figure. 3-17a. The 2D fluorescent spectra of TPPS-CDots@INHs were shown in Figures. 3-17b and 3-17c, which were similar to CDots synthesized from gemini tartrate. It means TPPS dopant could not significantly change the emission property of CDots. In Table. 3-1, the carbon percentage of TPPS doped CDot is around 18.6% which is higher than CDots synthesized from gemini tartrate (8.12%), however the carbon percentage decreases significantly after pyrolysis (from 28.7% to 18.6%). In addition, TPPS-CDots@INHs showed much higher retention of C and N than the S- or N-CDots@INHs, therefore N/C ratio was higher by ~ 0.07 . The Raman spectra of TPPS-CDots@INHs showed D and G bands with $I_D/I_G \sim 1.13$ which was higher than CDots from gemini tartrate (Figure. 3-17d), it suggested the increase in defects after incorporating TPPS molecule in HNHs before pyrolysis.

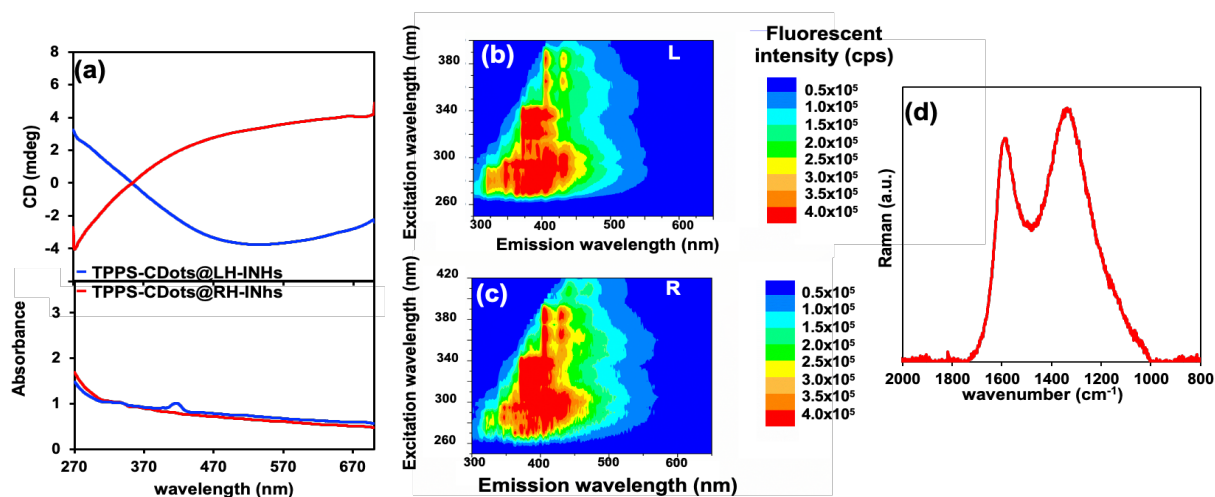


Figure. 3-17 CD-absorption (a) 2D fluorescent (b,c), and (d) Raman spectra (d, λ_{ex} 633 nm) of TPPS-CDots@INHs, (~ 1 mg/mL).

Apart from TPPS dopant, polymer with aromatic moieties²² were also considered as aromatic dopants. To synthesize optically active CDots with an aromatic dopant, polymer was introduced into the chiral nanospace of HNHs before pyrolysis at the same condition. The polymer-doped HNHs were prepared by *in-situ* polymerization of polymer in the HNHs system.

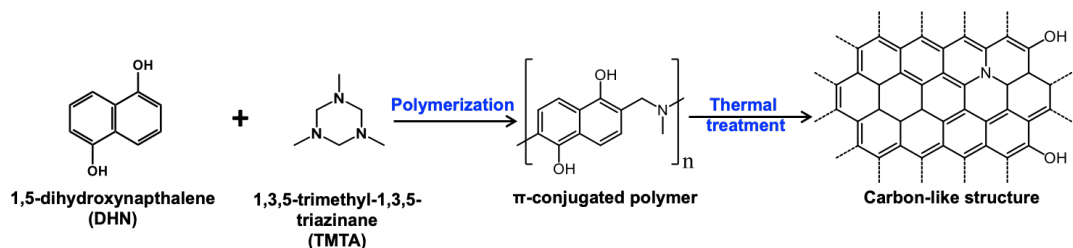


Figure. 3-18 Schematic illustration of the estimated reaction mechanism for polymerization of polymer from 1,5-DHN monomer and TMTA crosslinker and the chemical structure of carbon-like structure after thermal treatment.²²

The fluorescent polymer was *in-situ* polymerized using hydroxyaromatic organic molecular and a triazinane derivative as a monomer and crosslinker, respectively. It was previously reported that aromatic monomer units 2,6-dihydroxyanthracene (DHA), 1,5-dihydroxynaphthalene (1,5-DHN), 2,6-dihydroxynaphthalene (2,6-DHN) or 9,9-bis(4-hydroxyphenyl)fluorene (BHF) can be reacted with crosslinkers having structures such as 1,3,5-trimethyl-1,3,5-triazinane (TMTA) or hexamethylenetetramine (HMT) to create polymer nanoparticles by heating at 150-200 °C in microwave reaction.²³ In addition, these nitrogen-enriched polymers were fabricated to be coated on the outer surface of the spherical β -lactoglobulin for their stabilization in a basic aqueous solution.²⁴ This polymer was polymerized by a facile and versatile method in one pot for the formation of π -electron rich polymer, which fabricated the carbon-like layer after thermal treatment.²² The chemical structure of this carbon-like layer was similar to the graphene structure, as shown in Figure. 3-18. Therefore, this polymer was introduced into HNHs before pyrolysis at 600 °C, because we believed that this polymer containing aromatic moiety would enhance the forming sp^2 carbon-core in CDots@INHs.

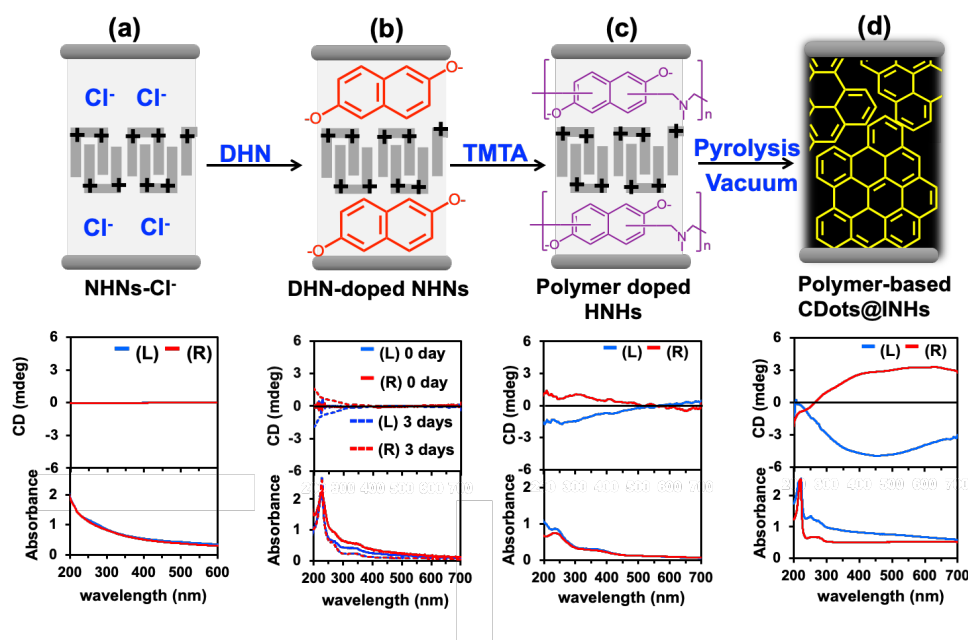


Figure. 3-19 CD and absorption spectra of HNHs-Cl⁻ (a), DHN-doped HNHs (b), polymer-doped HNHs (c), and polymer-based CDots@INHs (d).

For the preparation of polymer-doped HNHs, the polymer was *in-situ* synthesized in HNHs system. The tartrate anion in HNHs system was replaced by Cl⁻ anion at 4 °C and then DHN monomer was introduced into HNHs-Cl⁻ to obtain DHN-doped HNHs (Figure. 3-19a). DHN-doped HNHs showed a strong absorption peak of DHN at 228 nm with no CD signal (Figure. 3-19b), with the ratio of gemini-Cl₂:DHN (1:1) calculated from the difference in absorbance at 228 nm of soaking solution and supernatant (Figures. 3-20a and 3-20b). Surprisingly, we observed a progressive increment in CD signal after keeping it at 4 °C for 3 days, which suggested the better self-organization of DHN in the nanospace of HNHs system (Figure. 3-19b). Then, the *in-situ* polymerization was successfully carried out by adding 1 equivalent TMTA to DHN-doped HNHs and continuing the reaction at 4 °C for 12 hrs. After 24 hrs, polymer-doped HNHs were washed away by cold water 4 times to remove the excess TMTA. The helical morphology of polymer-doped HNHs was confirmed by TEM characterization, as shown in Figures. 3-20c to 3-20e, which suggested that the helical silica framework was retained after *in-situ* polymerization. The absorbance peak of polymer-doped DHNs with a boarded absorption in 200-700 nm implied the generation of extended polymer chain.²⁴ The CD response of polymer-doped HNHs enhanced significantly compared to DHN-doped HNHs (3 days), therefore we believed that the

polymerization obviously enhanced the chiral property in HNHs system. To prepare polymer-CDots@INHs, the polymer-doped HNHs were pyrolyzed to obtain the black powder, which showed CD signals with $g_{\text{abs}} -1.5 \times 10^{-4}$ (LH) and 1.5×10^{-4} (RH). The Raman spectra indicated I_D/I_G ratio was 0.94, which means doping aromatic polymer moiety could increase the degree of graphitic carbon of CDots (Figure. 3-20f). However, 2D fluorescent spectra of polymer-CDots@INHs did not show an obvious change in emission character as illustrated in Figure. 3-25a.

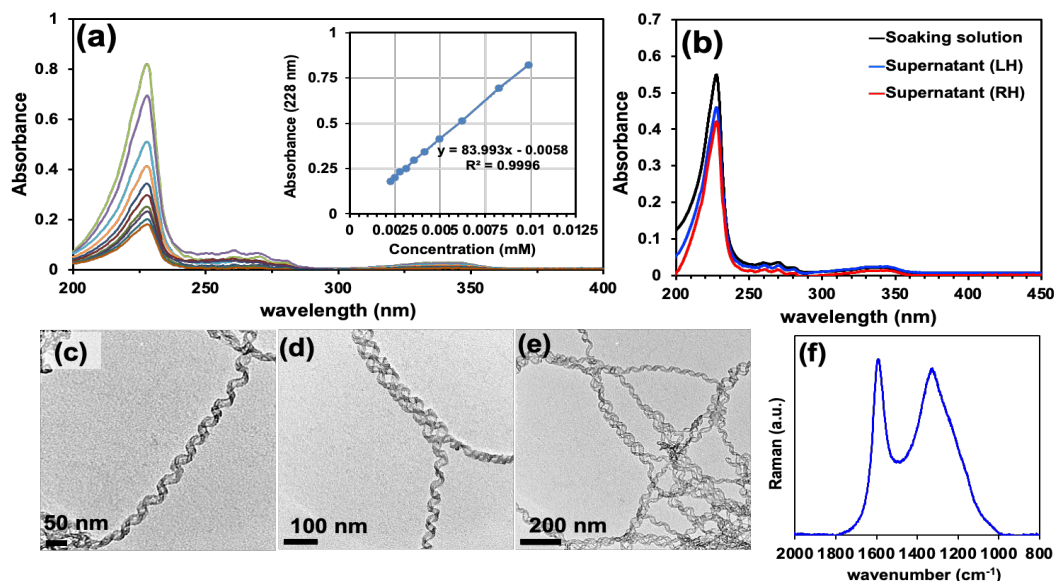


Figure. 3-20 (a) absorption spectra (insert; standard calibration curve) of DHN at different concentrations, (b) absorption spectra of soaking solution of DHN and supernatant (L-/R-), (c, d, e) TEM images of polymer-doped HNHs, (f) Raman spectra of polymer-based CDots@INHs.

The third family of dopant of CDots is the metal-complex. It was previously reported that metal ions such as Mn^{2+} , Zn^{2+} and Eu^{3+} could improve the luminescent property of CDots. For instance, Zn(II) could passivate the CDots surface resulting in a longer photoluminescent lifetime,²⁵ whereas Mn(II) served as a dopant in CDots with red-shifted orange emission.²⁶ Another metal complex to incorporate into CDots was Eu(III) due to its outstanding luminescent property from the f-f transition.²⁷ For sample preparation of metal-complex doped CDots, Mn^{2+} , Zn^{2+} and Eu^{3+} needed to be complexed with anionic ligands to obtain negative-charge metal complexes, because the negative charges of metal complexes are supposed to be attractive to cationic charges of gemini surfactant in HNHs system. Consequently, Mn^{2+} and Zn^{2+} were complexed with *meso*-

tetra-(4-sulfonatophenyl) porphyrin (TPPS) ligand containing four negative charges of sulfonate anion, while Eu^{3+} was complexed with ethylenediaminetetraacetic acid (EDTA) ligand as shown in Figure. 3-21.

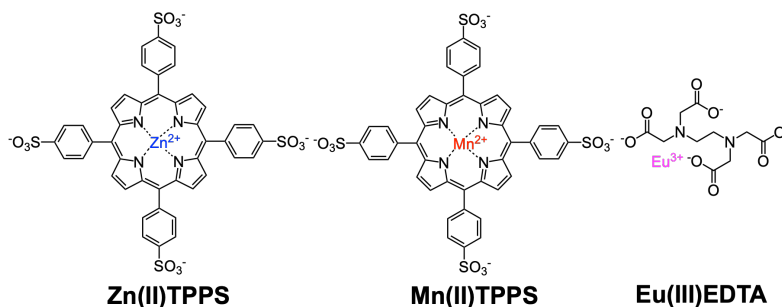


Figure. 3-21 Chemical structures of Zn(II)TPPS, Mn(II)TPPS and Eu(III)EDTA.

Subsequently, Mn(II)TPPS and Zn(II)TPPS complexes were introduced to HNHs-Cl₂ to obtain Mn(II)TPPS doped HNHs and Zn(II)TPPS doped HNHs, respectively. The Mn(II)TPPS and Zn(II)TPPS doped HNHs represented symmetrical CD signals for both LH- and RH-HNHs in Figure. 3-22, which could suggest that the chiral arrangement of gemini-type surfactant in HNHs induced the chirality to achiral Mn(II)TPPS and Zn(II)TPPS complexes. The ratio between Mn(II)TPPS/ Zn(II)TPPS complexes and gemini-Cl₂ was calculated as shown in the Table. 3-2.

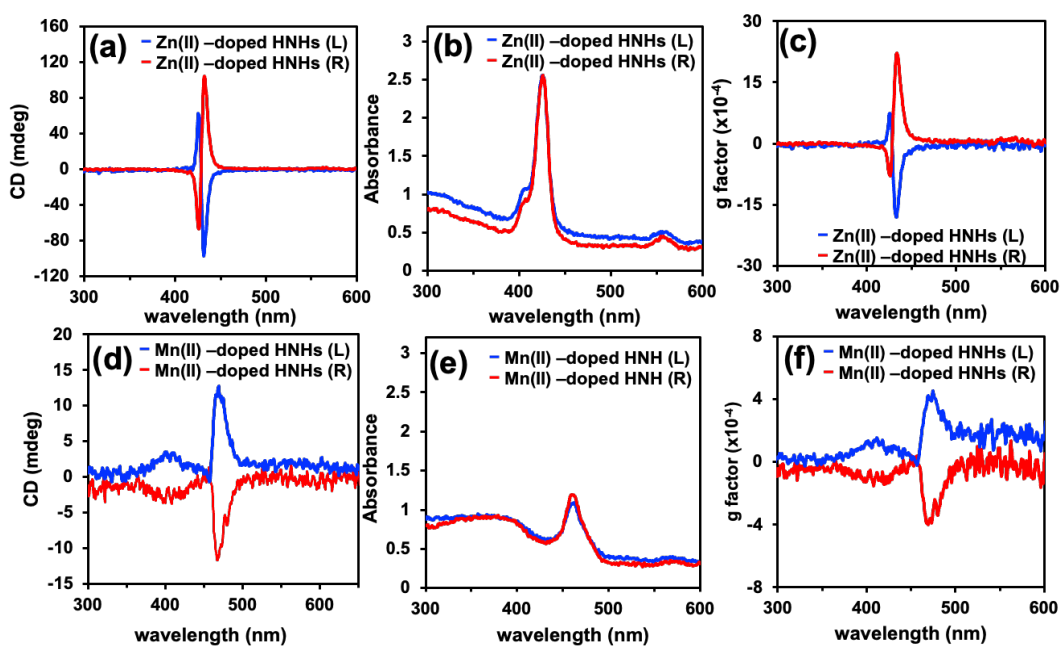


Figure. 3-22 CD, absorption, and g_{abs} spectra of Zn(II)TPPS (a,b,c) and Mn(II)TPPS (d,e,f).

Table. 3-2. the ratio between gemini-Cl₂:ion or molecule of polymer-doped HNHs, TPPS-doped HNHs, Zn(II)-doped HNHs, Mn(II)-doped HNHs and Eu(III)-doped HNHs.

Hybrid nanohelices (HNHs)	The ratio between gemini-Cl ₂ :ion or molecule
Polymer-doped HNHs	gemini-Cl ₂ :DHN = 1 (RH), 1 (LH)
TPPS-doped HNHs	gemini-Cl ₂ :TPPS = 3(RH), 3 (LH)
Zn(II)TPPS HNHs	gemini-Cl ₂ :Zn(II)TPPS = 3.7 (RH), 5 (LH)
Mn(II)TPPS doped HNHs	gemini-Cl ₂ :Mn(II)TPPS = 4 (RH), 3.3 (LH)
Eu(III)EDTA doped HNHs	gemini-Cl ₂ :Eu(III)EDTA = 26 (RH), 31 (LH)

In the case of Eu(III)EDTA doped HNHs, it showed a fluorescent emission peak relating to Eu(III) complex after ion-exchanging (Figure. 3-23). The ratio between gemini-Cl₂:Eu(III)complex was calculated from the difference between the soaking solution and supernatant as 26 (RH-HNHs) and 31 (LH-HNHs).

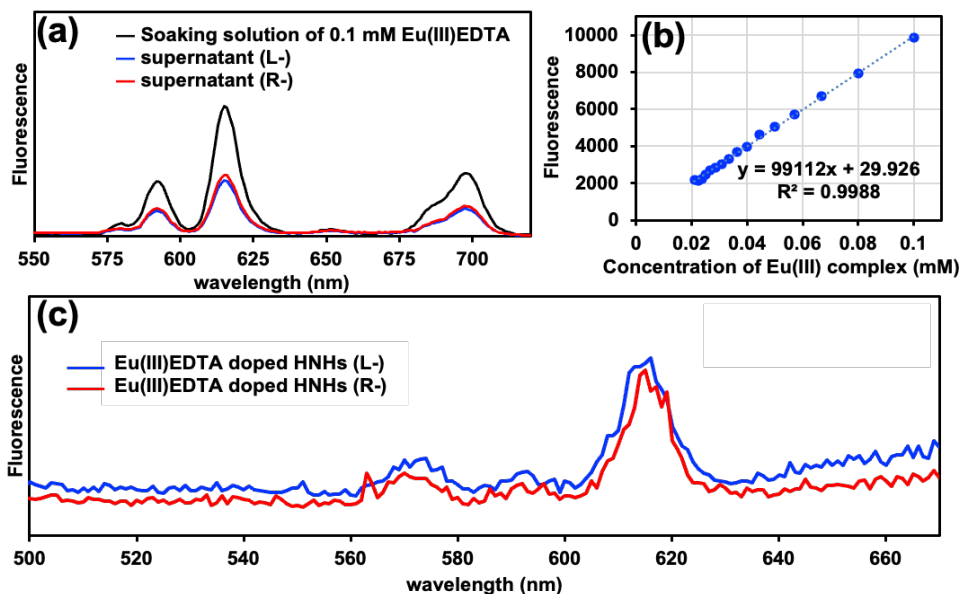


Figure. 3-23 (a) Fluorescent spectra of soaking solution of 0.1 mM Eu(III)EDTA and supernatant, $\lambda_{\text{ex}}365$ nm, (b) standard calibration curve, and (c) fluorescent spectra ($\lambda_{\text{ex}}365$ nm) of Eu(III)EDTA doped HNHs, (~ 1 mg/mL).

These three metal-doped HNHs were pyrolyzed at 600 °C to obtain Zn(II)-, Mn(II)- and Eu(III)-CDots@INHs with symmetrical CD signals in UV-visible range in Figure. 3-24. The 2D fluorescent spectra of metal-complex doped CDots were studied in Figures. 3-25b -3-25d.

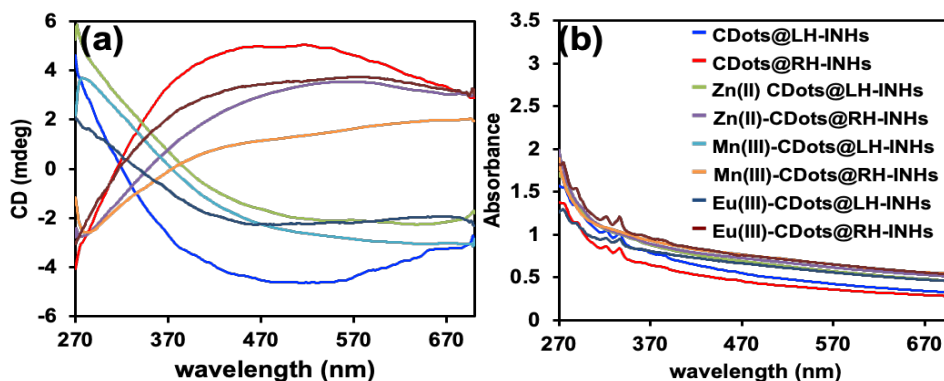


Figure. 3-24 CD (a), absorption (b) spectra of Zn(II)-, Mn(II)- and Eu(III)-CDots@INHs, (~1 mg/mL).

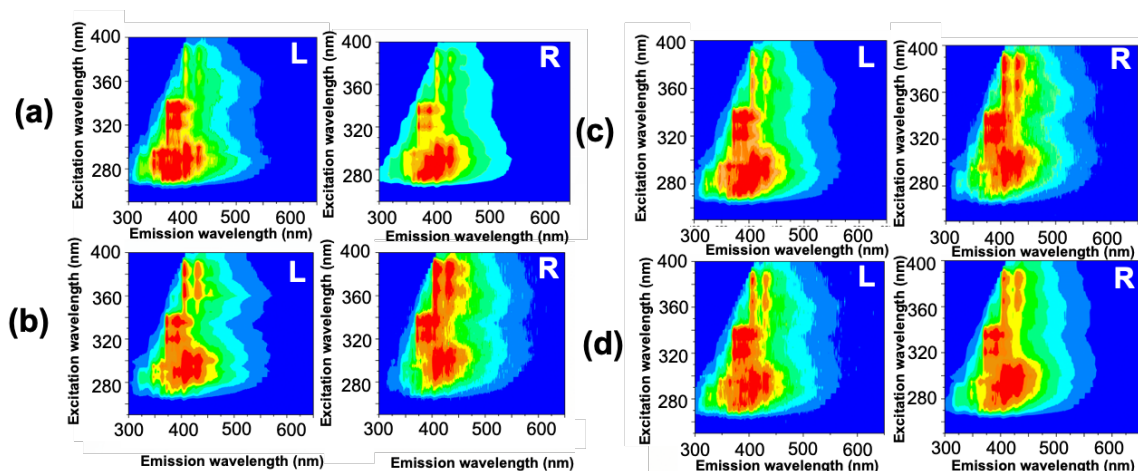


Figure. 3-25 2D Fluorescent spectra of polymer-based CDots@INHs (a), Zn(II)-doped CDots@INHs (b), Mn(III)-doped CDots@INHs (c), and Eu(III)-doped CDots@INHs (d) in DMF, (~1 mg/mL).

XPS was used for the comparison between various CDots. The C1s XPS spectra of N-CDots@INHs showed four different types of carbon content with C=C (283.8 eV, 61.48%), C-C (285.1,25.73%), C=O (286.6 eV, 7.89%) and O-C=OH (288.9 eV, 4.89%) in Figure. 3-26a. Therefore, most of the carbon content of CDots is C=C which could be confirmed as the π -domain

carbon core of CDots. These carbon percentages in high-resolution XPS spectra of N-CDots@INHs were similar to CDots@INHs (Figure. 3-7c). Meanwhile, N1s high-resolution XPS spectra of N-CDots@INHs indicated the percentages of pyrrolic nitrogen (399.7 eV, 68.83%), graphitic nitrogen (401.7 eV, 15.62%) and pyridinic nitrogen (397.6 eV, 15.55%) in Figure. 3-26b, it could be observed that the percentage of pyrrolic nitrogen was higher than that of CDots@INHs (from 54.82 % to 68.83%). Meanwhile, the percentages of graphitic nitrogen and pyridinic nitrogen of N-CDots@INHs decreased (from 24.2 % to 15.62% and 20.97 % to 15.55%) in Figure. 3-26f, compared to CDots@INHs from gemini tartrate. Furthermore, the carbon/silicon and nitrogen/silicon ratios were reported in Figures. 3-26c and 3-26d. Interestingly, the C/Si and N/Si ratio of N- and polymer-based CDots@INHs were higher than CDots@INHs around 2 times (59.83% and 1.22%, respectively), which is in agreement with the results in Figure. 3-27b.

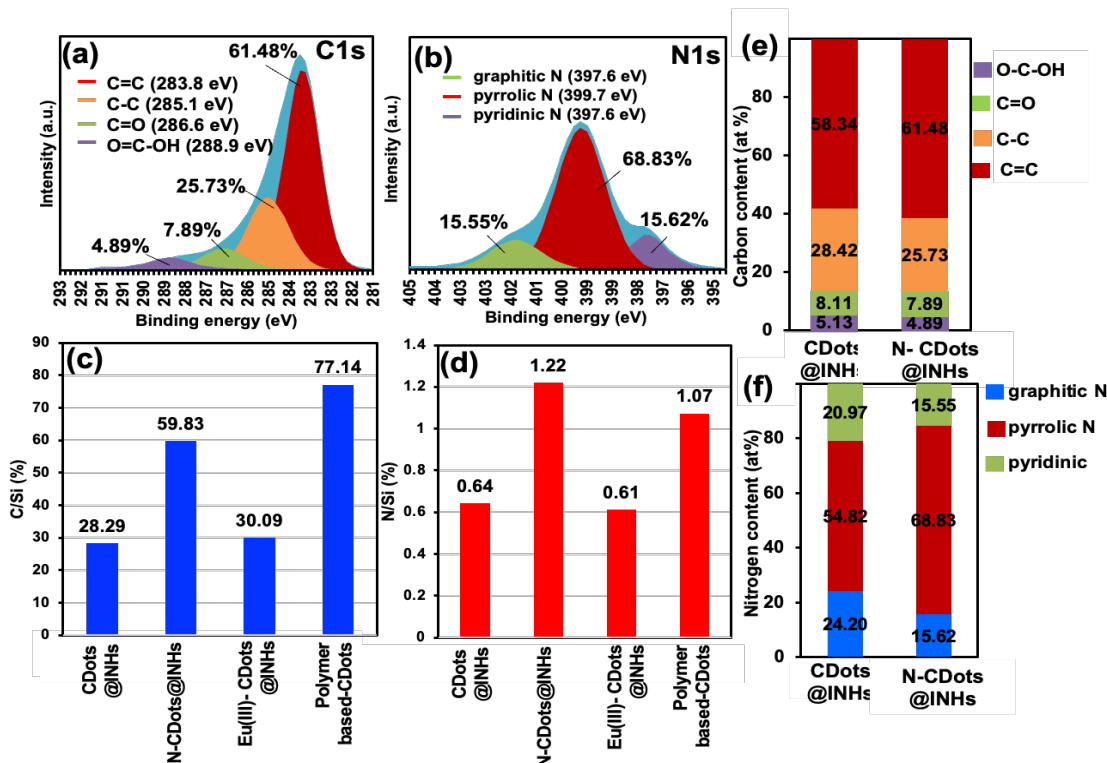


Figure. 3-26 C1s (a) and N1s (b) high-resolution XPS spectra of N-doped CDots@INHs, The C/Si (c) and N/Si (d) ratio of CDots@INHs, N-, Eu(III)-, and polymer-CDots@INHs measured by XPS, Comparison of carbon percentage (e) and nitrogen percentage (f) of CDots@INHs and N-CDots@INHs from XPS analysis.

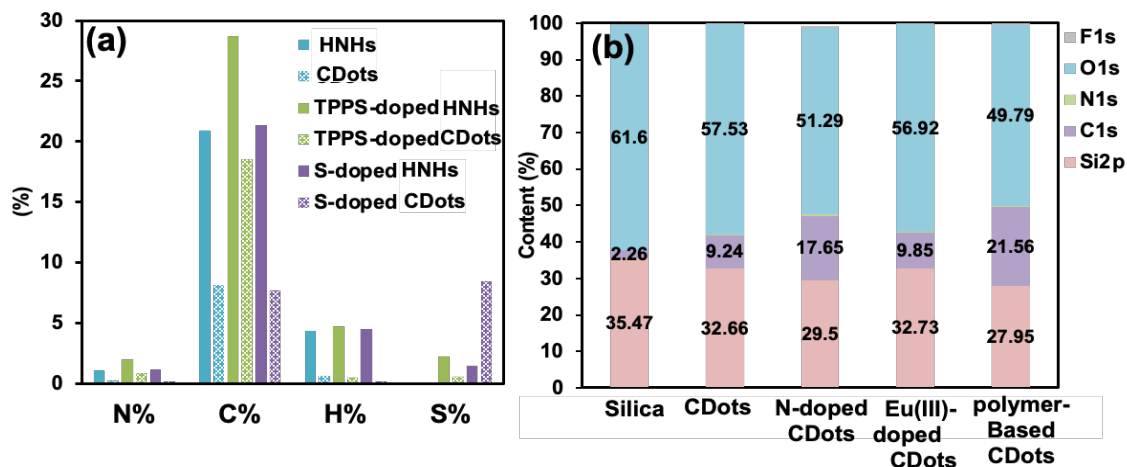


Figure. 3-27 (a) Elemental percentages from elemental analysis before and after pyrolysis. (b) The elemental percentages (%) from XPS analysis of silica, CDots@INHs, N-, Eu(III)-, and polymer-based CDots@INHs.

