Morphological transformation of nanocrystals

Wang, Shaoyan

2019

Wang, S. (2019). Morphological transformation of nanocrystals. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/136757>

<https://doi.org/10.32657/10356/136757>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 22:59:23 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

[Morphological Transformation of Nanocrystals]

[Wang Shaoyan]

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

[01. 08. 2019]

[Morphological Transformation of Nanocrystals]

[Wang Shaoyan]

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2019

Special Statement

The work presented in this thesis has been completed under the supervision of professor Dr. Chen, Hongyu.

01. Aug. 2019

.....
Date

.....
Chen Hongyu

01. Aug. 2019

.....
Date

.....
Wang Shaoyan

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

01. Aug. 2019

.....

Date

Wang Shaoyan

.....

Wang Shaoyan

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

01. Aug. 2019

.....
Date

.....
Zhao Yanli

Authorship Attribution Statement

This thesis contains material from 1 paper published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 2 is published as Y. Lei, S. Wang (co-first author), Z. Lai, X. Yao, Y. Zhao, H. Zhang and H. Chen. Two-dimensional C₆₀ nano-meshes *via* crystal transformation. *Nanoscale* 11, 8692-8698 (2019) DOI: 10.1039/C8NR09329F.

The contributions of the co-authors are as follows:

- Dr. Y. Lei and Dr. H. Chen designed and planned this project.
- I and Dr Lei performed most of the experiments and I prepared the manuscript drafts. The manuscript was revised by Dr Lei and Dr. Chen.
- I interpreted the mechanisms and analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Characterization, Testing and Simulation.
- Dr Yao and Dr. Zhao helped in TGA characterization.
- Dr Lai and Dr. Zhang helped in the HRTEM and SAED characterization

01. Aug. 2019

.....
Date

.....
Wang Shaoyan

Abstract

The structure of organic/molecular crystals plays an important role in their properties and applications. While myriads of organic compounds have been synthesized under the macroscopic scale, the shape control of organic crystals remains at a primitive level at the micro- or nanoscale. (**Chapter 1**). Thus, it is urgent to develop new synthetic handles for designing organic crystals.

A simple and effective solution-phase strategy has been developed to achieve hexagonal C₆₀ mesh networks made of aligned nanorods, which were obtained by crystal transformation from C₆₀ microplates (**Chapter 2**). The crystal transformation was caused by removing and embedding the co-solvent molecules. The epitaxial growth of rod on plate by the lattice matching leads to the ordered nanorod arrays. The unconventional role of solvents provides a good opportunity for exploring the morphologies of organic/molecular crystals.

Thus, we propose solvent exchange as a new synthetic handle for creating complex micro- or nano- structures of organic crystals. Understanding the mechanism of solvent exchange and the effect of solvent are basis for the generality of the synthetic method (**Chapter 3**). Here, we systematically explored the role of solvents and their competitive relationship during the destabilization and on-site crystallization of the crystals. Therefore, with mitigated driving force in solution phase, solvent loss or exchange in C₆₀ plates does not lead to structural collapse, but leads to crystal transformation to mesh networks.

The generality of crystal transformation has been explored. The C₆₀ nanorods also can transform to orthogonal plates with an overall rod shape. In addition, the C₆₀/ferrocene mesh networks were obtained by crystal transformation of the *fcc* C₆₀/ferrocene plates. Besides the hexagonal C₆₀ plates, the rhombic C₆₀·trichlorobenzene plates transformed to rhombic nano-meshes by solvent exchange. Interestingly, C₇₀ meshes were converted from C₇₀ cubes by incubation in the transformative solution.

However, this method is not only applied to molecular crystals (C_{60} or C_{70}), but also to most organic crystals with solvent incorporation. The TPE-4Br organic crystal has been demonstrated to form different shapes (plates, prism-like structures or wires) by tuning the embedded solvent molecules (**Chapter 4**). Furthermore, the *p*-xylene-rich TPE-4Br plate can undergo crystal transformation to microrod arrays by solvent exchange. In addition, the crystal transformation was accompanied by the luminescence changes.

Considering the wide variety of solvate crystals in the literature, our new synthetic handle and the understanding of mechanism opens a window for designing sophisticated crystal morphologies.

Acknowledgements

On the occasion of the completion of this thesis, I would like to express my sincere thanks to my supervisor, Prof. Chen Hongyu. He is smart and good at thinking. For scientific research, he is extremely serious and scrupulous about every detail. One of the great things about Prof. Chen is that he teaches students in accordance with their aptitude. He taught me the logic analysis and helped me improved my ability to analyze and solve problems. I want thank him again for his guidance and concern in my research and life during the four years for pursuit doctor's degree. Here, I wish Prof. Chen every success in his work, and then climb the peak in future researches.

Also, I want to thank Prof. Zhao sincerely, for all the care and supports he had provided for me after Prof. Chen left university. He also helps me a lot for the characterization and analysis in my first paper.

I really appreciate the Division of Chemistry and Biological Chemistry (CBC), School of Physical and Mathematical Sciences (SPMS), Nanyang Technological University (NTU), which support my 4 years scholarship for my PhD and provide the course learning.

In addition, I want to express my gratitude for my group members and collaborators. Discuss and learning with them has made great progress for me. I would like to especially thank Dr. FENG Yuhua, Dr. SONG Xiaohui, Dr. LAM Zhen-hui, Dr. WANG Ruoxu, Dr. LIU Jiawei, SU Dongmeng, HAN Fei, and XU Weichang. I also thank Dr. LAI Zhuangchai and TRAN Thu Ha for their help in characterization and data processing.

Finally, I am truly grateful for my family. Without their supporting, I am impossible to complete my PhD studies. I especially want to thank my wife for her support and trust over the years and for her care and encouragement in my life and spirit.

Table of Contents

Abstract	1
Acknowledgements	3
Table of Contents	4
 Chapter 1 Introduction.....	 8
1.1 The applications of organic crystals	8
1.2 General method of organic crystals	12
1.2.1 Additive control for organic crystals	13
1.2.2 The physical vapor transport (PVT) method	14
1.2.3 The melting method	17
1.2.4 Solution growth method.....	19
1.3 Crystal morphology controlling by solvent molecules	25
1.4 The effect of solvent molecules on florescence properties	29
1.5 Desolvation process in organic crystals	30
1.6 Single-crystal to single-crystal (SCSC) transformation.....	33
1.7 Summary	39
References.....	41
 Chapter 2 Two-Dimensional C₆₀ Nano-Meshes <i>via</i> Crystal Transformation ..	 48
2.1 Introduction	48
2.1.1 Mesh structure in inorganic crystal	49
2.1.2 Morphologies of fullerene crystals and their applications	56
2.2 Material and methods	61
2.2.1 Materials	61
2.2.2 Methods	61

2.2.3	Characterization	64
2.3	Results and discussion	64
2.3.1	Dependence of crystal morphologies on solvent ratio	64
2.3.2	The solvent environment causes structural transformation	69
2.3.3	Identification of crystal system and solvent	72
2.3.3.1	Characterization the crystal and solvent molecules by XRD and TGA	72
2.3.3.2	Investigating the incorporated solvent by spectra.....	74
2.3.4	The effect of solvent on the structural rearrangement	76
2.3.5	Lattice mismatching and epitaxial relationship	81
2.4	Conclusion	83
2.5	Appendix	84
	References.....	86

Chapter 3	Solvent Exchange as a Synthetic Handle for Controlling Molecular Crystals	90
3.1	Introduction	90
3.1.1	Morphology of molecular crystals and their applications	90
3.1.2	Well established size and shape control in inorganic nanocrystals ...	91
3.1.3	A new synthetic handle for organic nanocrystals	91
3.2	Material and methods	92
3.2.1	Materials	92
3.2.2	Methods	93
3.2.3	Characterization	97
3.3	Results and discussion	98
3.3.1	Morphologies of C ₆₀ depend on co-solvents ratio	98
3.3.2	Difficult to control the structural change in drying conditions.....	99

3.3.3	Stability of C ₆₀ crystals in various conditions.....	100
3.3.4	The effect of IPA on desolvation	101
3.3.5	Characterization by TGA and spectra.....	103
2.3.3.1	Characterization the solvent exchange by TGA	103
2.3.3.2	Characterization by spectra	104
3.3.6	Crystallographic characterization by XRD and SAED.....	106
3.3.7	The yield of mesh networks against the solvent ratio in transformative solution	110
3.3.8	Isolate the variables to understand the separate role of co-solvents ..	113
3.3.9	Mechanistic proposal	117
3.3.10	Intermediates during crystal transformation	117
3.3.10.1	T-shape and X-shape junctions	118
3.3.11	Atomic force microscope topographic images of C ₆₀ crystals.....	119
3.3.12	Thermodynamic driving force and kinetic factors.....	120
3.3.13	Generality of crystal transformation	121
3.4	Conclusion	126
3.5.	Appendix	127
	References.....	138

Chapter 4 Solvent Exchange Induced Crystal Transformation of AIE Crystals Accompanied by Tuning Emission

4.1	Introduction	143
4.1.1	The advantage of aggregation-induced emission (AIE)	143
4.1.2	Application of AIE molecules	146
4.1.3	Lack of synthetic method for morphologies control of AIE crystals.	152
4.1.4	The effect of solvent on the luminescence of AIE crystals	152
4.1.5	Solvent exchange for regulating AIE crystals	152

4.2	Material and methods	154
4.2.1	Materials	154
4.2.2	Methods	154
4.2.3	Characterization	156
4.3	Results and Discussion	157
4.3.1	Morphology of TPE-4Br crystals depend on the solvents	157
4.3.2	Identification the crystals and solvents by XRD and TGA	158
4.3.3	The stability of TPE-4Br crystals	160
4.3.4	Strategy for crystal transformation	161
4.3.5	Solvent exchange during crystal transformation	164
4.3.6	Temporal evolution during crystal transformation	164
4.3.7	Effect of solvent molecules on luminescence of TPE-4Br crystals ..	165
4.3.8	Characterization by Raman and IR spectra	168
4.3.9	The mechanism of crystal transformation	170
4.4	Conclusion	172
4.5	Appendix.....	174
	References.....	181
Chapter 5	Conclusion and Future Work	185
5.1	Conclusion	185
5.2	Future work	187
5.2.1	New morphologies for other organic crystals.....	187
5.2.2	The heterojunction structures for photoelectric application	191
	References.....	193
	List of Publications	194

Chapter 1 Introduction

Nanomaterials are defined as solid materials (elementals, compounds, alloys or crystals), which at least one of its dimensions is in the range of nanometer (nm). Nanomaterials exhibit different physical and chemical properties from their bulk counterparts, due to their specific surface area.¹⁻² Thus, many applications of nanostructures were explored in catalysis,³ sensors,⁴⁻⁵ and biomedical delivery.⁶ Despite the wide application of nanomaterials, people are not satisfied with the current situation of synthesis and hope to understand the mechanism of synthesis for the development of more complex structures. The synthesis of inorganic nanocrystals has been established,⁷⁻¹⁰ where size and shape are well controlled⁷⁻⁸ and new nano-architectures are rapidly emerging.⁹⁻¹⁰

1.1. The applications of organic crystals

Organic crystals have weak intermolecular interactions, Van der Waals forces. Thus, the weak intermolecular interactions give rise to different properties in organic crystals compared to inorganic nano materials (metallic or covalent bonds). However, due to sp² hybridization and delocalized π -electrons, organic molecules have semiconducting properties.¹¹ Charge transfer of organic semiconductor material occurs between donors and acceptors.¹² Thus, the organic crystals have developed rapidly in various fields, such as medicine,¹³⁻¹⁴ imaging,¹⁵⁻¹⁶ organic field-effect transistors (OFETs),^{11, 17-20} organic light-emitting diodes (OLEDs),²¹⁻²² and organic solar cells.²³⁻²⁷

Figure 1.1. (a) The chemical structures of organic molecules. (b) The images of BSB-Me, BSB-Me:Te, and BSB-Me:Pe organic crystals under 405 nm laser excitation. (c) Schematic diagram of the single-crystal-based OLED. (d) The fabrication procedures of template stripping technique for the OLEDs. Photographs of the (e) BSB-Me, (f) BSB-Me:Te, and (g) BSB-Me:Pe OLEDs driven at 10 V. Reprinted from ref 28, with permission. Copyright © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The electroluminescence phenomenon in organic materials has been found in the early 1950s. But the first practical OLEDs device was prepared by American physical chemist Ching W. Tang and his collaborators in 1987.²⁹ The device was used two-layer structure to separate the hole and electron transporting layers and thus the recombination and light emission would occur at the intermediate organic layer, leading to the reduction of voltage and the enhancement in efficiency. Since Tang developed the thin-film OLEDs, this field has made a great progress. However, single crystals for OLED fabrication has limited structures due to unbalanced carrier injection. Ding *et al.* demonstrated that three single crystals, 1,4-bis(4-methylstyryl)benzene (BSB-Me), tetracene (Te) and pentacene (Pe) could deposit onto the electrode to prepare light-

emitting devices.²⁸ The BSB-Me crystal acted as a host material, while the Te and Pe are applied to guest matrixes, Thus, the donor BSB-Me transferred the energy to the acceptor (Te and Pe) by dipole-dipole interaction. The initial BSB-Me shown blue emission. When the charge transfer occurred, the BSB-Me:Te, and BSB-Me:Pe have green and red emission, respectively (Figure 1.1). The pentacene doped BSB-Me single-crystal-based OLED exhibited high luminance (820 cd m^{-2}) and external quantum efficiency (EQE) (0.31 %), which were higher than the reported single crystal OLEDs without doping.³⁰⁻³²

General speaking, the donor-acceptor contacting mode of organic semiconductor is related to the photovoltaic phenomenon, which can convert light to electricity. The influence factors of the photovoltaic effects include excitons diffusion length, dissociation, and charge transport. However, the traditional of bilayer heterojunction had irregular arrangement. Thus, the drawbacks of the structure were the short of exciton diffusion length, leading to weak absorption of sunlight.³³ The small donor-acceptor interface area caused the low exciton dissociation efficiency. However, the ambipolar transport property of single crystal leads to high electron mobility and the regular structure give raise to a long exciton diffusion.

Karak *et al.* reported that rubrene single crystals were used to fabricate photovoltaic device.²⁶ The rubrene crystals were first prepared by the physical vapor transport process.³⁴ For the preparation of device, one thin single crystal was selected and laminated on the indium tin oxide (ITO) substrates. The ITO was pretreated by ultrasonication in water, acetone, and isopropyl alcohol (IPA), respectively. Then the ITO was treated with oxygen-plasma for 5 min treatment. Lithium fluoride (LiF) and aluminium (Al) are deposited on the crystals, which were used for cathode. During the deposition, a shadow mask was applied for deposited material on the rubrene crystals (Figure 1.2a). After LiF and Al were deposited on the substrate, a 200 μm channel formed between ITO and LiF/Al, which exposed rubrene crystals. The schematic diagram shown the lateral of the ITO-rubrene-LiF/Al device (Figure 1.2b). To investigate the

photovoltaic effect, different thickness of LiF layers (0-3.5 nm) were deposited onto the rubrene crystal, follow by Al deposition. Then the ITO–rubrene–LiF/Al device was tested I–V characteristics under AM 1.5 (100 mW/cm^2) simulated solar irradiation, as shown in Figure 1.2c-e. With the open-circuit voltage (V_{OC}) increase, the thickness of LiF interlayer increases. The V_{OC} of the device shown 0.47 V without inserting the LiF interlayer. However, when the device deposited with LiF interlayer, the V_{OC} increased to 1.16 V with 1.5 nm thickness and 1.28 V for 3.5 nm.

Figure 1.2. (a) The optical image of ITO-rubrene-Al device. (b) The schematic diagram of the ITO-rubrene-LiF/Al device. (c) The current-voltage curves of the ITO-rubrene-Al device was characterized with different thicknesses of LiF layers: (a) 0 nm, b) 1.5 nm, and c) 3.5 nm of LiF conditions under AM 1.5 simulated solar irradiation (100 mW cm^{-2}). Reprinted from ref 26, with permission. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As a popular application of organic crystals, field-effect transistor (FET) is favored by many scientists. The most common FETs are organic thin films transistors, which the thin film is

used to active layer.¹⁷ However, organic single crystals have good molecular packing and free of grain boundaries, resulting in high charge transport and mobility.³⁵ Thus, it is an ideal candidate for preparing FET. Bao's group have made great contributions to single crystal field-effect transistors.¹⁸⁻¹⁹ They reported a method that the large arrays of single crystals were directly prepared on the source-drain electrodes of transistor.¹⁸ In a typical experiment, the octadecyltriethoxysilane (OTS) was printed on Si/SiO₂ surfaces or poly-4-vinylphenol (PVP) dielectric (flexible plastic), then the single organic crystals were deposited on the OTS films (Figure 1.3). Based on this method, the pentacene, rubrene and fullerene (C₆₀) single crystals have been successfully used to fabricate transistors, whereas the device based on rubrene crystal has high mobilities with 2.4 cm² V⁻¹ s⁻¹.

Figure 1.3. Flexible single-crystal transistor arrays. (a) Schematic diagram of single-crystal transistor arrays on PVP dielectric. The bottom left of (a) shown the rubrene transistor array and the right exhibited the anthracene crystals array on the substrate of poly (ethylene terephthalate) (PET). Under a UV radiation, the pattern shown blue emission. (b) Electrical characteristics of the single-crystal transistor devices. Reprinted from ref 18, with permission. © 2006 Nature Publishing Group.

1.2. General method of organic crystals

Novel applications are based on designed synthetic methods. Therefore, investigating the growth method of organic crystals is conducive to deepen our understanding the physical

properties of materials and prepare on-demand device. The shape of inorganic crystal can be tuned by ligands⁷⁻⁸ and the manipulation of interfacial energy.⁹ But the synthetic control in organic crystal is far from ideal. There is no ligand known for specific facets.

1.2.1. Additive control for organic crystals

Some research works were reported that additives could absorb on the crystal facet to affect the growth of crystal.³⁶⁻³⁸ Weissbuch *et al.* discovered that the morphologies of glycine crystals were regulated by additives, which inhibited the growth of crystal facets by the steric effect of the side chain (Figure 1.4).³⁶ For example, the acetic acid, α -amino acid, and hexafluorovaline favored to absorb on $(00\bar{1})$, (010) (or $(0\bar{1}0)$), (011) facets of glycine crystals, respectively (Figure 1.4e-i). Despite the organic crystal structures could tune by the additives, the shapes were not well-defined compare to the ligand control in inorganic synthesis.⁷

Figure 1.4 Schematic diagram of packing arrangement and morphologies of different glycine crystals.

(a) α -form along the a axis, (b) γ -form along the c axis, (c) γ -form along the c axis. (d) r-Glycine

bipyramids formed in pure aqueous solution. (e, f) Twinned pyramidal γ -crystals in 4% acetic acid solution. (g) r-Glycine plate-like crystals formed at the aqueous solutions with both of (R)- α -amino acids and (S)- α -amino acids. (h) γ -glycine crystals grown from in 1-2% (w/w hexdfluorovaline/glycine) aqueous solutions. (i) 3% hexdfluorovaline/glycine aqueous solutions. Reprinted from ref 36, with permission. Copyright © 1994, WILEY-VCH Verlag GmbH.

Besides the additive control, a series of methods have been developed for preparing organic crystals to investigate the various properties and different morphologies. The ways for preparing large organic crystals include gas-phase, melt-growth, and solution methods.³⁹⁻⁴⁰

1.2.2. The physical vapor transport (PVT) method

In growth of organic crystal, people hope to prepare an entire and unbroken structure. But the impurities and defects will affect the intrinsic properties and morphologies of organic crystals.⁴¹⁻⁴² Therefore, it is crucial to develop a method for purifying organic crystals. The physical vapor transport (PVT) method was a popular method to prepare highly purified organic crystals.¹⁹⁻²⁰ Pioneered works about the PVT method have been developed by Kloc *et al.* in the 1990s.⁴³⁻⁴⁴ In this growth method, with the system pressure decreased, the solid materials changed to gas at low temperature. At a certain temperature, the materials reached the sublimation point, but it was lower than the melting point (Figure 1.5). Thus, when the carrier gas was pumped into the tube from the left side, the vapor of organic materials was carried to right side by the flow of gas. Then, the crystals were formed by decreasing the temperature. Thus, the impurities would be separated from the organic materials due to the different molecular weights.⁴⁵ Li *et al.* has demonstrated that the dibenzo[*d,d'*]thieno[3,2-*b*;4,5-*b'*]dithiophene (DBTDT) crystals obtained by the PVT method (Figure. 1.5b).⁴⁶ In a typical procedure, the DBTDT powders were maintained in a high-temperature zone of 140 °C for sublimation. With the temperature decrease to 85-140 °C, the crystals were spontaneously formed on the Si/SiO₂ substrate.

Figure 1.5. (a) Scheme of the physical vapor transport growth method. The dark blue crystals are pentacene crystals and the red and yellow crystals are impurities. (b-c) SEM images of the hexagonal DBTDT crystals. Reprinted from ref 45, 46 with permission. Copyright © 2005 American Chemical Society and 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, respectively.

The physical vapor transport method is suitable for crystals which are unstable at high temperatures. Thus, the crystal morphologies can be tuned by changing the temperature. As shown in the Figure 1.6, the pentacene crystals were prepared using the PVT method.⁴⁷ The pentacene formed wires or rods when the temperature at 350 °C. However, when the temperature decreased to 325 °C, many plates or disks were crystallized on the substrate. The possible explanation was that higher temperature caused the faster movement of molecules, leading to crystal growing along the direction with stronger intermolecular interactions.

Similarly, the dibenzo[d,d']thieno[3,2-b;4,5-b']dithiophene (DBTDT) crystal morphologies prepared by PVT method were also temperature-dependent.⁴⁸ When the DBTDT crystals grown at relatively high temperature (100 °C), the hexagonal plates formed. By decreasing the temperature to 85 °C, the hexagonal disks of the DBTDT crystals were changed to elongated hexagonal plates. When the DBTDT prepared at 70 °C, the diamond-like plates were obtained on the substrate. Thus, the temperature has a serious influence on the morphology of organic crystals. In addition, the rubrene crystals also exhibit similar phenomenon by affecting of temperature.⁴⁹⁻⁵⁰

Figure 1.6. (a) Schematic diagram of PVT synthesis method for preparing pentacene crystals. (b) SEM images of the pentacene wires. (c) SEM images of pentacene plates. Reprinted from ref 47 with permission. Copyright © 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 1.7. The crystal growth of dibenzo[d,d']thieno[3,2-b;4,5-b']dithiophene (DBTDT) at different temperature. SEM images of (a-c) hexagonal plates, (d-f) elongated hexagonal disks and (g-i) diamond-like plates. Reprinted from ref 48 with permission. Copyright © 2010 American Chemical Society.

1.2.3. The melting method

Some organic molecules have high melting point and chemical instability. Hence the melting methods are the most common methods for preparing of large organic crystals. Some organic molecules are not stable and oxidation, decomposition or polymerization will occur at high temperature. The melting methods can be used to prepare crystals, which suitable a few organic molecules.⁵¹⁻⁵³ The melts are usually naphthalene,⁵⁴ anthracene,⁵⁵ and pyrene.⁵⁶ There are three main melting methods, the Bridgman melting growth method, zone melting growth method, and Czochralski melting growth method.^{53, 57-58} We chose the zone melting growth method as an example to introduce the preparation of crystals. The schematic diagram of Figure 1.8a shown the zone melting method. At first, the organic powder was put in a quartz ampoule with an inert gas. After the whole ampoule was melted, the ampoule was moved through a temperature gradient. Then, the crystal nucleation spontaneously occurred at the tip of the ampoule. Finally, the crystallization propagated through the to the surrounding materials. In this method, only one or a few narrow zones are melted, and the crystal-melt interfaces move with the temperature gradient. Due to the solubility differences between crystals and impurities, the impurities are segregated at the crystal-melt interface, resulting in purification of the fresh crystal.^{51, 59} Therefore, the melting method are usually used to prepare large crystals. The N, N'-dimethylperylene-3,4: 9,10-bis(dicarboximide) (DM-PBDCI) molecules were melted in anthracene at a high temperature. With the glass ampoule cooling, the DM-PBDCI crystals grown to the size of almost 5 mm (Figure 1.8b, c).⁶⁰ In addition, the copper phthalocyanine (CuPc) can dissolve in melted anthracene at high temperature. When the temperature increased to 260 °C, the anthracene melts vaporized and sublimed to the top of the ampoule by elevating

the ampoule at low speed. After the temperature dropped, the CuPc raw materials were oversaturated and felled down to the bottom, thus CuPc wires were obtained with a large scale (about 11.6 mm in length).⁵²

Figure 1.8. (a) Schematic diagram of a typical melting growth method. Reprinted with permission from ref. 59. Copyright © 2013 Elsevier Science B.V. (b) DM-PBDCI crystals were formed at the bottom of the ampoule. (c) the separated DM-PBDCI crystals from solution. Reprinted with permission from ref. 60. Copyright ©2001 Elsevier Science B.V.

The morphology of organic crystals can be regulated and controlled by internal and external factors. The external factors affecting the crystal morphology include environment, temperature and pressure, which usually reflect in physical vapor transport and melting methods. On the other hand, the internal factor relates to intermolecular or intramolecular interactions and molecular structure. Due to the lack of ligands or regulators for controlling the facets and interaction, the size and shape of organic crystal would mostly depend on the intrinsic facets. The stacking of organic molecules favors their own structural characteristics. However, the adjustable space of solution method is large because the solvent molecules assist crystallization in solution phase.

1.2.4. Solution growth method

Solution growth method is a traditional way for preparing organic crystals. As we all know, most of organic molecules favor to dissolve in organic solvents due to the theory of similarity and intermiscibility. The most common organic solvents include dichloromethane, chloroform, carbon tetrachloride, toluene, xylene, mesitylene and benzene. With the changes of environment, the decrease of solubility will lead to crystallization. Thus, several solution methods were established to prepare crystals (Figure 1.9). First of all, the simplest way to obtain organic crystals is solvent evaporation method.⁶¹⁻⁶² A saturated solution was preserved in a vessel (beaker or glass bottle) with a loose cover (Figure 1.9a). With the slow evaporation of the solvent, the organic molecules aggregated to form nuclei. Then the nuclei kept growing to larger crystals by increasing the solvent concentration.⁶¹⁻⁶² The dithiophene-tetrathiafulvalene (DT-TTF) single crystals were synthesized by the evaporation of DT-TTF/chlorobenzene saturated solution on electrodes, which exhibited high hole mobilities in organic field effect transistors (OFETs).⁶² Jiang *et al.* demonstrated that the 1,4-bis((5'-hexyl-2,2'-bithiophen-5-yl)ethynyl)benzene (HTEB) 2D materials were fabricated by solution cast-assembly,⁶³ which was a modified slow evaporation method. The HTEB molecules were dissolved in chlorobenzene to make a saturated solution. Then, the stock solution was casted onto substrates. After that the mixture were stored in Petri dishes for 24h. Finally, the HTEB were formed a film crystal on the substrates. The thiophene units provided strong molecular interactions of the HTEB molecules, thus the HTEB assembled to a large crystal. The film could grown on the Si, SiO₂, quartz or the surface of water. The OFETs based on HTEB crystals shown high performance with mobility of $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. By using this method, the BPEA micro wires, BNEA microribbons, and BTEA polyhedron crystals were obtained.⁶⁴ When used these crystals to prepare FET device, the BPEA micro wires ($0.73 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) had higher mobilities than BNEA microribbons ($0.73 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), whereas the 3D BTEA crystals

exhibited the lowest mobilities with $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The thickness and disrupted π stacking of the 3D crystal account for hindering of charge transport.

Figure 1.9. Solution methods for the growth of organic single crystals. (a) Solvent evaporation method. (b) Slow cooling method. (c) Vapor diffusion method. (d) Liquid-liquid interfacial precipitation method. Reprinted from ref 39 with permission. Copyright © 2013, Cambridge University Press.

The slow cooling method was used to prepare single crystals, which the solubility changes obviously with temperature. The organic materials dissolve in solvent at room or high temperature. When the temperature decrease, the material molecules spontaneously precipitate to form seeds. Then, the additional materials will adhere to the seeds to give heterogeneous nucleation, leading to the formation of large crystals (Figure 1.9b). The large rubrene crystal was formed when cooled temperature of the rubrene/1-propanol stock solution.⁶⁵ The solubility of rubrene in 1-propanol is obviously dependent on temperature. Thus, the rubrene saturated solution was prepared at 60 °C. Then, the stock solution was heated to 90 °C for 10 h. As the temperature slowly decreased to 45 °C, the crystals spontaneously nucleated and grown to large one. These methods used one solvent (good solvent) to dissolve materials and the crystals were precipitated by evaporation. However, some organic solvents act as poor solvent to the organic materials.

As shown in Figure 1.9c, the organic materials were dissolved into a good solvent 2 in a small beaker, then the small beaker with saturated solution was placed in a large beaker with volatile solvent (poor solvent 1). Then, the large beaker was sealed to prevent volatile solvent gases from evaporating out. Afterward, the solvent 1 diffused to solvent 2, leading to the stock solution oversaturation. Finally, the nucleation and crystallization occur. The diffusion speed of vapor can be tuned by changing the system temperature. The copper phthalocyanine (CuPc) (Figure 1.10a) is soluble in a non-volatile sulfuric acid solution, but the CuPc has low solubility in water. Thus, the diffusion of water into stock solution would increase the concentration and give rise to crystal formation.⁶⁶ The diffusion has two different ways, the solution diffusion method and the vapor diffusion method (Figure 1.10c, d). Whereas, the CuPc favor to form relatively large crystals by using the vapor method, which has smaller contact area and lower diffusion velocity in comparison of solution diffusion method. In addition, the Cl₂-NDI crystals were prepared by the vapor diffusion method.⁶⁷ A vial of CH₃OH/CHCl₃ (v/v = 7:3) mixture with a cap was placed in a petri dish, then the petri dish was covered with a parafilm to prevent solvent vapor diffusing out of the system. The petri dish was heated to 40 °C for 1 h, and the container was filled of solvent vapor. After that, the stock solution of Cl₂-NDI/CHCl₃ dropped on the OTES modified Si/SiO₂ wafer. The container was sealed for 1-3 days. As the solvent slowly evaporated, the Cl₂-NDI molecules nucleated and kept growing to form ribbon-shaped crystals at the edge of droplet. For optoelectronic applications, the Cl₂-NDI crystals could be used to fabricate field-effect transistor devices. By using a 25 μm gold wire as shadow mask, two ends of the Cl₂-NDI ribbon were deposited with Au film, which acted as drain and source electrodes. The Cl₂-NDI ribbon exhibited high mobility with 8.6 cm² V⁻¹ s⁻¹, and the good ambient stability.

Figure 1.10. (a) Chemical structure of organic compounds. (b) Schematic diagram of liquid-liquid diffusion method. (c) Vapor diffusion method. The water vapor slowly diffuses to the CuPc solution in H_2SO_4 . Reprinted from ref 66 with permission. Copyright © 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Schematic diagram of the Cl_2 -NDI crystals formation by the vapor diffusion method. (e) SEM images of Cl_2 -NDI crystals. Reprinted from ref 67 with permission. © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Generally, when two solvents were gently and slowly mixed, the difference of density can make two kinds of solvents to form an interface. Based on this phenomenon, many research groups employed liquid-liquid interfacial precipitation (LLIP) methods to prepare organic crystals.⁶⁸⁻⁷¹ In the LLIP method (Figure 1.9d), there are several basic requirements: 1. the solubility of materials in two solvents differs greatly. 2. The good solvent and poor solvent are miscible with each other. 3. the poor solvent should be lighter than the good solvent. In a typical procedure, the materials were dissolved in the good solvent (toluene, chlorobenzene,

dichloromethane or chloroform) to give saturated solution, then the poor solvent (methanol, ethanol, isopropanol alcohol and hexane or water) was slowly added to beaker, leading to the formation of an interface.⁷⁰⁻⁷⁴ When the poor solvent diffused into stock solution, seeds were formed due to the decrease of solubility. Miyazawa *et al.* demonstrated that the C₆₀ nanowhiskers were formed at the interface between toluene and IPA (Figure 1.11a, b).⁶⁸ In addition, Guo *et al.* reported that the 6-methyl-anthra[2,3-b]benzo[d]thiophene (Me-ABT) crystals were synthesized at ethanol/chloroform interface. Firstly, the Me-ABT powders were dissolved in chloroform at 60 °C. Afterward, the system was stopped heating, and the ethanol was slowly added into the Me-ABT/chloroform solution (Figure 1.11c). With natural cooling, the Me-AB microribbons crystallized at the bottom of vial (Figure 1.11d, e).⁷⁰

Figure 1.11. (a) Optical photographs of C₆₀ nanowhiskers formed in the toluene/IPA interface. (b) SEM micrographs of the C₆₀ nanowhiskers. (c) The schematic diagram of Me-ABT microstructure self-assembly process. (d) SEM image of the Me-ABT microribbons. (e) TEM image of a Me-ABT microribbon. Reprinted from ref 68, 70 with permission. Copyright © 2002, Materials Research Society and 2010, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, respectively.

Perylenetetracarboxyldiimide (PTCDI) crystals, as n-type semiconductors, have been fabricated by using the LLIP method.⁷² Three PTCDI derivatives with different alkyl chains have good solubilities in chloroform. When the methanol slowly added to a vial, there was a

clear interface formed between the methanol and PTCDI derivatives solution in chloroform. As the solutions diffused, the interface became blurred and eventually merged (Figure 1.12b). Finally, the PTCDI derivatives generated nanowires at the bottom of the vial. The diameter of nanowire decreases with the length of alkyl chain increases. The reason was that the longer alkyl chain, the lower solubility in methanol. Thus, the longer alkyl chain PTCDI-13 generated more nucleation sites and crystallized narrower wires.

Compare with the vapor diffusion, the organic material molecules in LLIP method (solution diffusion process) have larger contact area with poor solvent molecules in solution phase than solvent vapor. Thus, the entropy increase should be larger when the organic molecules are mixed with alcohol solution than with vapor. In a word, the LLIP method can generate many nucleation sites and favor to form micrometer sized crystals. On the other hand, the gentle interface without pressure from the bottom of beaker leads to form high quality crystals.

Figure 1.12. (a) The chemical structures of PTCDI derivatives. (b) Optical photographs of the evolution of solution diffusion. The upper liquid is methanol and the lower liquid is the PTCDI/ CHCl_3 solution. The final image shows the PTCDI-C8 crystals in a large flask. The SEM images of (c) PTCDI-C5, (d) PTCDI-C8, and (e) PTCDI-C13 nanowires. Reprinted from ref 72 with permission. Copyright © 2007 American Chemical Society

1.3. Crystal morphology controlling by solvent molecules

Typically, solvent act as an intermediary for growing crystals. It exhibits indirect or passive role in crystal formation. However, the solvent molecules have been found to regulate crystal morphologies⁷⁵⁻⁷⁹ when the solvent molecules were embedded into crystal lattice during crystallization. With strong interaction with the neighboring organic molecules, the solvent molecules can tune parameters of crystal package, which affect the lattice constants, facets and the separation among the fluorescence centers. For example, the morphologies of fullerene (C_{60}), a molecular crystal, has been well studied in the past two decades. When the *m*-xylene⁷⁶ or pyridine⁸⁰ was embedded into C_{60} , the rod-like crystals formed. As shown in Figure 1.13a, the C_{60} nanorods were prepared when saturated solution of C_{60} /*m*-xylene injected into cetyltrimethylammonium bromide (CTAB)/IPA solution with vigorously stirring. The inclusion of *m*-xylene in crystals could change the original *fcc* C_{60} crystal system to the *hcp* crystal system. However, if the C_{60} crystals formed at the interface between CCl_4 and IPA, the CCl_4 molecules were trapped into crystal lattice to give hexagonal plates (Figure 1.13d, e).⁷⁷

Figure 1.13. TEM image of C_{60} crystals. (a) TEM images of C_{60} rod was prepared at the interface between *m*-xylene and IPA. (b) The selected area electron diffraction patterns (SAED) of (b). (c) High-resolution TEM image of the C_{60} rod. (d, e) TEM images of C_{60} plates formed at CCl_4 /IPA interface. Reprinted from ref 76, 77 with permission. Copyright © 2007 American Chemical Society and 2007 American Chemical Society, respectively.

Sathish *et al.* also reported the solvent dependent morphology of C_{60} structures, the hexagonal plates and rhombic plates.⁸¹ As previous results, the C_{60} could form hexagonal plates when IPA slowly injected in C_{60} saturated solution in CCl_4 (Figure 1.14a, d). However, if the tert-butyl alcohol (TBA) added into saturated C_{60} /toluene solutions, many rhombic plates were obtained at the bottom of the vessel (Figure 1.14b, e). When the C_{60} nucleated at the interface between benzene and TBA, polygonal structures (such as, triangular, quadrilateral or hexagonal plates) formed (Figure 1.14c, f).

Figure 1.14. Schematic diagram of the C_{60} crystals formation by the LLIP method. (a) Hexagonal C_{60} plates formed at interface of CCl_4 and IPA. (b) Rhombic C_{60} plates crystallized at TBA/toluene interface. (c) Mixed C_{60} plates formed at TBA/toluene interface. SEM images of C_{60} at (d) IPA/ CCl_4 , (e) TBA/toluene, and (f) TBA/benzene systems. Reprinted from ref 81 with permission. Copyright © 2009 American Chemical Society.

Besides C_{60} fullerene, C_{70} can also prepare solvates. Park *et al.* demonstrated that C_{70} molecules formed cube-shaped structures using LLIP method.⁸² In a typical experiment, the saturated solution of C_{70} in mesitylene was prepared in a vial. Then IPA solution was added into the saturated solution. However, the uniformity of crystals varies with the speed of the addition of IPA. When the IPA added fast, the stock solution and IPA merged quickly. After 30s, the brown color of mother liquor changed to dark, indicating the nucleation occur (Figure 1.15a-i), the SEM images shown the C_{70} cubes has uniform size distribution (Figure 1.15b). If added the IPA slowly, a clear interface formed between two solution. The vial was stood for 5 min without disturbance. After 5 min sonication, the solution was mixed together, and C_{70} cubes were precipitated with the color of solution changed. The SEM images of Figure 1.15 d shown the C_{70} cubes prepared by the LLIP method with broad size distribution. The thermal

gravimetric analysis (TGA) data shown that a sharp weight decreased at 80 °C and the final weight loss was 22.7% at about 230 °C, which proved that the existence of the solvent molecules.

The different size distribution can be explained by the classic theory of nucleation and growth.⁸³⁻⁸⁶ At the early stage, the monomer species collide with each other. But the monomers are not stable, and will dissolve and regenerate in the solution. When the concentration increases to one certain point (oversaturation), many clusters increase to large size with stable nuclei, which defined as homogeneous nucleation. With the growth materials consuming, the oversaturated stage only last for a short time. After the concentration decreases and falls below critical point, there is not enough materials for formation of new nuclei. Thus, the free monomers deposited on the stable nuclei to form heterogeneous nucleation. Take C₇₀ as an example, when the IPA mixed the stock solution of C₇₀ quickly, the C₇₀ molecules are unfavorable in the IPA solution, and fast nucleated and formed a lot of clusters. Thus, the C₇₀ molecules of heterogeneous nucleation grown to large crystals with uniform size. On the hand, the C₇₀ molecules at the interface of IPA and mesitylene has local aggregation. The C₇₀ solution and IPA convectively diffused with each other, but there is no high concentration of monomer to get the critical point. The new nucleation continuous generate and the additional C₇₀ monomers adhere to small crystals. Finally, different sizes of C₇₀ cubes formed at the bottom of vial.

Figure 1.15. (a) The experiment procedure of synthesis of C_{70} crystals by the LLIP method. (b, c) SEM images of C_{70} cubes. (d) Optical images of C_{70} cubes. Reprinted from ref 82 with permission. Copyright © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.4. The effect of solvent molecules on fluorescence properties

Solvent molecules can affect not only the morphology of crystals, but also the fluorescence properties.^{75, 87} As shown in Figure 1.16a, the amorphous of TPE carbazole and cyano-substituted TPE derivative had yellow emission. But when the amorphous of TPE derivatives

exposed to different solvent vapors, the yellow-emissive solids changed into green-emissive or blue-emissive crystals.⁸⁷ Hinoue *et al.* reported that the TPMA and anthracene-1,8-disulfonic acid (1,8-ADS) crystals shown various morphologies when different solvent molecules were embedded into gaps between two molecules. When the inclusion crystals exposed to the $\lambda=365$ nm UV irradiation, different emission colors (from blue to orange-yellow) were exhibited (Figure 1.16b). In addition, the fluorescence emission spectra of the inclusion crystals shown widely shifted from 452 nm to 570 nm (Figure 1.16c).

Figure 1.16. (a) Optical images of the amorphous and crystalline of carbazole and cyano-substituted TPE derivative under light (>365 nm) illumination. Reprinted from ref 87, with permission. Copyright © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Photos of solvate and guest-free crystals of 1,8-ADS and TPMA under UV irradiation ($\lambda=365$ nm). (c) Normalized fluorescence spectra of these crystals excited at 340 nm. Reprinted from ref 75 with permission. Copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, respectively.

1.5. Desolvation process in organic crystals

However, the solvates usually are unstable when the environment changes. The loss of solvent from organic crystals, i.e., the desolvation process, has been observed in air or under vacuum conditions. Hasell *et al.* found that the organic crystals of

$C_{54}H_{60}N_{12} \cdot (C_4H_8O_2)_3 \cdot CH_2Cl_2 \cdot H_2O$ (CC2·dioxane) were cracked by heating to 100 °C for 16 h under dynamic vacuum.⁸⁸ The broken crystals (CC2 β) shown a formula of $C_{54}H_{60}N_{12}$, indicating the loss of solvent molecules (Figure 1.17). A similar situation also presented in cortisone acetate co-crystals (Figure 1.17c).⁸⁹ With the temperature increasing, the embedded solvent molecules left the cortisone acetate (CTA·DMSO) crystals, and the surface of the crystals became weathered (Figure 1.17d-g).

Figure 1.17. (a, b) SEM images of CC2·dioxane and CC2 β crystals. (c) The formula of cortisone acetate (CTA). Reprinted from ref 88 with permission. Copyright © 2014 American Chemical Society. The Optical images of CTA·DMSO crystal under heating at (d) 20 °C, (e) 80 °C, (f) 140 °C and (g) 210 °C, the scale bar is 2 mm. Reprinted from ref 89 with permission. Copyright © 2007 Akadémiai Kiadó, Budapest.

Shrestha *et al.* reported that the C_{60} plates formed at the interface between IPA and co-solvents (benzene and CCl_4).⁷⁹ By tuning the solvent ratio of CCl_4 in benzene, the surface of plates became porous. When the solvent ratio of CCl_4 /benzene was lower than 50:50, the plates had a smooth surface (Figure 1.18). However, if the solvent ratio reached 70:30, a few of pores

appear on surface of the plates. With the percentage of CCl_4 increased, the number of pores increased and the size of pores became larger. For the cause of porous structure, they believe that the slow evaporation of the embedded solvent molecules may led to the pore formation. In addition, the C_{60} nanowhiskers, crystallized in benzene/IPA system, could become porous during drying process. Besides, the CCl_4 C_{60} plates shown many pores under vacuum conditions during TEM characterization (Figure 1.13d).

Figure 1.18. SEM images of C_{60} crystals formed at IPA/ $(\text{CCl}_4 + \text{benzene})$ interface. The structure formed in different solvent ratio (CCl_4 : benzene), (a) 30:70, (b) 50:50, (c) 70:30, (d) 80:20, and (e) 90:10. (f) The large-view image of macropore of (e). Reprinted from ref 79 with permission. Copyright © 2012 American Chemical Society.

The crack or pore formation lead to the increasing of surface area, which is unfavorable in thermodynamics. But the porous structure or crushed structure were formation after the environment changes. It was indicated that the pore formation of crack and solvent loss had close correlation. However, the mechanism of structural changes has not been discussed in detail.

1.6. Single-crystal to single-crystal (SCSC) transformation

Similar desolvation and dehydration occur in metal-organic frameworks (MOFs) and coordination polymer (CP). Solvent molecules were usually bound to the center molecules (metal ions).⁹⁰ However, the loss of solvent molecules by the external force factors (such as heat, light or mechanochemical force) leads to structural changes. This phenomenon was related to the single-crystal to single-crystal (SCSC) transformation. Zhang *et al.* reported that the $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ crystal transformed to $\text{Cu}_3\text{Cl}_6(1,4\text{-dioxane})_2$ crystal under desolvation.⁹¹ The $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ molecule was synthesized by dissolving the $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ into HCl, CH_3OH , and 1,4-dioxane mixture solution. After two weeks, the blue crystals were precipitated at the bottom of beaker (Figure 1.19a). The chemical structure shown that the each Cu^{2+} has coordinated with two Cl^- , two H_2O , and two O atoms (Figure 1.19c). The H_2O formed hydrogen bonds with Cl^- and 1,4-dioxane, respectively. When the crystals were heated to 120 °C for 3 min, the desolvation occurred to form $\text{Cu}_3\text{Cl}_6(1,4\text{-dioxane})_2$, which the molecular conformation changed to square-pyramidal geometry from octahedrally geometry. In the $\text{Cu}_3\text{Cl}_6(1,4\text{-dioxane})_2$, four Cl^- (two from the original coordination center, the other two form the neighbor center), and two O atoms were coordinated to the Cu^{2+} . Thus, two water molecules were left the blue crystals, leading to the formation of brown crystals. Not only heating the crystals but also exposing to air could induce the desolvation or dehydration

as well. It was indicated that the desolvation was accompanied by changing of crystal composition, color, structure, and magnetism.⁹¹

Figure 1.19. (a) The structure arrangement of $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$. Inset: optical image of $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ crystals. (b) The structure of $\text{Cu}_3\text{Cl}_6(1,4\text{-dioxane})_2$. Inset: optical image of $\text{Cu}_3\text{Cl}_6(1,4\text{-dioxane})_2$ crystals. Cu: blue, C: light gray, O: red, H: gray, Cl: green. (c) The schematic diagram of the possible transformation process. Reprinted from ref 91 with permission. Copyright © 2010 Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim.

Bloch *et al.* demonstrated that the $[\text{Ag}(\text{dpzm})]\text{ClO}_4 \cdot 1.1(\text{DMSO}) \cdot 0.9(\text{EtOAc})$ crystals with a porous structure (left structure in Figure 1.20a) was synthesized when the ethyl acetate vapor slowly diffused into the mixture solution, which the AgClO_4 and Di-2-pyrazinylmethane (dpzm) dissolved in the dimethyl sulfoxide (DMSO) solution.⁹² The five-coordinate silver(I) center was coordinated with 1 dpzm, 1.1 DMSO and 0.9 EtOAc to form trigonal bipyramidal structure. The ^1H NMR spectroscopy demonstrated the existence of DMSO and EtOAc and the solvent

ratio in the final crystal structure. TGA data shown that the 3.9% mass loss at initial stage was contributed to EtOAc molecules (Figure 1.20b). Whereas, a sharp mass loss (19.1%) at the second stage indicated the presence of DMSO solvent molecules. The differential scanning calorimetry (DSC) shown an exothermic peak at 184 °C (Dotted circle), indicating the DMSO lost from the crystal.

Figure 1.20. (a) The chemical structure changes upon the desolvation. (b) The TGA and DSC curves of $[\text{Ag}(\text{dpzm})]\text{ClO}_4 \cdot 1.1(\text{DMSO}) \cdot 0.9(\text{EtOAc})$ crystals. Reprinted from ref 92 with permission. Copyright © 2010 Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim.

However, the $[\text{Ag}(\text{dpzm})]\text{ClO}_4 \cdot 1.1(\text{DMSO}) \cdot 0.9(\text{EtOAc})$ crystals are not stable in the paratone oil. At first, the $[\text{Ag}(\text{dpzm})]\text{ClO}_4 \cdot 1.1(\text{DMSO}) \cdot 0.9(\text{EtOAc})$ crystals (Figure 1.21a) were placed on a glass slide, then the slide was immersed in the paratone-N oil. Then the crystals were partially dissolved in the solution and some crushed into small pieces. After the crystals stored in the oil for 1-2 weeks, the $[\text{Ag}(\text{dpzm})]\text{ClO}_4 \cdot 1.1(\text{DMSO}) \cdot 0.9(\text{EtOAc})$ crystals

transformed to $[\text{Ag}(\text{dpzm})]\text{ClO}_4$ crystals by desolvation. The $[\text{Ag}(\text{dpzm})]\text{ClO}_4$ crystals shown irregular rod-like structures (Figure 1.21c, d). However, the mechanism of structural changes was not clearly understood.

Figure 1.21. (a) Optical images of $[\text{Ag}(\text{dpzm})]\text{ClO}_4 \cdot 1.1(\text{DMSO}) \cdot 0.9(\text{EtOAc})$ crystals. (b) Optical images of the crystals of (a), which immersed in paratone-N oil, some crystals were broken into smaller pieces. (c, d) There are many rod-like structures generated when the crystals of (a) maintained in paratone-N oil for 1-2 weeks. Reprinted from ref 92 with permission. Copyright © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The lost solvent molecules also can recombine into crystal by exposing crystals to the solvent vapor. Aslani *et al.* have prepared a $[\text{Pb}_2(8\text{-Quin})_2(\text{NO}_3)_2(\text{MeOH})]$ (8-HQuin = 8-hydroxyquinoline) crystals by using branched tube method.⁹³ The branched tube has two interconnected parts, the vertical tube and the side tube. In a typical experiment, the 8-

hydroxyquinoline and lead (II) nitrate powders were put in the vertical tube. Then, the methanol was added into the two parts of the tube. Under heating 60 °C in the oil-bath for 10 days, light brown crystals were crystallized in the cooler tube (side tube), as shown in Figure 1.22c.⁹⁴

Figure 1.22. (a) Chemical structure of $[\text{Pb}_2(8\text{-Quin})_2(\text{NO}_3)_2(\text{MeOH})]$. (b) Chemical structure of $[\text{Pb}(8\text{-Quin})(\text{NO}_3)]$. The schematic diagram shown the structural change from $[\text{Pb}_2(8\text{-Quin})_2(\text{NO}_3)_2(\text{MeOH})]$ to $[\text{Pb}(8\text{-Quin})(\text{NO}_3)]$ by thermal desolvation. (c) The brown $[\text{Pb}_2(8\text{-Quin})_2(\text{NO}_3)_2(\text{MeOH})]$ crystals. (d) The yellow $[\text{Pb}(8\text{-Quin})(\text{NO}_3)]$ crystals. Reprinted from ref 94 with permission. Copyright © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In the chemical conformation, 4 lead(ii) ions were connected with 4 8-Quin⁻ by the N and O atoms and coordinated with 2 methanol molecules. However, the [Pb₂(8-Quin)₂(NO₃)₂(MeOH)] crystals could undergo transformation to [Pb(8-Quin)(NO₃)] crystals by heating to 160 °C. The Pb (II) center coordinated was an oxygen atom from the nitrate ligand after the methanol molecules left. In addition, the other side of nitrate ligand was chelated to Pb (II) from the neighboring chain. With the chemical structure changed, the color of crystals changed from brown to yellow (Figure 1.22c, d).