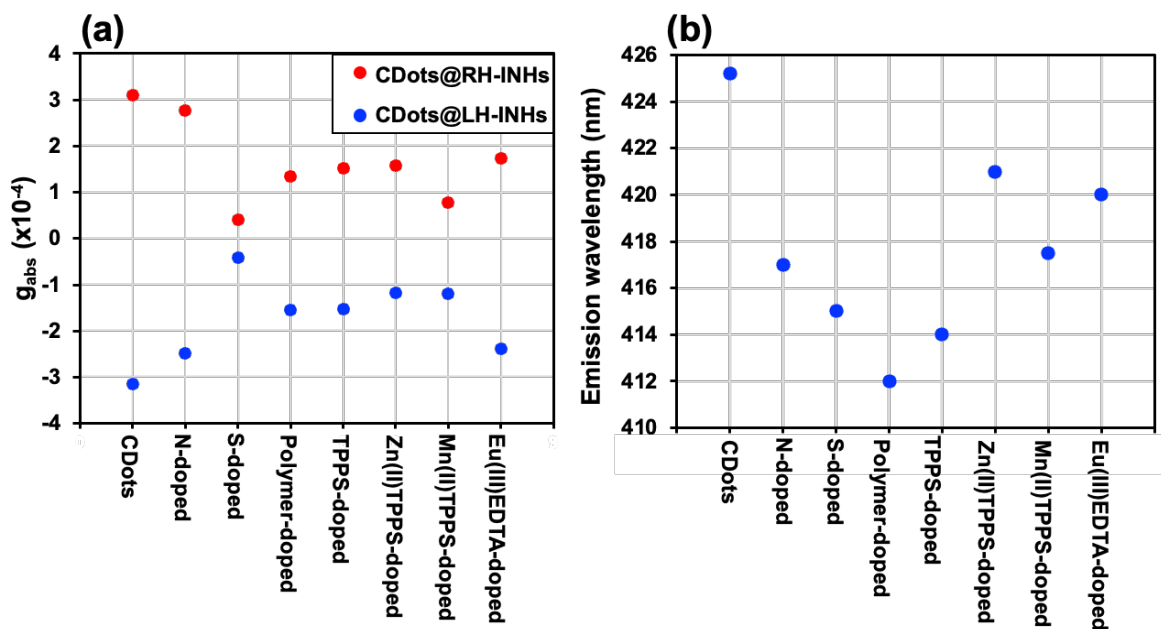


Figure. 3-28 Comparison of g_{abs} at 570 nm (a) and emission wavelength (b) of various CDots@INHs dispersed in DMF (λ_{ex} 290 nm).

It could be suggested that azide ion in N-doped HNHs and aromatic polymer in polymer-doped HNHs could retain the carbon and nitrogen content effectively in the pyrolysis step. Meanwhile, Eu(III)-CDots@INHs had percentages of C/Si and N/Si around 30.09% and 0.61%,

respectively, which are similar to CDots@INHs. In the case of elemental results (EA) in Figure 3-27a, the carbon content decreased dramatically by around 50% after pyrolysis at 600 °C under vacuum, it is possibly explained by losing organic matter in the form of gas during the thermal treatment.⁶

For chirality in CDots@INHs and doped CDots@INHs, the g_{abs} at 570 nm were compared in Figure. 3-28a. For most of the CDots@INHs, the CD signal was observed in the UV-visible range (200-700 nm) with $g_{\text{abs}} \sim 10^{-4}$. It was observed that the g_{abs} of doped CDots were dramatically lower than CDots from gemini tartrate ($\sim 3 \times 10^{-4}$), which possibly implied that the introduction of dopants into the HNHs system before pyrolysis has an impact on the chirality of CDots. The reason to explain why g_{abs} of doped CDots were lower than that of CDots is the self-assembly organization of gemini surfactant was not well-organized after the introduction of dopants via ion-exchanging method, then decrease g_{abs} of CDots after pyrolysis. In luminescence property, doped CDots dispersing in DMF were measured at different excitation wavelengths (Figures. 5-15, 5-17 and 5-25). Their emission under excitation at 290 nm slightly shifted to a shorter wavelength for some of the doped CDots (Figure. 3-28b), but it was unclear whether the dopants had been seen. The small effect of the various dopants on the chiral and luminescent properties of doped-CDots@INHs is probably due to the high carbon percentage from gemini surfactant which makes the effect of other elements negligible. The Circularly Polarized Luminescence (CPL) signals were not detectable from these CDots@INHs probably due to the low g_{abs} .

Previously, it was reported the chirality induction of perovskite nanocrystals using silica nanohelices using a drop-casting approach, which represents strong CD and CPL signals ($g_{\text{abs}} \sim \pm 2 \times 10^{-2}$).^{28, 29} Subsequently, the drop-casting method was used to develop chirality induction to carbon dots using silica nanohelices. INHs (100 μg) were deposited on a 1x1 cm² quartz plate and dried at room temperature for 1 hr. After that, precursors for the synthesis of CDots into the chiral space of silica nanohelices, as shown in Figure. 3-29. Unfortunately, the organic matter was lost after pyrolysis, possibly explained that the pyrolysis under N₂ flow was not effective to pyrolyze precursors on the substrate. Therefore, the method for thermal treatment of precursors prepared by a drop-casting method is in the process to be improved.

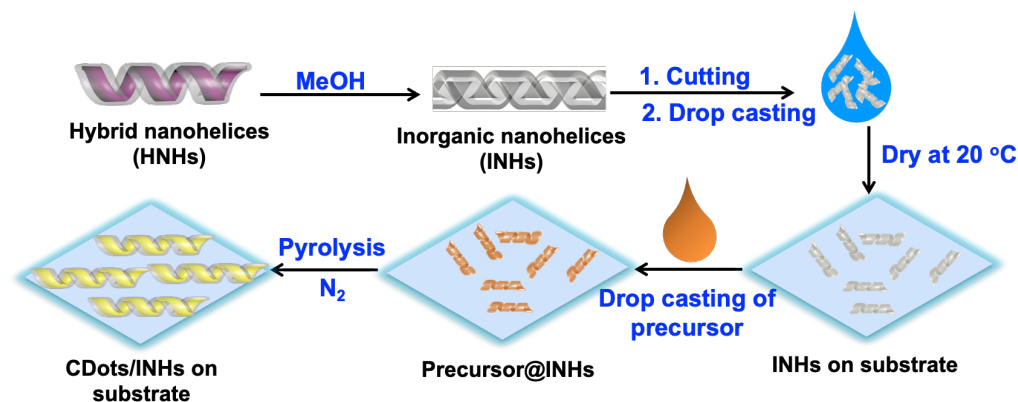


Figure. 3-29 Scheme of drop-casting method for synthesis of CDots/INHs on a substrate.

3.3 Conclusion

We have demonstrated the formation of chiral CDots *in-situ* in the nano-metrical helical silica framework. The silica nanohelices were prepared by supramolecular self-assembly of gemini-type surfactant with tartrate anion, which acts as a soft template to organize helical silica framework via sol-gel polycondensation. The helical silica nanohelices performed as chiral inducer to achiral graphenoid CDots, meanwhile the organic template inside silica nano-helices acts as a carbon source. We represented the first examples of CDots showing CD signals in the wavelength of 200 nm – 700 nm. Various dopants were doped in these CDots including heteroatom, aromatic dopant and metal-complex dopants by ion-exchange method in HNHs before pyrolysis. Interestingly the molecular chirality was not requisite for the chiral CDots, i.e. even when the chiral tartrate was exchanged to achiral anions, after the pyrolysis, similar CD signals were observed which was directly related to the morphology of silica helices. We believe that our results have a high potential for chiral induction from mesoscopic chiral frameworks to carbon-based nanoparticles. However, CDots@IHNs and doped CDots@INHs showed low $g_{\text{abs}} \sim \pm 10^{-4}$ without chirality in emission relating to CPL signal. Owing to these issues, we developed an approach for chirality induction of CDots by using drop-casting method. However, the organic matter was lost after pyrolysis. This work was recently published in *Chem. Commun.*, 2023, **59**, 9762-9765 (Sequential chiral induction between organic and inorganic supramolecular helical assemblies for the *in situ* formation of chiral carbon dots).

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Chapter 4

Chirality induction to achiral polymer using silica nanohelices

Chiral polymers have gained a lot of attention due to their potential for a variety of scientific and industrial applications, such as asymmetric catalysis,¹ chiral separation² and chiral sensors.³ The chiral property of polymers could originate at the molecular level such as in the presence of asymmetric carbons in polymer chains.^{4,5} Furthermore, the conformation of polymers at the supramolecular level could represent the chiroptical properties by helical folding conformationally⁶ or in the presence of chirality inducers such as ion interaction,⁷ pH⁸ and solvent.⁹ These optically active polymers could express their chiroptical property via CD and CPL signals.^{10,11}

Fluorescent polymers are widely used in fluorescent imaging, living-cell labelling and optical signaling.^{12,13} Recently, it was reported that aromatic monomer units 2,6-dihydroxyanthracene (DHA), 1,5-dihydroxynaphthalene (1,5-DHN), 2,6-dihydroxynaphthalene (2,6-DHN) or 9,9-bis(4-hydroxyphenyl)fluorene (BHF) could react with crosslinkers such as 1,3,5-trimethyl-1,3,5-triazine (TMTA) or hexamethylenetetramine (HMT) to create polymer by thermal treatment.¹⁴ Additionally, the polymer had been fabricated and deposited on proteins such β -lactoglobulin to enhance the stabilization in a strong basic solution.¹⁵ The coating of the porous silica by the polymer was used for selective retention of polycyclic aromatic hydrocarbon (PAHs) due to proton- π interactions.¹⁶ The mechanism of the polymerization was discussed in the previous publication.^{14,16,17}

One of the efficient ways to endow the chirality to achiral fluorescent polymer is to use chiral micro- and nano-structures with asymmetric architectures in their three-dimensional shapes, such as helical, spiral, pyramidal and nanoflower shapes.¹⁸⁻²⁰ In this research, we report how the chirality induction to achiral polymer was performed using helical silica-based nanomaterials. The INHs as previously introduced acted as a chiral inducer to induce chiral property to achiral polymer via drop casting.²¹ The achiral polymer was polymerized by using 2,6-dihydroxynaphthalene (DHN) as monomer and 1,3,5-trimethyl-1,3,5-triazine (TMTA) as a crosslinker, (called PolyDHN-TMTA hereafter).¹⁴ There were two main approaches for chirality induction of achiral polymer using silica nanohelices by drop-casting method, as illustrated in Figure. 4-1. The first

approach was *ex-situ* synthesis, in which case, the monomer and the crosslinker were mixed before depositing on INHs thin film. For the second method, *in-situ* synthesis, the polymerization reaction between DHN monomer and TMTA crosslinker occurred after being introduced inside INHs, therefore, INHs acted as both chiral inducer and chiral nano-reactor for the fabrication of optically active polymer.

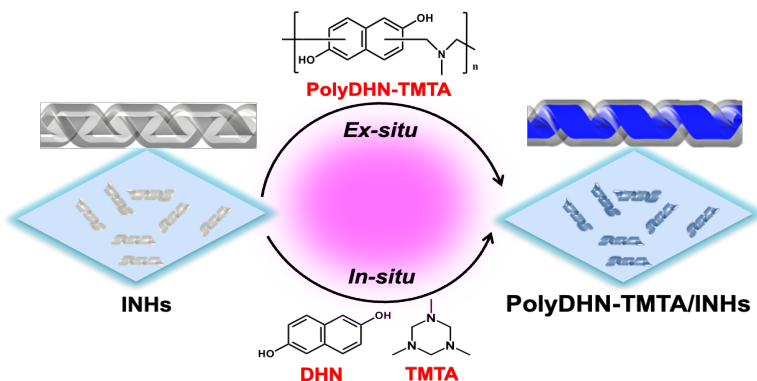


Figure. 4-1 Preparation of polymer with chiroptical properties using *ex-situ* and *in-situ* approaches.

4.1 Experimental section

4.2.1 Synthesis of gemini tartrate and preparation of helical silica nanohelices (INHs)

The synthesis of gemini (16-2-16) tartrate and the preparation of INHs has been described in Chapter 2 as well as in our previous publications.²²

4.2.2 Preparation of INHs thin film for chirality induction to achiral polymer

The morphology of INHs was first characterized by TEM. Then, helical INHs were cut and then drop-casted on a quartz slide in the 200 μg INHs/2x2 cm^2 ratio and dried at room temperature for 1 hr before using.

4.2.3 Preparation of PolyDHN-TMTA

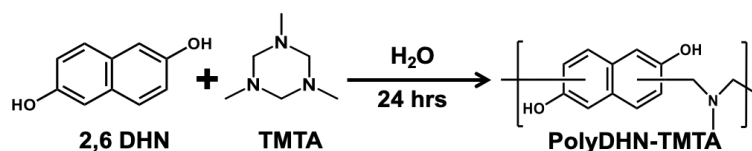


Figure. 4-2 Polymerization of DHN and TMTA.¹⁴

To prepare PolyDHN-TMTA, 2,6-dihydroxynaphthalene (DHN) from Sigma-Aldrich (98%) and 1,3,5-trimethyl-1,3,5-triazine (TMTA) from Tokyo Chemical Industry (TCI) acted as monomer and crosslinker, respectively. The DHN solution (2.5 mM) and TMTA solution (2.5 mM) were freshly prepared in H_2O before using.

4.2.4 *Ex-situ* synthesis of PolyDHN-TMTA/INHs

The PolyDHN-TMTA was prepared by polymerization by mixing DHN (2.5 mM, 1.0 mL), TMTA (2.5 mM, 1.0 mL) and H_2O (8.0 mL), respectively. The polymerization reaction in 15-mL tube was carried out on roller mixer at 20 °C for 24 hrs. The estimated mechanism of their polymerization and condensation to fabricate PolyDHN-TMTA was reported in previous publications.^{15, 17, 23, 24} Then, 200 μL of PolyDHN-TMTA solution was drop-casted on a quartz plate containing INHs (200 $\mu\text{g}/2 \times 2 \text{ cm}^2$). After that, the samples were dried at 20 °C, for 24 hrs before measuring CD and CPL signals.

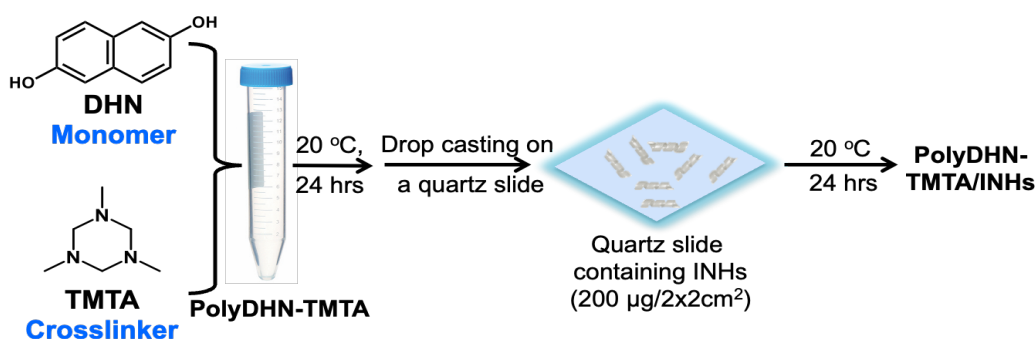
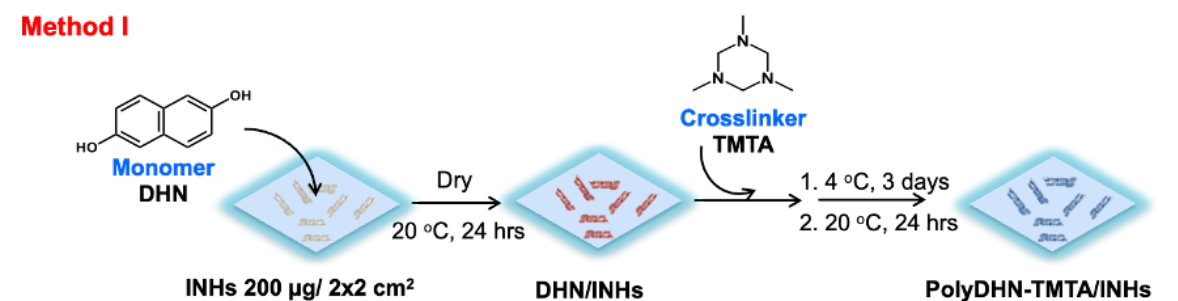


Figure. 4-3 *Ex-situ* synthesis of chiral PolyDHN-TMTA using INHs.

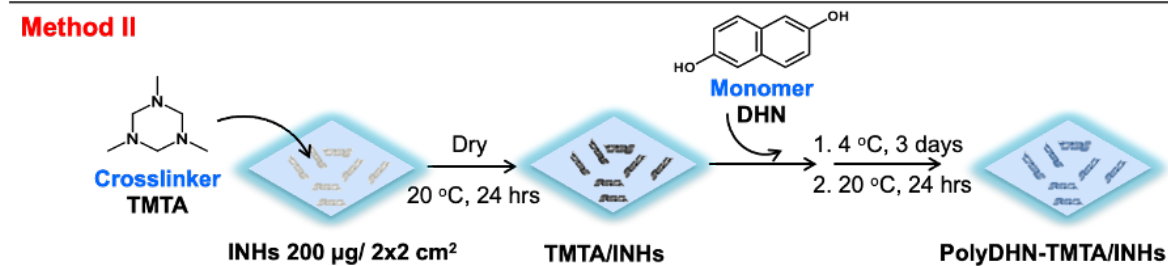
4.2.5 In-situ synthesis of PolyDHN-TMTA/INHs

The *in-situ* synthesis of PolyDHN-INHs was prepared in three methods as shown in Figure. 4-4. The *in-situ* method I was carried out by drop-casting DHN (2.5 mM, 400 μ L) on INHs thin film and letting it dry at 20 $^{\circ}$ C for 24 hrs. Then, the TMTA crosslinker (2.5 mM, 400 μ L) was drop-casted to DHN/INHs so as to let the polymerization occur at 4 $^{\circ}$ C for 3 days. Then, the samples of PolyDHN-TMTA/INHs were dried at 20 $^{\circ}$ C for 24 hrs before measuring CD and CPL signals. Meanwhile, method II was started by drop-casting of TMTA (2.5 mM, 400 μ L) on INHs thin film, then DHN monomer (2.5 mM, 400 μ L) was drop-casted and kept at 4 $^{\circ}$ C for 3 days. After that, the samples were dried at 20 $^{\circ}$ C for 24 hrs. In *in-situ* synthesis (method III), right after mixing the solutions of DHN and TMTA in H₂O, the mixture was drop-casted on INHs thin film and dried at 20 $^{\circ}$ C. After that, 500 μ L of H₂O was introduced on DHN+TMTA/INHs and continued polymerization at 4 $^{\circ}$ C for 3 days before drying at 20 $^{\circ}$ C for 24 hrs.

Method I



Method II



Method III

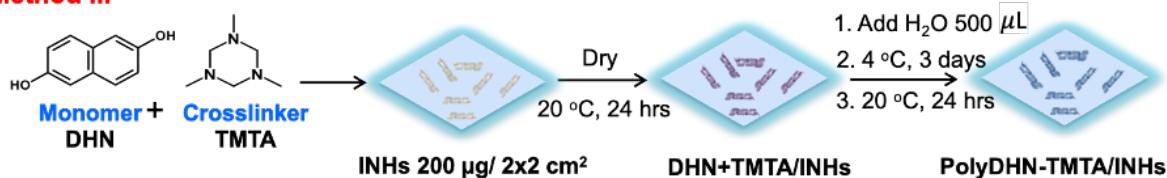


Figure. 4-4 Three *in-situ* approaches for *in-situ* synthesis of PolyDHN-TMTA/INHs.

4.2 Result and discussion

4.2.1 *Ex-situ* synthesis of chiral PolyDHN-TMTA using INHs.

The first approach for chirality induction to achiral polymer using silica nanohelices was called as *ex-situ* synthesis. The UV-vis absorption spectra of the DHN monomer in H₂O showed a strong peak at 225 nm with small peaks at 270 nm and 350 nm. Then, the modification of the UV-vis absorption spectra of PolyDHN-TMTA after mixing DHN and TMTA (1:1) for 24 hrs (Figure. 4-5a) was clearly observed with a broad continuous band extended in the UV-visible range. The broad absorption peak of PolyDHN-TMTA suggested the extension of the polymer chain²⁵ and π -stacking of naphthalene portions between the polymer chain.²⁶ Furthermore, the suspension of PolyDHN-TMTA clearly showed the scattering of a light beam due to the Tyndall effect (Figure. 4-5a insert), which could indicate the formation of polymer colloid particles.²⁷ Therefore, the UV-visible of achiral PolyDHN-TMTA not only originated from the absorption of chromophores in polymer chains but was also influenced by the particle's scattering.²⁷ TEM images in Figures. 4-5c and 4-5e indicated spherical particles, meanwhile, DLS results indicated that the diameter of achiral PolyDHN-TMTA dispersing in H₂O was 142 nm (Figure. 4-5b).

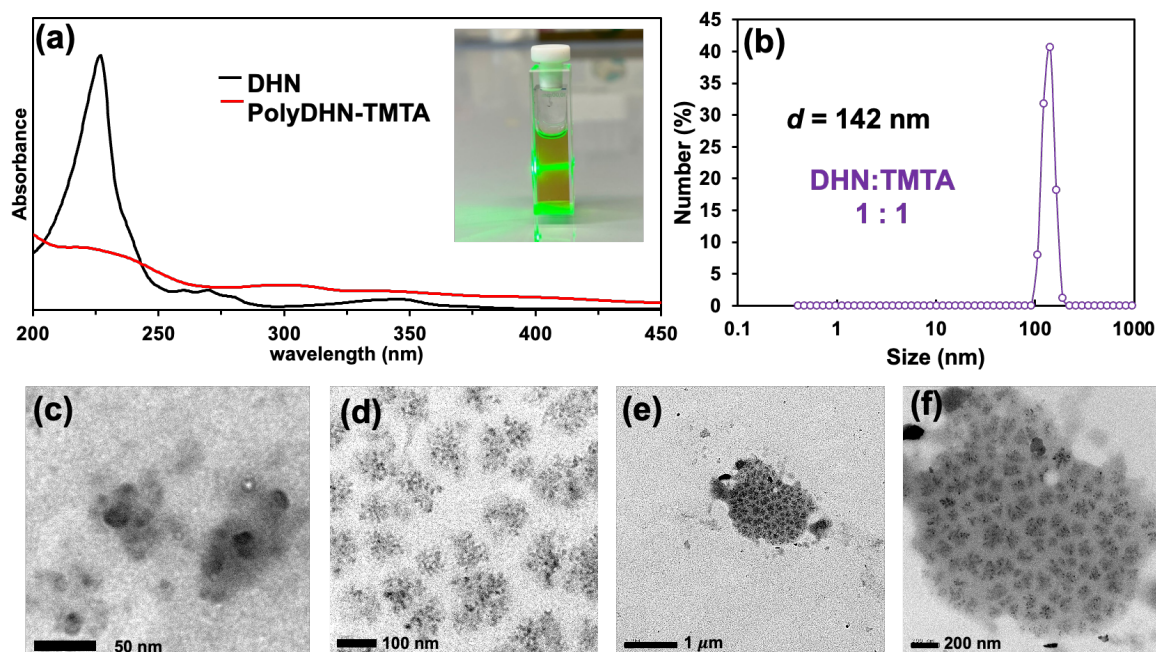


Figure. 4-5 (a) UV-visible spectra of DHN and PolyDHN-TMTA for 24 hrs, (b) DLS spectra and (c,d,e,f) TEM images of PolyDHN-TMTA, (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 24 hrs, 20 °C).

The fluorescent emission of PolyDHN-TMTA showed a peak at 435 nm under excitation at 290 nm (Figure. 4-6c). For fluorescent emission, the fluorescent peak at 387 nm of DHN decreased in Figure. 4-6b and show a red shift to 435 nm (λ_{ex} 290 nm) during polymerization for 24 hrs in Figure. 4-6a. This emission shift to a longer wavelength of achiral Poly-DHN-TMTA suggested the extension of the polymer chain after polymerization reaction in H₂O for 24 hrs at 20 °C.¹⁵

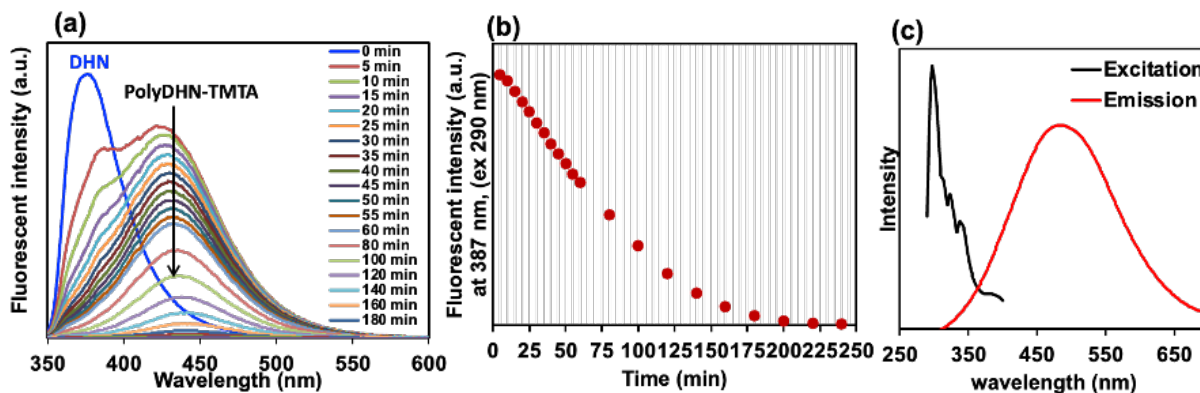


Figure. 4-6 (a) Fluorescent spectra of DHN and achiral PolyDHN-TMTA during polymerization in H₂O, (b) fluorescence decay (λ_{ex} 290 nm) of PolyDHN-TMTA during polymerization, (c) excitation and emission (λ_{ex} 290 nm) of PolyDHN-TMTA in H₂O, (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 24 hrs, 20 °C)

The polymerization reaction between DHN and TMTA was characterized by Nuclear Magnetic Resonance (NMR) in D₂O (Figure. 4-7). The NMR spectra showed peaks at 7.15-7.74 ppm, which are assigned as aromatic protons of DHN monomer. Subsequently, TMTA was introduced into DHN solution as a crosslinker and subsequently initiated an up-field shift of these aromatic proton signals since reaction time at 80 min. It suggested that TMTA reacted with photons at four reaction sites of DHN during polymerization.¹⁴ After 180 min, the NMR signals started to be ambiguous due to the decrease in solubility in D₂O, which proposed the formation of PolyDHN-TMTA. The estimated mechanism of their polymerization and condensation to fabricate PolyDHN-TMTA was reported in previous publications.^{15, 17, 23, 24}

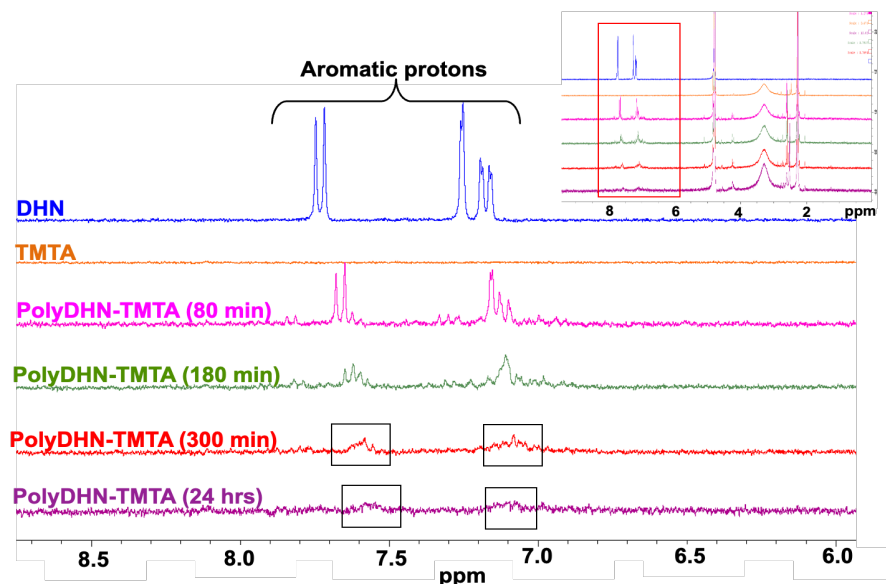


Figure. 4-7 NMR spectra of DHN, TMTA, and PolyDHN-TMTA at different reaction times (80 min, 180 min, 300 min and 24 hrs) in D_2O , (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H_2O (8.0 mL), 24 hrs, 20 °C)

Furthermore, PolyDHN-TMTA was characterized by Diffuse Reflectance Infrared Fourier Transform (DRIFT) in Figure. 4-8a. It was observed the peaks of ν_{O-H} (3393 cm^{-1}), $\nu_{C=C}$ (1600 cm^{-1} and 1376 cm^{-1}), ν_{C-N} (1269 cm^{-1}) and ν_{C-O} (926 cm^{-1}) caused by functional groups from DHN monomer and TMTA crosslinker.²⁴ Meanwhile, Raman spectra of PolyDHN-TMTA showed D and G bands in Figure. 4-8b relating to crystalline and amorphous phases of polymer, respectively. These Raman peaks implied the enhanced-raman active modes corresponding to the stretching vibration of single and double carbon-carbon bonds of the polymer chain.²⁸

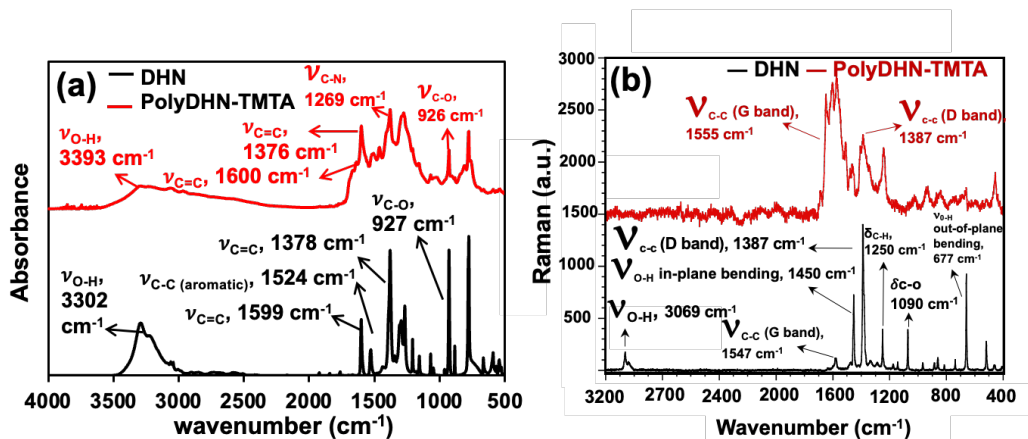


Figure. 4-8 DRIFT spectra (a) and Raman spectra (b) of DHN and PolyDHN-TMTA.