The structures changes of MOFs and CP by desolvation are different from that of solvents or H₂O lost in solvent embedded organic crystal. Generally speaking, the solvent molecules or O atoms of H₂O molecules were usually coordinated with central metal ions of the structure of MOF or CP. When the environment changes (e.g. crystals are placed in air, under vacuum, heating and immersed in other solvents or oil), the coordinated solvents or H₂O molecules left the metal ions center, which formed a vacant coordination site. Then the unused atoms or ligands in adjacent metal center could bind to the unoccupied site of the original metal. Thus, the structural transformation occurs when the chelated solvent molecules lost. However, despite the loss of coordinated solvent, the new formed molecular structure will prevent the original crystals from collapsing or creaking after desolvation. On the other hand, some desolvated crystals can re-embed the solvent molecules to restore the original appearance.

However, the single-crystal to single-crystal transformation has limitations in structural changes. In most situations, only a single path way leads to structural transformation from crystals A to crystals B. In a few cases, the crystal structure could undergo transformation or from B to A. But the structural transformation was different to form crystals C because there is no dependable template to regulate the removal and incorporation of solvents.

Furthermore, the crystal morphologies have not been well controlled. If the crystals lost solvent seriously, it would cause crystal structures were easily cracked or broken (Figure 1.21).

On the other hand, when the solvent was partially lost (such as $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ crystals lost the H_2O molecules), the morphology of crystal did not change. However, the chemical structure was changed after desolvation or dehydration, leading to the conversion of crystal color.

The single crystal can transform to another crystal by external stimuli, but the transformation mechanisms of such structural transformation are not clearly understood.⁹⁰ On the contrary, the solvent embedded crystals were liable to collapse or form pores. However, the resemblance for the two cases is that the underlying reasons has not been studied in detail. Although embedded solvents have clearly observed in many crystals, and the desolvation processes were also demonstrated by various characterizations, the puzzled question is whether the solvent loss is caused by the structural changes, or the opposite.

Understanding the mechanism of structural changes of organic crystals (including pore formation, crumble and single crystal to single crystal transformation) is of great importance for establishing more general synthetic control. Thus, we focus our efforts on two core mechanistic questions: 1. What is the role of solvents in crystal formation and morphological changes? 2. How to effectively tune solvent molecules and reduce the desolvation rate during structural changes.

1.7. Summary

In this chapter, the classic synthetic methods of organic or molecular crystals and their application in optics, electricity and medicine have been discussed and analyzed. Although the morphology, size and polymorphism of organic crystals have been extensively studied in macroscale or large scale. But few of synthetic handles focus on the morphologies on nano- or micro- structure. Thus, the control capability of organic crystal in nanoscale is of great importance and remains a huge challenge.

The traditional methods, such as PVT method or melting method, are usually used to prepare large crystals. It is very common that solvent as a media for growing organic crystals and could tune the morphology of organic crystals when it was embedded into crystal lattice. Despite the single crystal can transform to single crystal by tuning the solvent molecules, the transformation is limited in crystals A to crystals B or crystals B to crystals A due to lack of template. Otherwise, the desolvation process is not under control, which leads to structural collapse or pore formation. However, the pore formation inspired me to explore the structural changes by controlling solvent molecules. If we can effectively tune the solvent to prevent structural crumble, the other solvent can be introduced to change the crystal morphology.

In this thesis, we focus on understanding the environment factors and role of solvents to mitigate the loss of solvents and directional regulate the solvent molecules in crystals. Therefore, the first step is to select suitable systems by screening the solvate crystals. Then, we need to understand the underlying mechanism, which is a necessary step for developing a general synthetic method. Whereas, we will explore which species plays what role at which time point; how to effectively tune solvent molecules; how to prepare complex structures and why the orderly structure well-defined morphologies are formed. When the above problems are solved, the generality of the method become invincible.

Therefore, we will start from the special case, which devote ourselves to preparing and exploring the formation of new structures (chapter 2). By understanding the role of solvent molecules and studying the mechanism of crystal transformation, we put forward a new synthetic strategy, which can be used in other molecular crystals (chapter 3). Not only C₇₀ fullerene but also organic crystals can be used for the solvent exchange method to construct complex nano-architectures, which the fluorescence is tunable (chapter 4). Finally, the complex organic/molecular crystals are promising for fabricating organic photoelectric devices (chapter 5).

Reference

1. Roduner, E. *Chem. Soc. Rev.* **2006**, 35 (7), 583-592.
2. Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, 105 (4), 1103-1170.
3. Liu, X.; Astruc, D. *Adv. Mater.* **2017**, 29 (16), 1605305.
4. Saha, K.; Agasti, S. S.; Kim, C.; Li, X.; Rotello, V. M. *Chem. Rev.* **2012**, 112 (5), 2739-2779.
5. Wang, S.; Liu, C.; Wang, H.; Chen, G.; Cong, M.; Song, W.; Jia, Q.; Xu, S.; Xu, W. *Acs Appl. Mater. Inter.* **2014**, 6 (14), 11706-11713.
6. Elsabahy, M.; Wooley, K. L., Design of polymeric nanoparticles for biomedical delivery applications. *Chem. Soc. Rev.* **2012**, 41 (7), 2545-2561.
7. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. *Angew. Chem. Int. Edit.* **2009**, 48 (1), 60-103.
8. Wang, Y.; He, J.; Liu, C.; Chong, W. H.; Chen, H. *Angew. Chem. Int. Edit.* **2015**, 54 (7), 2022-2051.
9. Feng, Y.; Wang, Y.; He, J.; Song, X.; Tay, Y. Y.; Hng, H. H.; Ling, X. Y.; Chen, H. *J. Am. Chem. Soc.* **2015**, 137 (24), 7624-7627.
10. Tan, R. L. S.; Chong, W. H.; Feng, Y.; Song, X.; Tham, C. L.; Wei, J.; Lin, M.; Chen, H. *J. Am. Chem. Soc.* **2016**, 138 (34), 10770-10773.
11. Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2011**, 112 (4), 2208-2267.
12. T. Ishiguro; K. Yamaji; G. Saito, Organic Superconductors, 2nd ed. *Springer-Verlag, Berlin, Heidelberg, Germany.* **1998**.

13. Nicol, A.; Kwok, R. T.; Chen, C.; Zhao, W.; Chen, M.; Qu, J.; Tang, B. Z. *J. Am. Chem. Soc.* **2017**, *139* (41), 14792-14799.
14. Gao, H.; Zhao, X.; Chen, S. *Molecules* **2018**, *23* (2), 419-419.
15. Fateminia, S. A.; Wang, Z.; Goh, C. C.; Manghnani, P. N.; Wu, W.; Mao, D.; Ng, L. G.; Zhao, Z.; Tang, B. Z.; Liu, B. *Adv. Mater.* **2017**, *29* (1), 1604100.
16. Leung, C. W. T.; Hong, Y.; Chen, S.; Zhao, E.; Lam, J. W. Y.; Tang, B. Z. *J. Am. Chem. Soc.* **2013**, *135* (1), 62-65.
17. Klauk, H. *Chem. Soc. Rev.* **2010**, *39* (7), 2643-2666.
18. Briseno, A. L.; Mannsfeld, S. C.; Ling, M. M.; Liu, S.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. *Nature* **2006**, *444* (7121), 913.
19. de Boer, R. W. I.; Gershenson, M.; Morpurgo, A.; Podzorov, V. *Phys. Status Solidi A* **2004**, *201* (6), 1302-1331.
20. Reese, C.; Bao, Z. *Mater. Today* **2007**, *10* (3), 20-27.
21. Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16* (23), 4556-4573.
22. Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107* (4), 953-1010.
23. Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19* (7), 1924-1945.
24. Yang, F.; Sun, K.; Forrest, S. R. *Adv. Mater.* **2007**, *19* (23), 4166-4171.
25. Zhang, H.; Jiang, L.; Zhen, Y.; Zhang, J.; Han, G.; Zhang, X.; Fu, X.; Yi, Y.; Xu, W.; Dong, H. *Adv. Electron. Mater.* **2016**, *2* (6), 1500423.
26. Karak, S.; Lim, J. A.; Ferdous, S.; Duzhko, V. V.; Briseno, A. L. *Adv. Funct. Mater.* **2014**, *24* (8), 1039-1046.
27. Zhang, J.; Xu, W.; Sheng, P.; Zhao, G.; Zhu, D. *Acc. Chem. Res.* **2017**, *50* (7), 1654-1662.
28. Ding, R.; Feng, J.; Dong, F. X.; Zhou, W.; Liu, Y.; Zhang, X. L.; Wang, X. P.; Fang, H.

- H.; Xu, B.; Li, X. B. *Adv. Funct. Mater.* **2017**, *27* (13), 1604659.
29. Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51* (12), 913-915.
 30. Takenobu, T.; Bisri, S. Z.; Takahashi, T.; Yahiro, M.; Adachi, C.; Iwasa, Y. *Phys. Rev. Lett.* **2008**, *100* (6), 066601.
 31. Ding, R.; Feng, J.; Zhang, X. L.; Zhou, W.; Fang, H. H.; Liu, Y. F.; Chen, Q. D.; Wang, H. Y.; Sun, H. B. *Adv. Funct. Mater.* **2014**, *24* (45), 7085-7092.
 32. Nakanotani, H.; Saito, M.; Nakamura, H.; Adachi, C. *Appl. Phys. Lett.* **2009**, *95* (10), 235.
 33. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270* (5243), 1789-1791.
 34. Briseno, A. L.; Tseng, R. J.; Ling, M. M.; Falcao, E. H.; Yang, Y.; Wudl, F.; Bao, Z. *Adv. Mater.* **2006**, *18* (17), 2320-2324.
 35. Podzorov, V.; Menard, E.; Borissov, A.; Kiryukhin, V.; Rogers, J.; Gershenson, M. *Phys. Rev. Lett.* **2004**, *93* (8), 086602.
 36. Weissbuch, I.; Leisorowitz, L.; Lahav, M. *Adv. Mater.* **1994**, *6* (12), 952-956.
 37. Davey, R. J.; Blagden, N.; Potts, G. D.; Docherty, R. *J. Am. Chem. Soc.* **1997**, *119* (7), 1767-1772.
 38. Hamilton, B. D.; Weissbuch, I.; Lahav, M.; Hillmyer, M. A.; Ward, M. D. *J. Am. Chem. Soc.* **2008**, *131* (7), 2588-2596.
 39. Jiang, H.; Kloc, C. *MRS Bull.* **2013**, *38* (1), 28-33.
 40. Wang, C.; Dong, H.; Jiang, L.; Hu, W. *Chem. Soc. Rev.* **2018**, *47* (2), 422-500.
 41. Jurchescu, O. D.; Baas, J.; Palstra, T. T. *Appl. Phys. Lett.* **2004**, *84* (16), 3061-3063.
 42. Provencher, F.; Bérubé, N.; Laprade, J.-F.; Simard, G.; Tant, J.; De Halleux, V.; Geerts, Y.; Silva, C.; Côté, M. *J. Chem. Phys.* **2012**, *137* (3), 034706.
 43. Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J.-L.; Garnier, F.

- Chem. Mater.* **1995**, 7 (7), 1337-1341.
44. Kloc, C.; Simpkins, P.; Siegrist, T.; Laudise, R. *J. Cryst. Growth* **1997**, 182 (3-4), 416-427.
 45. Roberson, L. B.; Kowalik, J.; Tolbert, L. M.; Kloc, C.; Zeis, R.; Chi, X.; Fleming, R. *J. Am. Chem. Soc.* **2005**, 127 (9), 3069-3075.
 46. Li, R.; Jiang, L.; Meng, Q.; Gao, J.; Li, H.; Tang, Q.; He, M.; Hu, W.; Liu, Y.; Zhu, D. *Adv. Mater.* **2009**, 21 (44), 4492-4495.
 47. Park, J. E.; Son, M.; Hong, M.; Lee, G.; Choi, H. C. *Angew. Chem. Int. Edit.* **2012**, 51 (26), 6383-6388.
 48. Li, R.; Hu, W.; Liu, Y.; Zhu, D. *Acc. Chem. Res.* **2010**, 43 (4), 529-540.
 49. Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. *Science* **2004**, 303 (5664), 1644-1646.
 50. Zhang, Y.; Dong, H.; Tang, Q.; He, Y.; Hu, W. *J. Mater. Chem.* **2010**, 20 (33), 7029-7033.
 51. Tripathi, A. K.; Heinrich, M.; Siegrist, T.; Pflaum, J. *Adv. Mater.* **2007**, 19 (16), 2097-2101.
 52. Jiang, W.; Wang, X.; Chang, Y.; Yu, S.; Ma, C.; Ye, K.; Cheng, C.; Du, G. *J. Cryst. Growth* **2006**, 290 (2), 544-547.
 53. Arivanandhan, M.; Sankaranarayanan, K.; Sanjeeviraja, C.; Arulchakkaravarthi, A.; Ramasamy, P. *J. Cryst. Growth* **2005**, 281 (2-4), 596-603.
 54. Selvakumar, S.; Sivaji, K.; Arulchakkaravarthi, A.; Balamurugan, N.; Sankar, S.; Ramasamy, P. *J. Cryst. Growth* **2005**, 282 (3-4), 370-375.
 55. Probst, K.; Karl, N. *Phys. Status Solidi A* **1975**, 27 (2), 499-508.
 56. Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1956**, 29 (1), 131-133.
 57. Bridgman, P. W. *Proc. Am. Acad. Arts. Sci.* **1925**, 305-383.

58. Hoesterey, D. *J. Chem. Phys.* **1962**, *36* (2), 557-558.
59. Hong, I. H.; Tan, K. J.; Toh, M.; Jiang, H.; Zhang, K.; Kloc, C. *J. Cryst. Growth* **2013**, *363*, 61-68.
60. Miyahara, T.; Shimizu, M. *J. Cryst. Growth* **2001**, *226* (1), 130-137.
61. Jiang, H.; Yang, X.; Cui, Z.; Liu, Y.; Li, H.; Hu, W.; Liu, Y.; Zhu, D. *Appl. Phys. Lett.* **2007**, *91* (12), 123505.
62. Mas-Torrent, M.; Durkut, M.; Hadley, P.; Ribas, X.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126* (4), 984-985.
63. Jiang, L.; Dong, H.; Meng, Q.; Li, H.; He, M.; Wei, Z.; He, Y.; Hu, W. *Adv. Mater.* **2011**, *23* (18), 2059-2063.
64. Wang, C.; Liu, Y.; Ji, Z.; Wang, E.; Li, R.; Jiang, H.; Tang, Q.; Li, H.; Hu, W. *Chem. Mater.* **2009**, *21* (13), 2840-2845.
65. Matsukawa, T.; Yoshimura, M.; Sasai, K.; Uchiyama, M.; Yamagishi, M.; Tominari, Y.; Takahashi, Y.; Takeya, J.; Kitaoka, Y.; Mori, Y. *J. Cryst. Growth* **2010**, *312* (2), 310-313.
66. Wang, C.; Fang, Y.; Wen, L.; Zhou, M.; Xu, Y.; Zhao, H.; De Cola, L.; Hu, W.; Lei, Y. *Chem.–Eur. J.* **2014**, *20* (35), 10990-10995.
67. He, T.; Stolte, M.; Würthner, F. *Adv. Mater.* **2013**, *25* (48), 6951-6955.
68. Miyazawa, K.; Kuwasaki, Y.; Obayashi, A.; Kuwabara, M. *J. Mater. Res.* **2002**, *17* (1), 83-88.
69. Wakahara, T.; Sathish, M.; Miyazawa, K. i.; Hu, C.; Tateyama, Y.; Nemoto, Y.; Sasaki, T.; Ito, O. *J. Am. Chem. Soc.* **2009**, *131* (29), 9940-9944.
70. Guo, Y.; Du, C.; Yu, G.; Di, C. a.; Jiang, S.; Xi, H.; Zheng, J.; Yan, S.; Yu, C.; Hu, W. *Adv. Funct. Mater.* **2010**, *20* (6), 1019-1024.
71. Kim, K. H.; Bae, S. Y.; Kim, Y. S.; Hur, J. A.; Hoang, M. H.; Lee, T. W.; Cho, M. J.;

- Kim, Y.; Kim, M.; Jin, J.-I.; Kim, S.-J.; Lee, K.; Lee, S. J.; Choi, D. H. *Adv. Mater.* **2011**, *23* (27), 3095-3099.
72. Briseno, A. L.; Mannsfeld, S. C.; Reese, C.; Hancock, J. M.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. *Nano Lett.* **2007**, *7* (9), 2847-2853.
73. Hoang, M. H.; Kim, Y.; Kim, S. J.; Choi, D. H.; Lee, S. J. *Chem.–Eur. J.* **2011**, *17* (28), 7772-7776.
74. Yang, J.; Heo, M.; Lee, H. J.; Park, S.-M.; Kim, J. Y.; Shin, H. S. *ACS Nano* **2011**, *5* (10), 8365-8371.
75. Hinoue, T.; Miyata, M.; Hisaki, I.; Tohnai, N. *Angew. Chem. Int. Edit.* **2012**, *51* (1), 155-158.
76. Ji, H.-X.; Hu, J.-S.; Tang, Q.-X.; Song, W.-G.; Wang, C.-R.; Hu, W.-P.; Wan, L.-J.; Lee, S.-T. *J. Phys. Chem. C* **2007**, *111* (28), 10498-10502.
77. Sathish, M.; Miyazawa, K. i. *J. Am. Chem. Soc.* **2007**, *129* (45), 13816-13817.
78. Shrestha, L. K.; Shrestha, R. G.; Yamauchi, Y.; Hill, J. P.; Nishimura, T.; Miyazawa, K. i.; Kawai, T.; Okada, S.; Wakabayashi, K.; Ariga, K. *Angew. Chem. Int. Edit.* **2015**, *54* (3), 951-955.
79. Shrestha, L. K.; Yamauchi, Y.; Hill, J. P.; Miyazawa, K. i.; Ariga, K. *J. Am. Chem. Soc.* **2012**, *135* (2), 586-589.
80. Minato, J.-i.; Miyazawa, K. i.; Suga, T. *Sci. Technol. Adv. Mater.* **2005**, *6* (3-4), 272.
81. Sathish, M.; Miyazawa, K. i.; Hill, J. P.; Ariga, K. *J. Am. Chem. Soc.* **2009**, *131* (18), 6372-6373.
82. Park, C.; Yoon, E.; Kawano, M.; Joo, T.; Choi, H. C. *Angew. Chem. Int. Edit.* **2010**, *49* (50), 9670-9675.
83. LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72* (11), 4847-4854.
84. Yin, Y.; Alivisatos, A. P. *Nature* **2004**, *437* (7059), 664.

85. Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem. Int. Edit.* **2007**, *46* (25), 4630-4660.
86. Chiu, C.-Y.; Li, Y.; Ruan, L.; Ye, X.; Murray, C. B.; Huang, Y. *Nat. Chem.* **2011**, *3* (5), 393.
87. Wang, Y.; Zhang, G.; Zhang, W.; Wang, X.; Wu, Y.; Liang, T.; Hao, X.; Fu, H.; Zhao, Y.; Zhang, D. *Small* **2016**, *12* (47), 6554-6561.
88. Hasell, T.; Culshaw, J. L.; Chong, S. Y.; Schmidtman, M.; Little, M. A.; Jelfs, K. E.; Pyzer-Knapp, E. O.; Shepherd, H.; Adams, D. J.; Day, G. M. *J. Am. Chem. Soc.* **2014**, *136* (4), 1438-1448.
89. Petit, S.; Mallet, F.; Petit, M.; Coquerel, G. *J. Therm. Anal. Calorim.* **2007**, *90* (1), 39-47.
90. Kole, G. K.; Vittal, J. J. *Chem. Soc. Rev.* **2013**, *42* (4), 1755-1775.
91. Zhang, B.; Zhu, D.; Zhang, Y. *Chem.–Eur. J.* **2010**, *16* (33), 9994-9997.
92. Bloch, W. M.; Sumby, C. J. *Chem. Commun.* **2012**, *48* (19), 2534-2536.
93. Mahmoudi, G.; Morsali, A.; Hunter, A. D.; Zeller, M. *CrystEngComm* **2007**, *9* (8), 704-714.
94. Aslani, A.; Morsali, A. *Chem. Commun.* **2008**, (29), 3402-3404.

Chapter 2. Two-dimensional C₆₀ nano-meshes *via* crystal transformation

The two-dimensional (2D) nanostructures have many applications in the catalysis, electronics, and energy conversion. Thus, developing the 2D structures with a rational and general approach is of importance. Despite the many 2D nanostructures have been designed, the synthesis of 2D nanoscale superstructures remains a great challenge due to the difficulty by arranging the materials in a controllable way. Here, hexagonal mesh networks are obtained via crystal transformation of C₆₀ microplates. The transformation is triggered by the removal and inclusion of solvent molecules and hence, driven by a small free energy difference. The epitaxial growth of ordered nanorod arrays is due to the matching lattice between the (111) facet of *fcc* plate and the (10 $\bar{1}$ 0) facet of *hcp* rods.

Besides the 2D C₆₀ mesh networks with on-site recrystallization, the more complicated C₆₀ mesh networks are also obtained. The multi-layer hexagonal meshes were achieved by rationally regulated solvent molecules. Thus, this route of co-solvent induced crystal transformation provides a unique mechanistic perspective and a new direction for designing sophisticated 2D superstructures.

2.1. Introduction

In macroscopic world, mesh is an essential structural feature to achieve transparency (e.g., screen window), separation (e.g., sieve, fishnet), support (e.g., sewage grid), and decoration. It is conceivable that these functions can be exploited at the nanoscale. But the synthesis of nanoscale mesh is still a big challenge. There are a few of examples known in inorganic system.

2.1.1. Mesh structure in inorganic crystals

Pioneer works have been carried out meshes by different methods. For example, the Yu group self-assembled Te nanowires into a film by the Langmuir-Blodgett method.¹ Firstly, the Te nanowires were synthesized by using the previous method.² The Na_2TeO_3 and poly(vinyl pyrrolidone) (PVP) were mixed and dissolved in distilled water with vigorous stirring at room temperature. Then the mixed solution was transferred to a Teflon-lined stainless steel autoclave. After 5 min, the mixture formed a homogeneous solution. Then a certain amount of hydrazine hydrate solution was added into the homogeneous solution, followed by an aqueous ammonia solution was dropped into the solution. The container was sealed and heated to 180 °C for 3 h. Finally, the temperature was decreased to room temperature naturally. The Te nanowires characterized by TEM (As shown in Figure 2.1a).

The Te nanowires can be assembled to film. In a typical experiment, a certain amount of Te nanowires with mother liquor was centrifugated and removed the supernatant. Then, Te nanowires were washed by acetone and separated by centrifugation. Afterward, the Te nanowires was dispersed to N,N-dimethylformamide (DMF) solution. Then of DMF and chloroform were a mixed added into the Te nanowires solution. A small amount of DMF promotes Te nanowires precipitation. The mixture was transferred to the Langmuir-Blodgett trough and formed a homogeneous solution. Te nanowires had good dispersion and floated on the surface of water. The DMF promotes PVP-coated nanostructures during assembly. The Te nanowire formed a film by self-assembling (Figure 2.1b, c). The selected-area electron diffraction (SAED) patterns demonstrated that the nanowire was along [001] direction.

Figure 2.1. (a) TEM image of the Te nanowires. (b) TEM image of the monolayer assembly of Te nanowires (c) TEM image of self-assembled Te nanowires with high magnification, the insert image is corresponding SAED pattern of Te nanowires. (d-f) TEM images of the nanomeshes fabricated by packing two layers of films (Te nanowires). The two layers of films in (d) has 45° , (e) 60° , and (f) 65° crossed angles. Printed from ref 1 with permission. Copyright © 2010 American Chemical Society.

In order to separate the compressed monolayer from the interface air/water, the monolayer Te nanowires was transferred to a planar substrate. By overlaying the resulting films, the angle between the parallel nanowire arrays can be arbitrarily controlled,¹ giving macroscopic meshes with nanoscale aperture (nano-meshes). When the two monolayers packed with different angle, the nano-meshes with different shapes were obtained (Figure 2.1 d-f). The Te nanowire meshes exhibited reversibly switched photoelectric properties. In addition, the photocurrent was affected by the intensity of light and the number of monolayers. Such strategy can be used to Ag₂Te nanowires and Pt nanotubes systems.