Furthermore, X-ray photoelectron spectroscopy (XPS) technique indicated the element compositions of PolyDHN-TMTA with three main elements including carbon (80.45%), nitrogen (3.29%) and oxygen (16.02%). The deconvolution of C1s XPS spectra showed the presence of different types of carbons in Figure. 4-9a, C-C (284.9 eV) is the majority of the carbon (33.87%), with 20.32% of C-O-C (286.4 eV), 17.81% of C-OH (285.3 eV), 13.50% of C=C (284.3 eV), 7.07% of C=O (287.4 eV), 3.31% of O-C=O (288.5 eV), 1.74% of C=O-O (289.5 eV) and 2.38% of $\pi-\pi^*$ (291.3 eV). Therefore, the sp^3/sp^2 ratio was calculated to be ~ 2.51 (Table 2-1). In addition, N1s XPS spectra (Figure. 4-9b) revealed that PolyDHN-TMTA contained pyridinic N (388.8 eV, 24.12%), pyrrolic N (400.1 eV, 30.20%), graphitic N (401.2 eV, 16.90%), and oxidized N (402.2 eV, 28.78%). Owing to the characterization in DRIFT and XPS, the chemical structure of achiral PolyDHN-TMTA was roughly proposed in Figure. 4-9c.

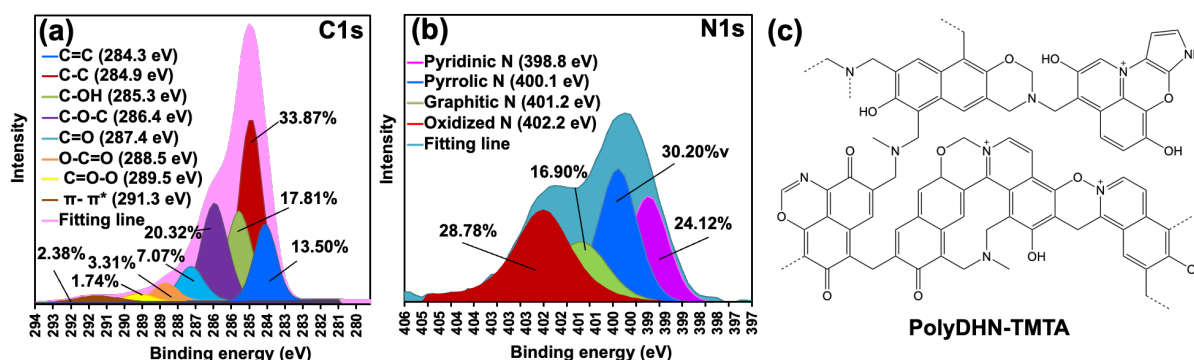


Figure. 4-9 High-resolution C1s (a) and N1s (b) XPS spectra of PolyDHN-TMTA, (c) Proposed chemical structure of achiral PolyDHN-TMTA. (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 24 hrs, 20 °C)

After preparing PolyDHN-TMTA, the achiral PolyDHN-TMTA solution in water (200 μ L) was drop-casted on the INHs thin film on the substrates. The INHs thin film was prepared by depositing INHs suspension (1 mg/mL, 200 μ L) on 2x2-cm² quartz substrate, then dried for 1 hour at room temperature. The thin film of DHN/INHs and PolyDHN-TMTA/INHs were measured with two azimuth angles at 0° and 90°, respectively, and accumulated to minimize the effect of LD.

To endow the chiroptical properties, both DHN monomer (2.5 mL, 400 μ L) and PolyDHN-TMTA solution (200 μ L) were drop-casted on a thin film of INHs (200 μ g in 2x2 cm²) and dried

at 20 °C for 24 hrs to obtain DHN/INHs and PolyDHN-TMTA/INHs, respectively. Surprisingly, DHN/INHs and PolyDHN-TMTA/INHs showed symmetrical CD signals in TCD and DRCD spectra in Figure. 4-10, the DHN and PolyDHN-TMTA on RH-(LH-) INHs represented negative (positive) signals, respectively. PolyDHN-TMTA/INHs and DHN/INHs showed an obvious difference in their CD and absorption spectra. The g_{abs} in DRCD of PolyDHN-TMTA/INHs ($\propto$ normalized CD signals by absorbance) were -1.9×10^{-3} and 2.1×10^{-3} (260 nm) for LH- and RH-INHs, meanwhile DHN/INHs showed g_{abs} in DRCD at $\sim -8.5 \times 10^{-4}$ and 1.1×10^{-3} (230 nm) for LH- and RH-INHs, respectively.. Furthermore, DHN/INHs and PolyDHN-TMTA/INHs showed luminescence. The emission peaks of DHN/INHs and PolyDHN-TMTA/INHs are at a wavelength of 385 nm and 500 nm (λ_{ex} 290 nm), respectively (Figure. 4-10c), which could possibly imply the stronger interchain electron interaction and longer chain length with good packing in polymer chain leading to a shift in emission.^{27, 29} Both DHN/INHs and PolyDHN-TMTA/INHs showed symmetrical CPL signals with g_{lum} ($\propto$ normalized CPL signals by fluorescence) at $\sim -1.1 \times 10^{-2}$ and 1.3×10^{-2} at 385 nm for DHN/LH-INHs and DHN/RH-INHs, respectively, and -7.8×10^{-3} and 5.4×10^{-3} at 435 nm for PolyDHN-TMTA/LH-INHs and PolyDHN-TMTA/RH-INHs, respectively. However, the CPL peaks were not at the same wavelength of the fluorescent emission due to the polydispersity of polyDHN-TMTA. For further characterization of morphology, TEM images (Figure. 4-11) illustrated the helical morphology of PolyDHN-TMTA/INHs with a darker contrast compared to INHs. Therefore, it could suggest the helical morphology of PolyDHN-TMTA was influenced by the helical morphology of INHs template.

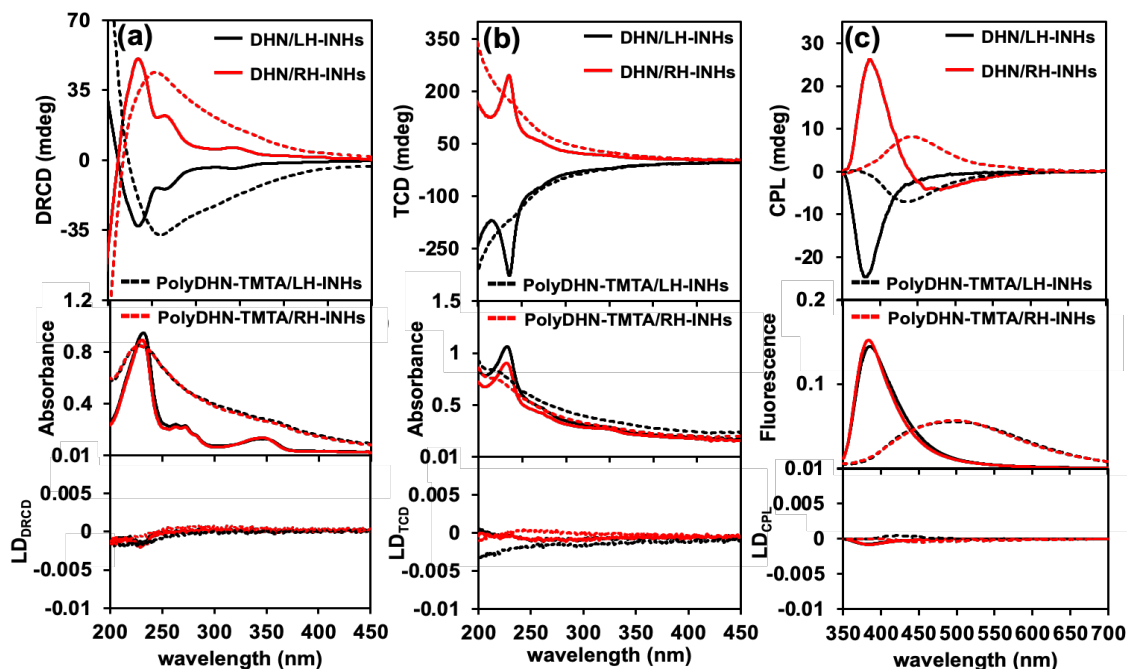


Figure. 4-10 DRCD, TCD and CPL (λ_{ex} 300 nm) spectra of DHN/INHs and PolyDHN-TMTA/INHs. (200 μL PolyDHN-TMTA on INHs 200 $\mu\text{g}/2 \times 2 \text{ cm}^2$).

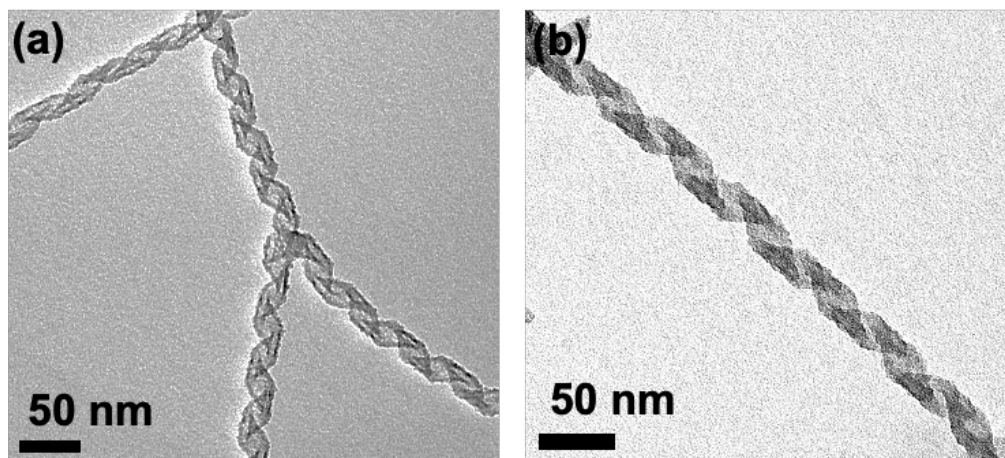


Figure. 4-11 TEM images of INHs and PolyDHN-TMTA/INHs. (200 μL PolyDHN-TMTA on INHs 200 $\mu\text{g}/2 \times 2 \text{ cm}^2$).

In general, the degree of polymerization is defined as the number of repeat units in the polymer chain corresponding to molecular weight and length of the polymer, therefore the turning extension of polymerization degree is strongly related to time in a polymerization reaction. The polymerization of PolyDHN-TMTA (DHN:TMTA =1:1) within different reaction times (80 min, 180 min, 300 min and 24 hrs) was carried out at 20 °C before being drop-casted on INHs thin film, and keeping dry at 20 °C for 24 hrs (Figure. 4-12).

PolyDHN-TMTA alone showed no chiroptical properties as shown in Figure. 4-13. Meanwhile, PolyDHN-TMTA/INHs showed both symmetrical CD (in TCD) and CPL signals for LH- and RH-INHs, which implied that the INHs played a crucial role in endowing chiroptical properties. During the polymerization time (80 min to 24 hrs), CD spectra of PolyDHN-TMTA/INHs for both LH and RH INHs obviously turned (from sharp peak at 80 min to boarded peak at 24 hrs), which was in agreement with a change in absorbance. Additionally, CPL signal of PolyDHN-TMTA/INHs shifted to a longer wavelength during polymerization time, which corresponded to a shift in fluorescent emission. The obvious change of PolyDHN-TMTA/INHs was clearly observed after polymerization for 24 hrs compared to DHN/INHs. These changes in CD and CPL signals (80 min to 24 hrs) could be proposed that the different reaction times had an impact on the chain extensions of PolyDHN-TMTA, which influenced the chirality induction using the INHs nano-template using drop-casting method.

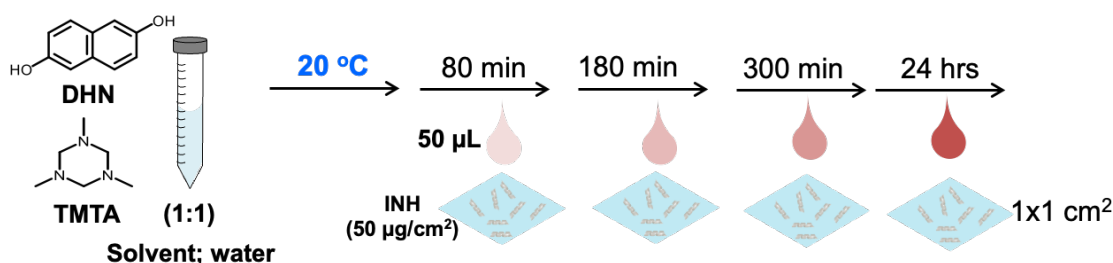


Figure. 4-12 Sample preparation of PolyDHN-TMTA/INHs within 80 min, 180 min, 300 min and 24 hrs via drop-casting method, (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 20 °C)

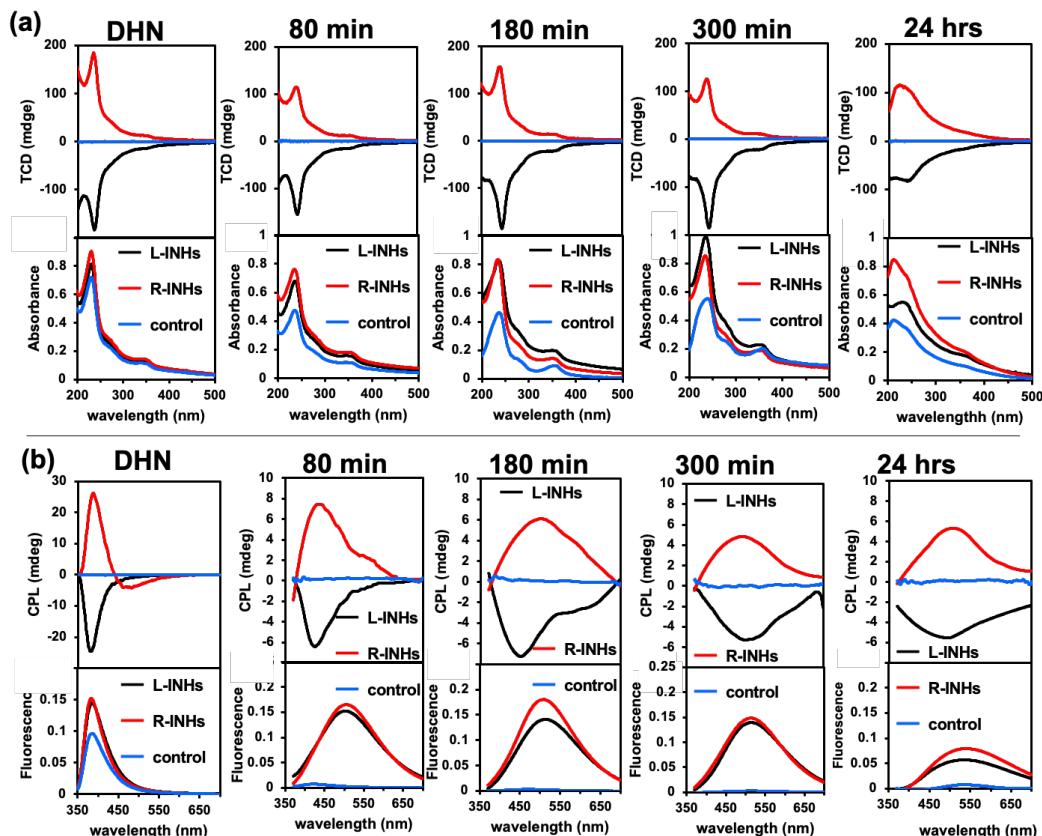


Figure. 4-13 TCD (a) and CPL, λ_{ex} 300 nm (b) of DHN/INHs and PolyDHN-TMTA/INHs within 80 min, 180 min, 300 min and 24 hrs, reaction temperature 20 °C, (100 μL PolyDHN-TMTA on INHs 100 $\mu\text{g}/1 \times 1 \text{ cm}^2$),

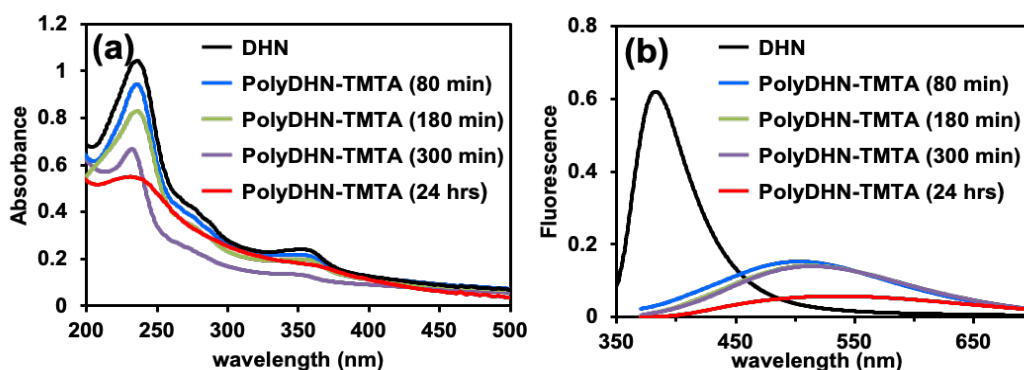


Figure. 4-14 Comparison absorbance (a) and fluorescence, λ_{ex} 300 nm (b) of DHN/INHs and PolyDHN-TMTA/INHs within 80 min, 180 min, 300 min and 24 hrs, reaction temperature 20 °C, (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H_2O (8.0 mL), 20 °C)

Besides the effect of reaction time on chirality induction, one of the important parameters dealing with polymerization kinetics is temperature as an increase in temperature will increase the polymerization rate.³⁰ Therefore, the polymerization reaction in H₂O between DHN and TMTA (DHN:TMTA =1:1) was studied at 60 °C compared to the polymerization reaction at 20 °C (Figure. 4-15). It showed that the CD and CPL signals of PolyDHN-TMTA/INHs were obviously different compared to DHN/INHs after a reaction time of 80 min, which was more rapid than the polymerization reaction at 20 °C. Thus, the reaction at a higher temperature (60 °C) could speed up the polymerization rate to synthesize achiral PolyDHN-TMTA before drop-casting on INHs thin film.

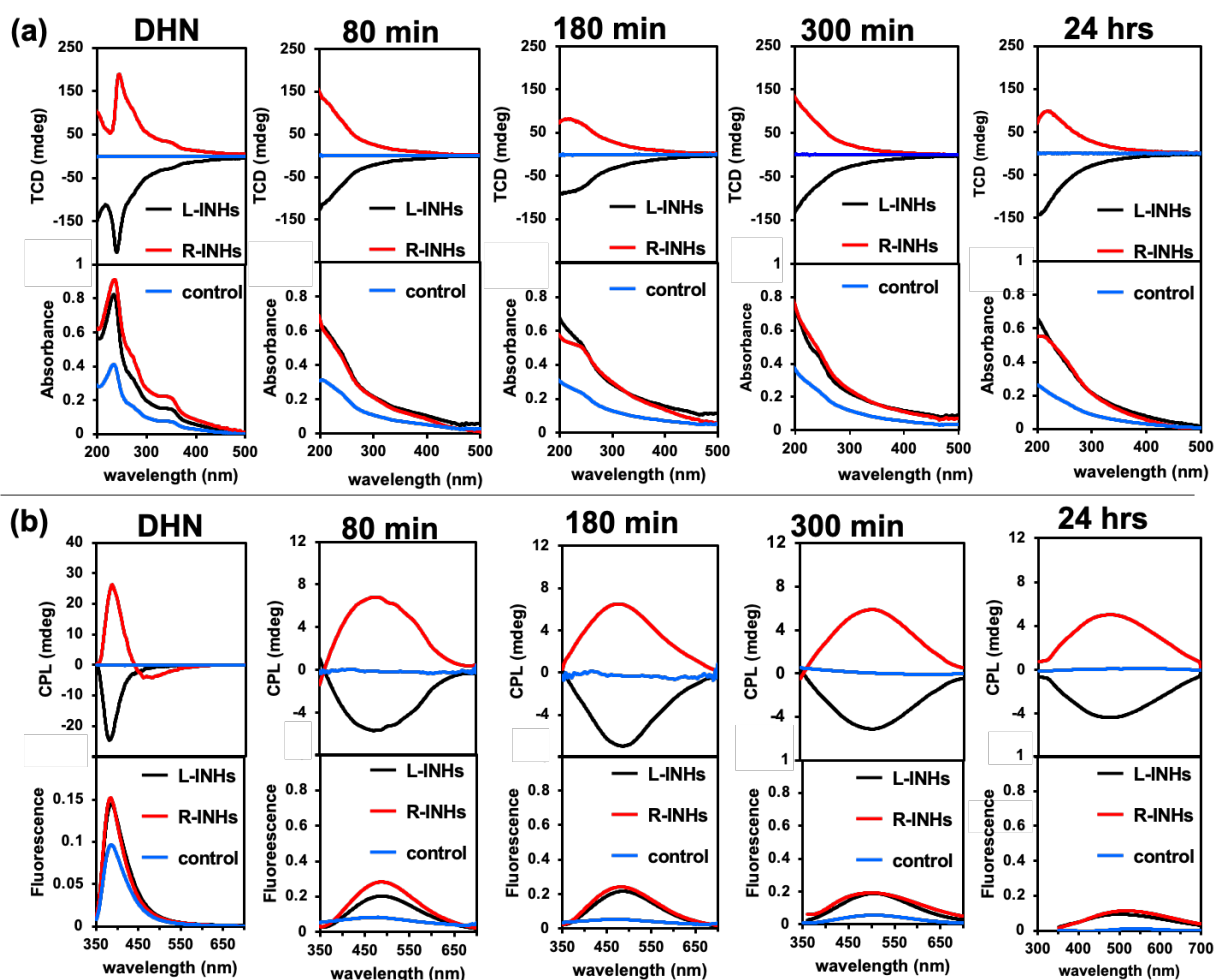


Figure. 4-15 TCD and CPL (λ_{ex} 300 nm) of DHN/INHs and PolyDHN-TMTA/INHs within 80 min, 180 min, 300 min and 24 hrs, reaction temperature 60 °C, (100 μ L PolyDHN-TMTA on INHs 100 μ g/1x1 cm²),

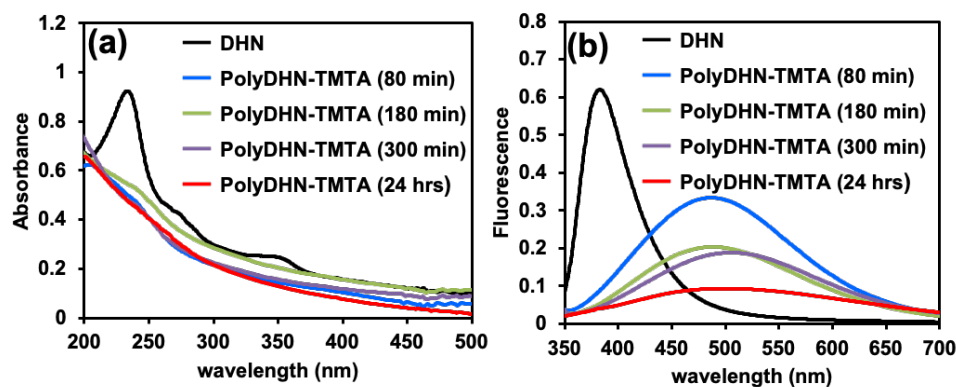


Figure. 4-16 Comparison of absorbance (a) and fluorescence spectra, λ_{ex} 300 nm (b) of DHN/INHs and PolyDHN-TMTA/INHs at different reaction times (80 min, 180 min, 300 min, 24 hrs), reaction time 60 °C, (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 60 °C)

Owing to the drop-casting method for chirality induction of achiral PolyDHN-TMTA, the temperature effect for drop-casting was investigated by variation at 20 °C, 40 °C, 60 °C and 80 °C (Figure. 4-17). It was found that the g_{abs} in DRCD decreased as the temperature for drop-casting increased in Figure. 4-17c, as PolyDHN-TMTA/INHs at 80 °C showed the lowest dissymmetry factor while PolyDHN-TMTA/INHs at 20 °C showed the highest in chirality. Therefore, these suggested that the chirality induction based on a drop-casting method was significantly influenced by temperature.

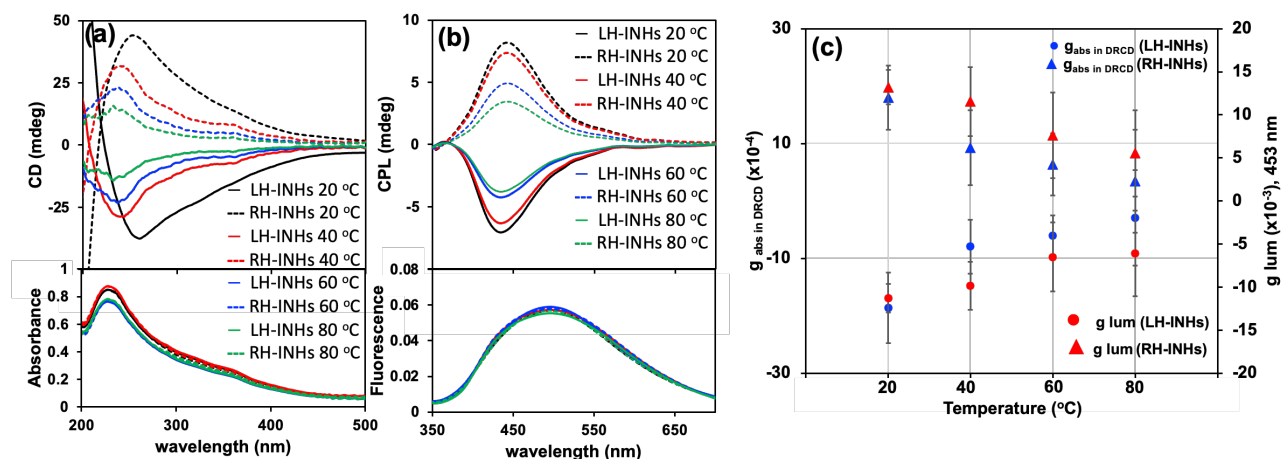


Figure. 4-17 CD-absorption (a), CPL-fluorescent, λ_{ex} 300 nm (b) spectra and g_{abs} in DRCD/ g_{lum} of PolyDHN-TMTA/INHs using drop-casting at different temperatures (20 °C, 40 °C, 60 °C, 80 °C).

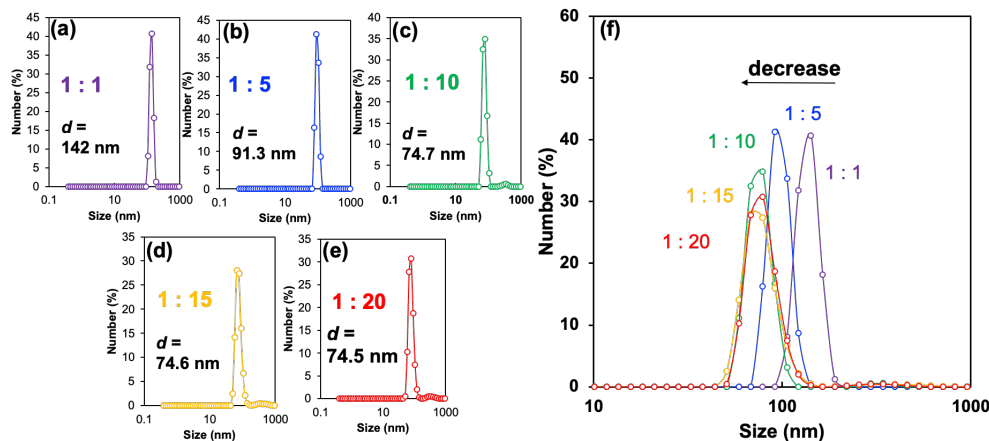


Figure. 4-18 DLS spectra of PolyDHN-TMTA with the different ratios of DHN:TMTA (reaction temperature 20 °C, 24 hrs)

Previously, it was reported that the size of PolyDHN-TMTA NPs could be controlled by the ratio between DHN monomer and TMTA crosslinker. The maximum size of polymer NPs was obtained by polymerization at an equivalence of DHN and TMTA (1:1), meanwhile the particle size decreased when DHN/TMTA ratio deviated from equivalence.²⁴ Subsequently, we are interested in studying the chirality induction of PolyDHN-TMTA, which was synthesized by different ratios between DHN and TMTA. Besides PolyDHN-TMTA from DHN and TMTA (1:1), PolyDHN-TMTA prepared by different ratios of DHN:TMTA were carried out at 1:1, 1:5, 1:10, 1:15 and 1:20. The DLS spectra in Figure. 4-18 showed the sizes of PolyDHN-TMTA at 142, 91.3, 74.7, 74.6 and 74.5 nm by using DHN:TMTA at 1:1, 1:5, 1:10, 1:15 and 1:20, respectively, at 20 °C for 24 hrs. The 1:1 DHN:TMTA could fabricate the largest size of PolyDHN-TMTA, while the size decreased when the DHN:TMTA deviated to 1:5, 1:10, 1:15 and 1:20.

To endow the chiroptical properties, PolyDHN:TMTA with different ratios of DHN:TMTA was drop-casted on INHs thin film resulting in the symmetrical CD response in Figure. 4-19a. In addition, g_{abs} in DRCD showed a correlation with the ratio of DHN:TMTA, when the g_{abs} in DRCD increased as the DHN:TMTA increased (Figure. 4-19b). In the case of CPL response, PolyDHN-TMTA/INHs with different ratios of monomer:crosslinker clearly represented CPL signals in Figure. 4-20a, which observed the shift in CPL peak to short wavelength when the DHN/TMTA ratio increased (Figure. 4-20b). The g_{abs} in DRCD and CPL peaks were turned corresponding to the DHN:TMTA ratio, possibly suggesting that the size of polymers has an impact on chirality induction using INHs via a drop-casting approach.

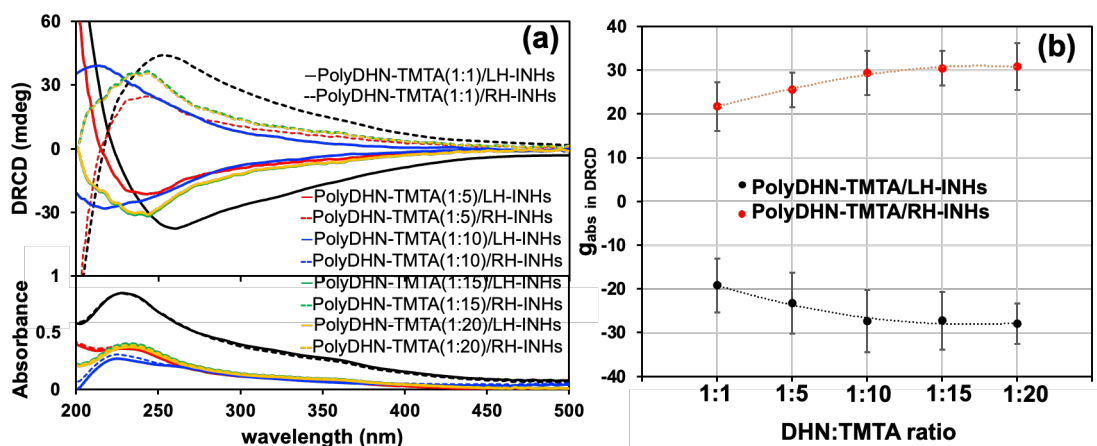


Figure. 4-19 (a) CD-absorption of PolyDHN-TMTA with the different ratios of DHN:TMTA, (b) the plot between g_{abs} in DRCD and DHN:TMTA ratio, (200 μ L PolyDHN-TMTA on INHs 200 μ g/2x2 cm^2)

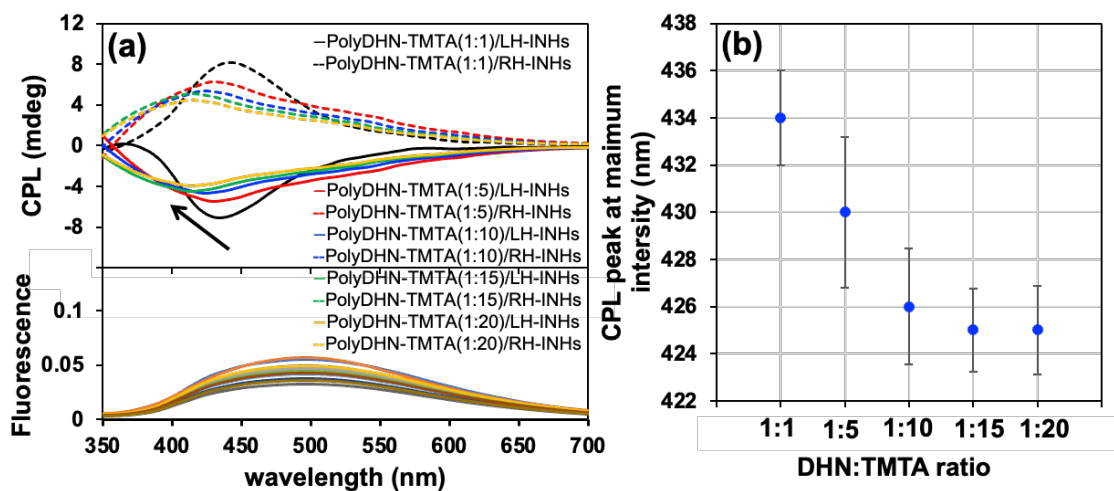


Figure. 4-20 (a) CPL-fluorescence, λ_{ex} 300 nm of PolyDHN-TMTA with the different ratios of DHN:TMTA, (b) the plot between CPL peak at maximum intensity and DHN:TMTA ratio, (200 μ L PolyDHN-TMTA on INHs 200 μ g/2x2 cm^2)

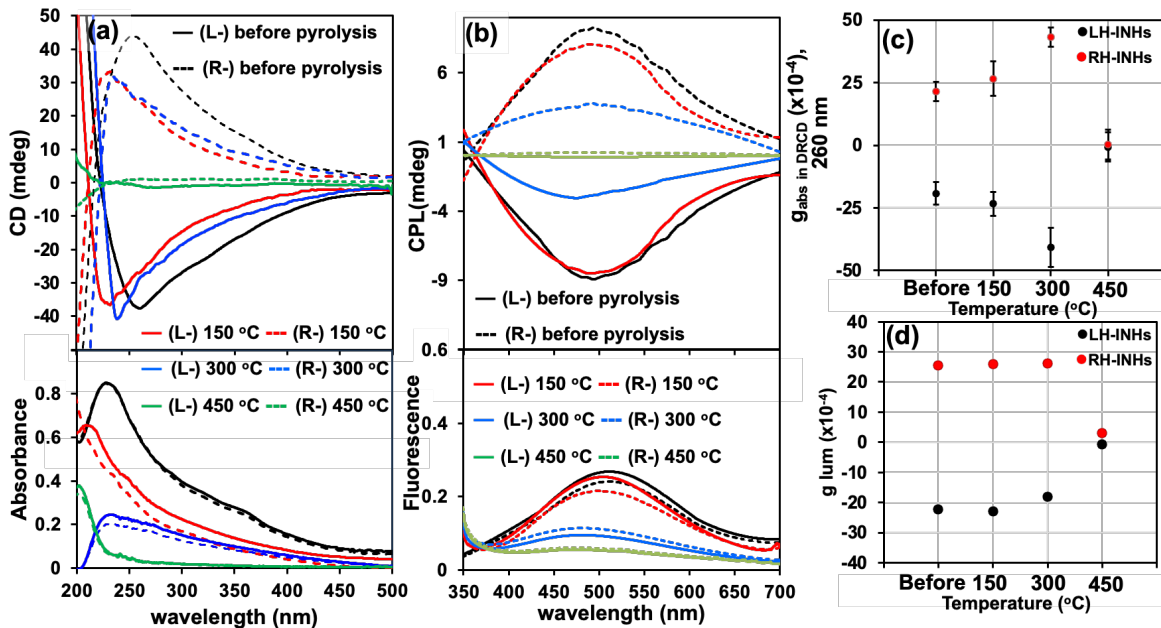


Figure. 4-21 DRCD-absorbance (a), CPL-fluorescence (λ_{ex} 300 nm) spectra (b), $g_{\text{abs in DRCD}}$ (c) and g_{lum} (f) of PolyDHN-TMTA before and after pyrolysis at 150, 300, 450 °C. (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 20 °C), (200 μ L PolyDHN-TMTA on INHs 200 μ g/2x2 cm²)

In general, polymers structurally contain amorphous and crystalline phase. The amorphous region could be refined where molecules arrange randomly while the crystalline region indicates a specific periodic pattern of polymer arrangement.³¹ In addition, it is obvious that thermal treatment has a strong impact on the structural arrangement of polymers. To know more information, the thermal treatment of PolyDHN-TMTA/INHs was investigated by pyrolysis at different temperatures (150 °C, 300 °C, 450 °C) under a nitrogen atmosphere in Figure. 4-21. Surprisingly, it could be observed that PolyDHN-TMTA/INHs after pyrolysis at 300 °C showed the highest $g_{\text{abs in DRCD}}$, as shown in Figure. 4-21c, while g_{lum} did not turn significantly related to temperature (Figure. 4-21d). Due to the highest $g_{\text{abs in DRCD}}$, PolyDHN-TMTA/INHs after pyrolysis at 300 °C were further characterized by DRIFT. It showed the bands at $\nu_{\text{O-H}}$ (3060 cm⁻¹), $\nu_{\text{C=C}}$ (1720 cm⁻¹ and 1605 cm⁻¹), $\nu_{\text{C-N}}$ (1229 cm⁻¹) and $\nu_{\text{C-O}}$ (752 cm⁻¹), as shown in Figure. 4-22a, compared to their DRIFT of PolyDHN-TMTA before thermal treatment. PolyDHN-TMTA/INHs after pyrolysis at 300 °C showed an obvious difference in DRIFT spectra, indicating that their molecular vibration of PolyDHN-TMTA was influenced by pyrolysis process. In addition, Raman spectra of

PolyDHN-TMTA in Figure. 4-22b showed G and D bands which were assigned to in-plane vibration of sp^2 carbon network and out-of-plane vibrations by structural defects, respectively.³² In addition, XPS analysis showed the elemental contents of C (80.16%), N (1.23%), and O (18.26%) with N/C $\sim$ 0.015. The high-resolution C1s XPS spectra (Figure. 4-23a) revealed the C=C (284.3 eV, 17.00%), C-C (284.9 eV, 31.62%), C-OH (285.3 eV, 15.51%), C-O-C (286.4 eV, 18.77%), C=O (287.4 eV, 4.94%), O-C=O (288.5 eV, 5.53%), C=O-O (289.5 eV, 3.30%) and $\pi-\pi^*$ (291.3 eV, 3.33%). Thus, the sp^3/sp^2 ratio is $\sim$ 1.86, which is lower than PolyDHN-TMTA before pyrolysis ($\sim$ 2.52). As a result of a change in sp^3/sp^2 ratio and Raman spectrum, it therefore suggested that PolyDHN-TMTA generated the creation of fused-ring aromatic structure during the thermal treatment at 300 °C. Furthermore, the nitrogen proportion in N1s of PolyDHN-TMTA after pyrolysis at 300 °C (Figure. 4-23b) showed a notable change compared to that of before pyrolysis. The percentages of oxidized nitrogen (402.2 eV) and graphitic nitrogen (401.2 eV) declined significantly from 28.78% to 8.03% and 16.90% to 8.71%, respectively. While the percentages of pyridinic nitrogen (398.8 eV) and pyrrolic nitrogen (400.1 eV) increased from 24.12% to 38.85% and 30.20% to 44.41%, respectively. These results indicated the transformation of the chemical structure of PolyDHN-TMTA by losing NO_3^- , NO_2^- , NO and graphitic nitrogen.

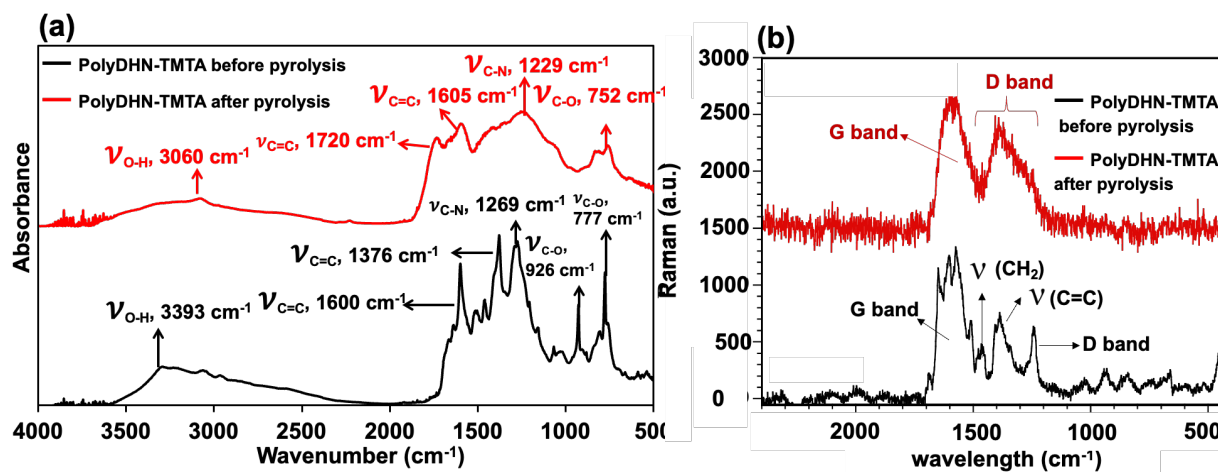


Figure. 4-22 DRIFT (a) and Raman spectra (b) of PolyDHN-TMTA before and after pyrolysis at 300 °, (PolyDHN-TMTA prepared by DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 20 °C)

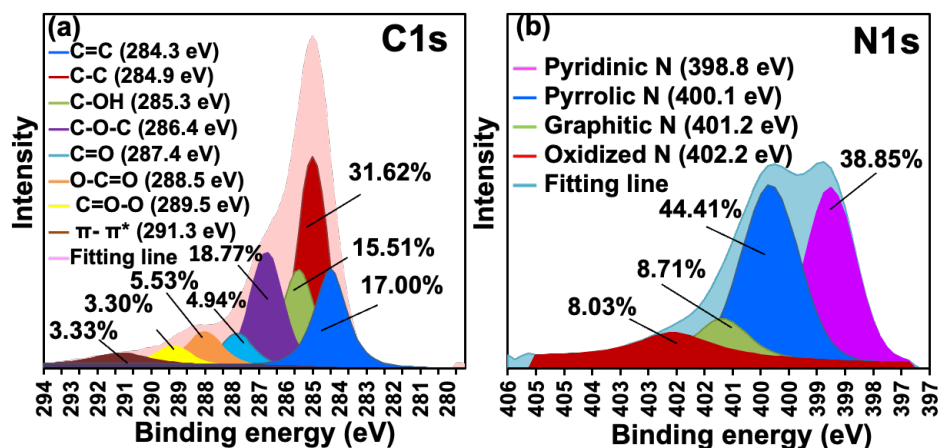


Figure. 4-23 HR-XPS C1s (a) and N1s (b) spectra of PolyDHN-TMTA after pyrolysis at 300 °C, (PolyDHN-TMTA prepared by The DHN solution (2.5 mM, 1.0 mL), TMTA solution (2.5 mM, 1.0 mL) and H₂O (8.0 mL), 20 °C)

Table. 4-1 sp²/sp³ carbon content (%) of polyDHN-TMTA before and after pyrolysis at 300 °C

	sp ²	sp ³	sp ³ /sp ² (%)
Before pyrolysis at 300 °C	13.50	33.87	2.51
After pyrolysis at 300 °C	17.00	31.62	1.86

4.2.2 *In-situ* synthesis of chiral PolyDHN-TMTA using INHs.

Beyond *ex-situ* synthesis, we attempted to address the *in-situ* synthesis of PolyDHN-TMTA with chiroptical properties using silica nanohelices. The *in-situ* synthesis of PolyDHN-TMTA was carried out by three different methods, as shown in Figure. 4-4. In method I, DHN monomer was firstly drop-casted on INHs and followed by drop-casting TMTA crosslinker. Meanwhile, method II was started by introducing TMTA crosslinker on INHs before adding DHN monomer. In the case of method III, it was carried out by drop-casting of the DHN:TMTA mixture before adding H₂O as a medium to continue the polymerization reaction.

For the *in-situ* (method I) synthesis of chiral PolyDHN-TMTA, DHN monomer was firstly drop-casted on the INHs thin film. Therefore, the optimized ratio between DHN and INHs was studied by the variation of DHN concentration (0.25-3.5 mM, 400 μL) to 200 μg INHs (on a substrate 2x2 cm²) in Figure. 4-24a. DHN/LH-INHs and DHN/RH-INHs showed negative and

positive CD signals, respectively. Meanwhile, the absorbance of DHN molecule as a function of concentration is shown in Figure. 4-24c.

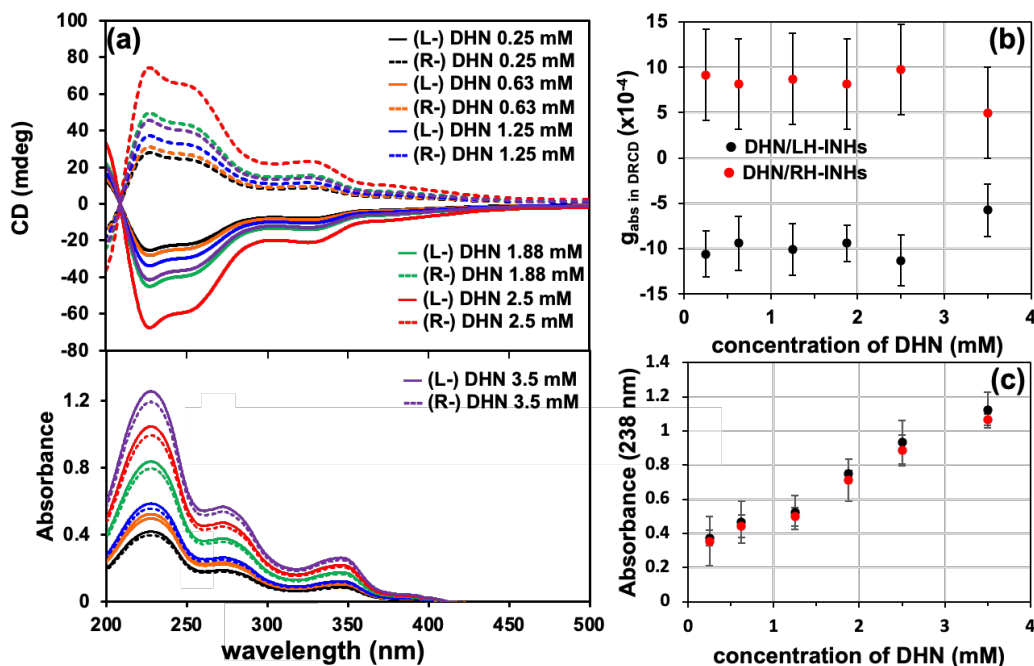


Figure. 4-24 (a) DRCD-absorption spectra of DHN/INHs (DHN; 0.25-3.5 mM, 400 μ L, on INHs 200 μ g in 2x2 cm²), (b) the plot between absorbance and DHN concentration (0.25-3.5 mM), (c) the plot between g_{abs} in DRCD and DHN concentration (0.25-3.5 mM).

The g_{abs} in DRCD of 3.5 mM DHN showed the lowest value which was explained by an excess DHN molecule on INHs, it increased to around $\pm 1.0 \times 10^{-4}$ for the lower concentration of DHN 0.25-2.5 mM. CPL spectra of 0.25 mM and 2.5 mM DHN/INHs were measured as shown in Figure. 4-25. While DHN/INHs at 2.5 mM expressed both high g_{abs} in DRCD and g_{lum} , 0.25 mM DHN showed no CPL signals which is likely due to the absence of stacking effect of the fluorophore.³³ Subsequently, 2.5 mM DHN (400 μ L) was chosen as the most optimized ratio for the 200 μ g INHs on a substrate (2x2 cm²).

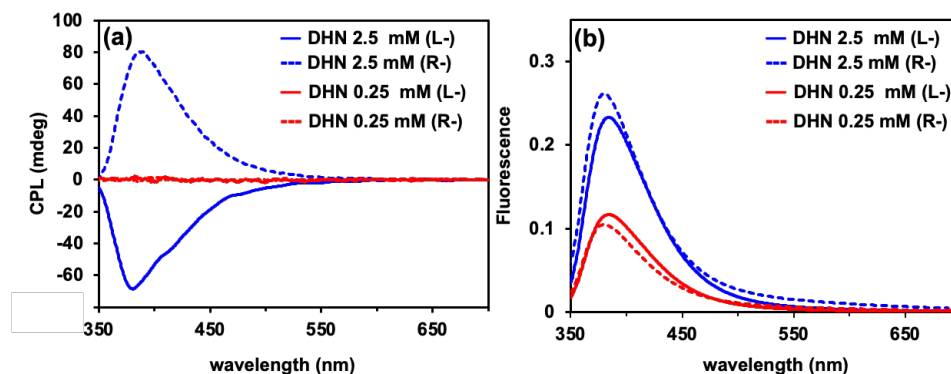


Figure. 4-25 (a) CPL and (b) fluorescent spectra of DHN/INHs (0.25 mM and 2.5mM), λ_{ex} 300 nm.

The next step was to add the TMTA crosslinker to induce polymerization on a substrate containing DHN/INHs thin film. TMTA was drop-casted on DHN/INHs in equivalence of DHN (1:1) to continue polymerization at 4 °C for 3 days. After that, samples were dried at 20 °C for 24 hrs to obtain PolyDHN-TMTA/INHs. The obvious change in CD and CPL spectra could be observed in Figure. 4-26, CD signal peaks at 238 nm decreased significantly compared to DHN/INHs while CPL signals shifted to longer wavelength after 24-hrs polymerization. Furthermore, the absorption of PolyDHN-TMTA/INHs was clearly changed compared to DHN/INHs, as the absorption at 228 nm decreased significantly with expressing a new peak of 357 nm. The obtained PolyDHN-TMTA/INHs showed two main fluorescent peaks at 387 and 475 nm, revealing the remaining DHN monomer and the formation of PolyDHN-TMTA, respectively. Thus, the *in-situ* polymerization (method I) could fabricate PolyDHN-TMTA with chiroptical properties but the polymerization was not completely finished corresponding to the fluorescent peak of DHN monomer at 387 nm. The reason to explain this incomplete polymerization by *in-situ* method I was the dominance of crystallinity in DHN monomer in INHs system.

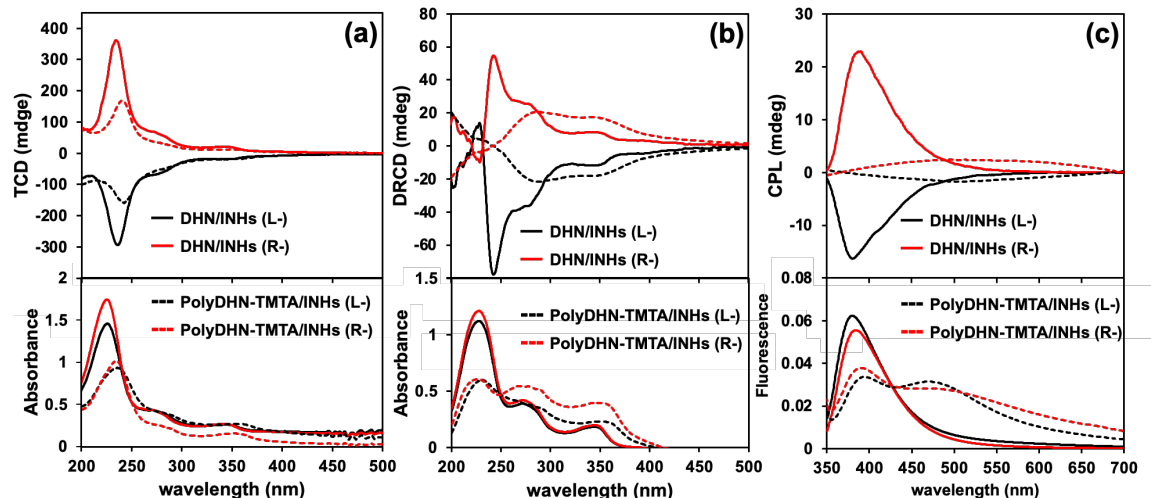


Figure. 4-26 (a) TCD-absorption, (b) DRCD-absorption, and (c) CPL-fluorescent spectra (λ_{ex} 300 nm) of DHN/INHs and PolyDHN-TMTA/INHs by *in-situ* synthesis method I (DHN:TMTA ratio = 1:1), (DHN 2.5 mM (400 μ L), TMTA 2.5 mM (400 μ L), INHs 200 μ g).

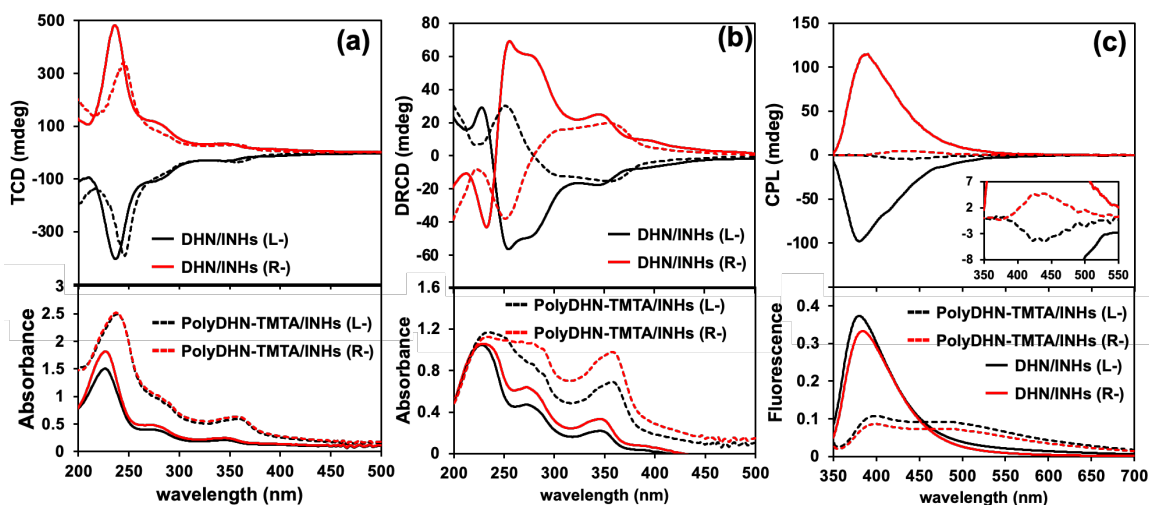


Figure. 4-27 (a) TCD-absorption, (b) DRCD-absorption, and (c) CPL-fluorescent (λ_{ex} 300 nm) spectra of DHN/INHs and PolyDHN-TMTA/INHs by *in-situ* synthesis method I (DHN:TMTA ratio = 1:10), (DHN 2.5 mM (400 μ L), TMTA 25 mM (400 μ L), INHs 200 μ g)

Due to the incomplete polymerization of *in-situ* synthesis (method I), we attempted to tackle this problem by changing the ratio between monomer and crosslinker. The DHN:TMTA ratio was adjusted to 1:10 in order to complete the polymerization of PolyDHN-TMTA. The results of *in-situ* synthesis (method I) in the ratio DHN:TMTA (1:10) were observed in Figure. 4-28, the CD and CPL signals were turned after polymerization however it was still observed the florescent peak of DHN monomer. Surprisingly, the shift in CPL peaks was clearly observed when PolyDHN-TMTA was fabricated by a difference in DHN/TMTA ratio (1:1 and 1:10) in Figure. 4-28b. The CPL peaks of PolyDHN-TMTA/INHs 1:10 shifted to a longer wavelength compared to PolyDHN-TMTA 1:1, which could originate from the different sizes of PolyDHN-TMTA synthesizing by the different ratios of DHN/TMTA.²⁴ Furthermore, the *in-situ* polymerization of chiral polymer based on chiral INH was carried out at a higher temperature (20 °C) instead of 4 °C (Figure. 4-29) in order to enhance the polymerization speed. However, it could be found that the polymerization was still not finished followed by the remaining emissive peak of DHN monomer at 387 nm.

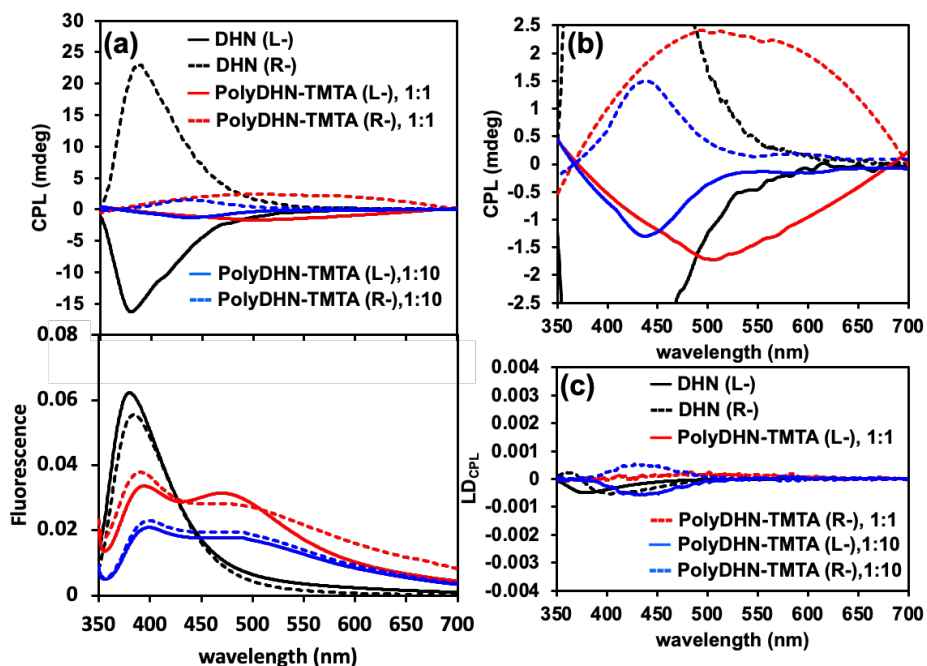


Figure. 4-28 (a,b) CPL, λ_{ex} 300 nm and (b) LD_{CPL} spectra of DHN/INHs and PolyDHN-TMTA/INHs by *in-situ* synthesis method I, (DHN:TMTA ratio = 1:10).