Figure 2.2. TEM image of (a) BiOCl plates. (b) The SAED patterns of (a). (c, d) The Bi₂S₃ nano-meshes were synthesized by mixing the BiOCl plates with TAA for 4 h (c) and 10 h (e). The (d, f) shown the SAED pattern of Bi₂S₃ meshes in (c, e), respectively. (g, h) The unit cell of BiOCl plates and Bi₂S₃ meshes. (i) The lattice matching between crystal BiOCl plates and Bi₂S₃ meshes. (j) The schematic illustration of topotactic transformation. Printed from ref 3 with permission. Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

However, creating such meshes by bottom-up method is more challenging, given the difficulty in dictating the criss-cross of nanorods in a controllable manner. To achieve this aim, a representative example has demonstrated that Bi₂S₃ nano-meshes made of aligned nanorods can be converted from 2D BiOCl plates, which transformation is driven by a chemical reaction and the mesh alignment determined by crystal epitaxy.³⁻⁶

In this approach, the preformed 2D plates as sacrificial templates were employed to grow

nanorods along specific orientations by crystal epitaxy. The 2D BiOCl plates were first formed before further transformation. The BiCl₃ will hydrolyze in H₂O, thus the BiCl₃ powder were dissolved in water to prepare 3 M BiCl₃ solution. After stood for 2h, the BiCl₃ reacted with the H₂O to produce the HCl and BiOCl. Then the BiOCl precipitated in the solution to form white plates (Figure 2.2a). The Figure 2.3b shown the SAED pattern of the BiOCl plate, corresponding the TEM images of the plate in the Figure 2.3a. Combined with the XRD data, the plates were demonstrated to have a tetragonal structure.³

When the (thioacetamide) TAA was added to mixture solution with BiOCl plates and incubated at 60 °C for 4 h, the BiOCl plates underwent crystal transformation to form Bi₂S₃ mesh networks (Figure 2.2c). However, the mixed SAED patterns of Bi₂S₃ mesh networks and BiOCl plates (e.g (200), (110)) indicated that the nano-meshes were partial formation (Figure 2.2d). After 10 h reaction, the structure of the BiOCl discs were completely transformed into mesh networks (Figure 2.2e). The SAED pattern proved that the Bi₂S₃ mesh networks was orthorhombic crystal system. By measuring the lattice distance, the d_{002} of Bi₂S₃ was equal to 1.99 Å, and the lattice distance of d_{200} of BiOCl was 1.94 Å. Thus, the good lattice matching between the [002] of Bi₂S₃ and [200] BiOCl indicated their epitaxial registry. In addition, the BiOCl disc plane has two equivalent directions, the [100] and [010] directions, which perpendicular to each other. As shown in the schematic diagram of unit cell and topotactic transformation in Figure 2.3, the lattice mismatching between the [001] direction of Bi₂S₃ ($d=3.98$ Å) and the [100] or [010] directions ($d= 3.89$ Å) promoted the epitaxial growth of nanorod on the plates along the [001] direction (Figure 2.3g-j).

Figure 2.3. (a) TEM image of the BiOCl/Bi₂O₃ heterostructure. The right part was BiOCl orthogonal networks, which was obtained by dipped in HCl solution on the β -Bi₂O₃ film. (b-d) SAED patterns of the β -Bi₂O₃ film, the interface, and the BiOCl network. (e) HRTEM image of the β -Bi₂O₃ precursor in

(a). (f) HRTEM image of two perpendicularly aligned nanowalls. (g) The schematic diagram of the BiOCl orthogonal networks, and the relationship between the BiOCl nanowall and β -Bi₂O₃ film. Printed from ref 4 with permission. Copyright © 2011 American Chemical Society.

By employing the top-down method, Guo *et al.* reported that the β -Bi₂O₃ films could transform to BiOCl orthogonal network nanowalls.⁴ The complex hierarchical superstructures also used sacrificial templates to carry out crystal transformation. In the first step, the β -Bi₂O₃ film serve as a template. When dipped the diluted hydrochloric solution on the film for several minutes, the BiOCl nanowall networks were obtained by epitaxial growth. In order to capture the intermediate, only one side of Bi₂O₃ film was dipped in HCl solution. A focused ion beam (FIB) milling was used to cut a slice of BiOCl/Bi₂O₃ heterostructure. As shown in the bright field TEM image (Figure 2.3a), the left side was β -Bi₂O₃ precursor, and the right part shown the BiOCl nanowalls with an interface between the two parts. Combining the HRTEM image with SAED patterns, the β -Bi₂O₃ precursor has tetragonal structure. The lattice distance d_{220} is 2.737 Å in β -Bi₂O₃, and the d_{002} is 2.817 Å. The lattice distance of BiOCl in [110] direction is 2.751 Å. Thus, there is small lattice mismatching ($f = 0.50\%$) between $[2\bar{2}0]$ of β -Bi₂O₃ and $[1\bar{1}0]$ of BiOCl. In addition, the growth direction [110] of BiOCl ($d_{110} = 2.75$ Å) and [002] of β -Bi₂O₃ ($d_{110} = 2.81$ Å) also has good matching. Thus, the BiOCl nanowalls grown epitaxially from β -Bi₂O₃ film. As shown in the schematic diagram, the (220) (or $(2\bar{2}0)$) and the (002) facet of β -Bi₂O₃ film are perpendicular to each other, and have an approximate lattice distance (Figure 2.3g). Thus, the BiOCl plates formed two sets of orthogonal networks nanowalls. Furthermore, the complex hierarchical superstructures can be prepared by using the BiOCl nanowalls as a template. Thus, the BiOCl nanowalls converted to Bi₂S₃ nanomeshes (Figure 2.3a-d), which was reported by Qi's group.³

Figure 2.4. (a) SEM image of a Bi_2S_3 N2DONW. (b) Tilt view of an orthogonal mesh networks. The mesh network was made up of nanorods. (c) TEM image of a Bi_2S_3 mesh network. The nano-meshes consisted of rods that are perpendicular to each other. (d) The SAED pattern of (c). The rods from the Bi_2S_3 nano-meshes grow along the $[001]$ growth direction. (e) The schematic diagram of the crystal transformation from the BiOCl plate to Bi_2S_3 mesh. Printed from ref 4 with permission. Copyright © 2011 American Chemical Society.

A further exploration demonstrated that the topotactic transformation has generality in the bismuth compounds.⁵ Not only the BiOCl but also the $\beta\text{-Bi}_2\text{O}_3$, BiOBr , and $\text{Bi}_2\text{O}_2\text{CO}_3$ nanowalls could transform to Bi_2S_3 nanomeshes. In addition, the intermediate template of $\text{Bi}_2\text{O}_2\text{CO}_3$ converted to $\beta\text{-Bi}_2\text{O}_3$ nanowalls by heating to 300 °C. When the mixture solution of TAA and HCl reacted with the $\beta\text{-Bi}_2\text{O}_3$, which can transform to Bi_2S_3 orthogonal networks

nanowalls directly. More importantly, the Bi_2S_3 nano-meshes formed an amorphous BiO_x nanowall structures by heating at 320°C for 3 h. The key factors of crystal transformation include two parts: (1) The precursor acted a sacrificial template. (2) Chemical reaction was prerequisite for the topotactic transformation. (3) The well-defined structures were obtained by the epitaxial growth with good lattice matching.

Figure 2.5. The schematic diagram of $\beta\text{-Bi}_2\text{O}_3$ crystals undergo topotactic transformation to various superstructure bismuth compounds. Printed from ref 5 with permission. Copyright © 2012 American Chemical Society.

Despite these recent successes, the related reports on nano-meshes still focus on inorganic crystals, such as bismuth compounds. However, the small lattice mismatch between 2D plate and 1D rod is commonly hard to satisfy.

2.1.2. Morphologies of fullerene crystals and their applications

Fullerene (C_{60} or C_{70}), a typical n-type semiconductor, has been widely used in high efficiency field-effect transistors (FETs), organic solar cells (OSCs), photovoltaics and

biomedical fields.⁷⁻¹⁸

In general, the devices usually consist of two main parts, the hole transporting and electron transporting which correspond to the p-type and n-type semiconductor materials, respectively. The ambipolar charge transport of single-crystalline p-n junction is desirable for designing the complementary circuits.¹⁹

As the typical electron transporting material, C₆₀ has good electron mobilities.^{8, 20-22} Fan *et al.* have been developed a FETs device by using the 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) as p-type and C₆₀ as n-type.¹² The p-n junction was fabricated by a droplet pinned crystallization (DPC) method.⁸ For preparation of p-n junctions, the C8-BTBT and C₆₀ were dissolved in mixed solution *m*-xylene and carbon tetrachloride. During the crystallization, the C₆₀ ribbons formed first and follow by C8-BTBT nucleation and growth (Figure 2.6a). The height profile of AFM image demonstrated that the C₆₀ ribbons were partial covered by C8-BTBT crystals (Figure 2.6d). As shown the optical images in Figure 2.6b-c, the two type crystals have two different colors. Whereas, the blue ones were identified as C₆₀ ribbons, and light-yellow crystals were C8-BTBT ribbons, which was proved by SAED (Figure 2.6f, g). On the other hand, the Raman intensity map demonstrated of C₆₀ with Raman shift at the region of 1355-1509 cm⁻¹. The transistors exhibited good charge transporting performance, the 0.16 cm² V⁻¹ s⁻¹ for hole mobility and 0.17 cm² V⁻¹ s⁻¹ for electron mobility.

Figure 2.6. (a) Schematic diagram of the DPC method. The bottom of (a) present the growth process of p-n junctions with well-aligned arrays. (b) Optical microscopy image of C8-BTBT and C₆₀ ribbon. The blue ribbons are C₆₀ crystals, and the yellow ones represent C8-BTBT crystals. (c) The p-n junctions of C8-BTBT and C₆₀ crystals. The inset of c shows the Raman intensity map of C₆₀ at the region of 1355-1509 cm⁻¹. (D) The AFM image of the C8-BTBT ribbon on the C₆₀ ribbon, which form p-n junction. (E) The TEM image p-n junction. SAED patterns of individual C8-BTBT crystal (f) and C₆₀ ribbon (g). Reprinted from ref 12, with permission. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Zhang *et al.* reported that the C₆₀/C₇₀-DPTTA cocrystals were used to prepare photovoltaic device by a drop-casting method.¹⁸ DPTTA and C₆₀ (or C₇₀) mixtures were dissolved in chlorobenzene. Then the solution was dripped on the Si/SiO₂ substrate. After the solvent evaporation, the crystal formed on the substrate. Afterward, aluminum (Al) was masked on one side of the crystal, and Au was evaporated on the other side (Figure 2.7 d). The current density-voltage (*J-V*) characterization shown that C₆₀-DPTTA cocrystal have a higher conversion efficiency (0.27%) than the C₇₀-DPTTA device (0.0005%). The co-crystals with a p-n junction donor-acceptor provide the good photovoltaic behavior.

Figure 2.7. (a) The DPTTA, C₆₀, and C₇₀ chemical structures. (b) The optical images DPTTA C₆₀, and C₇₀ crystals, and (c) C₆₀-DPTTA, C₇₀-DPTTA co-crystals. (d) Schematic diagram of device. (e) SEM image of the device. (f, g) *J-V* curves of C₆₀-DPTTA, C₇₀-DPTTA based devices. Reprinted from ref

So far, the well-established applications are based on the systems which process single-crystalline structure. Thus, we focus on the crystalline natures of fullerene in this work, which play a critical role in understanding the physical properties of materials and preparation of optoelectronic devices. In contrast to most of organic or inorganic materials, a typical feature of fullerene is forming a series of solvate crystals with various morphologies (such as rods and plates) by incorporating solvent molecules in its crystal lattice.²³⁻³⁴ As a consequence, its crystal phase deviates from the original fcc structure, giving rise to new crystal forms such as rods and plates. More complex fullerene superstructures remain a challenge, due to the lack of understanding in the crystallization process and the related solvated effects. The present synthetic methods towards fullerene crystals are mostly based on the liquid-liquid interface precipitation method (LLIP).³⁰⁻³² We believe that further exploration of methods and mechanisms would expand the synthetic freedom for more complex structures. Inspired by the successes of nano-meshes made of bismuth compounds, we wonder whether the 2D fullerene plates may also be used as sacrificial templates to afford the ordered alignment of 1D fullerene rods.

Figure. 2.8. (a) Schematic diagram of crystal transformation. SEM images of (b) The pure C_{60} plates and (c) pure rods synthesized from CCl_4 /IPA and *m*-xylene/IPA mixtures, respectively. (d) SEM image of the C_{60} mesh network.

In this work, we attempt to deconvolute the role of solvent molecules in the solvent mixture during the crystal transformation of fullerene nanocrystals. We demonstrate that the C_{60} microplates can undergo crystal transformation to nano-meshes (Figure. 2.8), in the absence of chemical reaction and by simply changing the solvents of crystallization. This on-site recrystallization generates epitaxial fullerene rods, which eventually emerge as an ordered network superstructure. The transformation was driven by small changes in van der Waals interactions resulting from the removal and inclusion of solvent molecules, in contrast to the reaction-driven transformation with much larger potential energy difference.³⁻⁶ Such a crystal transformation strategy can also serve as a simple yet available synthetic approach to achieve multi-layer nano-meshes. The present work provides a promising platform for studying the

formation mechanism of crystal transformation and offers an on-demand synthetic approach for establishing complex 2D mesh-like fullerene superstructures.

2.2 Material and methods

2.2.1. Materials

C₆₀ was purchased from Sigma-Aldrich, and used without further treatment. Carbon tetrachloride (CCl₄) (A.R.), *m*-xylene (A.R.) and isopropanol (IPA, A.R.) were purchased from Beijing Chemical Agent Ltd., China. 1,2,4-trimethylbenzene and 1,2,4-trichlorobenzene were purchased from Sigma-Aldrich and were used as received.

2.2.2 Methods

Synthesis of C₆₀ rods by mixing IPA and C₆₀ stock solutions. In a typical synthesis, 2 mL IPA was dropwise injected into a stock solution of C₆₀ in CCl₄/*m*-xylene mixture (1 mM, 2 mL) with gentle swirling until the purple C₆₀ solution turned into turbid suspension. And then, the mixture was kept undisturbed for 10 min, afterwards dark brown precipitation was formed. When the initial solvent ratio (CCl₄/*m*-xylene) was between 0:10 and 4:6 (v/v), only rods were obtained (Figure. 2.8c, 2.9a). The added IPA amount was dependent on the initial solvent ratio of the preparative solution, as shown in Table 2.1.

Synthesis of C₆₀ crystals plates. In a typical synthesis, 1 mL IPA was dropwise injected into a stock solution of C₆₀ in CCl₄/*m*-xylene mixture (1 mM, 2 mL) with gentle swirling until the purple C₆₀ solution turned into turbid suspension. When the ratio was between 6:4 and 10:0 (v/v), only plates (Fig. 2.8b, 2.9c).

Synthesis of mixed C₆₀ crystals (rods and plates). In a typical synthesis, 1 mL IPA was dropwise injected into a stock solution of C₆₀ in CCl₄/*m*-xylene mixture (1 mM, 2 mL) with gentle swirling until the purple C₆₀ solution turned into turbid suspension. when at 5:5 ratio, a

mixture of plates and rods formed (Fig. 2.9b).

Crystal transformation of the C₆₀ rods and plates obtained from CCl₄/*m*-xylene mixtures. The above C₆₀ crystal samples were concentrated by centrifugation at 1000 rpm and then remained in 0.3 mL of supernatant, and finally dispersed in 3 mL of transformative solution (2.7 mL IPA and 0.3 mL of supernatant) for crystal transformation.

During the transformation process of C₆₀ crystals from 6:4 plates to mesh networks, the residue *m*-xylene content in the transformative solution would be an important factor for the formation of C₆₀ mesh network. As a typical example, the residue CCl₄ and *m*-xylene in the solution was estimated to be around 4% and 2.7% v/v, respectively.

Especially, we choose the ratio of CCl₄/*m*-xylene = 6:4 (v/v) in stock solution as an example to clarify the detailed calculation process of the solvent ratio of CCl₄/*m*-xylene/IPA (v/v/v) in transformative solution, which is shown as follow:

Firstly, the CCl₄/*m*-xylene mixture with v/v = 6:4 (2 mL) is set as a stock solution. Considering that ratio of CCl₄ in stock solution is 60% and its corresponding volume should be 2 mL × 60% = 1.2 mL. While ratio of *m*-xylene in stock solution is 40% and its corresponding volume should be 2 mL × 40% = 0.8 mL. Then, the stock solution was diluted by 1 mL IPA to achieve C₆₀ crystals. The resultant solution was regarded as a preparative solution.

Thus, the solvent ratio of CCl₄/*m*-xylene/IPA (v/v/v) in the preparative solution =

$$\frac{V_{\text{CCl}_4}}{V_{\text{stock}} + V_{\text{IPA}}} : \frac{V_{\text{xylene}}}{V_{\text{stock}} + V_{\text{IPA}}} : \frac{V_{\text{IPA}}}{V_{\text{stock}} + V_{\text{IPA}}} = \frac{1.2 \text{ mL}}{2 \text{ mL} + 1 \text{ mL}} : \frac{0.8 \text{ mL}}{2 \text{ mL} + 1 \text{ mL}} : \frac{1.0 \text{ mL}}{2 \text{ mL} + 1 \text{ mL}} = 6:4:5$$

Next, the preparative solution was centrifuged and 0.3 mL supernatant was remained. Finally, 0.3 mL supernatant was dispersed in 2.7 mL IPA and the resultant solution was regarded as a transformative solution.

$$\text{Ratio of CCl}_4 \text{ in transformative solution} = \frac{V_{\text{CCl}_4}}{V_{\text{total}}} = \frac{0.3 \text{ mL} \times \frac{V_{\text{CCl}_4}}{V_{\text{stock}} + V_{\text{IPA}}}}{2.7 \text{ mL} + 0.3 \text{ mL}} = 4.0\%$$

$$\text{Ratio of } m\text{-xylene in transformative solution} = \frac{V_{\text{xylene}}}{V_{\text{total}}} = \frac{0.3 \text{ mL} \times \frac{V_{\text{xylene}}}{V_{\text{stock}} + V_{\text{IPA}}}}{2.7 \text{ mL} + 0.3 \text{ mL}} = 2.7\%$$

$$\text{Ratio of IPA in transformative solution} = \frac{V_{\text{IPA}}}{V_{\text{total}}} = \frac{2.7 \text{ mL} \times \frac{V_{\text{IPA}}}{V_{\text{stock}} + V_{\text{IPA}}}}{2.7 \text{ mL} + 0.3 \text{ mL}} = 93.3\%$$

Thus, the final solvent ratio of CCl₄/*m*-xylene/IPA (v/v/v) in transformative solution is 4.0:2.7:93.3.

The molar ratio of the incorporated solvent to C₆₀ for C₆₀ crystals at different CCl₄/*m*-xylene ratios was determined by thermal gravimetric analysis (TGA) performed in a nitrogen atmosphere. It can be expected that two stages of solvent loss should be included in the C₆₀ solvate crystals, namely, the removal of the solvent molecules at lower temperatures and the subsequent sublimation of the C₆₀ matrix at higher temperatures. In view of the possible overlap between the two processes, we first performed the TGA analysis for a pure C₆₀ sample under similar experimental conditions, as shown in Fig. S4a. It is obvious that the raw C₆₀ powder starts to lose weight at a temperature of 420 °C, suggesting that the weight loss of the C₆₀ solvate crystals below this temperature is due to the removal of solvent molecules. By means of this temperature as a reference point, we have examined the solvent content incorporated within the C₆₀ crystal. It can be determined that the 10:0 plates contained 4.0% w/w CCl₄ (Figure 2.15c), whereas the 0:10 rods had 9.3% w/w *m*-xylene (Figure 2.15b). Accordingly, the molar ratio of CCl₄ to C₆₀ and *m*-xylene to C₆₀ in the two C₆₀ crystals is estimated to be 1:5 and 2:3, respectively. Meanwhile, TGA data of 6:4 plates shown 2 phases of solvent loss, 2.2% and 8.3% w/w, respectively (Figure 2.15d).

Synthesis of crossed C₆₀•trimethylbenzene-based nano-meshes. Crossed C₆₀•trimethylbenzene-based nano-meshes were achieved following similar experimental procedures to the synthesis of C₆₀•xylene-based nano-meshes except the initial solvent ratio (CCl₄/1,2,4-trimethylbenzene) was 8:2.

2.2.3 Characterization

The samples were examined by using field-emission scanning electron microscopy (FESEM, JEOL 7600F) at an acceleration voltage of 5 kV. Before characterization by FESEM, the samples were coated with Pt layer by using an Edwards Sputter Coater. TEM images were obtained using a JEOL JEM-2100 electron microscope at an accelerating voltage of 200 kV. One drop of the as-prepared colloidal dispersion was deposited on a carbon-coated copper grid, and dried under high vacuum. The powder X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu K α radiation ($\lambda=1.54050$ Å) operated in the 2θ range from 3 to 30°, by using the samples spin-coated on the surface of a quartz substrate. Fourier transform infrared (FTIR) spectra were performed on Nicolet AVATAR 360 FT-IR spectrophotometer. The micro-Raman studies were measured under ambient conditions using 514.5 nm Ar ion excitation source. Thermogravimetric (TGA) curve was obtained using a STA 499 C Jupiter (NETZSCH) thermogravimetry analyzer. ^1H NMR spectra were measured on a Bruker BBFO-400 spectrometer. To obtain the average pore size of a mesh network and the width of the aligned rods, 60 and 80 samples were measured by the software of Nano Measurer 1.2, respectively. Then, the average values were exported from the reports. For the pore size, we measured the height of triangle or parallelogram. On the other hand, the width of the rod was collected by measuring the vertical distance between two opposite parallel lines of the rod in TEM image.

2.3 Result and discussion

2.3.1. Dependence of crystal morphologies on solvent ratio

Previous reported that the CCl_4 and *m*-xylene molecules could be embedded in the C_{60} crystals as solvents of crystallization,^{23-27, 30-32} leading to form different morphologies of

solvates. The C_{60} microplates crystallized at the interface between CCl_4 and IPA solution.^{30, 31} On the other hand, the C_{60} rods precipitated at IPA/*m*-xylene interface.³² In our modified method, the C_{60} powder was dissolved in the co-solvents of CCl_4 /*m*-xylene mixture, thus the crystals were formed by the inclusion of both solvent molecules. Compared with liquid-liquid interface precipitate (LLIP) method as pure fullerene crystal formation,^{31,32} IPA was dropwise added to a stock solution of C_{60} / CCl_4 /*m*-xylene mixture by continuous swirling. The quick diffusion of poor solvent of IPA into the stock solution reduced the solubility of C_{60} , which formed micrometer-sized crystals after 10 min. When the initial solvent ratio of CCl_4 /*m*-xylene at the range of 0:10 and 4:6 (v/v), only C_{60} rods were generated at the mixture, as shown in Figure 2.8c, 2.9a. if the ratio was between 6:4 and 10:0 (v/v), all the crystals were plates (Figure 2.8b, 2.9c); However, when the ratio was 5:5 ratio, both of plates and rods crystallized at the bottom of vessel (Figure. 2b). This dependence of crystal morphology on the solvent ratio indicated the influences of the embedded solvent molecules.

Figure 2.9. SEM images of C_{60} crystals prepared at different CCl_4/m -xylene ratio (a, d, 3:7; b, e, 5:5; c, f, 8:2; g, h, 6:4), before (a, b, c, g) and after crystal transformation (d, e, f, h). The dashed boxes in (e) highlight the unaffected C_{60} rods after the transformation. (i) TEM image shows of a mesh network.

As shown in Figure 2.9-2.11, the TEM and SEM were tested to characterize the morphologies of C_{60} crystals with different solvent ratio. It's worth noting that all the crystals are stable and had smooth surface, even under vacuum condition during characterization.

Figure. 2.10. TEM images of C_{60} crystals at different CCl_4/m -xylene ratio (a, 3:7; b, 5:5; c, 8:2; d, 6:4) before crystal transformation.

Figure S2.11. SEM images of C_{60} rods at different CCl_4/m -xylene ratio (a, b, 0:10; b, d, 1:9), before (a, c) and after (b, d) purifying by IPA.

The C_{60} crystals were stable in the preparative solutions and would not appear structural change (Table 2.1). But some crystals became unstable when left the preparative solutions. In a typical experiment, a small aliquot of the precipitate solution was dropped onto a substrate, then the supernatant was evaporated in a few minutes and the crystals were exposed in air. The 3:7 rods (Figure 2.9a and Fig. 2.10a) almost kept intact (Figure. S3a and S3b, ESI†).

Table 2.1. Dependence of crystal morphologies on solvent ratio

Solution types	CCl_4/m -xylene/IPA (v/v/v)			
Stock solution (2 mL)	3: 7: 0	5: 5: 0	6: 4: 0	8: 2: 0
Preparative solution (3-4 mL)	3: 7: 7.5 (rods)	5: 5: 6.5 (plates and rods)	6: 4: 5 (plates)	8: 2: 5 (plates)
Transformative solution (3 mL)	1.7: 4: 94.3 (rods)	3: 3: 94 (meshes and rods)	4: 2.7: 93.3 (meshes)	5.3: 1.3: 93.4 (crumbled plates)

Figure 2.12. SEM images of C_{60} crystals formed by evaporating small aliquots of the precipitate solutions at different CCl_4/m -xylene ratio (a, b, 6:4; c, d, 3:7) in air.