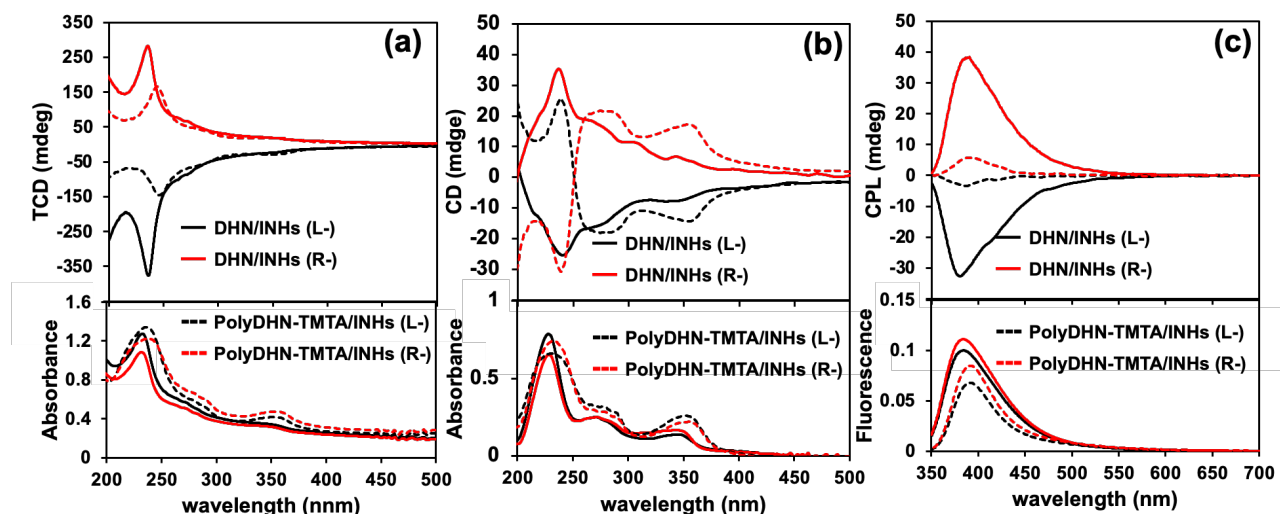


Figure. 4-29 TCD-absorption, (b) DRCD-absorption, and (c) CPL-fluorescent (λ_{ex} 300 nm) spectra of DHN/INHs and PolyDHN-TMTA/INHs by *in-situ* synthesis method I (DHN:TMTA ratio = 1:10), reaction at 20 °C, (DHN 2.5 mM (400 μ L), TMTA 2.5 mM (400 μ L), INHs 200 μ g)

The second approach for *in-situ* synthesis of PolyDHN-TMTA/INHs was carried out by firstly drop-casted TMTA and dried at 20 °C for 24 hrs. Then, DHN monomer was then drop-casted to react with crosslinker on TMTA/INHs at 4 °C for 3 days before drying at 20 °C for 24 hrs. CD and absorption spectra of TMTA/INHs were measured as shown in Figures. 4-30a and 4-30b, Then, DHN monomer was drop-casted on TMTA/INHs resulting in an absorption peak of DHN, however there were no symmetric CPL signals (Figure. 4-30c) with fluorescent emission at 387 nm. It is likely that there was no polymerization by using *in-situ* polymerization (method II).

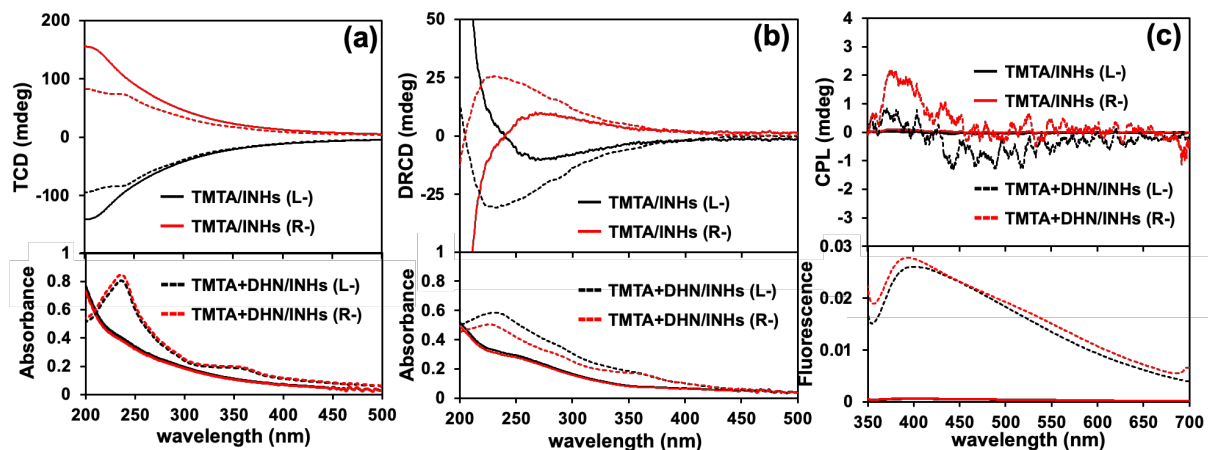


Figure. 4-30 TCD-absorption, (b) DRCD-absorption, and (c) CPL-fluorescent (λ_{ex} 300 nm) spectra of TMTA/INHs and PolyDHN-TMTA/INHs by *in-situ* synthesis method II (DHN:TMTA ratio = 1:1), (DHN 2.5 mM (400 μL), TMTA 2.5 mM (400 μL), INHs 200 μg)

Apart from *in-situ* methods I and II, the *in-situ* synthesis of PolyDHN-TMTA (method III) was investigated by mixing of DHN and TMTA before drop-casting on a chiral INHs template. The mixture of DHN and TMTA (1:1) was prepared in water to ensure good mixing and drop-casted on INHs thin film. Then, the polymerization reaction was monitored by introducing water as a medium. Therefore, H_2O (500 μL) was added on and kept at 4 $^{\circ}\text{C}$ for 3 days before drying at 20 $^{\circ}\text{C}$ for 24 hrs. The CD and CPL of PolyDHN-TMTA/INHs by *in-situ* polymerization (method III) were shown in Figure. 4-31, CD and CPL spectra were clearly different before and after polymerization suggesting the complete polymerization of PolyDHN-TMTA.

In a comparison of *ex-situ* and *in-situ* synthesis in Figure. 4-32, both methods could fabricate PolyDHN-TMTA with symmetrical CD and CPL signals, however they showed the difference in CD and CPL peaks. PolyDHN-TMTA/INHs by *ex-situ* method showed the maximum CD and CPL response at 260 and 432 nm, respectively. Meanwhile, PolyDHN-TMTA/INHs by *in-situ* method showed the highest CD and CPL responses at 350 and 420 nm. The g_{abs} in DRCD and g_{lum} of *ex-situ* synthesis were higher than that of *in-situ* approach in a wavelength of 200-500 nm, these results suggested that the *ex-situ* method is more effective in synthesizing optical active PolyDHN-TMTA.

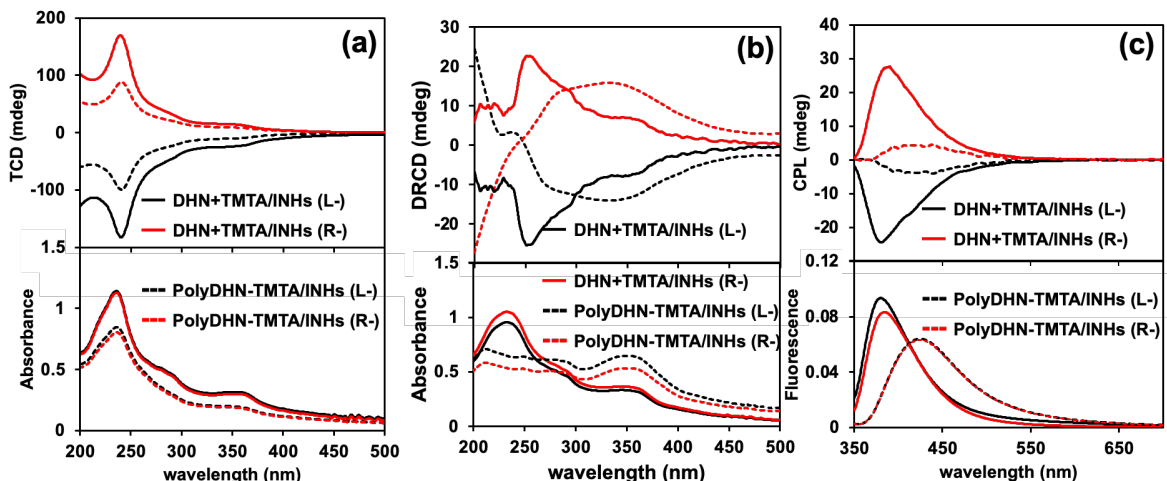


Figure. 4-31 (a) TCD-absorption, (b) DRCD-absorption, and (c) CPL-fluorescent (λ_{ex} 300 nm) spectra of DHN+TMTA/INHs and PolyDHN-TMTA/INHs by *in-situ* synthesis method III (DHN:TMTA ratio = 1:1).

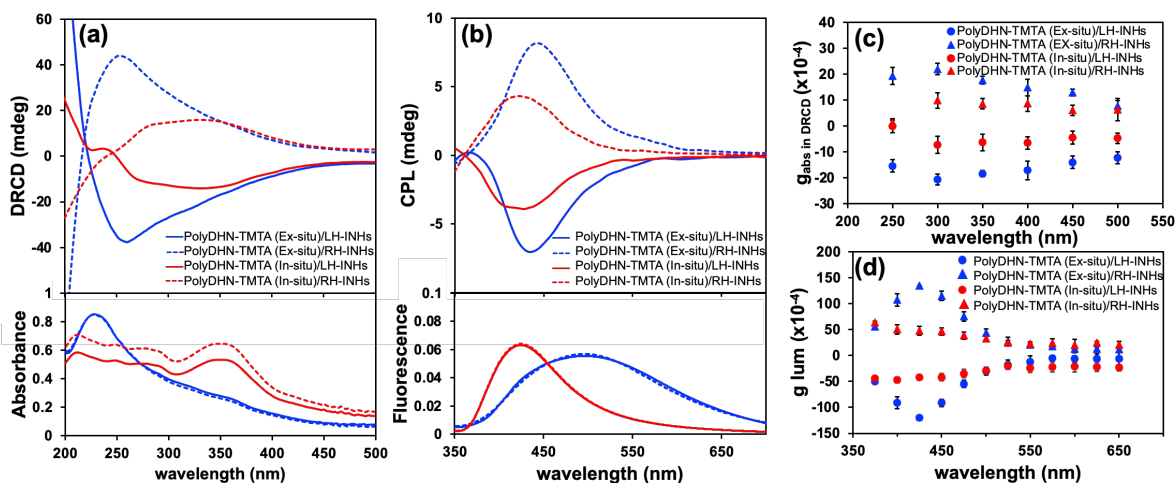


Figure. 4-32 (a) DRCD-absorption, and (b) CPL-fluorescence (λ_{ex} 300 nm) spectra of PolyDHN-TMTA by *in-situ* (method III) and *ex-situ* synthesis.

4.3 Conclusion

In conclusion, we have developed new approaches to endow chiroptical properties to achiral emissive polymer (PolyDHN-TMTA) by using silica inorganic nanohelices as a chiral nano-template. Chiral PolyDHN-TMTA was fabricated using INHs as chiral platform through two *ex-situ* and *in-situ* methods. The *ex-situ* method could fabricate PolyDHN-TMTA with strong CD and CPL signal (dissymmetric factor $\sim 10^{-3}$). It was found that the monomer/crosslinker ratio and the temperature for polymerization had an impact on chirality induction using silica nanohelices. The chiral property of PolyDHN-TMTA was enhanced after pyrolyzing at 300 °C under a nitrogen atmosphere, along with the decreasing sp^3/sp^2 ratio and oxidized-nitrogen percentage. We also investigated the effect of using the INHs not only as chiral inducer but chiral reactor, i.e. let the polymerization reaction occur inside the INHs. The *in-situ* polymerization was divided into three methods. It was observed that *in-situ* method III (prior mixing of the monomers and crosslinker before introducing them inside INHs to let polymerise inside) could generate a complete polymerization of PolyDHN-TMTA with symmetrical CD and CPL signals. However, the g_{abs} and g_{lum} from *in-situ* synthesis was lower than *ex-situ* approach.

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Chapter 5

Enantiomeric enrichment of racemic foldamers using silica nanohelices

Helical morphology DNA and peptide secondary¹ and tertiary structures² have been mimicked to build artificial chiral foldamers or polymers³ for example to develop therapeutic agents.⁴ Among which, the use of aromatic oligoamide foldamers has shown considerable development,^{5, 6} the mechanism of their folding in multiturn helical foldamers relies on backbone rigidity due to local electrostatic repulsion and hydrogen bonding between adjacent units, as well as intramolecular aromatic stacking. The aryl-amide bond rotation is restricted by specific attractive-repulsive interaction between amide and other functional groups at the ortho-position of aryl.⁷ Helical folding is governed by a combination of monomer shape, rigidity, and attractive and repulsive interactions.⁸ When synthesized from achiral monomers, they exhibit in an equilibrium between the left (*M*)- and right (*P*)-handed enantiomers, therefore showing no detectable chiroptical activity. The equilibrium bias of one-handed preference in helicity has been studied by appending chiral motifs at the end of foldamers,^{9, 10} binding chiral guests in helical cavities,¹¹ or inserting the chiral unit into the middle of folded sequences.¹² The efficiency for controlling the helical one-handed foldamers greatly impacts their applications in asymmetric catalysis¹³, photocatalysts¹⁴ and circularly polarized luminescence (CPL) laser.¹⁵

Quinoline-derived δ -amino acid (Q_n) was designed as helical oligomers with substituents oriented at 60°. ¹⁶ The intramolecular hydrogen bonding between the amide hydrogen and adjacent quinoline nitrogen could stabilize a bent and form a helix. Previously, Huc I. and co-workers demonstrated¹⁰ the control of the helical handedness of quinoline-derived aromatic oligoamide foldamers by their functionalization with chiral camphanyl moiety. The helical bias of right-handedness foldamers (de > 99%) was achieved by introducing (1*S*)-(-) camphanyl moiety at the N-terminus of helical oligomers. Furthermore, they found that incomplete chiral induction was influenced by the steric effect of chiral inducers at the N-terminus.¹⁷ Recently, Zheng D. and co-workers⁹ reported the absolute control helicity of quinoline oligoamide foldamers by attaching *S*- or *R*-oxazolylaniline enantiomers, resulting in CD and CPL signals with emission dissymmetry factors (g_{lum}) up to 0.038. In addition, they reported that their CD signal $|\Delta\epsilon|$ increased linearly

with the increase in the number of quinoline units. Consequently, $|\lg_{\text{abs}}| = \Delta\epsilon/\epsilon$ increased with the increasing foldamer length.

In this research, the effect of the chiral environment of helical silica nanostructure on the chirality of aromatic oligoamide foldamers was studied. After the preparation of a thin film of INHs as described in the previous chapters.¹⁸ The racemic oligoamide foldamers were drop-casted on the film, as shown in Figure. 5-1. The CD and CPL responses were measured with two azimuth angles (0° and 90°) and accumulated to obtain an average signal. The LD was also measured at two angles at 0° and 90° to minimize the LD effect.

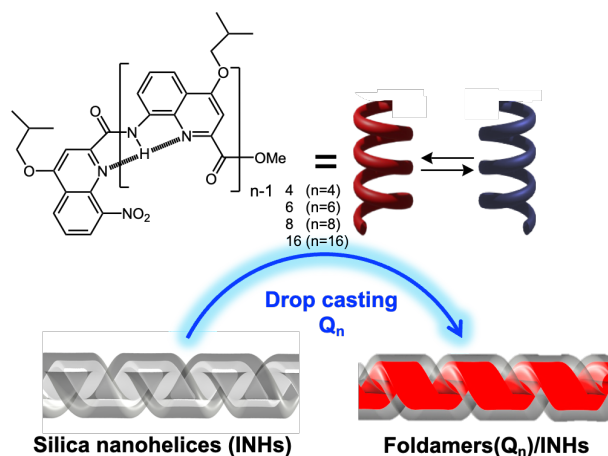


Figure. 5-1 Illustration of Enantiomeric enrichment of racemic foldamers using INHs.

5.1 Experimental section

5.1.1 Preparation of inorganic silica nanohelices (INHs)

Synthesis of gemini tartrate, preparation of helical silica nanohelices (INHs) and the preparation of a thin film by INHs are described in previous chapters.

5.1.2 Drop casting oligoamide foldamers (Q_n) on INHs

INHs (200 μg) in ETOH/iso-propanol was deposited on a quartz substrate ($2 \times 2 \text{ cm}^2$) by using a drop-casting method. Meanwhile, racemic foldamers (Q_n) was synthesized by BISE group (CBMN, university of Bordeaux) under supervision of Prof. Yann Ferrand.¹⁶ Then, 100 μL of 1.0 mM Q_n was drop-casted on a substrate containing INHs (200 μg) before drying at 20°C for 24 hrs.

5.1.3 Study on solvent effect for drop-casting of Q₄ on INHs

Q₄ was prepared at 1 mM by using different solvent including benzene, toluene, chlorobenzene, chlorotoluene, aniline and nitrobenzene. Then, Q₄ (1 mM, 100 μ L) was drop-casted on a substrate (2x2 cm²) containing INHs (200 μ g) before drying at 20 °C for 24 hrs.

5.1.4 Kinetic study for enantiomeric enrichment of Q₄ using INHs

Q₄ was prepared at 1 mM by using different solvent including toluene, chlorobenzene and aniline. Then, Q₄ (0.75 mM, 30 μ L) was drop-casted on a substrate (2x2 cm²) containing INHs (200 μ g) before drying at 20 °C for 24 hrs.

5.1.5 Optimization of the ratio between Q₄ and INHs

Racemic Q₄ was prepared at different concentrations (0.25, 0.50, 0.75, and 1.0 mM) by using toluene as a solvent. Then, 100 μ L of Q₄ solution was drop-casted on a quartz substrate (2x2 cm²) containing 200 μ g INHs and subsequently dried at 20 °C for 24 hrs.

5.1.6 Enantiomeric enrichment of racemic foldamers with different length

Q₄, Q₆, Q₈ and Q₁₆ were prepared at 1.0 mM by using toluene or aniline as a solvent. Then, 100 μ L of Q₄ solution was drop-casted on a quartz substrate (2x2 cm²) containing 200 μ g INHs and subsequently dried at 20 °C for 24 hrs.

5.2 Results and discussion

5.2.1 Solvent effect for drop-casting of Q₄ foldamers on INHs

Solutions of racemic oligoamide foldamers (Q₄) at 1 mM in various solvents were drop-casted (100 μ L) on INHs films (200 μ g INHs on 2x2 cm² to obtain Q₄/INHs thin film and dried at 20 °C for 24 hrs.^{18, 19} Six different solvents including benzene, toluene, chlorobenzene, chlorotoluene, aniline and nitrobenzene were used to dissolve Q₄. The boiling points vapor pressures and surface tensions of the solvents are shown in Table 5-1. After drop-casting of racemic Q₄ on INHs, clear CD signals were observed in all solvents (Figures. 5-2 and 5-3) although the original foldamers were racemic.

Table 5-1 Solvents for dissolving Q₄ before drop casting.

Solvent	Boiling point (°C)	Vapor pressure at 20 °C (Pa)	Surface tension (mM/m)
Benzene	80.3	10130	28.9
Toluene	110.8	2932	28.52
Chlorobenzene	132	1200	33.60
Chlorotoluene	157	359	33.42
Aniline	184.4	40	42.9
Nitrobenzene	211.1	27	46.34

Reference; MIDSIS-TROCS 4.0, Maritime Integrated Decision Support Information System on transport of Chemical Substance. (<http://midsis.rempec.org>)

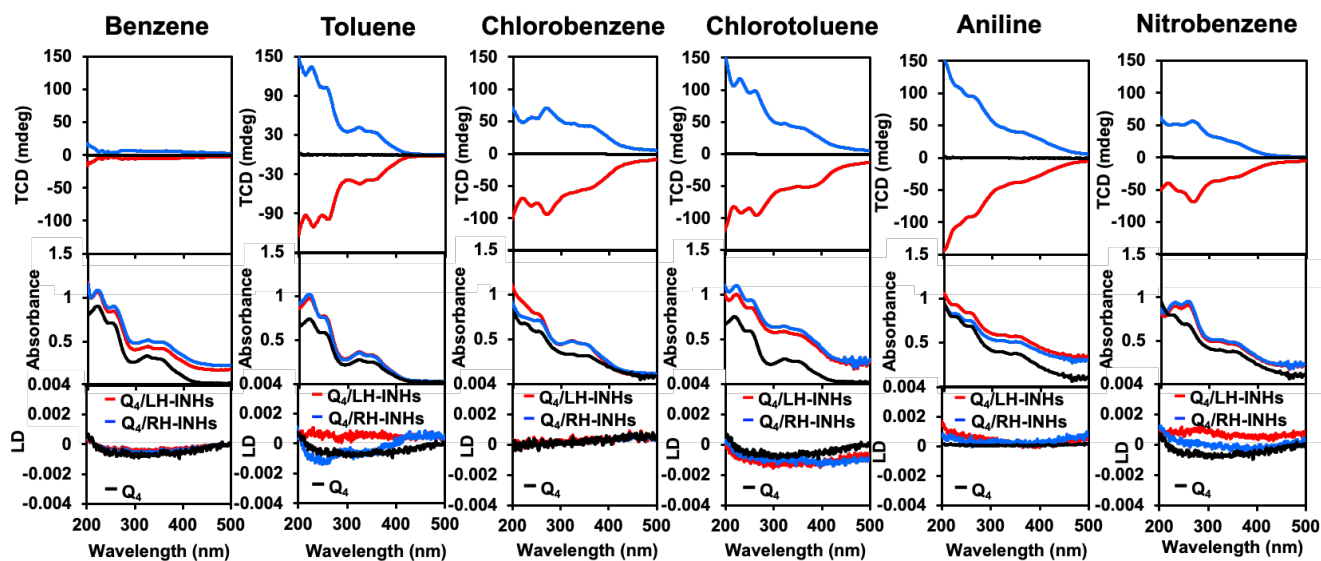


Figure. 5-2 TCD, Absorbance, and LD of Q₄/INHS by using different solvents for drop casting.

((Q₄ 1 mM, 100 μ L),(INHS 200 μ g/2x2 cm²))

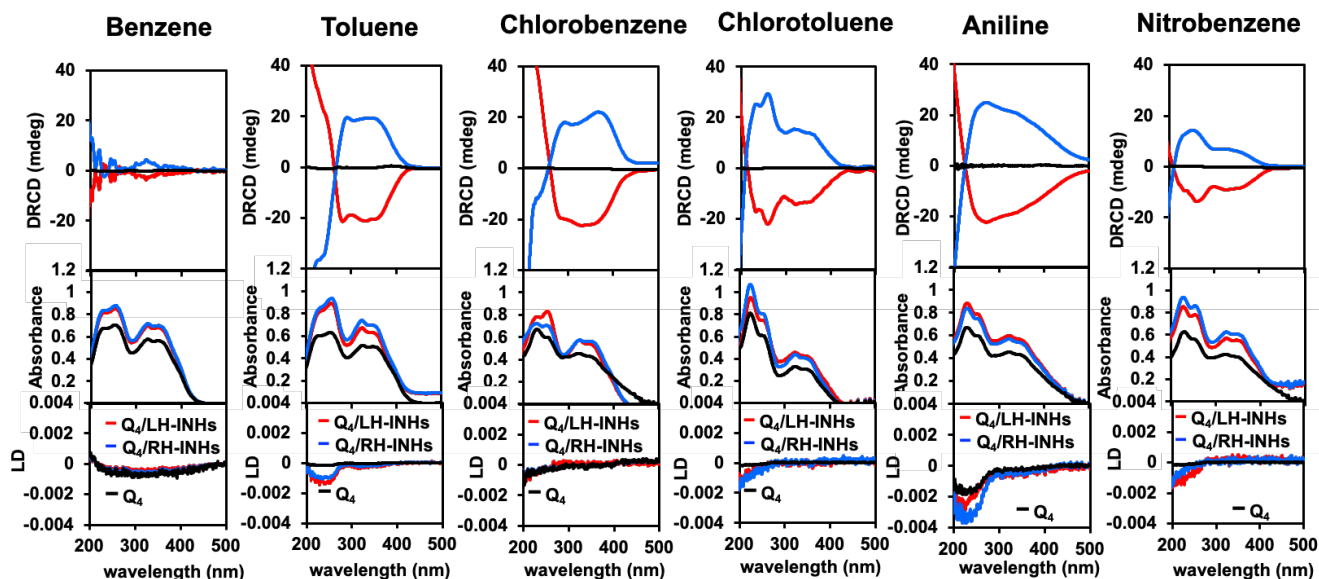


Figure. 5-3 DRCD, Absorbance, and LD of Q₄/INHs by using different solvents for drop casting.
 ((Q₄ 1 mM, 100 μ L),(INHs 200 μ g/2x2 cm²))

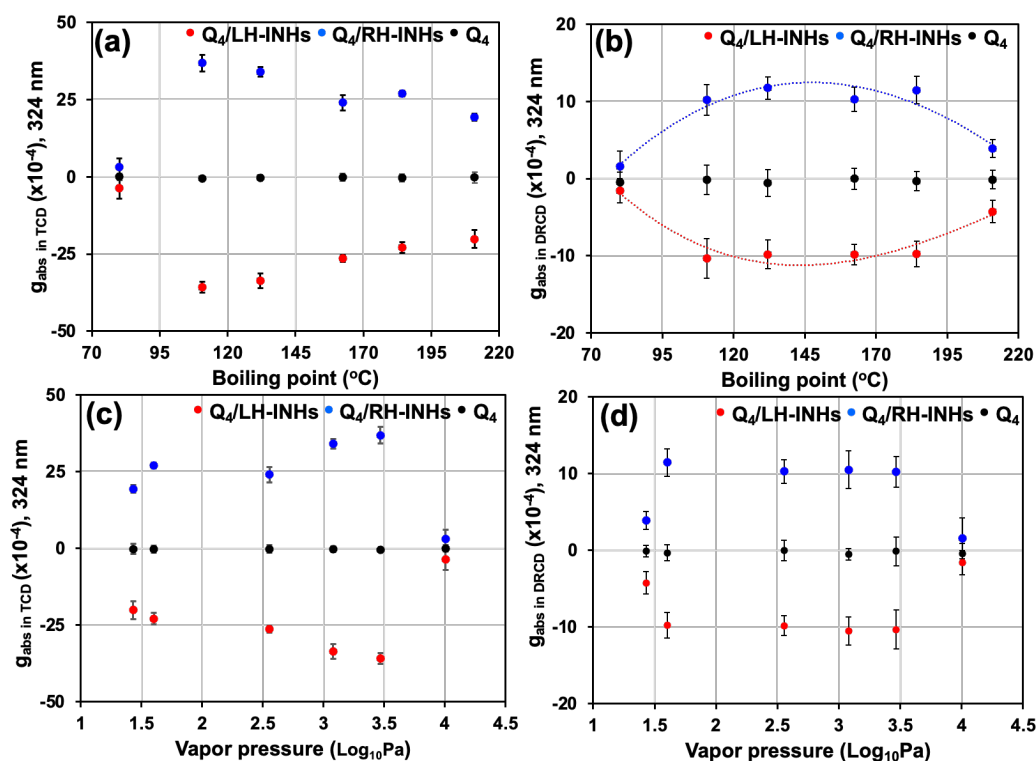


Figure. 5-4 The (a, c) g_{abs} in TCD, and (b, d) g_{abs} in DRCD of Q₄/INHs as a function of boiling points (°C) and vapor pressures of the solvents, respectively. ((Q₄ 1 mM, 100 μ L), (INHs 200 μ g/2x2 cm²))

The racemic Q₄ foldamers in different solvents (1 mM, 100 μ L) were drop-casted on INHs thin film (200 μ g/2x2 cm²), showed clear CD signs which were controlled by the handedness of INHs (Figures. 5-2 and 5-3). The foldamers (Q_n) with left-handed (right-handed) INHs presented negative (positive) CD signal, respectively. The dissymmetry g factors (g_{abs}) in TCD and DRCD spectra were calculated as $g_{\text{abs in TCD}}$ and $g_{\text{abs in DRCD}}$, respectively. Subsequently, the correlation between g_{abs} and boiling point ($^{\circ}$ C) or vapor pressure ($\log_{10}$ Pa) was plotted in Figures. 5-4. The $g_{\text{abs in DRCD}}$ of the lowest $\sim \pm 0.5 \times 10^{-4}$ in benzene (b.p. 80.3 $^{\circ}$ C, vapor pressure 10130 Pa), meanwhile the solvents having the b.p. in the range of 110.8-184.4 $^{\circ}$ C showed higher and similar $g_{\text{abs in DRCD}} \sim \pm 1.0 \times 10^{-3}$. Meanwhile, nitrobenzene with b.p. 211.1 $^{\circ}$ C (27 Pa) the Q₄ INHs film showed also low $g_{\text{abs in DRCD}} \sim \pm 0.5 \times 10^{-3}$. The solvents with both low and high b.p. were not suitable to induce chirality to racemic foldamers (Q₄) whereas the solvents including toluene, chlorobenzene, chlorotoluene and aniline with b.p (110.8-184.4 $^{\circ}$ C)/ vapor pressure (40-2932 Pa) were more effective to induce the chirality (Figure 5-4). In addition, these Q₄/INHs films showed the CPL signal as illustrated in Figure 5-5. The symmetrical CPL signals of Q₄/INHs on INHs were observed with negative (positive) signal on left-handed (right-handed) INHs, respectively. The dependence of solvents on the capacity to induce CPL signals from Q₄/INHs was similar to what was observed for the CD signals (Figure. 5-6). Solvents including toluene, chlorobenzene, chlorotoluene, and aniline showed high $g_{\text{lum}} \sim \pm 1.0 \times 10^{-3}$, whereas Q₄/INHs showed lower in g_{lum} using benzene and nitrobenzene. According to the above-mentioned results, Q₄/INHs showed clear CD and CPL signals, and the solvents in which Q₄ is dissolved before drop-casting has an important effect on chiroptical signals from racemic Q_n, which could be related to the solvent evaporation in drop-casting approach.

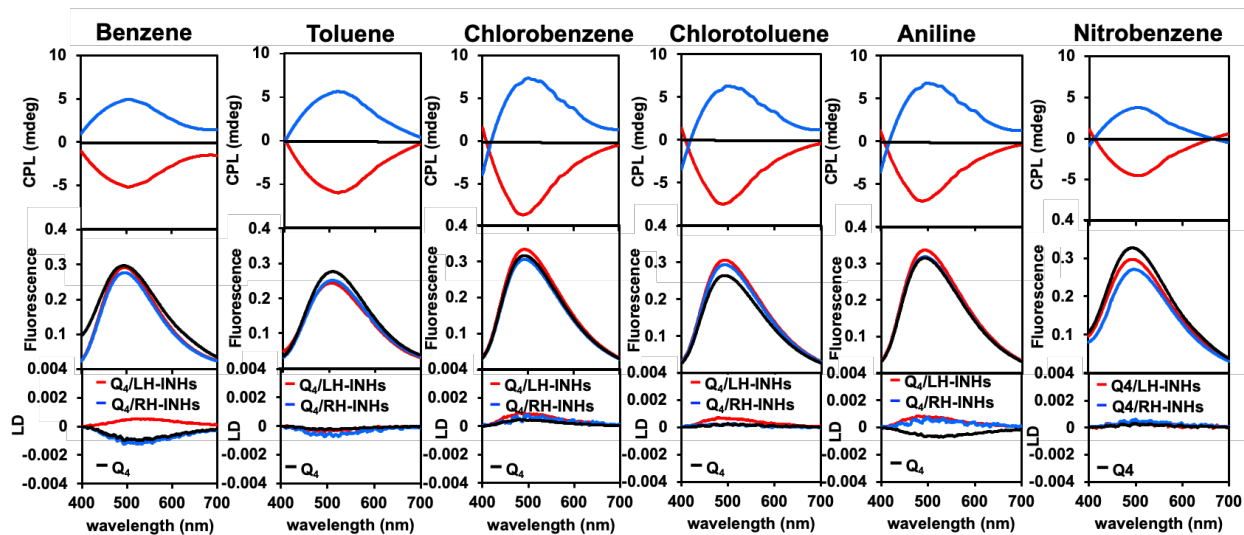


Figure. 5-5 CPL (λ_{ex} 320 nm), fluorescence and LD_{CPL} of Q_4/INHs by using different solvents.