However, the structures of 6:4 plates (Figure. 2.9g and Fig. 2.11d) were changed dramatically after the preparative solution evaporation (Figure 2.12a and 2.12b). Specifically, the C_{60} plates rapidly converted to mesh networks with close-packed nanorod arrays. The original appearance of hexagonal plate can still be recognized. We think the possible explanation is that the shift of the CCl_4/m -xylene ratio during the evaporation, which the CCl_4 (b.p. $76.8\text{ }^{\circ}\text{C}$) evaporate fast than the m -xylene (b.p. $138\text{ }^{\circ}\text{C}$). In addition, the difference in stabilities of C_{60} rods and plates in the solvent mixture may also promote the structural transformation.

2.3.2. The solvent environment causes structural transformation

After extensive experiments, we realized that the cause of structural transformation is not the intrinsic stabilities of the crystal morphologies, but the solvent environment.³⁵ Besides solvent evaporation, tuned co-solvents can also induce the structural transformation. However, it is

difficult to quantify the exact solvent ratio upon solvent evaporation. Thus, we sought to regulate the preparative solutions by diluting with IPA. The diluted solution with precise ratio was served as a transformative solution. In addition, the experiment was carried out in closed vessel to minimize evaporation during crystal transformation. More specifically, we synthesized C₆₀ plates at CCl₄/*m*-xylene = 6:4 (Figure 2.9g), then the plates with mother liquor were concentrated and removed the supernatant. Since residual solution is unavoidable, its volume was precisely controlled after dilution by IPA, the resulting preparative solution has an exact solvent ratio (Table 1). Different from the structures formed by solvent evaporation (Figure 2.12a and 2.12b), the mesh networks with perfect structural homogeneity (Figure 2.9h and 2.9i) were crystallized in the present transformative solution with small amount of CCl₄/*m*-xylene in about 2 h. The average pore size of the mesh is about 330 nm, and the average width of the rod is around 650 nm (Figure 2.13). In order to obtain a more homogeneous and smaller crystal size, we change solvent environment from room temperature condition to an ice bath. The mesh networks obtained from a low temperature shown smaller size (~ 12 μm) (Figure 2.22a-c in appendix) in comparison of the normal mesh with the size of 40-50 μm. The diameter of rods on mesh is about 420 nm and average pore size is 260 nm, which significantly decrease in size (Figure 2.22d, e). Thus, the size of pore and mesh can be tuned by the environment condition. On the other hand, the size of mesh networks also decreased when the IPA solution was adding quickly during the preparation of 6:4 plates. The fast nucleation gives small plates, which provide smaller templates for crystal transformation. Thus, the finally mesh network is 12-13 μm (Figure 2.23a). The pore size (~65 nm) and diameter of rods on mesh (~136 nm) is smaller than the mesh networks that fabricated in slowly adding IPA (Figure 2.23b-d).

Figure 2.13. The average pore size of a mesh network and the width of the aligned rods. (a) The average pore size of the mesh network is about 330 nm, and (b) the width of the rods from nano-mesh is about 650 nm.

Table 1 summarizes the solvent ratio during the process of crystal transformation. The C_{60} crystals were isolated by centrifugation and diluted by IPA, leading to the decreasing of the co-solvents. When the initial solvent ratio was 0:10, 1:9, and 3:7, the rods have smooth surface (Figure 2.9d and Figure 2.11) after dilution by IPA. If the ratio was 8:2, the plates were crumbled (Figure 2.9f), indicating severe structural relaxation. As shown in Figure 2.9e, the meshes were the main product at 5:5 ratio. But the co-existing rods were still unaffected, which highlighted using the dashed boxes (Figure 2.9e). Hence, the resulting morphologies at low solvent ratio shown that the rods were relatively more stable than the plates. Because all crystals were stable in their respective preparative solutions, the change in the solvent environment was responsible, upon dilution of C_{60} mother liquor by IPA.

Figure 2.14. SEM images of (a) the 6:4 plates after 4 rounds of purification by IPA; the purified plates were kept in an IPA solutions (b) with 1% v/v *m*-xylene for 24 h; and (c) with 2% v/v *m*-xylene for 30 min. The dashed lines in (c) highlight the orientations of the horizontal rods.

2.3.3. Identification of crystal system and solvent

2.3.3.1. Characterization the crystal and solvent molecules by XRD and TGA

XRD data shown that the 0:10 rods had *hcp* crystal system (Figure 2.15a and ii), which matched the C_{60} -xylene structures reported in the literature.^{23, 25, 32} The TGA data demonstrated that the pure rods incorporated 9.3% w/w *m*-xylene (Figure 2.16b), lower than that of the C_{60} rods prepared by LLIP method at the interface of IPA/*m*-xylene (12.8%).^{23, 25,}

Figure 2.15. (a) XRD, (b) Raman spectra, and (i-iv) optical microscopy images of C_{60} crystals: (i) 10:0 plate, (ii) 0:10 rods, (iii) 6:4 plate, and (iv) mesh network. (*) XRD pattern of pure C_{60} powder.

However, the 10:0 plates are *fcc* phase (Figure 2.15a and I), which match the XRD pattern of C_{60} powder (Figure 2.15a, *). Moreover, The TGA data demonstrated that the 10:0 plates had 4.0% w/w CCl_4 (Figure 2.16c), which was lower than the C_{60} crystals prepared from pure CCl_4 (29.9% solvent embedded in to plates).^{36, 37} Thus, the low level of solvent inclusion explained why the plates did not have the *hcp* crystal system of the $C_{60} \cdot 2CCl_4$ crystals.³⁶ The rods and plates in the modified method with rapid crystallization (< 10 min) resulted in reducing solvent content than the LLIP method.³⁸

Figure 2.16. TGA characterization of C_{60} crystals. TGA curves of (a) C_{60} powder and (b-d) crystals involving (b) 0:10 rods, (c) 10:0 plates, and (d) 6:4 plates.

2.3.3.2. Investigating the incorporated solvents by spectra

The critical issue in the crystal transformation is to understand the change in material composition from the 6:4 plates to meshes. These 6:4 plates had similar XRD pattern with the 10:0 plates (Figure 2.15a and iii). TGA data shown two different stages of solvent loss, about 2.2% and 8.3% w/w, respectively (Figure 2.16d). The co-solvents contents were higher than the pure 10:0 plates and pure 0:10 rods, which indicated that mixed solvent inclusion. FT-IR and NMR were also proved that the existence of embedded co-solvents. The peaks at 525 , 576 , 1182 and 1427 cm^{-1} of IR spectra were the characteristic bands of C_{60} molecules. In addition, the 6:4 plates shown two strong IR peaks at 761 and 784 cm^{-1} , which can be assigned to CCl_4 (Figure 2.17).

Figure 2.17. FT-IR spectra of C₆₀ crystals involving (black) 10:0 plates, (red) 0:10 rods, (blue) 6:4 plates, and (cyan) mesh networks.

Moreover, the ¹H NMR data of the 6:4 plates exhibited a chemical shift at around 2.1 ppm, indicating the *m*-xylene (Figure 2.18). Hence, these data demonstrate the mixed solvent incorporation. It is known that *m*-xylene and CCl₄ could replace C₆₀ molecules or insert in the interstitial holes in the lattice.^{37, 38} Low level doping with random distribution is not expected to lead to obvious XRD peak shifts. In addition, the faster diffusion of smaller CCl₄ within the interstitial space explains the less stability of plates than rods.

Figure 2.18. ^1H NMR spectra of C_{60} crystals involving (pink) 0:10 rods, (cyan) 6:4 plates, and (blue) mesh networks. The blue and red dashed boxes show the corresponding ^1H NMR peaks originated from -CH- and -CH₃ groups of *m*-xylene, respectively.

After crystal transformation, the XRD pattern of the meshes resembled the *hcp* phase of the C_{60} ·xylene solvate crystals.^{23, 25, 32} However, some small peaks still derive from the plate shown *fcc* crystal system (Figure 2.15a). It meets the SEM image of mainly rod-based structures with residual plate domains (Figure 2.9h). Figure 2.15b shown the Raman spectra of the C_{60} crystals. The absence of major peak shift indicates that the C_{60} molecules remained intact and without polymerization.^{23, 25, 31, 35, 38}

2.3.4. The effect of solvent on the structural rearrangement

To completely remove the co-solvents and understand their effects on the structural rearrangement, the initial C_{60} crystals were washed by repeated purifying by IPA (typically 4 rounds of centrifugation and re-dispersion in IPA). After purification, many pores³¹ appeared

on the surface of C₆₀ plates (Figure 2.14a). Notably, prolonged storage of the plates in IPA solution after several time purification would not transform to meshes. It was reported that fullerene and its derivatives could undergo structural transformation to give hierarchically structures.^{33, 34, 39} These structural changes were related to heating or solvent washing (IPA or 1-butanol).

The formation of these pores is of importance. Crystal dissolution is typically a layer-by-layer process retaining the stable facets (unless there are ligands blocking the surface unevenly).⁴⁰ The formation of pores should be unfavorable because it exposes unfavorable facets, increases the surface area and thus, the surface energy.⁴¹

However, when one component of the co-crystal dissociates, either by evaporation or dissolution, and the other component cannot, the residue would be forced to pile up, sometimes forming crystalline structures. Thus, the process is reminiscent of the weathering of hydrated minerals, driven by the loss of the solvent from the crystals. Here, the plates can remain their smooth surface in the preparative solution because the incorporated solvents are at equilibrium with the solution. With CCl₄ and *m*-xylene concentration greatly reduced in the transformative solution, the equilibrium shifts and the incorporated solvents are slowly lost. Hence, the increase of entropy during the escape of the incorporated solvent was the driving force. The pores probably result from the structural relaxation after the solvent loss.

The weathering process causes the collapse of the crystals, giving rise to powders. The formation of the crystalline rods in the nano-meshes suggests that the residue component (i.e., C₆₀) could reorganize or recrystallize. It is conceivable that the C₆₀ molecules would have more freedom in a solution than under vacuum conditions.

In order to investigate the role of solvent molecules, the CCl₄ was removed from the solution. The 6:4 plates were washed 4 times purification by IPA, then the purified plates were dissolved in *m*-xylene/IPA (1% v/v) solution for 24h. the plates were converted to mesh networks (Figure

2.14b). Thus, it demonstrated that the *m*-xylene could lead to crystal transformation, which match the evidence of C₆₀-xylene-based meshes. When we increase the ratio of *m*-xylene concentration to 2%, the transformation occurs faster (only 30 min). The higher solubility of C₆₀ material in high concentration of *m*-xylene/IPA solution promote the rapid recrystallization. Thus, it formed out-of-plane growth, resulting the vertical rods on the mesh (Figure 2.14c). However, the mesh formed at 1% *m*-xylene/IPA solution are predominantly horizontal rods, which show on-site recrystallization. The eventual loss of the plate materials within the triangular aperture obviously requires C₆₀ diffusion, but their inability to move out of the plane suggests short-distance rearrangements, in contrast to the cases of C₇₀ hierarchically structures formed by the control of diffusion kinetics of IPA.³⁴

Figure 2.19. Crystal transformation of 5:5 C₆₀ plates. SEM images of C₆₀ mesh networks at (a and c) low- and (b and d) high-magnification formed by transferring the 5:5 plates after 4 rounds of washing into an IPA solution with *m*-xylene (1% v/v) for 24 h.

Besides the 6:4 plates, the plates formed at the range of 5:5-10:0 solvent ratio can transform

to mesh in 1% v/v *m*-xylene/IPA solution. But the resulting mesh networks were often messy. Whereas, the 5:5 plates favour to crack. It may be caused by the strains during transformation (Figure 2.19). However, the 10:0 plates after transformation were crumbled and with longer transformation process (Figure 2.20). Thus, it indicated that the *m*-xylene embedded inside the plate is key factor, likely by modifying the local solvent environment during the on-site recrystallization.

Figure 2.20. Crystal transformation of C_{60} plates obtained from CCl_4 /IPA mixture after solvent washing. SEM images of C_{60} plates obtained in (a and b) CCl_4 /IPA mixture; (c and d) after 4 rounds of washing; the washed plates of c and d were transferred into IPA solutions (e and f) with *m*-xylene (1% v/v); and

(g and h) with *m*-xylene (2% v/v) for 24 h.

2.3.5. Lattice mismatching and epitaxial relationship

HRTEM and SAED studies were carried out to investigate the epitaxial relationship between the initial plate and the emerging rods. The 6:4 plate (Figure 2.21a) showed scattering pattern characteristic of *fcc* phase; its top/bottom surfaces are bound by (111)/($\bar{1}\bar{1}\bar{1}$) planes. The 0:10 rod was confirmed to have *hcp* phase, with its long axis pointed at the [001] direction (Figure 2.21b). Thus, it appears that the [001] direction of the rods are aligned along the three symmetrically equivalent directions of $[\bar{1}10]$, $[10\bar{1}]$, and $[0\bar{1}1]$ on the plate (Figure 2.21c). The lattice distances $d_{\bar{1}10} = d_{10\bar{1}} = d_{0\bar{1}1}$ of the *fcc* plate were determined from the SAED data to be 9.96 Å, whereas the lattice distance d_{001} of the *hcp* rods was 10.18 Å (Figure 2.21d), both of which are consistent with the literature data.^{37, 42} Hence, the co-solvent expands the *hcp* more than the *fcc* lattice, causing the above d spacings to match (2.1% mismatch), explaining the epitaxial growth of the rod arrays.

Figure 2.21. TEM images of single C_{60} plate and rod obtained from 6:4 (a) and 0:10 (b) solutions, respectively. (c) A schematic illustration of nanorod alignment along $[001]$ direction in a C_{60} mesh network. (d) Crystal lattice orientation and lattice spacings of fcc and hcp phases along $\bar{1}10$ and $[001]$ directions, respectively.

To achieve C_{60} mesh networks by adjusting the preparative solution with different solvent molecules, the 1,2,4-trimethylbenzene was used instead of *m*-xylene in the co-solvents. It was reported that the C_{60} ·trimethylbenzene crystal has similar XRD pattern with the C_{60} ·xylene.⁴³ The hexagonal C_{60} plates crossed with each other (Figure 2.22a) were formed by mixing the IPA with the C_{60} stock solution with 8:2 CCl_4 /1,2,4-trimethylbenzene (v/v) solution. Then the mixture was isolated and re-dispersed in IPA. Finally, the mesh networks consist of C_{60} ·trimethylbenzene nanorods were obtained (Figure 2.21b and 2.21c). Thus, the 1,2,4-

trimethylbenzene shown key factor during transformation, which assemble to *m*-xylene.

Figure 2.21. Crossed C_{60} -trimethylbenzene-based nano-meshes formed by crystal transformation. SEM images of C_{60} crystals synthesized at $CCl_4/1,2,4\text{-trimethylbenzene} = 8:2$ before (a) and after crystal transformation (b and c).

2.4 Conclusions

In summary, we developed a fascinating and versatile crystal transformation strategy to achieve complex 2D C_{60} mesh superstructures comprising aligned C_{60} nanorods from the preformed C_{60} plates. The synthetic freedom is expanded with further understanding of the underlying mechanisms. The change in the solvent environment drives the structural relaxation of 2D fullerene plates, which is followed by crystal transformation from *fcc* plate to *hcp* rod. Well lattice matching between the initial plates and the emerging rods allows the epitaxial growth of C_{60} nanorods on the plates, forming oriented nanorod arrays. There is a wide variety of solvate crystals in the literature and recrystallization is often reversible and easy to control, thus greatly expanding the potential of the crystal transformation strategy. Our discovery and the understanding of the on-site recrystallization open a new window for designing sophisticated 2D superstructures and potentially functional architectures.

In this part, we demonstrate that could undergo crystal transformation to prepare complex structures. However, some questions about the desolvation, structural change and solvent ratio still puzzled us. Thus, we will systematically study the effect and environment of solvents on morphology control to develop a generally synthetic handle.

2.5 Appendix

Figure 2.22. (a, b) C₆₀ mesh networks formed in an ice bath. (c) The average size of mesh networks is 12 μm. (d) The pore size of mesh is about 260 nm. (e). The average diameter of rods is 420 nm.

Figure 2.23. (a, b) C₆₀ mesh networks formed by adding IPA quickly. (c) The average diameter of rods is 136 nm. (d) The pore size of mesh is about 65 nm.

Reference

1. Liu, J.-W.; Zhu, J.-H.; Zhang, C.-L.; Liang, H.-W.; Yu, S.-H. *J. Am. Chem. Soc.* **2010**, *132* (26), 8945-8952.
2. Qian, H.-S.; Yu, S.-H.; Gong, J.-Y.; Luo, L.-B.; Fei, L.-f. *Langmuir* **2006**, *22* (8), 3830-3835.
3. Li, L.; Sun, N.; Huang, Y.; Qin, Y.; Zhao, N.; Gao, J.; Li, M.; Zhou, H.; Qi, L. *Adv. Funct. Mater.* **2008**, *18* (8), 1194-1201.
4. Guo, C. F.; Cao, S.; Zhang, J.; Tang, H.; Guo, S.; Tian, Y.; Liu, Q. *J. Am. Chem. Soc.* **2011**, *133* (21), 8211-8215.
5. Guo, C. F.; Zhang, J.; Tian, Y.; Liu, Q. *ACS Nano* **2012**, *6* (10), 8746-8752.
6. Zhao, Y.; Xie, Y.; Jie, J.-S.; Wu, C.-Y.; Yan, S. *J. Mater. Chem.* **2009**, *19* (21), 3378-3383.
7. Dodabalapur, A.; Katz, H.; Torsi, L.; Haddon, R. *Science* **1995**, *269* (5230), 1560-1562.
8. Li, H.; Tee, B. C.; Cha, J. J.; Cui, Y.; Chung, J. W.; Lee, S. Y.; Bao, Z. *J. Am. Chem. Soc.* **2012**, *134* (5), 2760-2765.
9. Li, H.; Fan, C.; Vosgueritchian, M.; Tee, B. C.-K.; Chen, H. *J. Mater. Chem. C* **2014**, *2* (18), 3617-3624.
10. Wu, K. Y.; Wu, T. Y.; Chang, S. T.; Hsu, C. S.; Wang, C. L. *Adv. Mater.* **2015**, *27* (29), 4371-4376.
11. Briseno, A. L.; Mannsfeld, S. C.; Ling, M. M.; Liu, S.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. *Nature* **2006**, *444* (7121), 913.
12. Fan, C.; Zoombelt, A. P.; Jiang, H.; Fu, W.; Wu, J.; Yuan, W.; Wang, Y.; Li, H.; Chen, H.; Bao, Z. *Adv. Mater.* **2013**, *25* (40), 5762-5766.
13. Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258* (5087),

- 1474-1476.
14. Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *J. Am. Chem. Soc.* **2008**, *130* (11), 3619-3623.
 15. Heeger, A. J. *Adv. Mater.* **2014**, *26* (1), 10-28.
 16. Hu, Z.; Wang, C.; Zhao, F.; Xu, X.; Wang, S.; Yu, L.; Zhang, D.; Huang, Y. *Nanoscale* **2017**, *9* (25), 8825-8833.
 17. Hu, Z.; Zhang, D.; Yu, L.; Huang, Y. *J. Mater. Chem. B* **2018**, *6* (3), 518-526.
 18. Zhang, H.; Jiang, L.; Zhen, Y.; Zhang, J.; Han, G.; Zhang, X.; Fu, X.; Yi, Y.; Xu, W.; Dong, H. *Adv. Electron. Mater.* **2016**, *2* (6), 1500423.
 19. Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H.; Li, W. *Nature* **2000**, *403* (6769), 521.
 20. Anthopoulos, T. D.; Singh, B.; Marjanovic, N.; Sariciftci, N. S.; Moutagne Ramil, A.; Sitter, H.; Cölle, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **2006**, *89* (21), 213504.
 21. Zhang, X.-H.; Kippelen, B. *J. Appl. Phys.* **2008**, *104* (10), 104504.
 22. Li, C.-Z.; Chueh, C.-C.; Yip, H.-L.; Zou, J.; Chen, W.-C.; Jen, A. K.-Y. *J. Mater. Chem.* **2012**, *22* (30), 14976-14981.
 23. Wang, L.; Liu, B.; Yu, S.; Yao, M.; Liu, D.; Hou, Y.; Cui, T.; Zou, G.; Sundqvist, B.; You, H. *Chem. Mater.* **2006**, *18* (17), 4190-4194.
 24. Vimalanathan, K.; Shrestha, R. G.; Zhang, Z.; Zou, J.; Nakayama, T.; Raston, C. L. *Angew. Chem. Int. Edit.* **2017**, *56* (29), 8398-8401.
 25. Kim, J.; Park, C.; Park, J. E.; Chu, K.; Choi, H. C. *ACS Nano* **2013**, *7* (10), 9122-9128.
 26. Park, C.; Park, J. E.; Choi, H. C. *Acc. Chem. Res.* **2014**, *47* (8), 2353-2364.
 27. Wang, L.; Liu, B.; Liu, D.; Yao, M.; Hou, Y.; Yu, S.; Cui, T.; Li, D.; Zou, G.; Iwasiewicz, A. *Adv. Mater.* **2006**, *18* (14), 1883-1888.

28. Geng, J.; Zhou, W.; Skelton, P.; Yue, W.; Kinloch, I. A.; Windle, A. H.; Johnson, B. *F. J. Am. Chem. Soc.* **2008**, *130* (8), 2527-2534.
29. Wei, L.; Yao, J.; Fu, H. *ACS Nano* **2013**, *7* (9), 7573-7582.
30. Sathish, M.; Miyazawa, K. i. *J. Am. Chem. Soc.* **2007**, *129* (45), 13816-13817.
31. Shrestha, L. K.; Yamauchi, Y.; Hill, J. P.; Miyazawa, K. i.; Ariga, K. *J. Am. Chem. Soc.* **2013**, *135* (2), 586-589.
32. Ji, H.-X.; Hu, J.-S.; Tang, Q.-X.; Song, W.-G.; Wang, C.-R.; Hu, W.-P.; Wan, L.-J.; Lee, S.-T. *J. Phys. Chem. C* **2007**, *111* (28), 10498-10502.
33. Zheng, L.; Han, Y. *J. Phys. Chem. B* **2012**, *116* (5), 1598-1604.
34. Bairi, P.; Minami, K.; Nakanishi, W.; Hill, J. P.; Ariga, K.; Shrestha, L. K. *ACS Nano* **2016**, *10* (7), 6631-6637.
35. Sathish, M.; Miyazawa, K. i.; Hill, J. P.; Ariga, K. *J. Am. Chem. Soc.* **2009**, *131* (18), 6372-6373.
36. Aksenova, V.; Nikonova, R.; Lad'yanov, V.; Mukhgalin, V. *Russ. J. Phys. Chem. A* **2014**, *88* (10), 1726-1731.
37. Rana, M.; Bharathanatha, R.; Gautam, U. K. *Carbon* **2014**, *74*, 44-53.
38. Céolin, R.; Agafonov, V.; André, D.; Dworkin, A.; Szwarc, H.; Dugué, J.; Keita, B.; Nadjo, L.; Fabre, C.; Rassat, A. *Chem. Phys. Lett.* **1993**, *208* (3-4), 259-262.
39. Shrestha, L. K.; Sathish, M.; Hill, J. P.; Miyazawa, K. i.; Tsuruoka, T.; Sanchez-Ballester, N. M.; Honma, I.; Ji, Q.; Ariga, K. *J. Mater. Chem. C* **2013**, *1* (6), 1174-1181.
40. Feng, Y.; Wang, Y.; He, J.; Song, X.; Tay, Y. Y.; Hng, H. H.; Ling, X. Y.; Chen, H. *J. Am. Chem. Soc.* **2015**, *137* (24), 7624-7627.
41. Wang, Y.; He, J.; Liu, C.; Chong, W. H.; Chen, H. *Angew. Chem. Int. Edit.* **2015**, *54* (7), 2022-2051.

42. Bürgi, H. B.; Blanc, E.; Schwarzenbach, D.; Liu, S.; Lu, Y. j.; Kappes, M. M.; Ibers, J. A. *Angew. Chem. Int. Edit.* **1992**, *31* (5), 640-643.
43. Park, C.; Song, H. J.; Choi, H. C. *Chem. Commun.* **2009**, (32), 4803-4805.

Chapter 3. Solvent Exchange as a Synthetic Handle for Controlling Molecular Crystals

Organic/molecular crystals have been widely applied in medicine, imaging, explosives, and optoelectronics, but there are very limited methods for controlling their size and shape at the micro- or nanoscale. Herein, we develop solvent exchange as a new synthetic handle for creating complex morphologies in molecular crystals. With mitigated driving force in solution phase, solvent loss or exchange in C₆₀ plates does not lead to structural collapse, but leads to crystal transformation to mesh networks. Different morphologies of C₆₀ crystals and C₇₀ crystals show similar transformation upon solvent exchange. We study the co-solvents and uncover their competing roles in the destabilization of the crystal structure and the on-site crystallization towards rods. This unconventional role of co-solvent is of importance not only for understanding the pore formation and crumbling, but also a new step towards regulating the desolvation and recrystallization processes. Rational transformation of organic crystals would open a new synthetic route for designing complex structures and new properties.