((Q_4 1 mM, 100 μL), (INHs 200 $\mu\text{g}/2 \times 2 \text{ cm}^2$))

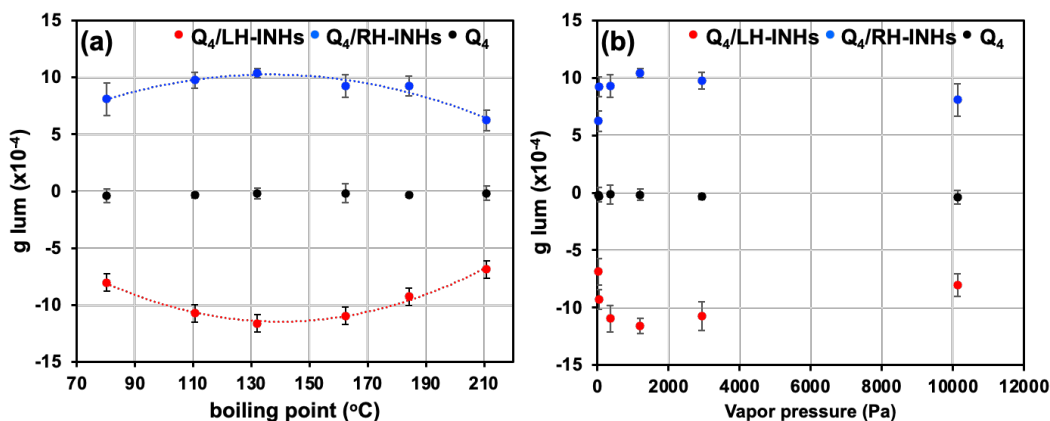


Figure. 5-6 The plot between g_{lum} and boiling point (a) vapor pressure (b) after drop-casting of Q_4/INHs by using difference solvent (λ_{ex} 320 nm), ((Q_4 1 mM, 100 μL), (INHs 200 $\mu\text{g}/2 \times 2 \text{ cm}^2$))

5.2.2 Kinetic studies for enantiomeric enrichment of Q_4 using INHs.

Kinetic study is crucial to understand the process of chirality induction to racemic foldamers on thin film of INHs. The Q_4 was dissolved in three different solvents including toluene, chlorobenzene, and aniline at the concentration of 0.75 mM. Toluene, chlorobenzene and aniline have a difference in boiling point and vapor pressure. Subsequently, 30 μL of Q_4 was drop-casted

on INHs thin film and the CD response was measured during the solvent evaporation at 20 °C. In Figure 5-7, the $g_{\text{abs in TCD}}$ of Q₄/INHs in toluene with the highest vapor pressure remained stable rapidly after drop-casting for 10 min, while $g_{\text{abs in TCD}}$ in chlorobenzene and aniline with lower vapour pressure took a longer time (~30 min) before remaining stable. Owing to this kinetic study, it could be summarized that the speed of chirality induction using INHs via a drop-casting method was influenced by solvent evaporation, which was significantly related to the physical properties of solvent; boiling point and vapour pressure.

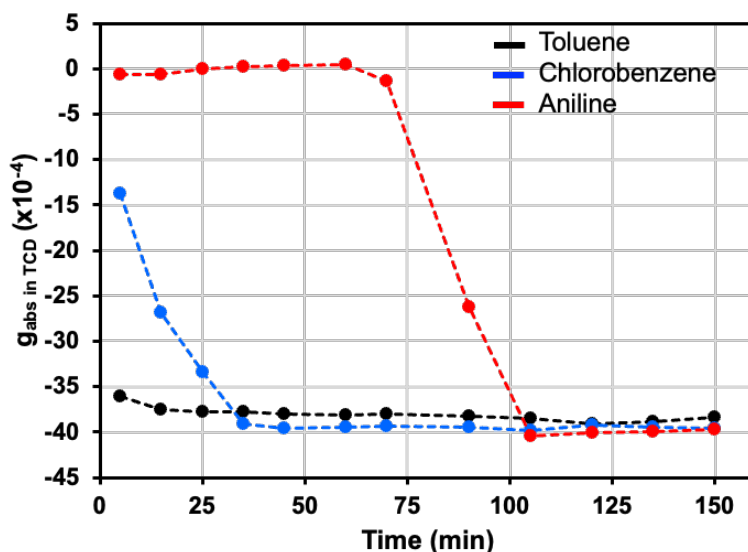


Figure. 5-7 Kinetic studies of Q₄ molecule after drop-casting on INHs thin film at 20 °C. (Q₄ 0.75 mM, 30 μ L).

5.2.3 Optimization of the ratio between Q₄ and INHs

In order to induce the chirality of racemic foldamers by using chiral INHs, the ratio between racemic Q₄ molecules to INHs needed to be optimized. The amounts of INHs were fixed at 200 μ g on a substrate (2x2 cm²), meanwhile racemic Q₄ was prepared at different concentrations (0.25, 0.50, 0.75, and 1.0 mM) by using toluene as a solvent. Then, 100 μ L of Q₄ solution was drop-casted on a quartz substrate containing 200 μ g INHs and subsequently dried at 20 °C for 24 hrs.

Owing to the variation of Q₄ concentration to 200 μ g of INHs, the detectable absorbance of Q₄ was corresponding to the Q₄ concentration, as illustrated in Figures. 5-15c and 5-15d. The CD

signals of Q₄/INHs in DRCD and TCD were converted to obtain g_{abs} in TCD and g_{abs} in DRCD, respectively. In Figures. 5-16a and 5-16b, the results showed that 0.50 mM and 0.75 mM had the highest g_{abs} . In terms of CPL, it was observed a relation between g_{lum} and Q₄ concentration (Figure. 5-16c). It was found that Q₄ at 0.75 mM with 200 μg INHs expressed the highest in $g_{\text{lum}} \pm 1.5 \times 10^{-3}$. Meanwhile, Q₄ at 0.25 mM showed a blue shift in emission which was possibly related to the less stacking or packing of Q₄ in chiral environment of INHs. Therefore, it was summarized that the Q₄ (0.25-0.5 mM) provided vacant INHs after drop-casting of Q₄, meanwhile Q₄ at 1.0 mM could generate the excess Q₄ in Figure. 5-17. Consequently, the optimized ratio between Q₄ and INHs was 0.75 mM (100 μL) to 200 μg INHs. It was previously reported that the volume of INHs was $2.83 \times 10^{-4} \text{ cm}^3$ to 1 mg of INHs.¹⁸ Thus, the optimized ratio was Q₄ 7.50×10^{-8} mole to $5.66 \times 10^{-5} \text{ cm}^3$ volume of hollow INHs.

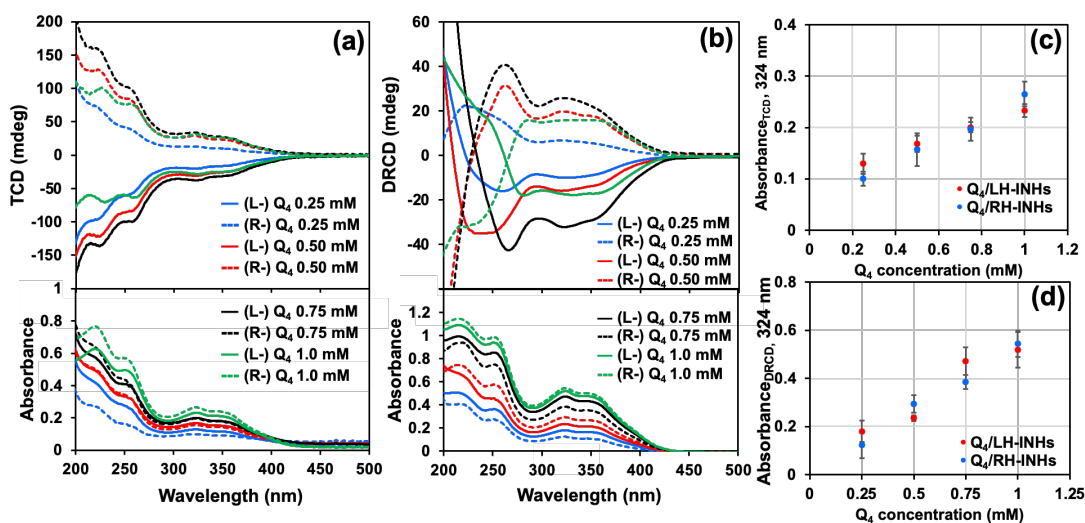


Figure. 5-15 (a) TCD-absorption, (b) DRCD-absorption, (c) CPL-fluorescent (λ_{ex} 320 nm) spectra of Q₄/INHs, (c,d) plot between absorbance at 324 nm and Q₄/INHs. ((Q₄ 0.25-1.0 mM, 100 μL), (INHs 200 μg /2x2 cm^2))

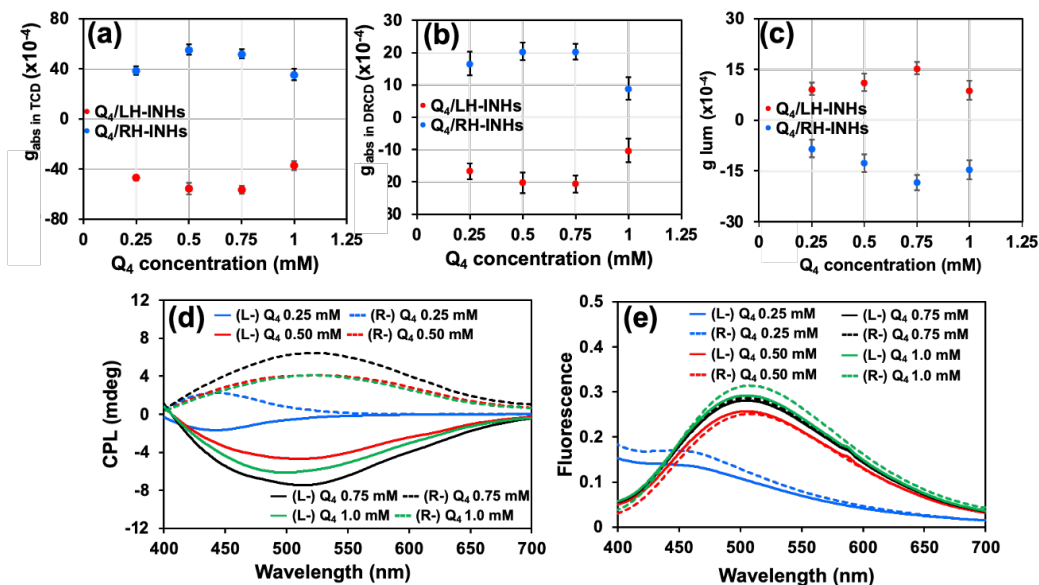


Figure. 5-16 The plot between g_{abs} in TCD (a), g_{abs} in DRCD (b), g_{lum} (c) with various Q_4 concentrations (0.25-1.0 mM), CPL (d) and fluorescent spectra (e) of Q_4 /INHs. ((Q_4 0.25-1.0 mM, 100 μL), (INHs 200 $\mu\text{g}/2 \times 2 \text{ cm}^2$))

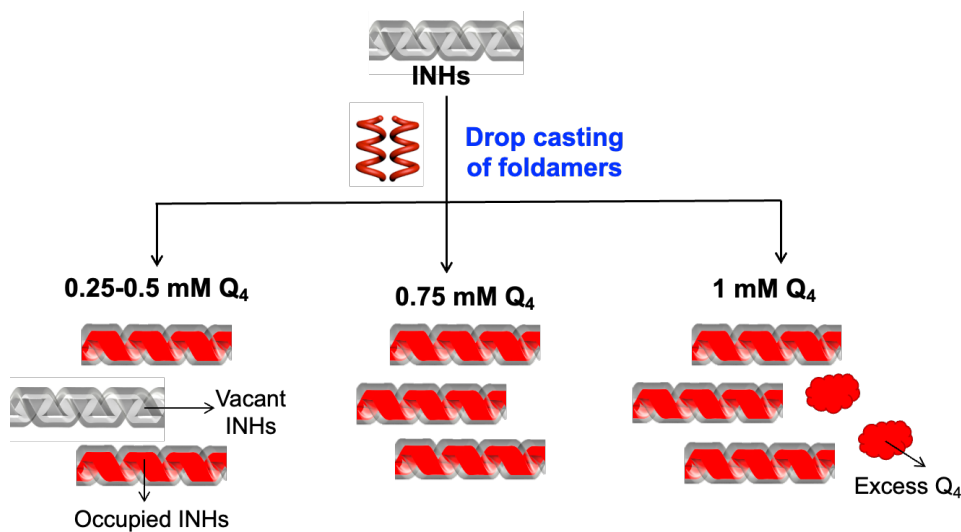


Figure. 5-17 Illustration of Q_4 at different concentrations (0.25-1.0 mM, 100 μL), drop-casted on INHs (200 μg)/ $2 \times 2 \text{ cm}^2$ substrate.

5.2.4 Enantiomeric enrichment of racemic foldamers with different length

According to these results, both CD and CPL signals were observed from racemic Q_4 foldamers after drop-casting on INHs thin film. There are two possible origins for such observations as shown in Figure. 5-8, racemic Q_n could be deracemized when they are in interaction with INHs to be richer in one enantiomer, or racemic Q_n form chiral aggregation in the chiral nano-space of INHs.

Structurally, the longer foldamers show stronger shielding of aromatic amide, amide and ester proton, with tight contact between aromatic rings.⁷ Therefore, longer foldamers have higher free racemization energy, meanwhile the shorter foldamers need lower energy to flip their handedness.

In order to elucidate the origin of the chiroptical signals observed by such racemic foldamers as discussed above, the effect of the foldamer length was observed. If the foldamers (Q_n) remain racemate and form helical aggregates inside INHs, the chirality of the helical silica template is dominant to generate a helical organization. Therefore, g_{abs} of longer foldamer/INHs should be larger than that of shorter foldamers/INHs due to the stronger π - π stacking of quinoline monomer in the foldamers chain. On the other hand, if enantiomeric enrichment occurred after drop-casting INHs, the g_{abs} with the foldamers which have lower racemization energy (easier switching in helical sense), should be higher.

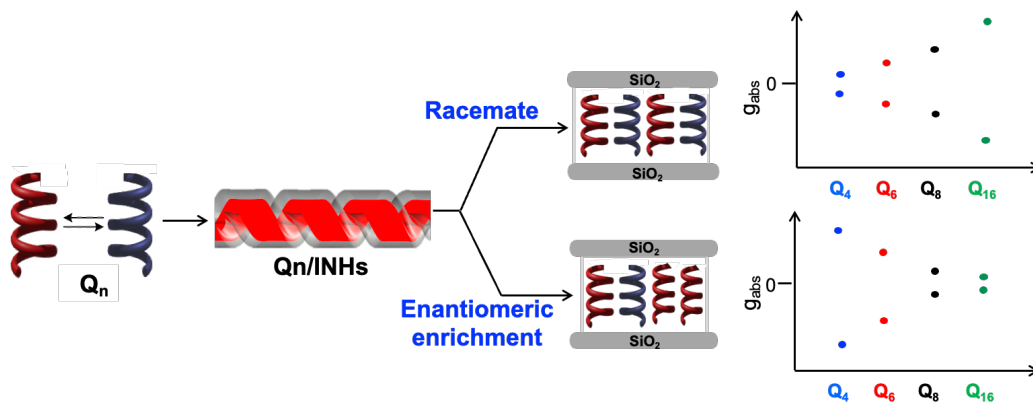


Figure. 5-8 Illustration of two possibilities of chirality induction of racemic Q_n using INHs.

The chirality induction of aromatic oligoamide foldamers with different lengths (Q_4 , Q_6 , Q_8 , and Q_{16}) was thus studied using INHs. The Q_4 , Q_6 , Q_8 , and Q_{16} (1 mM, 100 μ L) were drop-casted on a substrate containing INHs thin film (200 μ g/ 2x2 cm²). After drying samples at 20 °C for 24 hr, CD and CPL signals of Q_n /INHs were measured as shown in Figures. 5-9, using toluene and aniline as a solvent, respectively. While the chirality induction was observed for all the foldamers,

an interesting correlation was observed between dissymmetric factors (g_{abs} in TCD and g_{abs} in DRCD) with the length of the foldamers, since the former decreased with the increasing length of the foldamers. The Q_4 molecule showed the highest g_{abs} in TCD, g_{abs} in DRCD and g_{lum} whereas Q_{16} showed the lowest value (Figures. 5-10).

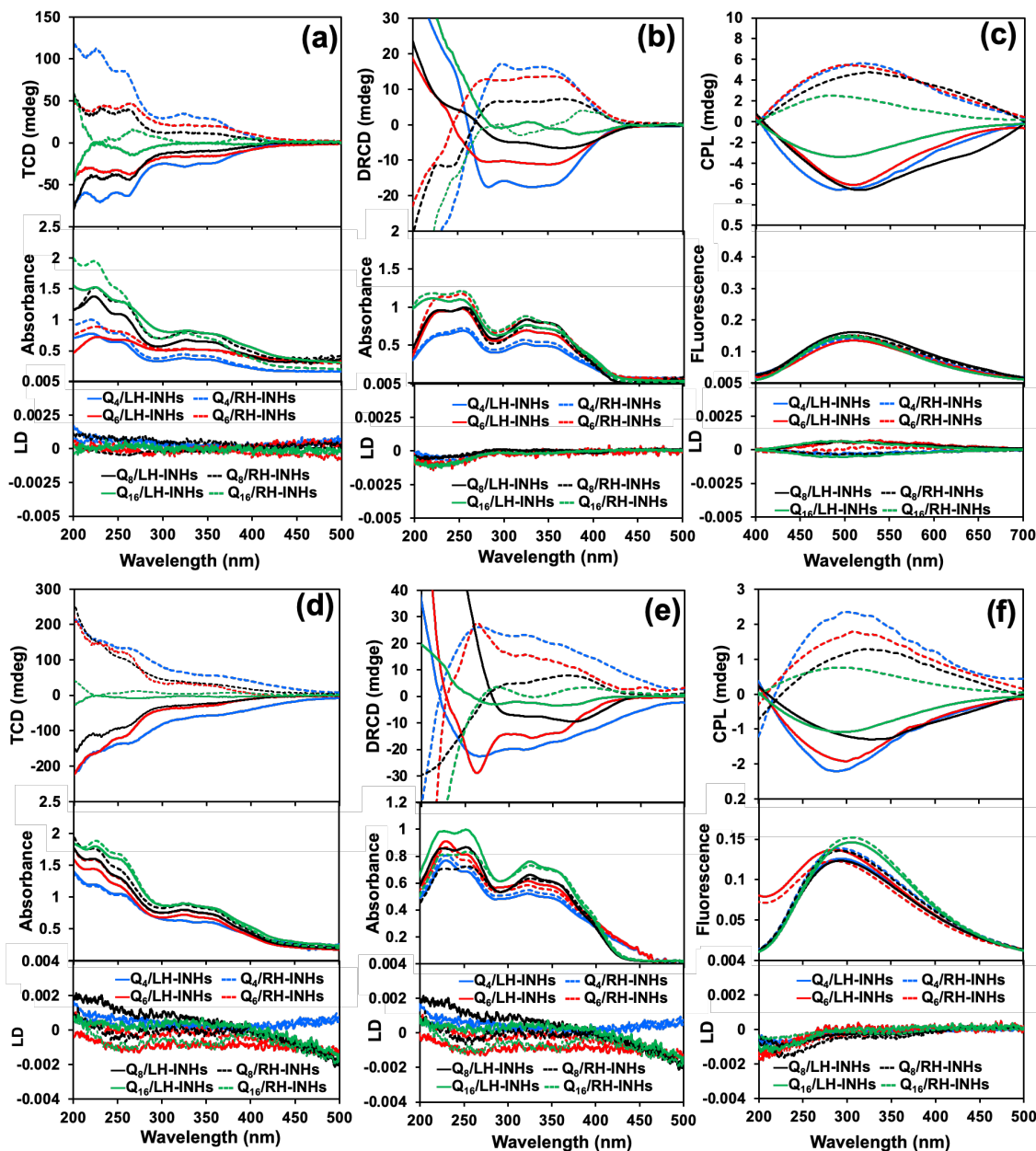


Figure. 5-9 TCD-absorption, DRCD-absorption, CPL-fluorescent (λ_{ex} 320 nm) spectra of Q_4 /INHs, Q_6 /INHs, Q_8 /INHs and Q_{16} /INHs using solvents as toluene (a, b, c) and aniline (d, e, f), ((Q_n 1.0 mM, 100 μ L),(INHs 200 μ g/2x2 cm^2))

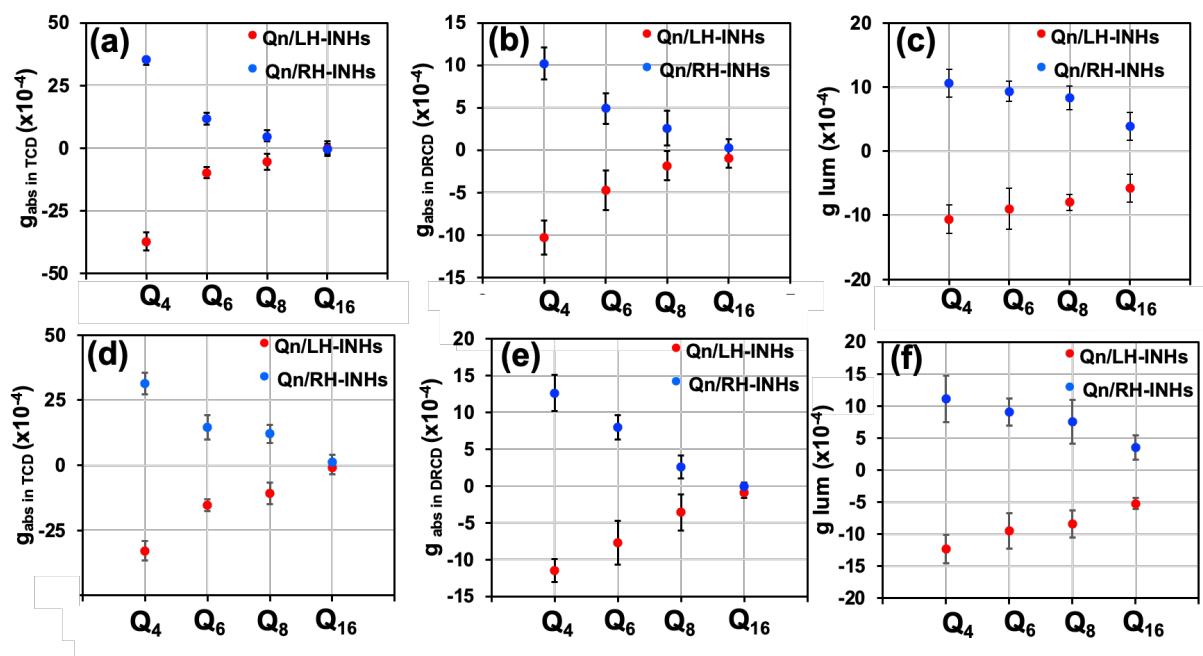


Figure 5-10 Comparison of g_{abs} in TCD, g_{abs} in DRCD, g_{lum} of Q_4 /INHs, Q_6 /INHs, Q_8 /INHs and Q_{16} /INHs using solvents as toluene (a, b, c) and aniline (d, e, f), ((Q_n 1.0 mM, 100 μ L),(INHs 200 μ g/2x2 cm^2))

In order to directly investigate if the foldamers inside INHs are enriched in one of the enantiomers (enantiomeric excess is not zero), we then washed out the foldamers from the INHs film, then measured the CD in solution. One aspect we needed to be careful about is that these foldamers would go under racemization as soon as they are separated from INHs in solution. Therefore, we needed to choose the foldamer which racemizes slowly enough so that we could measure the eventual CD signal after separating them from the INHs. For that, longer foldamers were better (slower racemization). However, as we saw above, the longest foldamer, Q_{16} do not show the induced CD or CPL. As a best compromise, Q_8 was chosen. DMF was chosen as the optimized solvent for washing out Q_8 from INHs.

First, Q_8 was drop-casted on INHs using toluene as a solvent. Then, the Q_8 was washed out from INHs by DMF and then filtrated to remove INHs (Figure. 5-11). After that, the obtained Q_8 in DMF solution was measured the CD signal in Figure. 5-12, in addition, it was observed the decay of CD response during the time (Figure. 5-13). Unfortunately, the CD signals of Q_8 after washing by DMF were unclear and reproducible. This issue could be assigned to the fast

racemization of Q₈ foldamers in DMF after removing from chiral INHs templates. Meanwhile, the average CD signal of Q₈ in DMF (from 20 times of experiments) was shown in Figure. 5-14, which could be calculated the percentage of enantiomeric excess (ee%) $\geq 2.5\%$ (by comparing to the chiral Q₈ molecule)

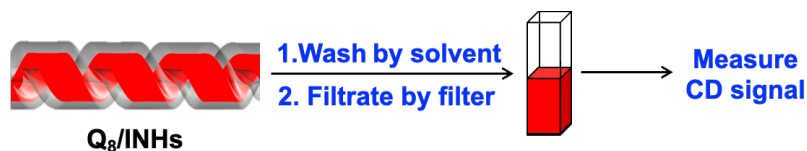


Figure 5-11 Removing Q₈ from chiral INHs by washing and filtrating.

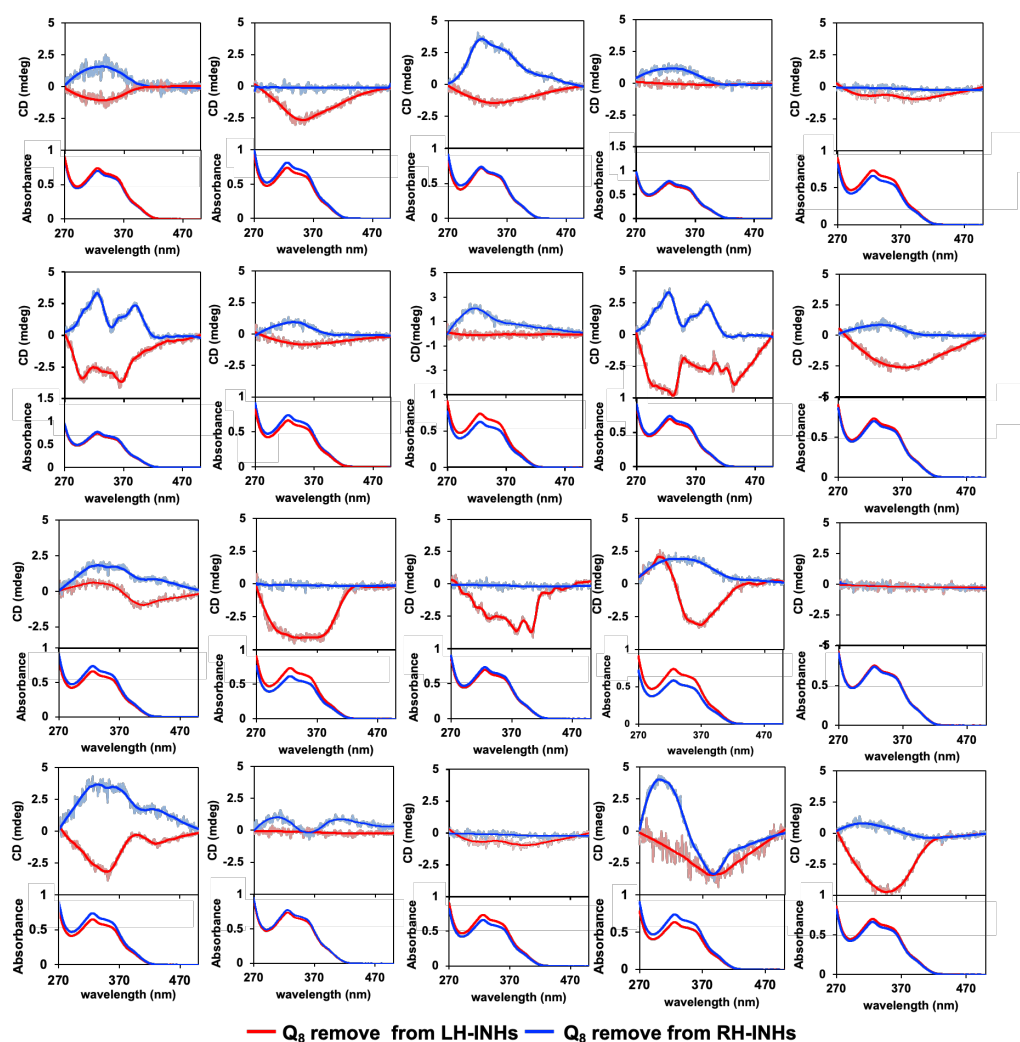


Figure 5-12 CD and absorption spectra of Q₈ foldamers after washing from chiral INHs using DMF as a solvent.