3.1. Introduction

3.1.1. Morphologies of molecular crystals and their applications

Molecular crystals find broad applications in fields such as medicine,¹ imaging,^{2, 3} explosives,^{4, 5} organic light-emitting diodes,⁶ organic photovoltaics,⁷ field-effect transistor,^{8, 9} and flexible electronics.¹⁰ While the size, polymorphism, and morphology of molecular crystals have been intensely studied,¹¹⁻¹⁶ the synthetic control at the nanoscale is still far from ideal. Facet control remains the only method of shape control, and we lack methods to construct complex nano-architectures.

3.1.2. Well established size and shape control in inorganic nanocrystals

This is in contrast to the synthesis of inorganic nanocrystals,¹⁷⁻²³ where size and shape control have been well established^{17, 18} and new nano-architectures are rapidly emerging.¹⁹ One of the most important reasons is the advance of synthetic handles, for example, the use of ligands to control facets;^{17, 18, 23} the manipulation of interfacial energy for controlling Janus growth;^{18, 21} and the exploitation of defects²⁴ and novel lattice types^{25, 26} for breaking high symmetry. Variations and combinations of these synthetic handles then give rise to myriads of possible structures.

3.1.3. A new synthetic handle for organic nanocrystals

For organic crystals, however, few synthetic handles are available. There is no ligand known for specific facets and we have to rely on the intrinsic facets for shape control. Further controls beyond facets are in urgent demand. In chapter 2, we found that exchange of the embedded solvents in a C₆₀ crystal could transform plates into mesh networks,²⁷ indicating an unconventional role of solvents. It provides an interesting opportunity where the manipulation of solvent could be developed into a new synthetic handle for designing molecular crystals. Thus, exploring the solvent effect and solvent environment is of importance.

In the conventional view, solvent is only a media for growing organic crystals, with only an indirect or passive role in affecting their properties. Only recently, it was found that solvents could tune the morphology of organic crystals²⁸⁻³² and their fluorescence properties.³³ Such solvent molecules are embedded in the crystal lattice,³⁴ with strong interactions with the neighboring organic molecules. Thus, they affect the lattice constants, facets and the separation among the fluorescence centers.

Structural collapse or pore formation has been reported in molecular crystals,^{31, 35-37} but the underlying reasons have not been studied in detail. The loss of solvent from organic crystals,

i.e., the desolvation process, has been observed in air or under vacuum conditions. While correlation has been established between the two phenomena, the key mechanistic question is whether the solvent loss is caused by the structural changes, or the opposite. From the point of view of surface energy, the appearance of pores or cracks would increase the surface area and thus should not be a spontaneous process. A more plausible explanation is that the change of the lattice structure is caused by the composition changes as a result of the entropy-driven loss of solvent. From this perspective, the structural collapse or pore formation in organic crystals would be similar in nature to the weathering of solvated mineral crystals.³⁸⁻⁴⁰

In this work, we systematically study the solvent environment during the crystal transformation of C₆₀ plates to mesh networks. Understanding the roles of solvents would be a first step towards the manipulation of the solvents as a new means of synthetic control. In comparison to the irreversible desolvation in gas phase or under vacuum conditions, the solvent environment can be more precisely controlled in a solution phase. With mitigated driving force, structural collapse can be avoided and desolvation and recrystallization can be dynamically regulated for synthetic purposes.

To clarify, we define desolvation as the net loss of solvent from crystals; and recrystallization as the dissolution and re-formation of crystals. In contrast, crystal transformation is defined as the on-site change of shape or composition, for example, in our case the dissolution of plate and reformation of rods all build upon and rely on the initial form of the hexagonal plates.

3.2. Material and methods

3.2.1. Materials

C₆₀, C₇₀, and 1,2,4-trichlorobenzene, *m*-xylene (A.R.) were purchased from Sigma-Aldrich, and used without further treatment. CCl₄ (A.R.) was purchased from Beijing Chemical Agent Ltd., China. Isopropanol alcohol (IPA, A.R.) were purchased from J.T.Baker® brand.

3.2.2. Methods

Synthesis of C₆₀ crystals (including rods and plates) by mixing IPA and C₆₀ stock solutions. In a typical synthesis, IPA was dropwise injected into a stock solution of C₆₀ in CCl₄/*m*-xylene mixture (1 mM, 2 mL) with gentle swirling until the purple C₆₀ solution turned into turbid suspension. And then, the mixture was kept undisturbed for 10 min, afterwards dark brown precipitation was formed. When the ratio was between 6:4 and 10:0 (v/v), only plates (Figure 3.1b, 3.4a). When the initial solvent ratio (CCl₄/*m*-xylene) was 0:10, only rods were obtained (Figure 3.4d). The added IPA amount was dependent on the initial solvent ratio of the preparative solution, as shown in Table 2 in appendix.

Crystal transformation during drying. The Figure 3.3 shown the results of transformation during drying. In a typical procedure, 50-100 μ L mother liquor (46% CCl₄, 31% *m*-xylene and 23% IPA) with small amount of plates was directly dropped on slide glass. Then, the crystal transformation was recorded by optical microscope during the solvent evaporating.

Crystal transformation from C₆₀ plates to mesh networks. In a typical synthesis, IPA was dropwise injected into a stock solution of C₆₀ in CCl₄/*m*-xylene mixture (1 mM, 2 mL) with gentle swirling until the purple C₆₀ solution turned into turbid suspension. The initial solvent ratio of CCl₄/*m*-xylene is 5.9:4.1, in order to conveniently describe the products, we named it 6:4 plates in this paper.

The above mother liquor with 6:4 C₆₀ plates were concentrated at 1000 rpm and then remained in 0.24 mL of supernatant, and finally re-dispersed in 3.0 mL IPA solution for crystal transformation. The optimal transformation condition occurs when a significant amount of mother liquor is diluted in IPA, to give a transformative solution containing 3.39% CCl₄ and 2.33% *m*-xylene (as shown in Figure 3.1, 3.2, and 3.13).

Dependence of C₆₀ plates in different environment conditions. The 6:4 C₆₀ plates were prepared as above method, and the plates were isolated by centrifugation and redispersed in

3.0 mL IPA. Then the plates were isolated (Figure 3.4a) and exposed in different environment.

1. The isolated 6:4 plates were preserved in IPA solution for 2 h (Figure 3.4b). 2. The isolated 6:4 plates exposed to air for 2 h (Figure 3.4c). 3. The 6:4 plates were purified 3 times by IPA (Figure 3.4d). 4. The isolated 6:4 plates were dispersed in an IPA solution with 3.39%/CCl₄ for 2 h (Figure 3.4e). 5. The isolated 6:4 plates were immersed in 2.33% *m*-xylene/IPA for 2 h (Figure 3.4f). 6. Crystal transformation in transformative solution with 5.38%/2.33% (CCl₄/*m*-xylene) solvent ratio (Figure 3.4g). 7. Crystal transformation in transformative solution with 3.39%/0.72% solvent ratio (Figure 2h). 8. The intermediate at 1 min with 3.39%/2.33% (CCl₄/*m*-xylene) solvent ratio (Figure 3.4i).

Yield of C₆₀ mesh networks with different solvent ratio. The C₆₀ plates were prepared as above method. On the blue arrow, the solvent ratio keeps constant. By decreasing the volume of residual solution, the total percentage of CCl₄ and *m*-xylene in transformative solution decrease, and the detailed solvent ratios were shown in Table 2 in appendix.

For the red arrow, the CCl₄ concentration increased when the *m*-xylene concentration remains unchanged. Therefore, the final percentage of *m*-xylene in transformative solution was kept at 2.33%, then different volume of CCl₄ was supplemented into the solution. In addition, the red box on the red dot line was 2.33% *m*-xylene without CCl₄.

However, the green arrow shown that the *m*-xylene ratio decreased under CCl₄ remain unchanged. The detailed experiments were performed to prepare transformative solution with different CCl₄/*m*-xylene solvent ratio (3.14/2.15; 2.04/1.40; 1.04/0.72), as shown in Table S1. Then certain amount CCl₄ was added into transformative solution to change the solvent ratio (3.39/2.15; 3.39/1.4; 3.39/0.72), which kept the same ratio of CCl₄ in transformative solution (Figure 3.13a). At the opposite direction of green line, upon increase of *m*-xylene concentration with CCl₄ unchanged (green dotted line) (Figure 3.18).

Synthesis of the nanostructures with overall rod shape. The 0:10 C₆₀ rods were formed in *m*-

xylene/IPA mixture using above experimental procedures. And then, the rods were separated by centrifugation at 1000 rpm and washed one time with IPA. The freshly prepared C₆₀ rods were mixed with 200 μ L of a saturated supernatant of 10:0 C₆₀ plates formed in CCl₄/IPA mixture as the transformative solution, and the mixtures were allowed to stand for 10 min.

Synthesis of C₇₀ networks. The C₇₀ cubes were formed in mesitylene/TBA mixture using liquid-liquid interfacial precipitation (LLIP) method.⁴⁷ Typically, 5 mL TBA was slowly injected into a stock solution of C₇₀ in mesitylene (1 mg/mL, 1 mL) to form an interface. The mixture was kept at 25 °C for 3 h without mechanical agitation. Then the mixture was treated by sonication for 30 s with shaking, and stored in the incubator at 25 °C for 24 h. And then, the cubes were separated by centrifugation at 5000 rpm. The networks were obtained when the C₇₀ cubes were immersed in an IPA-*m*-xylene mixture (V/V = 1:1 or 65:35, 1 mL mixture contains 0.5 mL IPA and 0.5 mL *m*-xylene; or 1 mL mixture contains 0.65 mL IPA and 0.35 mL *m*-xylene), and the mixtures were allowed to stand for 20 min. In addition, when the TBA-rich C₇₀ cubes were isolated and redispersed in an IPA-CCl₄ mixture (V/V = 3:7, 1 mL mixture contains 0.3 mL IPA and 0.7 mL CCl₄) for 20 min, many pores and small irregular plates appeared on the cube surface.

Synthesis of multi-layer hexagonal C₆₀ nano-meshes by using C₆₀ crystals formed in CCl₄/IPA mixture as the initial plates. The 10:0 C₆₀ crystals with *fcc* phase were first formed in CCl₄/IPA mixture using above experimental procedures. And then, the *fcc* plates were separated by centrifugation at 1000 rpm and washed one time with IPA. The freshly prepared C₆₀ plates were mixed with 200 μ L of a saturated supernatant of 0:10 C₆₀ rods formed in *m*-xylene/IPA mixture as the transformative solution, and the mixtures were allowed to stand for 10 min.

Synthesis of multi-layer hexagonal C₆₀ nano-meshes by using C₆₀/ferrocene crystals obtained at toluene/IPA interface as the initial plates. The C₆₀/ferrocene crystals were

formed at toluene/IPA interface following the previous reported experimental procedures and were heated at 120 °C for 15 min to remove the excess ferrocene.¹ And then, the resulting *fcc* plates were mixed with 200 µL of a saturated supernatant of C₆₀ rods formed in *m*-xylene/IPA mixture as the transformative solution, and the mixtures was allowed to stand for 10 min.

Synthesis of rhombic C₆₀ nano-meshes by using C₆₀•trichlorobenzene crystals formed in 1,2,4-trichlorobenzene/IPA mixture as the initial plates. The rhombic C₆₀•trichlorobenzene crystals were obtained following similar experimental procedures to the synthesis of C₆₀ plates formed in CCl₄/IPA mixture. After that, the C₆₀•trichlorobenzene plates were separated by centrifugation at 1000 rpm and washed one time with IPA. The freshly prepared C₆₀ plates were heated at 120 °C for 30 min to remove the incorporated 1,2,4-trichlorobenzene solvent. Finally, the *fcc* plates were mixed with 200 µL of a saturated supernatant of C₆₀ rods formed in *m*-xylene/IPA mixture as the transformative solution, and the mixtures were allowed to stand for 10 min.

The solvate C₆₀ crystals at different CCl₄/*m*-xylene ratios were determined by thermal gravimetric analysis (TGA) performed in a nitrogen atmosphere. In view of the possible overlap between the two processes, we first performed the TGA analysis for a neat C₆₀ powder under similar experimental conditions, as shown in Figure 3.7. It is obvious that the raw C₆₀ powder starts to lose weight at a temperature of 268 °C, suggesting that the weight loss of the C₆₀ solvate crystals below this temperature is due to the removal of solvent molecules. By means of this temperature as a reference point, we have examined the solvent content incorporated within the C₆₀ crystal. It can be determined that the 10:0 plates contained 3.90% w/w CCl₄ (Figure 3.6a), whereas the 0:10 rods contained 8.01% w/w *m*-xylene (Figure 3.6b). Meanwhile, TGA data of 6:4 plates showed two stages of solvent loss, about 4.97% and 7.42% w/w, respectively, while the mesh networks contained 3.25% CCl₄ and 8.26% *m*-xylene (Figure 3.6). It indicated that the CCl₄ came out of the plates and the *m*-xylene was included into crystal

lattice to give rods.

3.2.3. Characterization.

The morphologies and sizes of the samples were examined using field-emission scanning electron microscopy (FESEM, JEOL 7600F) at an acceleration voltage of 5 kV. Prior to analysis, the samples were coated with a thin gold layer using an Edwards Sputter Coater. TEM images and Selected Area Electron Diffraction (SAED) pattern were obtained using a JEOL JEM-2100 electron microscope at an accelerating voltage of 200 kV. One drop of the as-prepared colloidal dispersion was deposited on a carbon-coated copper grid, and dried under high vacuum. The X-ray diffraction (XRD) patterns were measured by Bruker D8 Advance Powder with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). We operated in the 2θ range from 5 to 40°, by using the samples spin-coated on the surface of a quartz substrate. Thermogravimetric analysis (TGA) curve was obtained using a TGA Q500 thermogravimetry analyzer. The Raman studies were measured under ambient conditions by using 488 nm excitation with integration time of 10 s. IR spectra were taken on a FTIR Perkin Elmer Frontier. For the UV-vis absorption spectra, the sample were dropped on a quartz wafer and tested by UV-vis-NIR Lambda 950. AFM images were taken on the Asylum Research Cypher Scanning Probe Microscope system with a tapping mode.

3.3. Results and discussion

3.3.1. Morphologies of C₆₀ depend on co-solvents ratio

In our experiments, we used the C₆₀ crystals as the model system to study the role of solvent. First, C₆₀ (Figure 3.1a) was dissolved in CCl₄/*m*-xylene mixture (*v/v* = 6:4) to near saturation. Then, isopropanol (IPA) was slowly added into the solution to give precipitate of micro-plates. While the plates were stable in this mother liquor (Figure 3.1b), *i.e.*, the solution from which they were prepared, their morphology changed dramatically upon changes of the environment.

Figure 3.1. The morphology of C₆₀ crystal depends on solvent ratio. (a) C₆₀ molecule. (b) 6:4 plates. (c) Messy networks. (d) Porous plates. (e) Mesh networks. The scale bar is 10 μm.

However, when the conditions were not right, pores and cracks would form (Figure 3.1d), or the transformation has a very low yield. Only with the right solvent ratio and procedure, were the mesh networks obtained (Figure 3.1e and 3.2). Hence, it is critical to understand which factors at which stages of the process are critical to the transformation. Analysis of the underlying mechanism would help future design of synthetic conditions.

Figure 3.2. C₆₀ mesh networks. SEM images of (a, b) mesh networks. TEM images of (c, d) mesh networks.

3.3.2. Difficult to control the structural change in drying conditions

When a droplet of the mother liquor containing C₆₀ plates was dried directly, sometimes messy networks could be observed (Figure 3.1c). Figure 3.3 shows the results of C₆₀ plates transformation during drying. But the result has low reproducibility in our hands, because the amount of mother liquor and the extract drying conditions are difficult to control. In contrast, the results obtained in the solution-phase processes have much higher reproducibility and hence, it becomes the focus of our study. In the following, we carry out a series of experiments to compare the degradation and transformation under various conditions, in an attempt to gain

insight in the underlying processes.

Figure 3.3. SEM images of messy networks formed by evaporating small aliquots of the precipitate solutions ($\text{CCl}_4/m\text{-xylene}$ ratio = 6:4). (a) At low magnification. (b) At high magnification.

3.3.3. Stability of C_{60} crystals in various conditions

When the plates were isolated by centrifugation and redispersed in IPA, they still appeared to have smooth surface (Figure 3.4a), even after the vacuum conditions during scanning electron microscope (SEM) characterization. After 2 h in the IPA solution, the plates appeared partially crumbled with many large pores (Figure 3.4b). In comparison, simply exposing the plates to air for 2 h gave only small and shallow pores (Figure 3.4c). When the purification cycle of centrifugation-redispersion was repeated 3 times, many large pores formed without making the plates crumble (Figure 3.4d). On the basis of these observations, we speculate that the loss of solvent should be the key factor. The resulting contraction induces strain in the crystal lattice, which depends on the degree of desolvation. Thus, the formation of pores, cracks, and even crumbling reflect the degree of structural relaxation to release the internal strain. The rate of loss appears to be less in air or vacuum than in an IPA solution. It agrees with the expectation that the entropy increase should be larger when the solvent molecules are mixed with IPA than with air molecules, which are much less in number. Repeated dilution in IPA is expected to further reduce the residual concentration of CCl_4 and $m\text{-xylene}$, thus promoting the

desolvation of the crystals.

Figure 3.4. 6:4 plate preserve in different conditions. SEM images of (a) 1 time purification by IPA, then the isolated plates were (b) preserved in IPA solution for 2 h. (c) The isolated plates were exposed to air for 2 h. (d) The plates were purified 3 times by IPA. (e) The isolated plates were dispersed in an IPA solution with 3.39% CCl_4 for 2 h. (f) The isolated plates were immersed in 2.33% *m*-xylene/IPA for 2 h. (g) Crystal transformation in IPA solution at 5.38%/2.33% (CCl_4 /*m*-xylene) solvent ratio, (h) at 3.39%/0.72% solvent ratio. (i) The intermediate at $t = 1$ min in transformative solution with 3.39%/2.33% ratio. The scale bar is 10 μm , and the scale bar of insert is 1 μm . See figure 3.27-3.35 in appendix for large-view images.

3.3.4. The effect of IPA on desolvation

As known previously, the C_{60} crystals synthesized in neat CCl_4 (i.e., $v/v = 10:0$) are plates,^{30,}

³² and those in neat *m*-xylene are rods^{29, 41} (i.e., $v/v = 0:10$) (Figure 3.5). They remained intact in their respective mother liquor. The rods were stable in air and vacuum, and even after repeated centrifugation-redispersion cycles in IPA (Figure 3.5d-f). From the thermogravimetric analysis (TGA) data, the purified rods contained 8.0% *m*-xylene (w/w, Figure 3.6b). After they were preserved in air for 2 days there was still 6.1% remaining (Figure 3.7b). It has reported that two distinct sites of C₆₀ crystals were occupied by the *m*-xylene molecules. A thermally disordered *m*-xylene occupies trigonal prismatic cavities. On the other hand, the heavily disordered solvent molecules replaced one C₆₀ molecule.⁴² It appears that this low level of desolvation is insufficient in causing morphological changes.

Figure 3.5. The stability of C₆₀ crystals. SEM images of (a) 10:0 plates, (b) the pure plates were purified 1 time by IPA and (c) purified 3 times by IPA. (d) 0:10 rods, (e) the pure rods were purified 1 time by IPA and (f) purified 3 times by IPA. The scale bar is 1 μm .

On the other hand, the purified 10:0 plates contained 3.9% CCl₄ (w/w, Figure 3.6a), which decreased to 0.85% after three rounds of purification (Figure 3.7c). The 10:0 plates started to show pores after one round of purification and severe degradation set in when they were exposed in air or after multiple rounds of purification. It is known that CCl₄ molecules only

occupy the prismatic sites in C₆₀ molecular packing.⁴³ The desolvation was obviously faster than the 6:4 plates. These results indicate that *m*-xylene has longer retention time within the C₆₀ crystals than CCl₄, likely because of its larger molecular size, higher boiling point (lower vapor pressure), and/or stronger interactions with C₆₀. As a result, the rods are generally more stable than the plates.

Figure 3.6. TGA of (a) 10:0 plates, (b) 0:10 rods, (c) 6:4 plates, and (d) mesh networks.

3.3.5. Characterization by TGA and spectra

3.3.5.1. Characterization the solvent exchange by TGA

During the formation of the 6:4 plates, the crystallization of C₆₀ includes both CCl₄ and *m*-xylene in the crystal lattice. The combined ratio of the co-solvents (4.97% CCl₄ and 7.42% *m*-xylene by TGA, Figure 3.6c) is higher than the ratios achieved with the respective neat solvents.²⁴ After transformation, the mesh networks contain lower CCl₄ (3.25%) and higher *m*-xylene (8.26% w/w) than the original 6:4 plates (Figure 3.6d), indicating solvent exchange. The

relative molar ratio of CCl₄: *m*-xylene decreases from the 1:2.1 in the plates, to 1:3.7 in the mesh networks (Table 3.1). Hence, some of the CCl₄ is lost as *m*-xylene is included during the crystal transformation.

Figure 3.7. TGA of (a) C₆₀ powder. (b) 0:10 rods were preserved 2 days before test. (c) 10:0 plates were purified three rounds by IPA. (d) Mesh networks were obtained from the transformation solution with solvent ratio of 5.38/3.70 (CCl₄/*m*-xylene).

Table 3.1. Dependence of crystal morphologies on solvent ratio.

C ₆₀ crystal	CCl ₄ % (w/w)	<i>m</i> -xylene (w/w)	n _{CCl₄} /n _{<i>m</i>-xylene}
10:0 plates	3.90	0	---
0:10 rods	0	8.01	---
6:4 plates	4.97	7.42	1:2.1
Mesh networks	3.25	8.26	1:3.7

3.3.5.2. Characterization by spectra

IR spectroscopy was used to investigate the embedded solvents (Figure S3.8a). Besides the characteristic C₆₀ bands at 526, 576, 1181, 1428, and 1536 cm⁻¹, the IR spectra of the 10:0

plates and 6:4 plates showed two strong peaks at 761 and 783 cm^{-1} , which can be ascribed to CCl_4 . In the 0:10 rods, three main peaks at 690, 697 and 769 cm^{-1} should originate from *m*-xylene.⁴¹ After transformation, the *m*-xylene peaks remained in the spectrum of the mesh networks, while only one CCl_4 peak (783 cm^{-1}) with much reduced intensity could be observed. Thus, the IR data support solvent exchange during crystal transformation.

Figure S3.8. FT-IR and Raman spectra of C_{60} crystals. (a) FT-IR, (b) Raman spectra of C_{60} crystals involving (I) 10:0 plates, (II) 6:4 plates, (III) 0:10 rods, and (IV) mesh networks.

In the Raman spectra (Figure S3.8b), the major peak at 1466 cm^{-1} characteristic of C_{60} is observed in all samples. The lack of the 1459 cm^{-1} band indicates the absence of polymerization in C_{60} .^{32, 41, 44-46}

Figure 3.9. UV-vis spectra of C_{60} crystals involving (I) 10:0 plates, (II) 6:4 plates, (III) 0:10 rods, and (IV) mesh networks.

The UV-vis spectra of the C_{60} crystals show four distinct transitions at 344, 613, 642, and 670 nm (Figure 3.9).^{47, 48} The absorption band at 314 nm (marked Δ) is observed in the 0:10 rods, 6:4 plates and mesh networks, which is contributed by *m*-xylene.⁴¹

3.3.6. Crystallographic characterization by XRD and SAED

In XRD, the 6:4 plates have *fcc* structure, similar to the 10:0 plates.⁴⁰ After transformation, the resulting mesh networks were mainly indexed to the *hcp* phase, *i.e.*, same as the rods, and the remaining weak peaks (marked by stars *) are assigned as the residual plates (Figure 3.10). According to the SAED observations, both the 10:0 and 6:4 plates show *fcc* pattern (Figure 3.11), consistent with the above XRD data. It appears that the different co-solvent inclusion

does not significantly disrupt the lattice structure, especially considering that their levels of co-solvent inclusion are much less than the *hcp* plates in the literature.⁴⁹ The rods inside the mesh networks show similar pattern as the 0:10 rods, which is indexed to *hcp* phase.²⁹ Therefore, the solvent exchange from the 6:4 plates to mesh networks leads to significant lattice reorganization from *fcc* to *hcp* phase.

Figure 3.10. XRD patterns of (i) 10:0 plates, (ii) 6:4 plates, (iii) 0:10 rods, and (iv) mesh networks.

Interestingly, in XRD the (220) peak of the 6:4 plates and the (002) peak of the mesh networks have matching 2θ angles (Figure 3.11), corresponding to lattice distances of 5.02 and 5.04 Å, respectively. Measured from SAED patterns, the d_{110} of the rod is 12.01 Å. Whereas the lattice distance d_{002} of the *hcp* rods on the mesh network is 5.01 Å, corresponding to lattice distance of 10.02 Å at the [001] growth direction. The d_{220} of the *fcc* plates is 4.98 Å, thus the three symmetrically equivalent directions of $[\bar{1}10]$, $[10\bar{1}]$, and $[0\bar{1}1]$ have lattice distance $d_{\bar{1}10} = d_{10\bar{1}}$

$= d_{011} = 9.96 \text{ \AA}$. The lattice matching (0.6% mismatch) leads to a low strain along the growth direction of rod, which promotes nucleation. It explains that the alignment of rods parallel to the edge of hexagonal plates and their 120° included angle with respect to each other (Figure 3.11c, 3.12a).

Figure 3.11. TEM images of (a) 6:4 plate, (b) mesh network (c) 10:0 plate, and (d) 0:10 rod, respectively. The insert images are the corresponding SAED patterns of TEM images.

On the other hand, the lattice mismatching rate between $[110]$ direction of the rod and the $[110]$ direction of plate is 17.07% (Figure 3.12b). It is expected that such poor lattice matching would generate high strain, preventing conformal coating of one on the other. The growth of a rod on a plate would differ from the coating of one crystal on another, in particular regarding

to the interface. When a 2D lattice sits on another, mismatch at any direction would cause strain. However, when a rod sits on a 2D lattice, the initial line of contact would be important for nucleation. We believe that once the rod stick to the plate, the (111) facet of the *fcc* plate matches the (10 $\bar{1}$ 0) facet of the *hcp* rod at the [001] direction. As the original plate gradually dissolve, the criss-cross of rods eventually lead to hexagonal mesh networks.

Figure S3.12. Schematic of crystal lattice orientations and lattice spacings of *fcc* and *hcp* phases. (a) The lattice matching between *fcc* [$\bar{1}10$] and *hcp* [001]. (b) The lattice mismatching between *fcc* [110] and *hcp* [110].

3.3.7. The yield of mesh networks against the solvent ratio in transformative solution

Given the importance of the co-solvents, their concentration is precisely controlled. The optimal transformation occurs when a significant amount of mother liquor (240 μL) is diluted in 3 mL IPA, to give a transformative solution containing 3.39% CCl_4 and 2.33% *m*-xylene (Figure 3.13). Since these concentrations are much reduced from those in the mother liquor (46% CCl_4 and 31% *m*-xylene), there is sufficient driving force for solvent exchange and thus crystal transformation. In comparison, transformation or etching cannot occur in the mother liquor, because the high concentration of the co-solvents would cause the process of solvent inclusion to have the same driving force as that of the desolvation process. Thus, near equilibrium is reached.

Figure 3.13. The solvent ratio of transformative solution versus the yield of mesh networks. The solvent

ratio keeps constant in the blue arrow. The red arrow shows that the ratio of CCl_4 increases in transformative solution when the *m*-xylene ratio remains unchanged. The *m*-xylene ratio decreases under CCl_4 remains the same in the green arrow.

Going beyond the stability problem, we have to understand the solvent effects during the crystal transformation. As shown in Figure 3.13a, the solvent ratio CCl_4/m -xylene was kept constant in an IPA solution (blue line). The optimal transformation condition occurs when *m*-xylene ratio is in the 1.40-2.33% range, and the CCl_4 ratio between 2.04-3.39% (Figure 3.14), where mesh networks were obtained with high yield (> 89%). With both of the co-solvents reduced in concentration, the yield decreased significantly. With 0.60% CCl_4 and 0.41% *m*-xylene, severe desolvation caused pore formation and no crystal transformation occurred (Figure 3.15). On the other hand, increase of co-solvent concentration from the optimal conditions left most of the plates unchanged, and thus caused rapid decrease of yield (Figure 3.14).

Figure 3.14. SEM images of C₆₀ mesh networks (a-f) with different solvent ratios during transformation. (a-b) Increase of co-solvent concentration from the optimal conditions caused rapid decrease of yield. (c-f) When *m*-xylene ratio is in the 1.40-2.33% range (the CCl₄ ratio between 2.04-3.39%), the mesh networks have high yield (> 89%) (Blue in in Figure 3.13). The lower left corner shows the yield of mesh networks. The upper right corner shows the *m*-xylene/CCl₄/IPA solvent ratio in transformative solution. The scale bar is 50 μm.

3.3.8. Isolate the variables to understand the separate role of co-solvents

Considering the three solvents (CCl_4 , *m*-xylene and IPA) involved, it would be important to isolate the variables in order to understand the separate role of co-solvents. In the follow experiments, purified plates were transformed in solutions where only one of the co-solvents was varied. During typical purification, the residue mother liquor is reduced to less than 5 μL , so that the remaining solvents would be negligible after dilution. After one round of purification, CCl_4 is estimated to be $< 0.08\%$ and *m*-xylene $< 0.05\%$; after two rounds, the residue co-solvents are expected to be negligible.

Figure 3.15. SEM images of C₆₀ crystals (a-f) with different solvent ratios during transformation. (a-b) With both of the co-solvents reduced in concentration, the yield decreased significantly. (c) Severe desolvation caused pore formation and no crystal transformation occurred. (d-f) Upon decrease *m*-xylene of concentration with CCl₄ unchanged (green line in Figure 3.13), the yield sharp decrease. The scale bar is 50 μ m.

When the 6:4 plates after one round of purification were dispersed in 3.39% CCl₄/IPA mixture, the CCl₄ concentration was retained and *m*-xylene was removed as compared to the optimal condition. After 2 h, the plates remained unchanged (Figure 3.3e). On the other hand, when the plates were dispersed in 2.33% *m*-xylene/IPA solution, they completely transformed to mesh networks (Figure 3.3f, 3.16). In the former experiment, CCl₄ has the same tendency to diffuse out as in the optimal transformation, but the lack of *m*-xylene prevented the rod formation and therefore the transformation was unsuccessful. The latter experiment shows that *m*-xylene by itself was sufficient to cause the transformation and CCl₄ was not required in the solution.

Figure 3.16. SEM images of C_{60} crystals (a-d) with different solvent ratios during transformation. (a-b) Upon increase of CCl_4 concentration with *m*-xylene unchanged (blue dotted line in Figure 3.13), the yield sharp decrease. (c) Without CCl_4 in the transformative solution, the plates can still transform to mesh networks, which has high yields. (d) The plates remained unchanged when the CCl_4 concentration was retained at 3.39% and *m*-xylene was removed.

We believe that the pore or crack formation reflects the destabilization of the plates, which is also an important requirement for the crystal transformation (in addition to the requirement of *m*-xylene). To test this hypothesis, the CCl_4 concentration was increased while maintaining the *m*-xylene concentration (the red line in Figure 3.13a): the 6:4 plates were dispersed in an IPA solution with 5.38% CCl_4 and 2.33% *m*-xylene. Several long rods appeared but the majority of the plate surface remained unchanged (Figure 3.3g, 3.16b), even after incubation for more than 6 months (Figure 3.17). Hence, *m*-xylene is not solely responsible. The slight increase of CCl_4 concentration significantly reduced the rate of crystal transformation, consistent with the hypothesis. On the other hand, when an IPA solution with 3.39% CCl_4 and 0.72% *m*-xylene was used, some rods appeared on the plates but the plate surface remained smooth after long incubation (Figure 2h, 3.15). Hence, decrease of *m*-xylene concentration and increase of CCl_4 can both impede crystal transformation, as reflected by the reduction of yield (the green and red lines in Figure 3.13a).

Figure 3.17. SEM images of the 6:4 plates dispersed in an IPA solution with 5.38% CCl_4 and 2.33% *m*-xylene, which remained unchanged even after 6 months incubation.

At the opposite direction, upon increase of *m*-xylene concentration with CCl_4 unchanged

(green dotted line), the yield remained above 95% (Figure 3.18). With *m*-xylene unchanged and decrease of CCl₄ concentration, the yield remained high, though with some side effects: Many vertical and tilted rods appeared (Figure 3.3f, 3.16). The low concentration of CCl₄ and the relative high concentration of *m*-xylene lead to fast recrystallization. The resulting high local concentration of C₆₀ near the plate surface would diffuse outward, promoting the out-of-plane growth of rods.

Figure 3.18. SEM images of mesh networks (a-d) with different solvent ratios during transformation. Upon increase of *m*-xylene concentration with CCl₄ unchanged (green dotted line in Figure 3.13), the yield remained above 95%. In contrast, with *m*-xylene unchanged and decrease of CCl₄ concentration, the yield remained high (~95%). The scale bar is 50 μ m.

As summarized in Figure 3.13, high CCl₄ concentration always inhibits transformation, even in the presence of high *m*-xylene concentration. On the other hand, high *m*-xylene concentration promotes transformation, with further assistance by lowering CCl₄ (the red dotted line). The

incompletely transformed products (16% yield at (3.7, 5.38)) were characterized by TGA. It shows that the plates still contain high percentage of CCl_4 (6.1%) and *m*-xylene (9.55%). The relative molar ratio of CCl_4 :*m*-xylene is 1:2.2 in the incompletely meshes, which is close to the 6:4 plates. Thus, it can explain their inability to transform (Figure 3.6).

3.3.9. Mechanistic proposal

Figure 3.19 gives our mechanistic proposal. There are several preconditions for the crystal transformation: desolvation of the plates and the presence of *m*-xylene. The former destabilizes the plate and promotes solvent exchange; whereas the latter is needed to form C_{60} rods. The co-solvents CCl_4 and *m*-xylene compete in this solvent exchange process and their relative concentration is the critical factor.

Figure 3.19. The illustration shows the relative stability of C_{60} plates.

3.3.10. Intermediates during crystal transformation

We captured the intermediates during crystal transformation at the optimal solvent ratio 3.39%/2.33% (CCl_4 /*m*-xylene), as shown in Figure S22. At 1 min, the plates generated lots of

rods on their surface along with many hexagonal holes in the plates (Figure 2i). The holes are inverse pyramids with hexagonal cross-section, obviously different from the random pores with circular cross-section formed during desolvation. These inverse pyramids are well aligned with the hexagonal plates, similar to the faceted holes reported in the literature.⁵⁰ With the transformation going on, the holes became larger and the rods extended in length, their interconnection eventually gives the first layer of mesh network at around 10 min (Figure S22).

Figure 3.20. SEM images of the crystal transformation from plate to mesh networks. (a) $t = 1$; (b) 10; (c) 30 and (d) 60 min. (e-h) High-magnification SEM images, corresponding to (a-d). The cyan lines and yellow lines in (e, f) show the T-shape and X-shape junctions, respectively. The dashed boxes in (e-h) highlight the diameter changes of the C_{60} rods during growth.

3.3.10.1. T-shape and X-shape junctions

At the cross point of the nanorods, there are T-shape and X-shape junctions (Figure 3.20e, f), with the former being more frequent. It is conceivable that the critical matter is whether the crossing occurs at early or late stage of nanorod growth: When two rods encounter at an early stage, the subsequent growth is extensive enough that the rod growth would continue on the other side of the obstacle, with similar width on both sides (Figure 3.20e). Such an X-shape

junction would be an interesting case where two crystals are well aligned before the encounter, and one has to cross over the other, forming a twinning plane at their interface. If two rods encounter at a late stage, the limited growth would be insufficient to overcome the obstacle, leading to a T-shape junction. For intermediate cases, the rod is able to cross over to the other side, but the lack of growth leads to much thinner rods than the opposite side (Figure 3.20f).

From occasional plates in stand-up orientation, it can be seen that both sides of the plates were converted to mesh network (Figure 3.21). The fact that the rods on the two sides do not overlap suggests that the transformation occurs independently from both sides. We believe that the inverse pyramids are the consequence of etching/dissolution, and the dissolved C_{60} then recrystallizes as rods on the plate surface.

Figure 3.21. SEM images of the intermediates of mesh networks, indicating that the transformation was carried out at both sides of plates.

3.3.11. Atomic force microscope topographic images of C_{60} crystals

Figure 3.22 presents the atomic force microscope (AFM) topographic images of C_{60} crystals. The thickness of the original 6:4 plate is 130 to 160 nm and the average diameter of the rod in the resulting mesh network is 100-150 nm. The overall thickness of the mesh network (450-500 nm) is well consistent with the combined thickness of an empty layer of the original plate

and two layers of mesh network on both sides.

Figure 3.22. AFM images of (a, b) 6:4 plate and (e, f) mesh network. The thickness of plate (c, d) is about 130-160 nm. The thickness of mesh network (g, h) is 450-500 nm, and the diameter of rod (g) is 100-150 nm.

In essence, the crystal transformation is akin to ripening, except that one type of crystal is dissolved to form a closely related, but different crystal. In contrast, the dissolved and recrystallized materials in ripening have the same composition. Moreover, the on-site recrystallization differs from the typical ripening. It is the critical factor in fitting the newly generated rods in/on the initial framework of hexagonal plates, rather than forming new particles in the solution.

3.3.12. Thermodynamic driving force and kinetic factors

On the basis of these understanding, the thermodynamic driving force for the crystal transformation is the relative stability of crystals in the different solvent environment.¹⁸ More specifically, it includes the loss of CCl₄ driven by entropy and the inclusion of *m*-xylene driven by the favorable stabilization energy of the rods. Both factors depend on the concentration of the co-solvents. In terms of kinetics, the critical factors are the rates of desolvation, C₆₀ dissolution, and recrystallization. The fact that these three processes can occur at the same location leads to the conclusion of on-site recrystallization. The epitaxy between the rods and plates leads to the alignment of rods and thus, the mesh networks. Lastly, the degradation of plates is also an important kinetic factor determining how much of the plates can be retained for crystal transformation.

3.3.13. Generality of crystal transformation

Solvates are common in organic and molecular crystals.^{32, 46, 51} Thus, we hope to develop a generate method to obtain mesh networks. Based on the understanding of crystal transformation, we found that two necessary conditions are of critical importance: 1) the template with pretreatment; 2) a transformative solution with certain amount of *m*-xylene. To decrease the dissolution of C₆₀ plate in transformative solution, we prepared a saturated

supernatant of pure C₆₀/*m*-xylene rods, which as the transformative solution.

In order to test the generality, 10:0 C₆₀ plates (Figure 3.23a) were dissolved in the transformative solution. the C₆₀ plates converted to hexagonal mesh networks in a few minutes. The SEM images of Figure 3.23c shown that meshes had multi-layers and closely combined together. It is because that the higher *m*-xylene concentration (50% v/v) leads to the vertical rods because of the long-distance diffusion of C₆₀.

Figure. 3.23. SEM images of C₆₀ crystals obtained from CCl₄/IPA mixture (a); the 10:0 plates were mixed with a saturated supernatant of C₆₀ rods formed from *m*-xylene/IPA mixture (b, c) for a few minutes. SEM images of C₆₀/ferrocene plates obtained at toluene/IPA interface (d); the cocystal plates after heat treatment at 120 °C were mixed with a saturated supernatant of C₆₀ rods formed from *m*-xylene/IPA mixture (e, f) for a few minutes.

Except that *m*-xylene is more stable in C₆₀ crystals than CCl₄, the two solvents appear to have symmetrical roles in the system. It is conceivable that CCl₄ should be able to transform xylene-rich crystals, just as xylene transforms CCl₄-rich crystals. Thus, we prepared rods in neat *m*-xylene (0:10, Figure 3.24a) to maximize the extent of co-solvent incorporation. A high concentration of CCl₄ (50%) in IPA solution was used as the transformative solution, to provide a larger driving force to exchange for the more stable *m*-xylene. The resulting nanostructures

contain lots of orthogonal plates with an overall rod shape (Figure 3.24b-d). It appears that multiple plates were epitaxially grown on the rod surface, so that its original shape is retained during the on-site recrystallization. These results confirm that the transformation is a two-way process.

Figure 3.24. SEM images of 0:10 C_{60} rods obtained from the *m*-xylene/IPA mixture (a); the rods were mixed with a saturated supernatant of C_{60} plates formed from the CCl_4 /IPA mixture (b-d) for a few minutes.

To further confirm the generality the strategy, different material composition of C_{60} plates have been tested. The C_{60} /ferrocene charge-transfer (CT) plates (Figure 3.23d) were prepared by using previous method.⁵² It was demonstrated that the C_{60} /ferrocene plates could transfer to *fcc* crystal system by heating to 120 °C for a few minutes.⁵² The ferrocene would sublime during this process. After heating, the C_{60} /ferrocene plates kept the original appearance. The

treated *fcc* plates were immersed in transformation solution. Then the multi-layer C_{60} nano-meshes were formed (Figure 3.23e and f). In addition, the rhombic $C_{60} \cdot 2C_6H_3Cl_3$ microplates (Figure 3.25a) were formed at the IPA and 1,2,4-trichlorobenzene mixture. The $C_{60} \cdot$ trichlorobenzene plates have to a triclinic phase with the unit cell parameters: $a = 9.878 \text{ \AA}$, $b = 9.941 \text{ \AA}$, $c = 12.334 \text{ \AA}$, and $\alpha = 70.99^\circ$, $\beta = 75.17^\circ$, $\gamma = 63.05^\circ$. The XRD of $C_{60} \cdot$ trichlorobenzene plates (Figure 3i.) fit the triclinic crystal system.²⁷ Upon heating treatment the plates at 120°C for 6 h, the $C_{60} \cdot 2C_6H_3Cl_3$ plates have *fcc* phase by the removal of 1,2,4-trichlorobenzene (Figure 3.26ii). Thus, the surface of rhombic plate is (111) facet with three equivalent growth directions at the side of plates and the long axis of *m*-xylene-rod has [001] growth direction. The small lattice mismatching leads to (Figure 3.25b and c) nano-meshes formation in the transformative solution.

Figure 3.25. Rhombic C_{60} nano-meshes formed by using $C_{60} \cdot$ trichlorobenzene crystals as the initial plates. SEM images of C_{60} crystals obtained in 1,2,4-trichlorobenzene/IPA mixture (a); the $C_{60} \cdot$ trichlorobenzene plates after heat treatment were mixed with a saturated supernatant of C_{60} rods formed in *m*-xylene/IPA mixture (b and c) for a few minutes.

To explore the generality of the transformation, we used C_{70} cubes, which were formed between *tert*-butyl alcohol (TBA) and mesitylene by liquid-liquid interfacial precipitation (LLIP) method (Figure S25a).⁵³ When the TBA-rich C_{70} cubes were isolated and redispersed in an IPA- CCl_4 mixture ($V/V = 3:7$), many pores and small irregular plates appeared on the cube surface (Figure S25b-d). Obviously, similar desolvation and recrystallization processes are occurring. On the other hand, when the TBA-rich cubes were immersed in an IPA-*m*-xylene

mixture (V/V = 1:1), the C₇₀ cubes underwent crystal transformation to networks, with thick perpendicular nanorods on their surface (Figure S25e). With lower *m*-xylene concentration of (V/V = 65:35), the rods become smaller in diameter indicating slower rate of recrystallization (Figure S25f). As previously reported, the C₇₀ cube has *cubic* crystal system⁵¹ with the cell dimension ca. *a* = 1.05 nm. The six surfaces of cube are (100) facets, and the lattice distance of *d*₁₀₀ is 1.05 nm. It was found that the *m*-xylene-C₇₀ nanowires or nanotubes have *fcc* phase⁵⁴ with lattice parameters ca. *a* = 1.492 nm. The longitudinal growth direction is [110] with *d*₁₀₀ = 1.055 nm. Thus, the lattice matching (~0.5%) leads to epitaxial growth of rod on the cube. The two equivalent directions of (100) explains that the alignment of rods are orthogonality with each other. The fact that the method can be applied to different morphologies of C₆₀ and C₇₀ crystals demonstrates the generality of the synthetic handle.

Figure 3.26. SEM images of C₇₀ crystals. (a) C₇₀ cubes obtained from the mesitylene/TBA mixture. (b-d) The cubes were isolated and redispersed in an IPA-CCl₄ mixture (V/V = 3:7). (e) The cubes were immersed in an IPA-*m*-xylene mixture (V/V = 1:1) and (f) in lower *m*-xylene concentration of (V/V = 65:35) for 20 minutes.

3.4. Conclusion

Molecular crystals contain co-solvents are very common.³⁴ Our model study shows that the degree of solvent inclusion can be continuously tuned, rather than only at stoichiometric ratios. Moreover, two different co-solvents can be incorporated with varying ratios. The combination of these two synthetic handles thus gives freedom in tuning the properties of molecular crystals. Bringing the desolvation process from the typical air or vacuum conditions to the solution phase would allow more precise control of the solvent environment, enhancing the reliability and reproducibility. Understanding the desolvation and solvent exchange processes would help design future synthetic routes, for example, putting co-solvents as tunable space-filler and then removing them to induce strain; tuning the strain to create pores and cracks; and tuning the solvent exchange to cause crystal transformation. Considering the wide-spread use of molecular crystals, we believe that rational manipulation of co-solvents would open door to a new horizon of synthetic control for molecular crystals.

In this chapter, we demonstrated the role of solvent molecules and the relationship between mesh yeild and the solvent ratio. In addition, we concluded the driving force and the critical limited factors. Finally, we proposed the general method that use solvent to fill the space of crystals, and a high concentration of another solvent was used as the transformative solution. Thus, the method can be used to different C₆₀ and C₇₀ crystals. However, the sythetic handle is limited to molecular crystal syetem. It is urgent for us to extend the new method to organic crystal system.

3.5. Appendix

Table 2. Dependence of crystal morphology on solvent ratio

Solvent ratio	Stock solution (mL)	IPA (mL)	Residue (mL)	IPA (mL)	CCl ₄ (%)	<i>m</i> -xylene (%)
10:0	2.0	0.70	0	3.0	---	---
5.9:4.1	2.0	0.59	0.40	3.0	5.38	3.70
5.9:4.1	2.0	0.59	0.30	3.0	4.16	2.86
5.9:4.1	2.0	0.59	0.24	3.0	3.39	2.33
5.9:4.1	2.0	0.80	0.24	3.0	3.14	2.15
5.9:4.1	2.0	1.00	0.24	3.0	2.93	2.01
5.9:4.1	2.0	0.59	0.14	3.0	2.04	1.40
5.9:4.1	2.0	0.59	0.10	3.0	1.48	1.01
5.9:4.1	2.0	0.59	0.07	3.0	1.04	0.72
5.9:4.1	2.0	0.59	0.04	3.0	0.60	0.41
0:10	2.0	1.80	0	3.0	---	---

Figure 3.27. SEM images of (a-c) 6:4 plates, which were purified 1 time by IPA.

Figure 3.28. The isolated 6:4 plates were preserved in IPA solution for 2 h. SEM images of (a-c).

Figure 3.29. The isolated 6:4 plates were exposed to air for 2 h. SEM images of (a-c).

Figure 3.30. The 6:4 plates were purified 3 times by IPA. SEM images of (a-c).

Figure 3.31. The isolated 6:4 plates were dispersed in an IPA solution with 3.39% CCl_4 for 2 h. SEM images of (a-c).

Figure 3.32. The isolated 6:4 plates were immersed in an IPA solution with 2.33% *m*-xylene for 2 h. SEM images of (a-c).

Figure 3.33. Crystal transformation in an IPA solution with 5.38%/2.33% (CCl₄/*m*-xylene) solvent ratio. SEM images of (a-c).

Figure 3.34. Crystal transformation in an IPA solution with 5.38%/2.33% (CCl_4/m -xylene) solvent ratio. SEM images of (a-c).

Figure 3.35. The intermediate at $t = 1$ min with 3.39%/2.33% ratio. SEM images of (a-c).

Figure 3.36. The XRD of (i) $C_{60} \cdot 2C_6H_3Cl_3$ microplates and (ii) $C_{60} \cdot 2C_6H_3Cl_3$ microplates by heating 120°C for 6h.

Reference

1. Nicol, A.; Kwok, R. T.; Chen, C.; Zhao, W.; Chen, M.; Qu, J.; Tang, B. Z. *J. Am. Chem. Soc.* **2017**, *139* (41), 14792-14799.
2. Fateminia, S. A.; Wang, Z.; Goh, C. C.; Manghnani, P. N.; Wu, W.; Mao, D.; Ng, L. G.; Zhao, Z.; Tang, B. Z.; Liu, B. *Adv. Mater.* **2017**, *29* (1), 1604100.
3. Fateminia, S. A.; Mao, Z.; Xu, S.; Yang, Z.; Chi, Z.; Liu, B. *Angew. Chem. Int. Edit.* **2017**, *56* (40), 12160-12164.
4. Zhang, C.; Wang, X.; Huang, H. *J. Am. Chem. Soc.* **2008**, *130* (26), 8359-8365.
5. Ma, Y.; Zhang, A.; Xue, X.; Jiang, D.; Zhu, Y.; Zhang, C. *Cryst. Growth Des.* **2014**, *14* (11), 6101-6114.
6. Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16* (23), 4556-4573.
7. Zhang, H.; Jiang, L.; Zhen, Y.; Zhang, J.; Han, G.; Zhang, X.; Fu, X.; Yi, Y.; Xu, W.; Dong, H. *Adv. Electron. Mater.* **2016**, *2* (6), 1500423.
8. Fritz, S. E.; Mohapatra, S.; Holmes, B. T.; Anderson, A. M.; Prendergast, C. F.; Frisbie, C. D.; Ward, M. D.; Toney, M. F. *Chem. Mater.* **2007**, *19* (6), 1355-1361.
9. Zhang, J.; Xu, W.; Sheng, P.; Zhao, G.; Zhu, D. *Acc. Chem. Res.* **2017**, *50* (7), 1654-1662.
10. Li, D.; Zhang, H.; Wang, Y. *Chem. Soc. Rev.* **2013**, *42* (21), 8416-8433.
11. Jiang, H.; Kloc, C. *MRS Bull.* **2013**, *38* (1), 28-33.
12. Hong, Y.; Lam, J. W.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40* (11), 5361-5388.
13. Wang, C.; Dong, H.; Jiang, L.; Hu, W. *Chem. Soc. Rev.* **2018**, *47* (2), 422-500.
14. Shtukenberg, A. G.; Ward, M. D.; Kahr, B. *Chem. Rev.* **2017**, *117* (24), 14042-14090.
15. Briseno, A. L.; Mannsfeld, S. C.; Ling, M. M.; Liu, S.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. *Nature* **2006**, *444* (7121), 913.