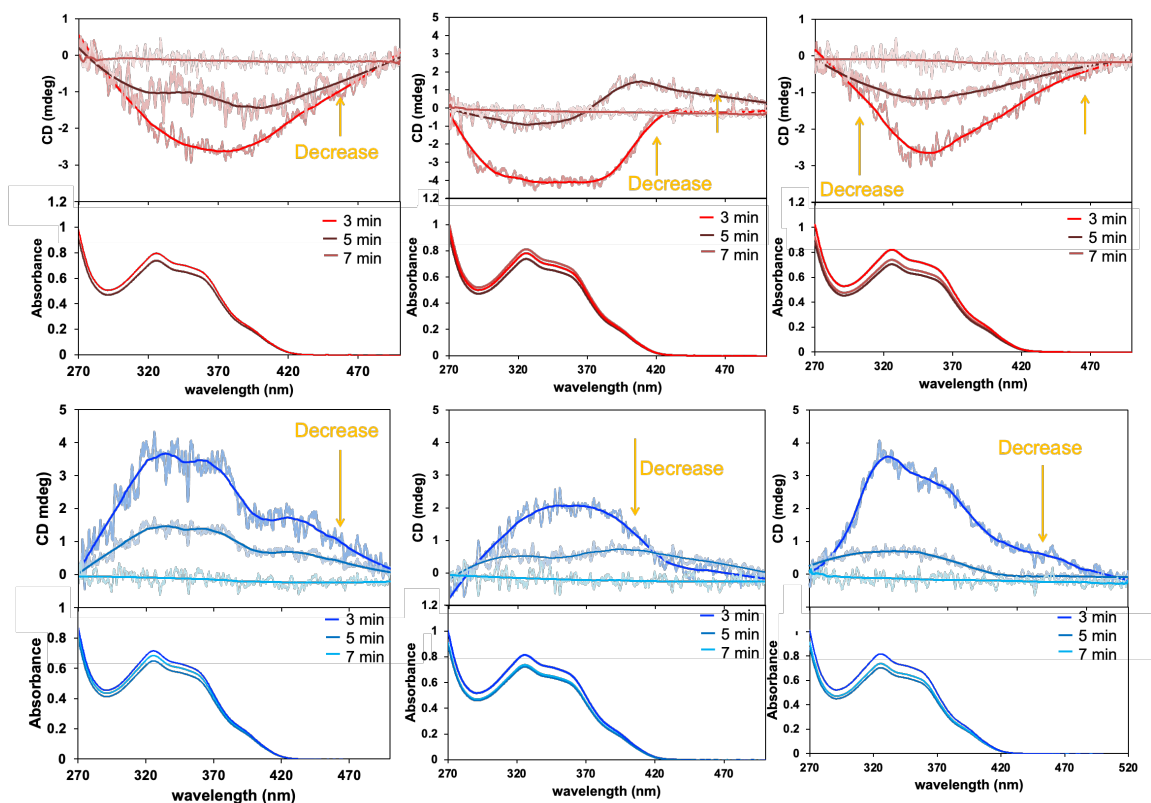


Figure 5-13 CD-absorption spectra of Q₈ foldamers after washing from chiral INHs using DMF during time.

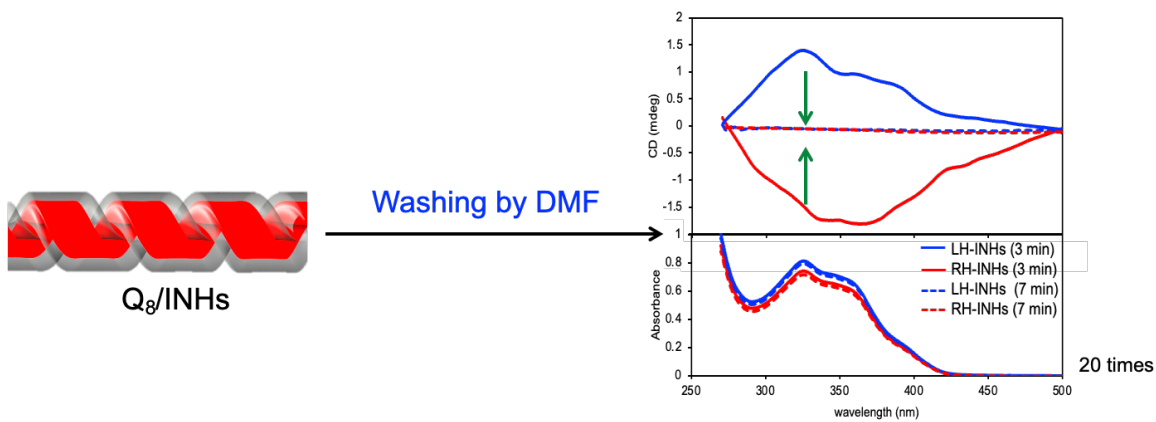


Figure 5-14 CD-absorption spectra (average) of Q₈ foldamers after washing from INHs (20 times).

5.2.5 Surface variation of chiral silica nanohelices for enantiomeric enrichment of foldamers.

The surface of chiral INHs played a crucial role in the interaction between foldamers and INHs. Subsequently, the modification of surface properties of INHs was studied (Figure 5-15); I) Inorganic silica nanohelices (INHs), II) Inorganic silica nanohelices containing amine functional groups, which were prepared by grafting (3-aminopropyl)triethoxysilane (APTES) molecule on the surface of INHs (called INHs-NH₂),^{20, 21} III) Inorganic silica nanohelices with less hydroxyl functional group (called INHs-calcinated), which was prepared by calcination of INHs at 600 °C for 2 hrs to remove most of the hydroxy functional group on the helical silica surface.

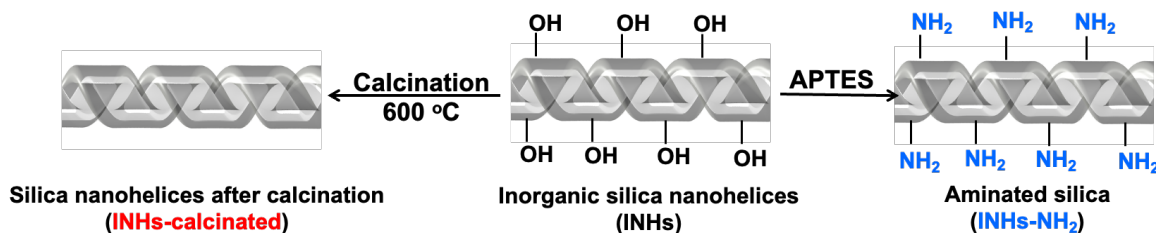


Figure. 5-15 Three kinds of helical templates including INHs, INHs-NH₂ and INHs-calcinated.

INHs, INHs-NH₂ and INHs-calcinated were characterized by FT-IR in Figure. 15-16a. The IR results suggested that INHs contained hydroxyl functional groups (3365.7 cm⁻¹ and 953.7 cm⁻¹) and O-Si-O (1044.7 cm⁻¹ and 791.6 cm⁻¹). Meanwhile, INHs-NH₂ showed peaks of NH₂ (1567.7 cm⁻¹), CH₂ (1493.3 cm⁻¹) and C-N (1333.5 cm⁻¹), which confirms the presence of amine functional groups on the surface of silica template (density; 0.7-1 amine group per nm²).²² After calcination of INHs at 600 °C, the decrease in OH peaks (~3365.6 cm⁻¹) suggested the decrease in the amounts of hydroxyl functional groups on the surface of the silica template. Furthermore, the thermal treatment of INHs at 600 °C originated the shank morphology of the helical silica framework. It was previously reported that the helical pitch and width decreased ~84% (from 69.4 nm to 58.6 nm) and ~87% (from 33.6 to 29.1 nm), respectively. Therefore, calcinated silica showed higher chirality ~1.9 times than that of INHs.²³ After preparing three different chiral templates including INHs, INHs-NH₂ and INHs-calcinated (200 μg), racemic foldamers including Q₄, Q₆ and Q₈ were dissolved in toluene at 1 mM for drop casting. The interaction between racemic Q₄ and

INHs/INHs-NH₂ was characterized by FT-IR as illustrated in Figures. 5-16b and 5-16c. No detectable peak shift in IR spectra of Q₄/INHs was observed compared to Q₄.

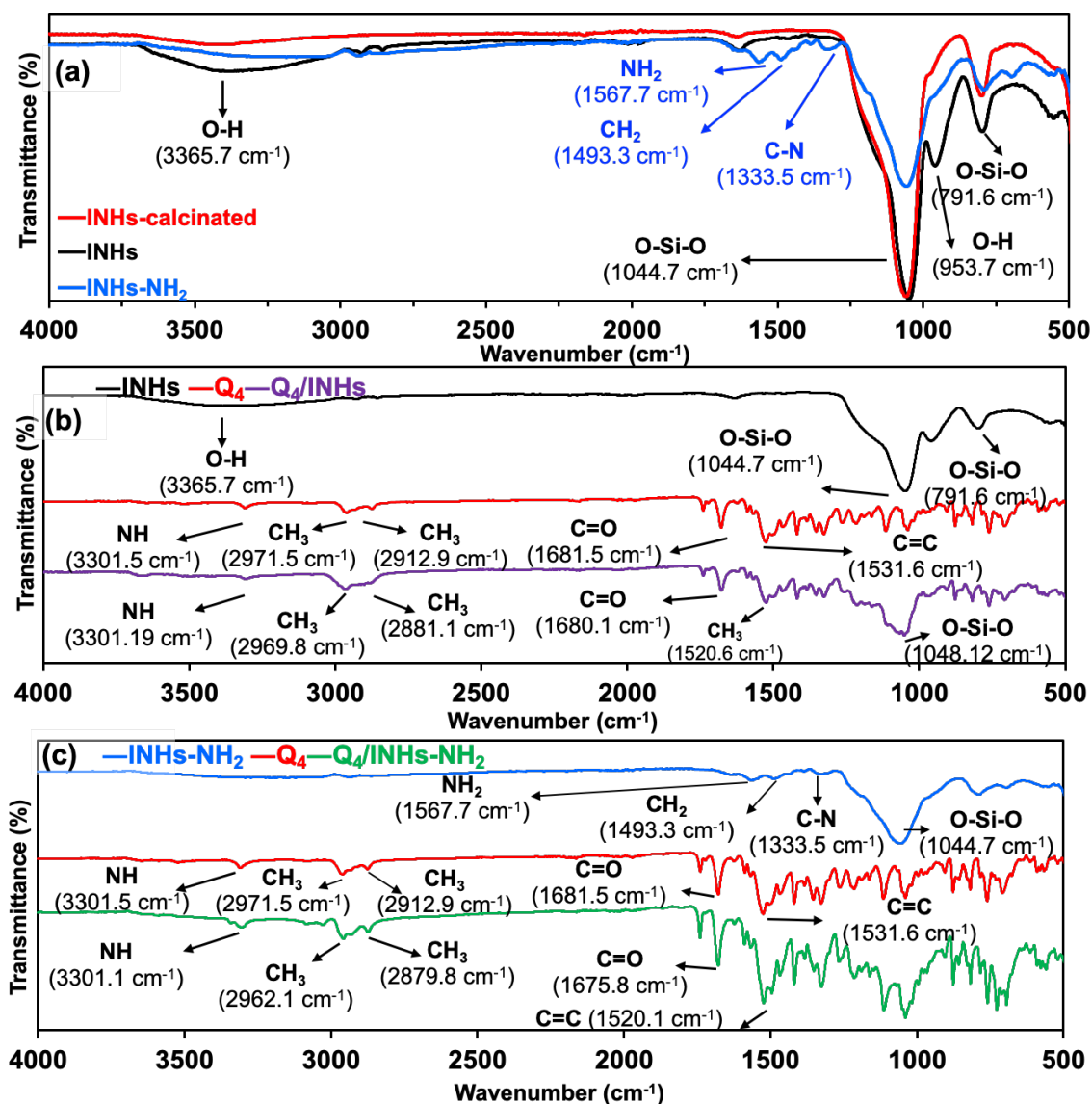


Figure. 5-16 FT-IR spectra (a) of INHs, INHs-NH₂, INHs-calcinated, (b) of Q₄/INHs and (c) Q₄/INHs-NH₂

The CD and CPL signals of Q₄, Q₆ and Q₈ showed similar patterns (Figures. 5-17 and 5-18) but INHs-INH₂ provided the highest in g_{abs} in TCD, g_{abs} in DRCD, and g_{lum} , INHs-calcinated showed the lowest efficiency for chirality induction of Q_n. These results implied that the silica surface of helical template had an important impact on enantiomeric enrichment of foldamers.

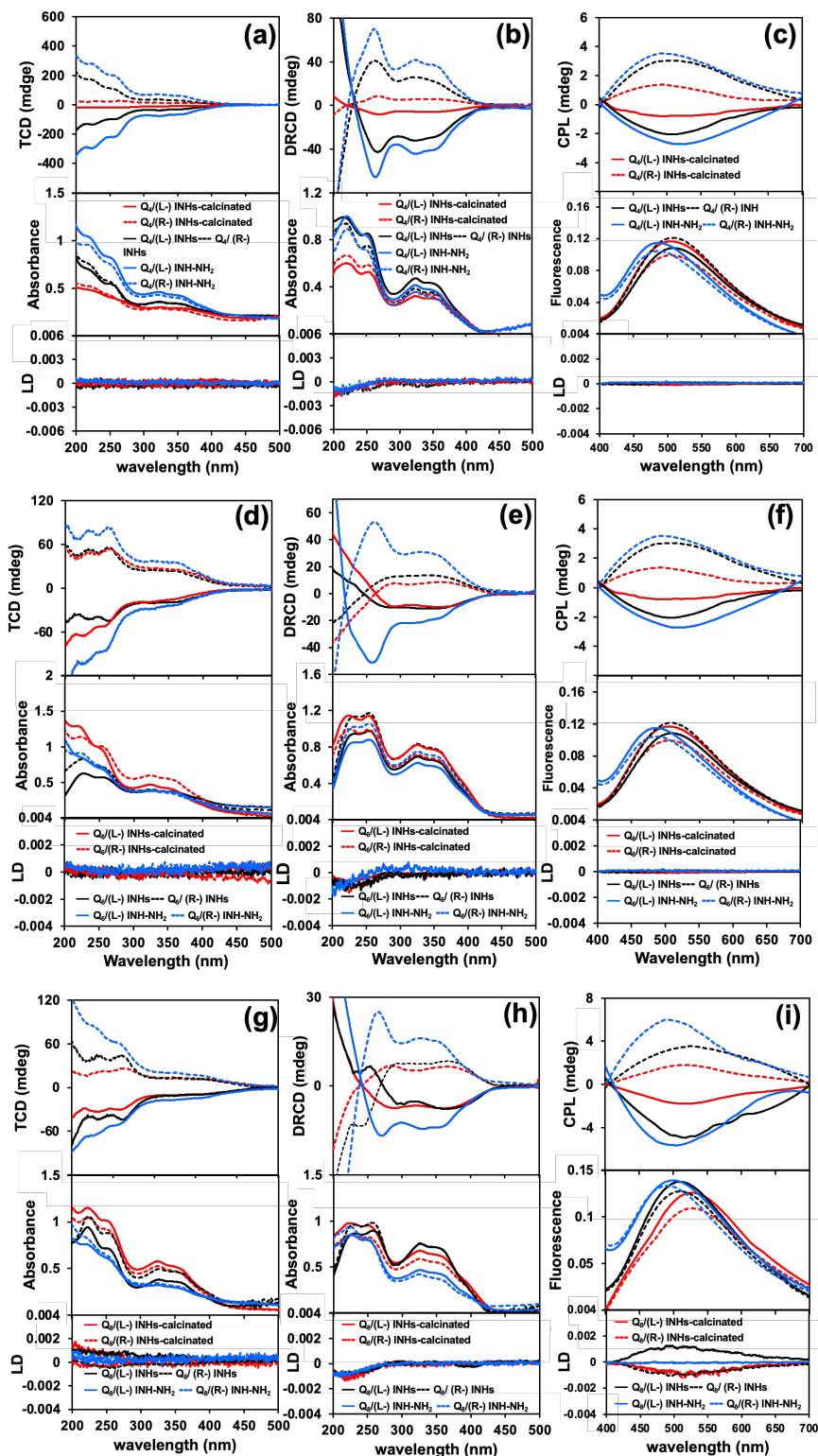


Figure. 5-17 TCD-absorption, DRCD-absorption, CPL-fluorescent (λ_{ex} 320 nm) spectra of Q₄/INHs (a,b,c), Q₆/INHs (d, e, f), Q₈/INHs (g, h, i). (Q_n 1 mM, 100 μ L to chiral silica template 200 μ g/2x2-cm² substrate), (solvent : toluene)

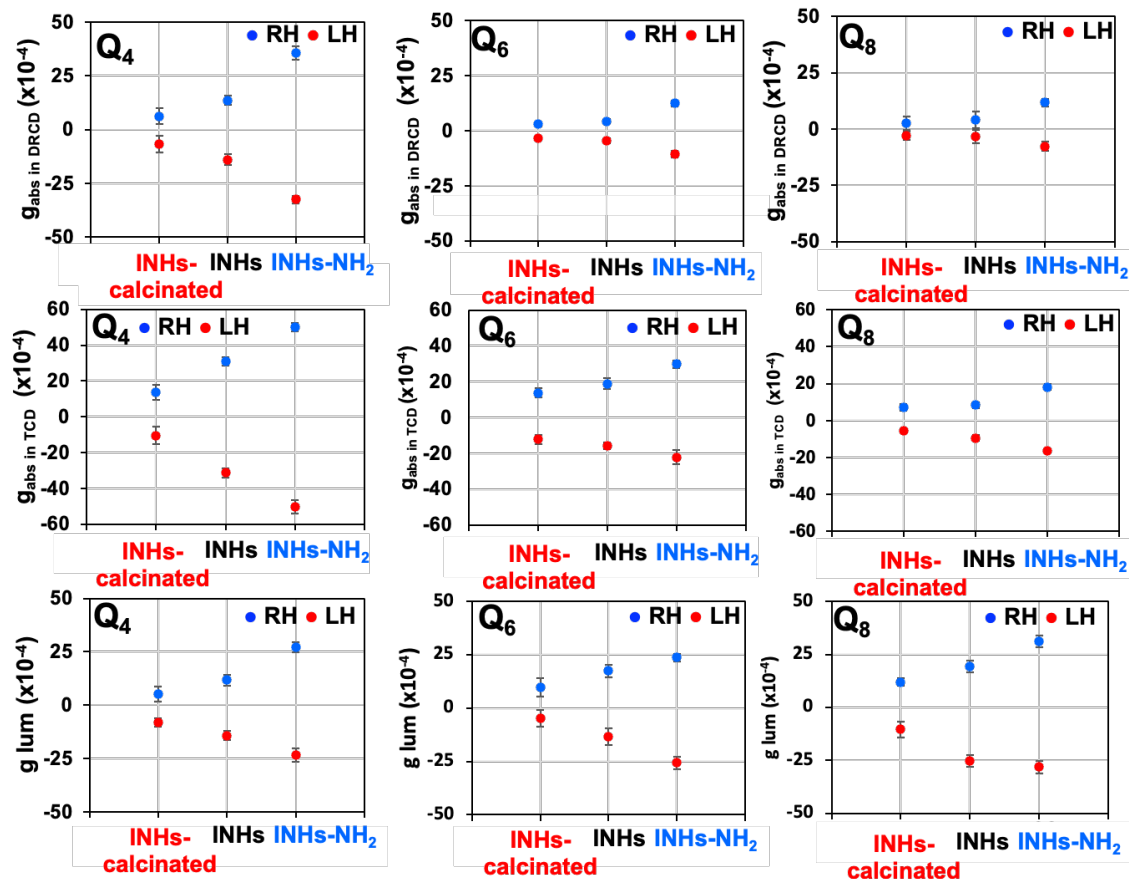


Figure. 5-18 Comparison of g_{abs} in DRCD, g_{abs} in TCD, g_{lum} of racemic Q_4 , Q_6 and Q_8 after drop casting on INHs-calcinated, INHs and INH-NH₂. (Q_n 1 mM, 100 μ L to chiral silica template 200 μ g), (solvent : toluene)

5.2.6 Temperature effect on enantiomeric enrichment of racemic foldamers

Apart from the solvent effect for chirality induction of racemic foldamers (Q_n), it suggested that the physical properties of a solvent such as boiling point and solvent evaporation had a strong impact on drop-casting approach. Therefore, it is important to study the temperature effect for chirality induction of Q_n . The Q_4 foldamer was dissolved in toluene at 1 mM and then drop-casted on a quartz slide (2x2 cm²) containing INHs thin film (200 μ g). After drop casting, the samples were dried at different temperatures including at 4 $^{\circ}$ C, 20 $^{\circ}$ C, and 60 $^{\circ}$ C. In Figure. 5-19, the results revealed that low temperature (4 $^{\circ}$ C) showed the highest chirality relating to g_{abs} in TCD, g_{abs} in DRCD and g_{lum} , while the high temperature (60 $^{\circ}$ C) resulted in the lowest dissymmetric factors. The correlation between the dissymmetric factors and temperature for drying samples (Figure. 5-20)

showed that the chirality induction of Q₄ using INHs via a drop-casting method was strongly resulted by temperature and lower the drying temperature, the higher g factors (g_{abs} and g_{lum}), probably due to the slow drying kinetics.

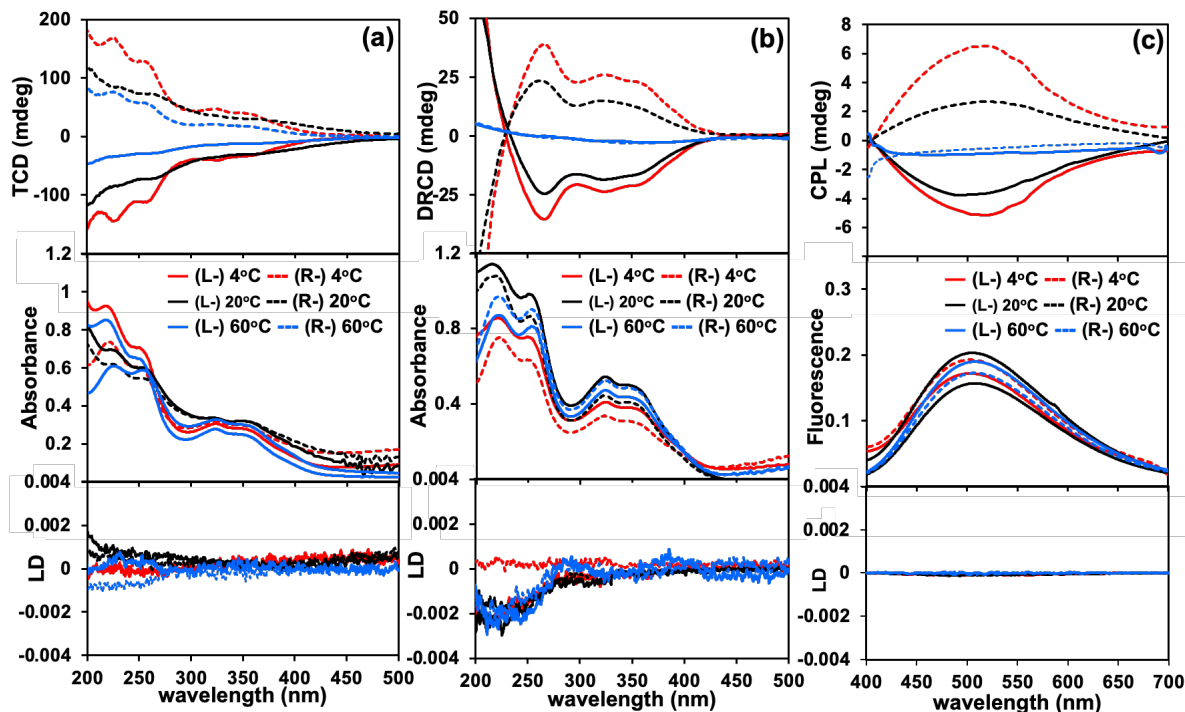


Figure. 5-19 (a) TCD-absorption, (b) DRCD-absorption and (c) CPL-fluorescent (λ_{ex} 320 nm) spectra racemic Q₄ foldamers after drop-casting on INHs at different temperatures (4 °C, 20 °C, 60 °C). (Q_n 1 mM, 100 μL to chiral silica template 200 μg), (solvent : toluene)

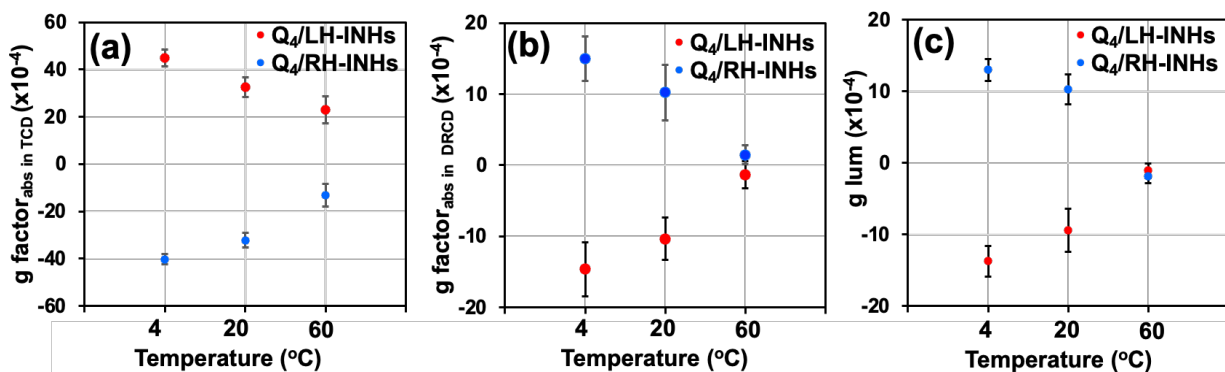


Figure. 5-20 Comparison of g_{abs} in DRCD, g_{abs} in TCD, g_{lum} of Q₄ after drop-casting on INHs at 4 °C, 20 °C, 60 °C, (Q_n 1 mM, 100 μL to chiral silica template 200 μg), (solvent : toluene)

5.2.7 TEM characterization of Q_n/INHs

The morphology of Q_n/INHs was characterized by TEM as shown in Figure. 5-21. INHs showed helical morphology (Figure. 5-21a) with the clear edge of silica wall. After drop-casting of Q_n, it was obviously observed the dark contrast with helical morphology, which is influenced by the helical morphology of silica nanohelices. The racemic foldamers in the chiral nanospace of INHs were amorphous because there was no observed crystalline pattern in selected area electron diffraction (SAED).

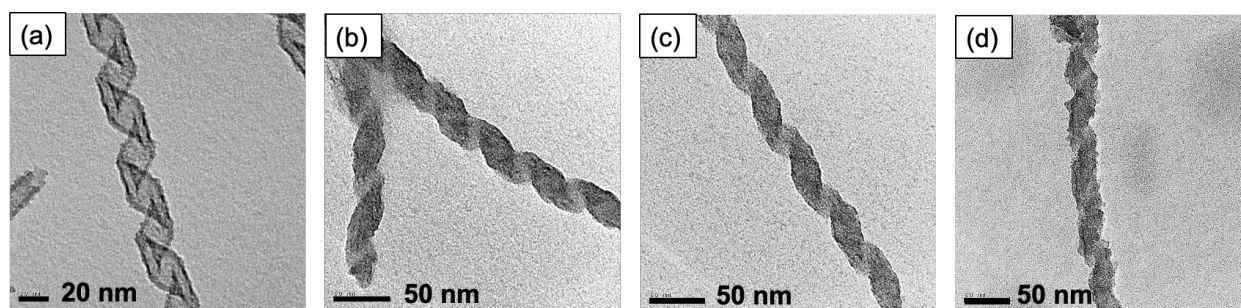


Figure. 5-21 TEM images of INHs (a), Q₄/INHs (b), Q₆/INHs (c), Q₈/INHs (d) (Q_n 1 mM, 100 μ L to INHs 200 μ g), (solvent : toluene).

5.2.8 Chiral foldamers (Q₄R and Q₄S) in chiral environment of helical silica template

The increasing length of racemic foldamers (Q₄, Q₆, Q₈, Q₁₆) showed a decline in g_{abs} , therefore it was possible that the shorter foldamers, easier the INHs could control the organization of racemic foldamers (are they enriching one of the enantiomers? We are not yet able to conclude). To investigate the difference in interaction between the right- or left-handed INHs with right- or left-handed foldamers, chiral foldamers (Q₄R and Q₄S) containing camphenyl moiety as a chiral inducer¹⁰ were synthesized and put in interaction with INHs. The oligoamide foldamers with *R*-camphanyl group (Q₄R) expressed helical left-handedness while Q₄ attaching with *S*-camphanyl moiety (Q₄S) shows the right-handed morphology (Figure 5-22).

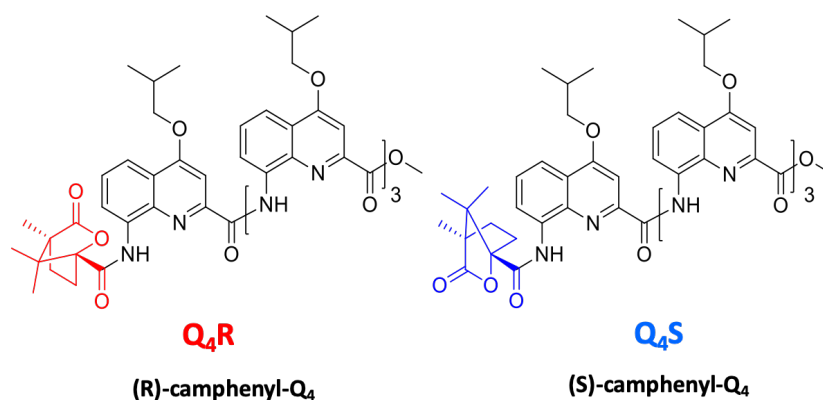


Figure. 5-22 Chemical structures of chiral foldamers (Q₄R and Q₄S).

The optical property of Q₄R and Q₄S was investigated in CHCl₃ and on a substrate in Figure. 5-23. Q₄R and Q₄S in CHCl₃ showed three CD peaks at 260, 310, 405 nm, the peaks at 260 nm and 310 were assigned the chiral chemical structure of foldamers while the CD peak at 405 nm was related to the helicity of foldamers. The g_{abs} of Q₄R and Q₄S in CHCl₃ (405 nm) was calculated as -1.3×10^{-2} and 1.4×10^{-2} , respectively. Q₄R and Q₄S also expressed CPL signal in Figure. 5-22b with g_{lum} (447 nm, λ_{ex} 320 nm) -5.3×10^{-3} and 5.9×10^{-3} , respectively. Furthermore, the CD and CPL spectra of Q₄R and Q₄S on solid state were detectable on a substrate in Figures. 5-23c and 5-32d. The CD spectra in the solid state indicated a primary peak at 405 nm with two small peaks at 260 and 310 nm, meanwhile the CPL signal showed symmetrical peaks at 447 nm (λ_{ex} 320 nm).

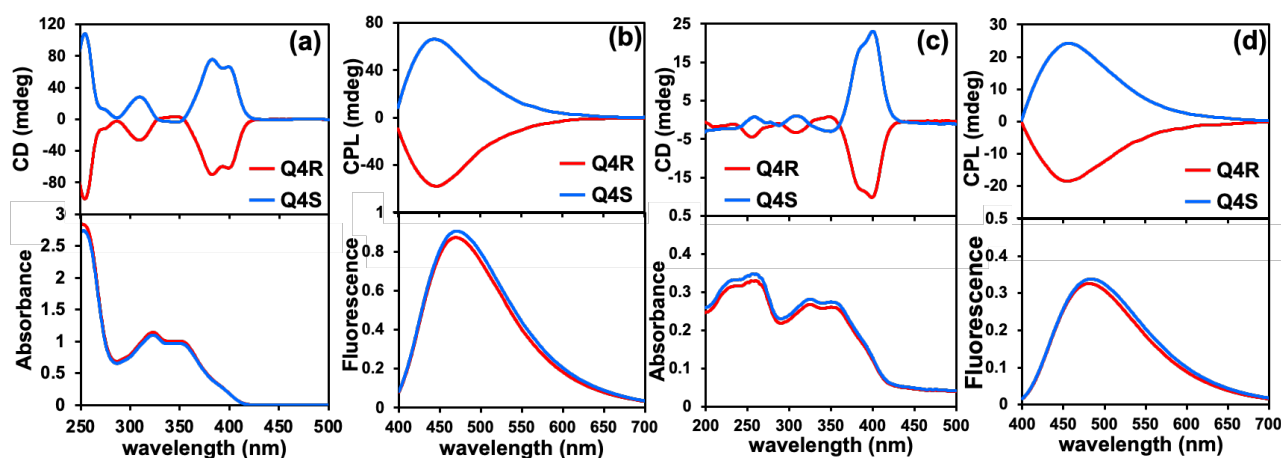


Figure. 5-23 CD and CPL (λ_{ex} 320 nm) spectra of Q₄R and Q₄S in CHCl₃ (a,b) and on a substrate (c, d).

Consequently, the Q₄R and Q₄S were drop-casting on INHs and let dry at 20 °C for 24 hrs. The CD signal was detected in Figure. 5-23, which showed that Q₄R/LH-INHs and Q₄S/RH-INHs expressed strong CD signals in a range of 250-450 nm, while Q₄R/RH-INHs and Q₄S/LH-INHs showed cotton peaks at 387 nm. In addition, it was clearly observed that Q₄R/LH-INHs and Q₄S/RH-INHs expressed strong symmetrical peaks in CPL, however Q₄R/RH-INHs and Q₄S/LH-INHs showed two CPL signal peaks with the opposite signal.

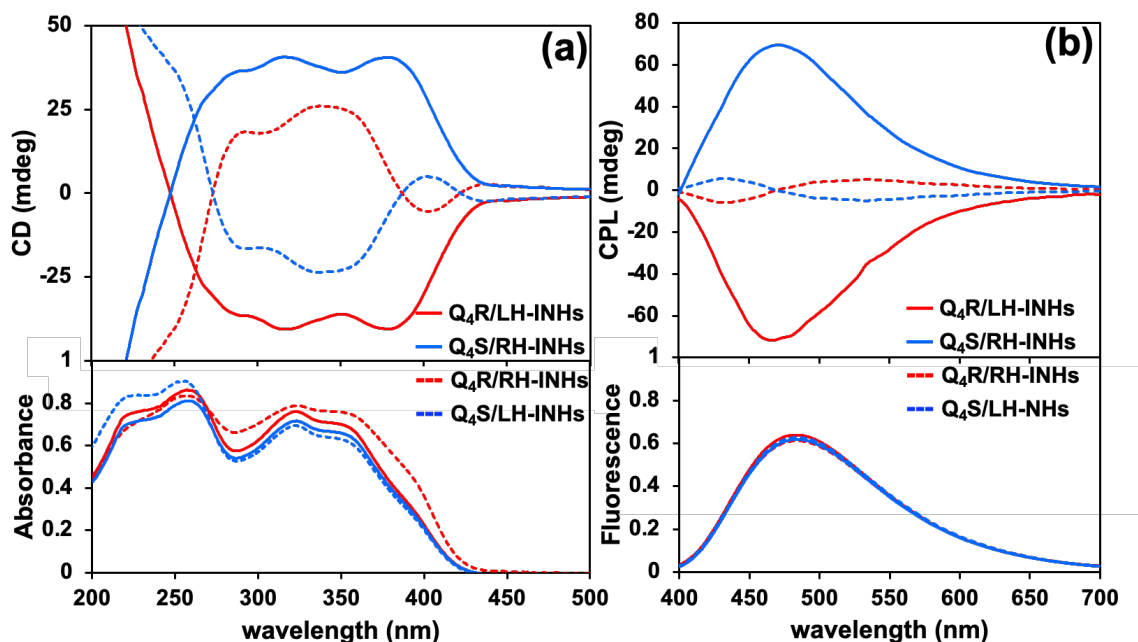


Figure. 5-24 CD (a) and CPL (b) spectra of Q₄R/INHs and Q₄S/INHs. (Q₄R/Q₄S 0.75 mM, 100 μ L to INHs 200 μ g), (solvent : toluene)

These results suggested that the chiral foldamers in INHs with the same handedness showed the strong cooperative chiral property in CD and CPL signals (Q₄R with left-handed helicity in LH-INHs and Q₄S with right-handed helicity in RH-INHs), chiral foldamers in INHs with the opposite handedness (Q₄R/RH-INHs and Q₄S/LH-INHs) showed the destructive effect between chirality from foldamers and chirality from helical silica nanostructures. Clearly, chiral foldamers (Q₄R and Q₄S) are sensitive to the chiral environment of the helical silica template.

5.3 Conclusion

The chirality induction of quinoline-derived oligoamide foldamers was studied using a helical silica-based nano-template as a chiral inducer. The silica nanohelices were fabricated by supramolecular self-assembly of organic molecules as a soft template. The racemic foldamers were introduced into the chiral environment of helical silica-based thin film using a drop-casting approach, resulting in the symmetrical CD and CPL response. The effects of temperature of drying, foldamer concentration, the nature of the silica surface and solvent for drop-casting were investigated. The foldamer's length showed strong correlation to the induced chiroptical properties, as dissymmetry factor increases when the foldamer length decreases. Chiral foldamers functionalized with chiral camphenyl moiety were introduced into chiral system of silica-based materials, which subsequently expressed the competitive effect between molecular chirality from foldamers and supramolecular chirality from silica nano-template. Therefore, the research proposed a novel concept to bias equilibrium in racemic foldamers using chiral silica nanohelices as a chiral environment.

5.4 Appendix

All of Raman results was obtained from Prof. Theirry Buffleteau (ISM, university of Bordeaux, France)

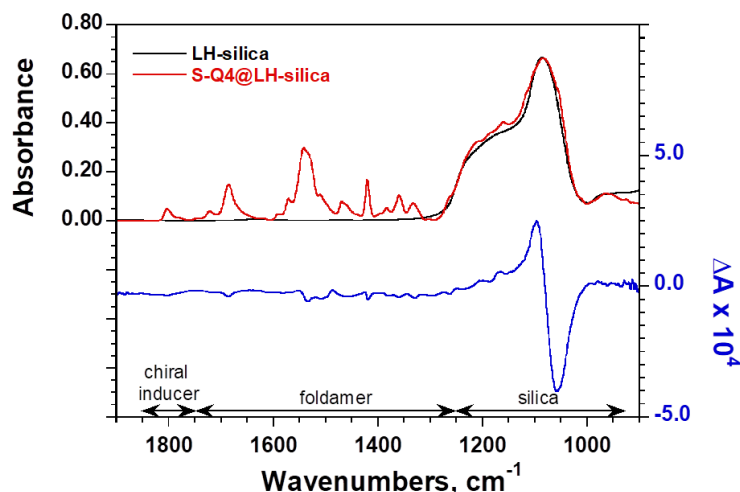


Figure. 5-25 Top) IR spectra of LH-silica and S-Q₄@LH-silica Bottom) Raw VCD spectrum of S-Q₄@LH-silica sample.

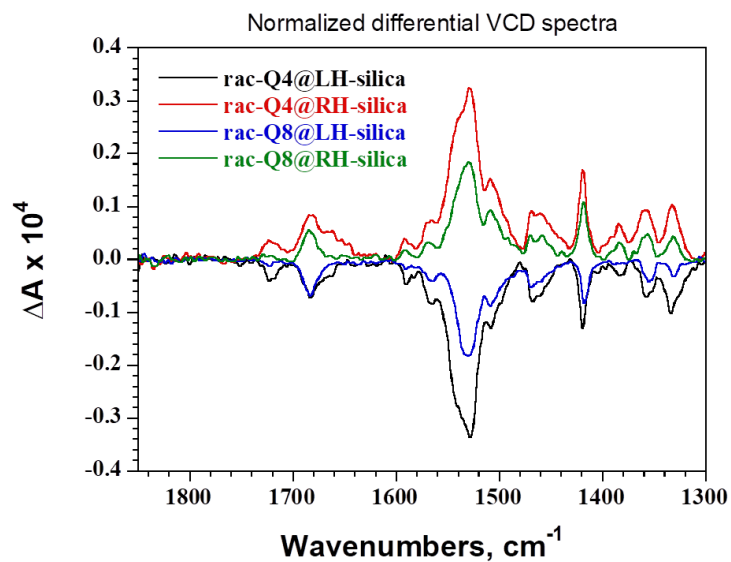


Figure. 5-26. Normalized differential VCD spectra of RH-silica (black spectrum) and LH-silica (red spectrum) samples.

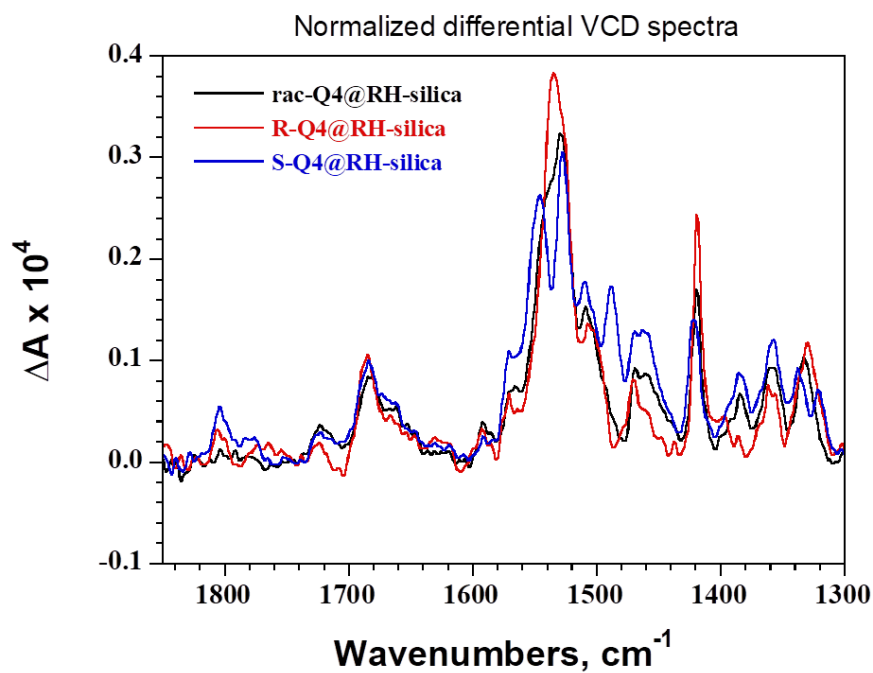


Figure. 5-27. Normalized differential VCD spectra of rac-Q₄@RH-silica (black spectrum), R-Q₄@RH-silica (red spectrum) and S-Q₄@RH-silica (blue spectrum) samples.

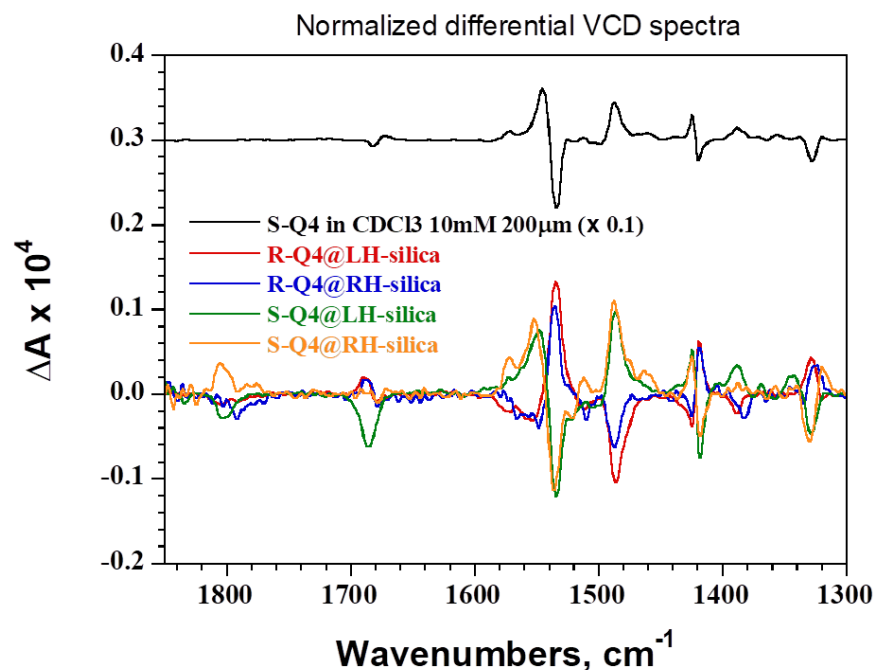


Figure. 5-28 Top) VCD spectrum of S-Q₄ foldamer in CDCl₃ solution (10mM), Normalized differential VCD spectra of R-Q₄@LH-silica (red spectrum), R-Q₄@RH-silica (blue spectrum), S-Q₄@LH-silica (green spectrum) and S-Q₄@RH-silica (orange spectrum) samples.

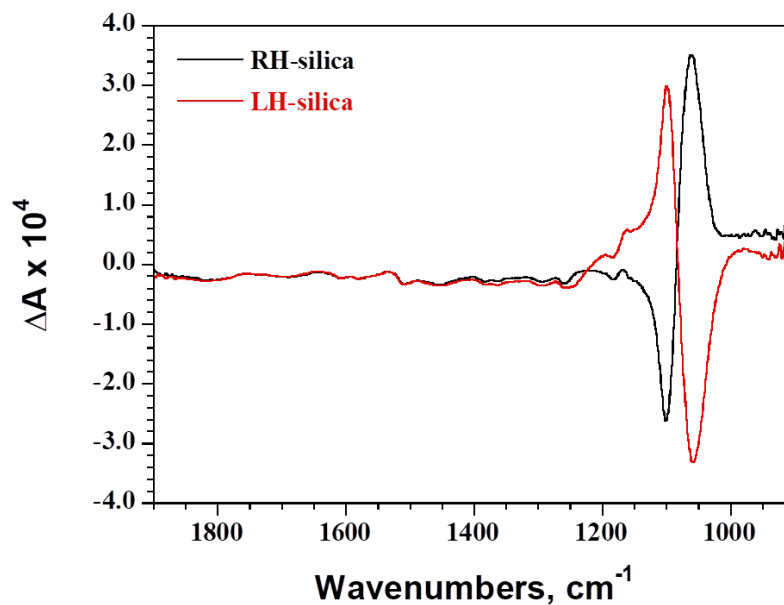


Figure. 5-29. Raw VCD spectra of RH-silica (black spectrum) and LH-silica (red spectrum) samples.

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Chapter 6

Conclusion and perspectives

In this work, we focused how chiroptical properties can be observed from achiral carbon materials and oligoamide foldamers when they are in interaction with helical silica-based materials. The cationic surfactant (called 16-2-16 or gemini-type surfactant) with chiral tartrate counterion self-assembles to helical nanostructure, the handedness of which can be controlled by the enantiomer of tartrate. This helical self-assembly serves as a soft template to construct silica-based material via sol-gel polycondensation of TEOS to obtain hybrid silica nanohelices. These silica nanohelices with helical morphology are used as chiral nano-template to induce chiral property onto achiral carbon dots (CDots), achiral polymer (PolyDHN-TMTA) and to do enantiomeric enrichment of racemic oligoamide foldamers (Q_n).

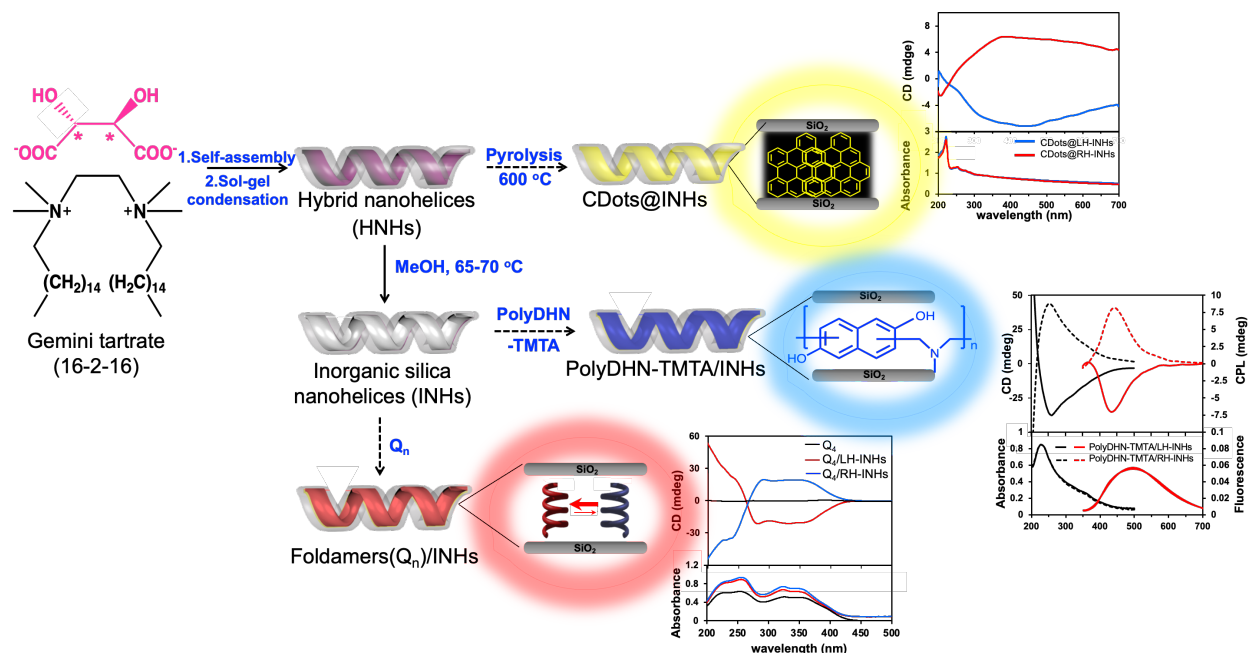


Figure. 6-1 Summary illustration for chirality induction to achiral carbon dots, achiral polymer and enantiomeric enrichment of racemic oligoamide foldamers.

The first part of my thesis is about the fabrication of chiral carbon dots (CDots) using silica nanohelices. The organic template of 16-2-16 was used as carbon source, meanwhile the helical morphology of silica nano-template acted as a chiral inducer. For preparation of optically active

CDots, the hybrid nanohelices were pyrolyzed at 600 °C under a vacuum to obtain CDots@INHs. Interestingly, CDots@INHs showed symmetrical CD signals in a wide wavelength range of 200-700 nm. The CDots@LH-INHs and CDots@RH-INHs showed negative and positive CD signals, respectively. The control experiment using pyrolyzed 16-2-16 without silica nanohelices, resulted in no CD response of CDots. Therefore, the silica nanohelices played a crucial role in endowing chiral property of CDots. The obtained CDots were characterized by several techniques including XPS, Raman and TEM. XPS analysis indicated that the major carbon content in CDots@INHs was sp^2 carbon, meanwhile Raman spectra showed two main peaks of D and G bands corresponding to an amorphous and crystalline phase of CDots. The high-resolution TEM indicated the average size of CDot was ~ 4 nm confined in nanospace of silica template. We attempted in doping the CDots with other atoms (Doped-CDots@INHs) by replacing tartrate ions with other dopants via an ion-exchanging method. The dopants were achiral hetero atoms, aromatic molecules and metal-ion complexes. The symmetrical CD signals of doped-CDots@INHs were observed even when the chiral tartrate anion was replaced by other achiral dopants, therefore, it suggested that the chiral property of CDots@INHs was not influenced by the asymmetric carbon from tartrate. When we exchanged the tartrate counterions with polymerizable monomers DHN, then crosslinker was introduced successively, we could also observe CD signals from the resulting polymer after the polymerizing reaction, confined in the chiral nanospace. No CPL was observed from these CDots@INHs or polymer@INHs. This work has been published in *Chem. Commun.*, 2023, **59**, 9762-976.

In the second part of my PhD research, we report chirality induction of achiral polymer (PolyDHN-TMTA) using silica nanohelices as a chiral template. Hollow inorganic silica nanohelices (INHs) were drop-casting on a quartz substrate to create a thin film of INHs. Two approaches, *ex-situ* and *in-situ* methods were used to induce the chiral property to achiral PolyDHN-TMTA.

In the case of the *ex-situ* method, PolyDHN-TMTA was prepared by polymerization between 2,6-hydroxyphthalene (DHN) and TMTA crosslinker (1:1) in H_2O prior to their introduction inside INHs. The absorption spectra of PolyDHN-TMTA showed a broad continuous band extended in the UV-visible range suggesting the extension of polymer chains. Furthermore, the suspension of PolyDHN-TMTA clearly showed the scattering of a light beam due to Tyndall effect corresponding to the formation of polymer colloid particles. The fluorescent emission of

PolyDHN-TMTA shifted to a longer wavelength from DHN monomer, corresponding to the extension of the polymer chain after polymerization. The elemental compositions of PolyDHN-TMTA represented three main elements including carbon, nitrogen and oxygen. The sp^3/sp^2 ratio was calculated to be ~ 2.51 . Then, PolyDHN-TMTA suspension was drop-casted on INHs thin film and dried to obtain PolyDHN-TMTA/INHs which showed symmetrical CD and CPL signals with $g_{abs} \sim -8.5 \times 10^{-4}$ and 1.1×10^{-3} (230 nm), and $g_{lum} \sim -7.8 \times 10^{-3}$ and 5.4×10^{-3} (435 nm). The helical morphology of PolyDHN-TMTA/INHs with a darker contrast, suggesting the helical morphology of PolyDHN-TMTA was influenced by the helical morphology of INHs. Furthermore, the thermal treatment of PolyDHN-TMTA/INHs (300 °C) was studied resulting in the enhancement in chiral properties along with the decreasing sp^3/sp^2 ratio and oxidized-nitrogen percentage. This work is in the process of preparation of manuscript.

In the case of the *in-situ* method, the helical INHs served both as a chiral inducer and chiral nanoreactors for synthesis of PolyDHN-TMTA with chiroptical properties. There were three sub-methods in *in-situ* synthesis. In *in-situ* synthesis in method I, DHN monomer was firstly drop-casted on INHs and followed by drop-casting TMTA crosslinker. Whereas, method II was started by introducing TMTA crosslinker on INHs before adding DHN monomer. In method III in *in-situ* synthesis, DHN and TMTA were mixed in H₂O just before drop-casting on the INHs films and let continue the polymerization reaction. Method I and method II could not completely polymerize PolyDHN-TMTA due to the strong crystallinity of DHN and the degradation of TMTA, respectively. Meanwhile, the method III method could generate the complete polymerization of PolyDHN-TMTA with symmetrical CD and CPL signals. Therefore, this part of my research demonstrated a versatile design chirality induction to achiral polymers using silica nano-template. This work is in the process of preparation of manuscript.

In the final part of my thesis, I was interested in the effect of INHs to the racemic oligoamide foldamers (Q_n). The racemic oligoamide foldamers conformationally exist in a dynamic system between two enantiomers between *P*- and *M*-form. When the solution of racemic foldamers was drop-casted on INHs thin film to obtain Q_n/INHs with clear CD and CPL signals, the signs of which is determined by the handedness of silica nano-template as it showed negative (positive) signal in LH (RH)-INHs, respectively. It was observed that different solvents and drying temperatures have an important effect for chirality induction from the racemic Q₄. The films dried at 4 °C showed the highest chirality of racemic Q₄, while the high temperature at 60 °C showed

the least performance to endow the chiroptical properties. Similarly, the drying of the sample in the least volatile solvent showed the highest chiroptical signals except for nitrobenzene. The speed of drying is, therefore a crucial factor inducing the chiroptical signals. The kinetic study for chirality induction of racemic Q₄ foldamers was related to the physical properties of solvent; boiling point and vapor pressure. The optimized ratio between Q₄ and INHs was studied as Q₄ 7.50x10⁻⁸ mole to 5.66x10⁻⁵ cm⁻³ volume of hollow INHs. There were two possibilities why we could observe chiroptical properties of racemic Q_n after drop-casting on INHs thin film. One, the enantiomeric enrichment happened, meanwhile another possibility is the Q_n remain racemate while organizing chirality in the chiral nano-space of INHs. The induction of chiroptical signals from racemic foldamers with different lengths (Q₄, Q₆, Q₈ and Q₁₆) was investigated. The results indicated the g_{abs} decreased as the foldamers length increased, as Q₄/INHs expressed the highest chirality while Q₁₆/INH had the lowest in g_{abs}. It assigned that it is more difficult to control the handedness of longer foldamers by INHs meanwhile the CD signals of shorter foldamers are easily controlled expressing in higher g_{abs}. We attempted to get rid of chiral INHs by washing them with DMF in order to evidence the enantiomeric excess of the Q₈ in the INHs nanospace before their racemization (if there is any deracemization). If racemic foldamers were deracemized by INHs, the decrease in CD signal should be observed due to their racemization. Unfortunately, the CD signals of Q₈ after washing by DMF were unclear and reproducible, which could be assigned to the fast racemization of Q₈ foldamers after removing chiral INHs templates. Meanwhile, there seems to be some tendencies, which could suggest partial deracemization. The surface variation of INHs was investigated in three kinds of INHs, bare INHs, aminated INHs and INHs-calcinated. It was found that aminated INHs provided the highest in g_{abs} and g_{lum} from the racemic Q_n, and the INHs-calcinated showed the lowest efficiency to induce the chiroptical signals from the racemic foldamers. Consequently, it implied that the surface polarity had a huge impact on the chirality induction using silica-based nano-template. The interaction between chiral foldamers with camphenyl moiety and INHs was investigated. The results clearly indicated that chiral foldamers show highly different interaction with INHs having different handedness. The INHs and the foldamer with the same handedness showed strong chiral property in CD and CPL signal, i.e. Q₄R with left-handed helicity in LH-INHs and Q₄S with right-handed helicity in RH-INHs. On the other hand, chiral foldamers in INHs with the opposite handedness (Q₄R/RH-INHs and Q₄S/LH-INHs) showed the competitive effect between molecular chirality from foldamers and chirality from

helical silica nanostructures. Therefore, it suggested that the chiral foldamers were strongly sensitive to the chiral environment of the helical silica template. This part of my thesis indicated that chiral environment of silica nanohelices at nano-scale could be used for enantiomeric enrichment of racemic oligoamide foldamers. Therefore, this work was regarded as a starting point in order to fabricate chiral nano-materials for enantiomeric separation, which gained a lot of attention in pharmaceutical industries.

In summary, silica nanohelices show a strong effect on the chirality induction of achiral carbon materials, achiral polymer and racemic foldamers. This work represents a developed approach for endowing the optical activities including CD and CPL response of optical inactive materials/molecules, which could be extremely beneficial for further applications in the future.

Publications and communication

Publications

1. Sequential chiral induction between organic and inorganic supramolecular helical assemblies for the *in situ* formation of chiral carbon dots, *Chem. Commun.*, 2023, **59**, 9762-9765
2. Chiral Perovskite Nanocrystal Growth inside Helical Hollow Silica Nanoribbons, *Nano Lett.* 2023, **23**, 8, 3174–3180
3. *In-situ* and *Ex-situ* fabrication of optically active polymer thin film using silica nanohelices (Manuscript preparation)
4. Chirality induction of oligoamide foldamers based on silica nanohelices (Manuscript preparation)

Communication

1. Poster presentation “**Chirality induction to achiral carbon-based materials and foldamers by artificial chiral silica nanohelices**” Conference Chirality2023, Rome, Italy 24-27 July, 2023
2. Oral presentation “**Chirality induction to achiral carbon-based materials and foldamers by artificial chiral silica nanohelices**” Chemistry-meet-Biology meeting, 27 April, 2023, IECB, Pessac, France
3. Poster presentation “**Chirality induction to achiral carbon-based materials and foldamers by artificial chiral silica nanohelices**” Journee Andre Collet de la Chiralite 2022, 4-7 October, Biarritz, France
4. Oral presentation “**Chirality induction to achiral carbon-based materials and foldamers by artificial chiral silica nanohelices**” Journée du pole CBSC, IECB, Pessac, Bordeaux, 2022
5. LICORICE, Summer school Life is chiral: Biological and Chemical fundamentals and novel approaches in chiral recognition, 26-30 June 2022, Lecce, Italy.
6. Oral presentation “**Chiral Carbon dots based on silica nanohelices**” kickoff CHIMERA, European Institute of Chemistry and Biology, Pessac, Bordeaux, France, 2022

7. Poster presentation “**Chiral induction of Carbon nanomaterials by artificial silica nanohelices**” the 24th of 24th Day of the Doctoral School of Chemical Sciences, Pessac, Bordeaux, France, 2022
8. Participant (viewer) in the Global Young Scientists Summit (GYSS) 2022, Virtual meeting
9. Oral presentation of poster presentation “Chiral Carbon dots obtained using silica nanohelices” Materials Research meeting (MRM2021), Yokohama, Japan, 2021
10. Poster presentation “**Chiral Carbon dots obtained using silica nanohelices**” CBMN’s scientific day, Bordeaux, Pessac, France
11. Oral presentation “**Chiral Carbon nanodots using silica nanohelices**” CBMN seminar, 2021, Pessac, Bordeaux, France

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