16. Reese, C.; Bao, Z. *Mater. Today* **2007**, *10* (3), 20-27.
17. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. *Angew. Chem. Int. Edit.* **2009**, *48* (1), 60-103.
18. Wang, Y.; He, J.; Liu, C.; Chong, W. H.; Chen, H. *Angew. Chem. Int. Edit.* **2015**, *54* (7), 2022-2051.
19. Feng, Y.; Wang, Y.; He, J.; Song, X.; Tay, Y. Y.; Hng, H. H.; Ling, X. Y.; Chen, H. *J. Am. Chem. Soc.* **2015**, *137* (24), 7624-7627.
20. Tan, R. L. S.; Chong, W. H.; Feng, Y.; Song, X.; Tham, C. L.; Wei, J.; Lin, M.; Chen, H. *J. Am. Chem. Soc.* **2016**, *138* (34), 10770-10773.
21. Sun, Z.; Liao, T.; Kou, L. *Sci. China Mater.* **2017**, *60* (1), 1-24.
22. Zheng, M.; Xiao, X.; Li, L.; Gu, P.; Dai, X.; Tang, H.; Hu, Q.; Xue, H.; Pang, H. *Sci. China Mater.* **2018**, *61* (2), 185-209.
23. Feng, Y.; Wang, Y.; Song, X.; Xing, S.; Chen, H. *Chem. Sci.* **2017**, *8* (1), 430-436.
24. Wiley, B.; Sun, Y.; Xia, Y. *Acc. Chem. Res.* **2007**, *40* (10), 1067-1076.
25. Wang, Y.; Wang, Q.; Sun, H.; Zhang, W.; Chen, G.; Wang, Y.; Shen, X.; Han, Y.; Lu, X.; Chen, H. *J. Am. Chem. Soc.* **2011**, *133* (50), 20060-20063.
26. Cheng, H.; Yang, N.; Lu, Q.; Zhang, Z.; Zhang, H. *Adv. Mater.* **2018**, *30* (26), 1707189.
27. Lei, Y.; Wang, S.; Lai, Z.; Yao, X.; Zhao, Y.; Zhang, H.; Chen, H. *Nanoscale* **2019**, *11* (18), 8692-8698.
28. Shrestha, L. K.; Yamauchi, Y.; Hill, J. P.; Miyazawa, K. i.; Ariga, K. *J. Am. Chem. Soc.* **2012**, *135* (2), 586-589.
29. Ji, H.-X.; Hu, J.-S.; Tang, Q.-X.; Song, W.-G.; Wang, C.-R.; Hu, W.-P.; Wan, L.-J.; Lee, S.-T. *J. Phys. Chem. C* **2007**, *111* (28), 10498-10502.
30. Sathish, M.; Miyazawa, K. i. *J. Am. Chem. Soc.* **2007**, *129* (45), 13816-13817.
31. Shrestha, L. K.; Shrestha, R. G.; Yamauchi, Y.; Hill, J. P.; Nishimura, T.; Miyazawa,

- K. i.; Kawai, T.; Okada, S.; Wakabayashi, K.; Ariga, K. *Angew. Chem. Int. Edit.* **2015**, *54* (3), 951-955.
32. Shrestha, L. K.; Yamauchi, Y.; Hill, J. P.; Miyazawa, K. i.; Ariga, K. *J. Am. Chem. Soc.* **2013**, *135* (2), 586-589.
 33. Wang, Y.; Zhang, G.; Zhang, W.; Wang, X.; Wu, Y.; Liang, T.; Hao, X.; Fu, H.; Zhao, Y.; Zhang, D. *Small* **2016**, *12* (47), 6554-6561.
 34. Stahly, G. P. *Cryst. Growth Des.* **2009**, *9* (10), 4212-4229.
 35. Couderc, G.; Hertzsch, T.; Behrnd, N.-R.; Krämer, K.; Hulliger, J. *Micropor. Mesopor. Mat.* **2006**, *88* (1-3), 170-175.
 36. Dawson, C.; Horton, P. N.; Hursthouse, M. B.; James, S. L. *CrystEngComm* **2010**, *12* (4), 1048-1050.
 37. Hasell, T.; Culshaw, J. L.; Chong, S. Y.; Schmidtman, M.; Little, M. A.; Jelfs, K. E.; Pyzer-Knapp, E. O.; Shepherd, H.; Adams, D. J.; Day, G. M. *J. Am. Chem. Soc.* **2014**, *136* (4), 1438-1448.
 38. Birkefeld, A.; Schulin, R.; Nowack, B. *Geochim. Cosmochim. Acta* **2006**, *70* (11), 2726-2736.
 39. Bertrand, G.; Comperat, M.; Lallemant, M.; Wattle, G. *J. Solid State Chem.* **1980**, *32* (1), 57-66.
 40. Favergeon, L.; Pijolat, M.; Valdivieso, F.; Helbert, C. *Phys. Chem. Chem. Phys.* **2005**, *7* (21), 3723-3727.
 41. Wang, L.; Liu, B.; Yu, S.; Yao, M.; Liu, D.; Hou, Y.; Cui, T.; Zou, G.; Sundqvist, B.; You, H. *Chem. Mater.* **2006**, *18* (17), 4190-4194.
 42. Ramm, M.; Luger, P.; Zobel, D.; Duczek, W.; Boeyens, C. A. *Cryst. Res. Technol.* **1996**, *31*(1) 43-53.
 43. Céolin, R.; Agafonov, V.; André, D.; Dworkin, A.; Szwarc, H.; Dugué, J.; Keita, B.;

- Nadjo, L.; Fabre, C.; Rassat, A. *Chem. Phys. Lett.* **1993**, *208* (3-4) 259-262.
44. Kim, J.; Park, C.; Park, J. E.; Chu, K.; Choi, H. C. *ACS Nano* **2013**, *7* (10), 9122-9128.
 45. Sathish, M.; Miyazawa, K. i.; Hill, J. P.; Ariga, K. *J. Am. Chem. Soc.* **2009**, *131* (18), 6372-6373.
 46. Geng, J.; Zhou, W.; Skelton, P.; Yue, W.; Kinloch, I. A.; Windle, A. H.; Johnson, B. *J. Am. Chem. Soc.* **2008**, *130* (8), 2527-2534.
 47. Jin, Y.; Curry, R. J.; Sloan, J.; Hatton, R. A.; Chong, L. C.; Blanchard, N.; Stolojan, V.; Kroto, H. W.; Silva, S. R. P. *J. Mater. Chem.* **2006**, *16* (37), 3715-3720.
 48. Rana, M.; Bharathanatha, R.; Gautam, U. K. *Carbon* **2014**, *74*, 44-53.
 49. Céolin, R.; Agafonov, V.; André, D.; Dworkin, A.; Szwarc, H.; Dugué, J.; Keita, B.; Nadjo, L.; Fabre, C.; Rassat, A. *Chem. Phys. Lett.* **1993**, *208* (3-4), 259-262.
 50. Wang, H.; Zhang, Z.; Wong, L. M.; Wang, S.; Wei, Z.; Li, G. P.; Xing, G.; Guo, D.; Wang, D.; Wu, T. *ACS Nano* **2010**, *4* (5), 2901-2909.
 51. Shrestha, L. K.; Sathish, M.; Hill, J. P.; Miyazawa, K. i.; Tsuruoka, T.; Sanchez-Ballester, N. M.; Honma, I.; Ji, Q.; Ariga, K. *J. Mater. Chem. C* **2013**, *1* (6), 1174-1181.
 52. Wakahara, T.; Sathish, M.; Miyazawa, K. i.; Hu, C.; Tateyama, Y.; Nemoto, Y.; Sasaki, T.; Ito, O. *J. Am. Chem. Soc.* **2009**, *131* (29), 9940-9944.
 53. Park, C.; Yoon, E.; Kawano, M.; Joo, T.; Choi, H. C. *Angew. Chem. Int. Edit.* **2010**, *49* (50), 9670-9675.
 54. Liu, D.; Yao, M.; Wang, L.; Li, Q.; Cui, W.; Liu, B.; Liu, R.; Zou, B.; Cui, T.; Liu, B.; Liu, J.; Sundqvist B.; Wågberg, T.; *J. Phys. Chem. C* **2011**, *115* (18), 8918-8922.

Chapter 4. Solvent exchange induced crystal transformation of AIE crystals accompanied by tuning emission

The aggregation-induced emission (AIE) concept became the focus of attention since its debuts. Widespread applications, including the cancer theranostics, bioimaging, organic light-emitting diode (OLED), were explored based on AIE phenomenon. However, many researches focus on the new AIE molecules design and the potential application, the preparation of AIE crystal morphologies has seldom been studied. Therefore, the synthetic methods for controlling the size and shape of AIE crystal was still in preliminary stage. We have developed a new synthetic handle for preparing complex micro- or nano- molecular crystal structure by solvent exchange. Further development to new areas (e.g. organic crystal) is urgently needed. AIE crystal is a good candidate for studying the solvent effect on its morphology and luminescence due to its good luminescent properties and solvent sensitivity.

In this work, we have prepared a series of tetrakis(4-bromophenyl)ethylene (TPE-4Br) crystal shapes (plates, prism-like structures or wires) and studies the luminescence of crystals by tuning solvent molecules. Furthermore, the *p*-xylene-rich TPE-4Br plate can undergo crystal transformation to microrod arrays by solvent exchange. The crystal transformation was accompanied by the luminescence changes. The good lattice matching between the *orthorhombic* TPE-4Br plate and *monoclinic* TPE-4Br rods leads to epitaxial growth on the plates. The present work provides a promising platform for designing complex organic crystals and tuning the emission, which is promising to develop many organic photoelectric applications.

4.1. Introduction

4.1.1. The advantage of aggregation-induced emission (AIE)

The luminescence of organic molecules has attracted great interests over the past decades.¹⁻⁸ Many luminophores shown strong photoluminescence in dilute solution. However, since Förster and Kasper found that the fluorescence of pyrene weakens with increasing concentration, the phenomena were commonly discovered in many aromatic molecules.¹⁻⁴ As shown in Figure 4.1a, the fluorescence photograph of perylene in THF solution shown intense emission.⁹ With increased in the fraction of water (f_w), the luminescence became weaken. The luminescence was quenched at the $f_w = 80\%$. These molecules commonly had planer structures, which were similar to the discs (Figure 4.2a). When the planar molecules aggregated, the well stack between the molecules led to emission quenching. The reason was that the collisional interactions in the excited states and ground states among the promote the formation of excimers and exciplexes.¹ Thus, the strong $\pi-\pi$ interaction between the cores of aromatic molecules formed the quenching effect.^{10, 11} Due to the luminescence is often quenched at high concentrations or aggregation, this phenomenon widely referred as “aggregation-caused quenching” (ACQ). In the condition of aggregation or crystallization, the ACQ effect is unfavorable for luminous emission and optical applications.

Figure 4.1. (a) Fluorescence images of perylene (20 μM) in THF/water mixtures with different fractions of water (f_w), which shows ACQ effect. (b) Fluorescence images of hexaphenylsilole (HPS; 20 μM) at different f_w . The HPS exhibit typical AIE effects. Reprinted from ref 9, with permission. Copyright © 2015 American Chemical Society.

To reduce the ACQ effect, a series of strategies have been proposed to address this issue,¹²⁻¹⁴ such as the formation of J-aggregates by tuning the molecular stacking,¹³ controlling of triplet,¹² and introducing long chain to prevent π - π interaction.¹⁴

Figure 4.2. (a) The schematic diagram of planar luminogens during aggregation. A typical example is pyrene molecules, which the aggregation is resemble the piling up process of discs. The strong π - π stacking interactions between the planar molecules leads to the light emission turn “off”. (b) The schematic diagram exhibits the aggregation of nonplanar propeller-shaped luminogens. The hexaphenylsilole (HPS) molecules shows opposite behave that the restricted intramolecular rotation turned “on” light emissions during aggregation. Reprinted from ref 5, with permission. Copyright © 2009 The Royal Society of Chemistry.

However, the emergence of AIE materials has solved this problem very well.⁵⁻⁸ Contrary to the ACQ, the AIE molecules has weak luminescence in solution and emit efficiently in aggregate formation. A typical example is hexaphenylsilole (HPS) molecules, the diluted solution of HPS has no emission. When the f_w reach to 80%, the turbid liquid of HPS exhibit strong luminescence (Figure 4.1b).

The main theory emission mechanism for AIE phenomenon, which includes three aspects, the restriction of intramolecular rotations (RIR), the restriction of intramolecular vibrations

(RIV), and the restriction of intramolecular motions (RIM).⁹ For the HPS molecules emission in HHF/water solution, the most recognized explanation is the restriction of intermolecular rotation (RIR) (Figure 4.2b). The hexaphenylsilole (HPS) molecules are isolated in dilute solution and the phenyl rings rotate freely along the single bond against the ethene center. Thus, the rotation of phenyl rings provides active intermolecular motion that consume absorbed energy, leading the excited states to the ground state with non-radiatively decay. But the intramolecular rotations are restricted due to close packing of molecules in aggregate state, which blocks the radiationless relaxation channel and opens the radiative decay pathway.

Thus, the strong luminescence in aggregated or solid state makes AIE molecules have good application prospects.

4.1.2. Application of AIE molecules

Recently, many research groups focused on design new AIE molecules, explored their applications in various fields.¹⁵⁻²¹ The main applications of AIE molecules fall into several categories, such as the cancer theranostics,^{15, 16} bioimaging,^{17, 18} organic solar cells,¹⁹ organic light-emitting diode (OLED),²⁰⁻²² and contaminant detection.²³

The most prevalent applications of AIE are cancer imaging and theranostics. Hu *et al.* developed an AIE-mito-TPP probe, which was targeted to mitochondria and light-up by aggregating in the mitochondria.¹⁵ Moreover, the probe has the selective anticancer activity. In order to prepare the AIE-mito-TPP probe, the synthetic procedure was shown in the Figure 4.4a. The compound 2 was formed by the reaction of 2,4-dihydroxybenzaldehyde and 1,6-dibromohexane, then the compound 2 further reacted with hydrazine hydrate to generate the AIE-Br molecules. Finally, the AIE-Br combined with TPP to give the AIE-mito-TPP probe. Due to AIE-mito-TPP has positive charge, thus the AIE-mito-TPP favor to aggregate on the surface of mitochondria, which have negative charge. When the rotation of the N-N bond in

the AIE-mito-TPP was restricted during aggregation and the intramolecular hydrogen bonds formed, hence the luminescence of probe turned on with red fluorescence.

Figure 4.3. (a) The synthetic process of AIE-mito-TPP. (b) The schematic diagram shown the therapeutic process of AIE-mito-TPP treating cancer in cells. Confocal microscopy images of different cells. (c, d) The HeLa cells were incubated with AIE-mito-TPP probe. (e, f) The normal cells (NIH-3T3) were incubated with AIE-mito-TPP. The cells were co-stained with (c, e) MitoTracker or (d, f) LysoTracker. Scale bar for all images are 20 μm . Reprinted from ref 15, with permission. Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Because the main component of cancer molecule (such as HeLa) is mitochondria, the AIE-mito-TPP probe molecule can effectively aggregate in HeLa cells. The Figure 4.3c-f shown that the emission of AIE-mito-TPP probe had overlap with MitoTracker emission. Thus, compared with NIH-3T3 cells, the AIE-mito-TPP had good binding ability with the mitochondria of HeLa. The cell viability demonstrated that the AIE-Br molecules had low cell toxicity to HeLa and NIH-3T3 cells. However, the AIE-mito-TPP probe shown high cytotoxicity to HeLa (Figure 4.4). With probe binding to mitochondria, the level of intracellular

reactive oxygen species (ROS) increased, resulting in the mitochondria dysfunction. Thus, the dysfunction of mitochondria inhibited ATP production and led to cells death.

Figure 4.4. (a) The cell viabilities of HeLa cells by incubation with AIE-Br (white bars) and AIE-mito-TPP (shaded bars) for 24 hours, respectively. (b) The cell viabilities of NIH-3T3. (c-h) Confocal microscopy images of the death process of HeLa cell when combined with AIE-mito-TPP for 1 h. Reprinted from ref 15, with permission. Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The AIE materials also have good photoelectrical properties. Liu *et al.* reported that the a tetraphenylethylene core based AIE molecule could serve as acceptor to fabricate organic solar

cells.¹⁹ The TPE-PDI₄ molecule was synthesized by mixing the PDI-Br, TPE-Bpin₄ (formation under the reaction of tetrakis(4-bromophenyl)ethene (TPE-4Br) with bis(pinacolato)diboron and Pd(PPh₃)₄ in water/THF solution under 80 °C for 48 h. The TPE-PDI₄ shows the typical AIE structural characteristics which has propeller-shaped structure (Figure 4.5a). In comparison with the dimer BP-PDI₂ molecule with a 2D structure (Figure 4.5b), the 3D TPE-PDI₄ has a charge-transport network that provide the good electron-transport ability. Thus, when the two donor molecules were used to combine with acceptor of PBDTT-F-TT to fabricate solar cells, the TPE-PDI₄: PBDTT-F-TT cells exhibited higher power-conversion efficiency (PCE) of 5.53% and lower V_{OC} of 0.91 V (Figure 4.5 d-e). But the V_{OC} was still significantly higher than the previous results of PBDTT-F-TT: PCBM cells.²⁴

Figure 4.5. (a-b) Chemical structures of TPE-PDI₄ and BP-PDI₂. (c) Chemical structure of PBDTT-F-TT polymer, which act as the donor. (d) J - V curves of different solar cells under AM 1.5G irradiation at 100 mW cm⁻²; and (e) External quantum efficiency against the wavelength of the two devices. Reprinted from ref 19, with permission. Copyright © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The high fluorescence quantum yields facilitate the AIE materials for OLED applications.

Recently, Qin *et al.* reported a non-doped OLEDs by using the red emissive AIE luminogens. The AIE molecules of TPE-TPA-BTD (TTB) was synthesized by the combination building blocks of tetraphenylethene (TPE) and arylamines (Figure 4.6a). Thus, the TPE unit provided the non-planar conformations for the TTB, which shown fluorescence quantum yields with 48.8% in the solid state. A typical configuration of OLEDs device was ITO/NPB (80 nm)/TTB (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm). Whereas, the NPB was applied to the hole-transporting layer (HTL), TTB was used to the emitting layer (EML), the TPBi acted as electron-transporting and hole-blocking material, and LiF was employed to enhance electron injection. However, the TTB has hole-transporting arylamino moieties. Therefore, the TTB can be used not only as an HTL but also as an EML. Compared with the OLEDs device (NPB serves as HTL), the non-doped OLEDs exhibited good electroluminescent (EL) and external quantum efficiencies (3.2%), which were very closed to the NPB-doped device (Figure b-e).

Figure 4.6. The chemical structure of TPE-TPA-BTD (TTB). (b) The EL spectra of TTB. (c) Current density-voltage-luminance characteristics of TTB devices. (d) Current efficiency against the current density. (e) External quantum efficiencies characteristics of the OLED devices. Device configuration: ITO/(NPB)/TTB/TPBi/LiF/Al. Reprinted from ref 25, with permission. Copyright © 2015 The Royal Society of Chemistry.

Many AIEgens have been prepared by using the HPS unit.^{26, 27} However, the Tetraphenylethene (TPE)^{7,28} is also a well-known AIE luminogen, which act as building block

to synthesize complex luminophores and regulate the luminescence.²⁹ Thus, a series of TPE based metal-organic frameworks (MOFs)³⁰⁻³² and conjugated microporous polymers (CMPs)^{33, 34} were prepared for retaining high luminescence efficiency and fluorescent sensor applications.

4.1.3. Lack of synthetic method for morphologies control of AIE crystals

Despite the rapid development of AIE system, a great number of studies focus on changes of fluorescence in solutions/suspensions mixture during aggregation. Few people pay attention to the shape and morphology of the AIE crystals, only the plates, wire and nanoparticles were reported.^{35-37, 38} The structure formation can only depend on the intrinsic facets, but no ligands for shape control. Thus, the synthetic control remains at a primitive level, which need new synthetic method for extend crystal morphologies.

4.1.4. The effect of solvent on the luminescence of AIE crystals

It was found that the organic crystal structures³⁹ and their florescence properties^{39, 40} could be tuned by the solvent molecules. In crystallization, the solvent molecules will embed into the interstitial void or exchange the host molecules, leading the change of unit-cell parameters and facets.⁴¹

4.1.5 Solvent exchange for regulating AIE crystals.

In previous chapters, we proposed solvent exchange as a new handle for regulating molecular crystals. By effectively controlling the removal and inclusion of solvent molecules in C₆₀ crystals and hence, the hexagonal mesh networks are obtained via crystal transformation of C₆₀ microplates.⁴² Based on systematically studying the solvent environment and understanding the roles of solvents during the crystal transformation, we found that the synthetic method has generality. Not the C₆₀ plates but also C₇₀ cubes can undergo transformation to complex

nanostructures. As a good candidate, AIE crystal has a large space to regulate solvent molecules and fluorescent properties. Thus, we spare no effort to develop new AIE morphology by using the solvent exchange method.

Figure 4.7. (a) Schematics illustrating the transformation of TPE-4Br plate to nanorod arrays. SEM image of (b) TPE-4Br plate and (c) TPE-4Br nanorod arrays.

Here, different shapes of TPE-4Br crystals (plates, prism-like structures or wires) have been prepared by tuning the embedding solvent molecules. Based on the understanding of the effect of solvent on the morphologies of TPE-4Br crystals. We put forward a method for preparing complex structures, i.e. the plate-like structures are combined with an IPA solution toluene or acetone molecules which can be converted plates into rods. Thus, we demonstrated that the TPE-4Br crystals microrod arrays underwent crystal transformation from *p*-xylene-rich TPE-4Br plates by the solvent exchange (Figure 4.7). The epitaxial growth of ordered nanorod arrays caused by the small lattice match between the (001) facet of *orthorhombic* plate and the (100) facet of *monoclinic* rods. In addition, the structural transformation was accompanied by the emission changes.

Rational transformation of organic crystals would open a new synthetic route for designing

complex micro- or nano- organic crystals and changing the luminous properties.

4.2. Material and methods

4.2.1. Materials

Tetrakis(4-bromophenyl)ethylene (TPE-4Br) (>97.0%(GC)), 3-methylpyridine, and tert butyl alcohol (TBA) were purchased from Tokyo Chemical Industry (TCI). Dioxane, *p*-xylene, acetone and toluene were purchased from Sigma-Aldrich, CCl₄ (A.R.) was purchased from Beijing Chemical Agent Ltd., China. Isopropanol (IPA, A.R.) were purchased from J.T.Baker® brand. All the chemicals are used without further treatment.

4.2.2. Methods

Synthesis of TPE-4Br plates. The TPE-4Br crystals were prepared by using LLIP method. In a typical synthesis of *p*-xylene-rich or 3-methylpyridine-rich plates, 50 mg TPE-4Br powder was dissolve in 3 mL *p*-xylene or 3-methylpyridine by sonication. 0.5 mL IPA was slowly injected into the stock solution of TPE-4Br in *p*-xylene or 3-methylpyridine (16.7 mg/mL, 0.5 mL), which formed an interface between the stock solution and the IPA. Then, the vial was kept undisturbed for 5 min. Next, the two solvents were mixed together by sonication for 30 s. Afterwards, mixture was stored in an incubator at 25 °C for 12 h. Finally, the colorless plates were formed at the bottom of vial (as shown in Figure 4.8 a, b).

Synthesis of TPE-4Br prism-like structures. Preparation of dioxane-rich prisms. 1.5 mL IPA was slowly injected into a stock solution of TPE-4Br in dioxane (14 mg/mL, 0.5 mL). The same procedure as above. Then the prism-like structures were formed at the dioxane/IPA interface.

Synthesis of TPE-4Br wires. In a typical experiment for synthesis of CCl₄ wires, 1.5 mL IPA was slowly injected into a stock solution of TPE-4Br in CCl₄ (40 mg/mL, 0.5 mL). The

same procedure as above. Then the rods were formed at the dioxane/IPA interface. In synthesis of toluene-rich rods, 1.0 mL IPA was slowly injected into a stock solution of TPE-4Br in toluene (30 mg/mL, 0.5 mL). The same procedure as above. Then the rods were formed at the bottom of vial. In synthesis of acetone wires and ribbons, 1.0 mL IPA was slowly injected into a stock solution of TPE-4Br in acetone (10 mg/mL, 0.5 mL). The same procedure as above. Then the ribbons and wires were formed at the bottom of vial. (Figure 4.8).

Synthesis of TPE-4Br microrod arrays. The TPE-4Br plates were formed in *p*-xylene/IPA mixture as mentioned above. Typically, 0.5 mL IPA was slowly injected into a stock solution of TPE-4Br in *p*-xylene (16.7 mg/mL, 0.5 mL) to form an interface. The mixture was kept at 25 °C for 5 min without mechanical agitation. Then the mixture was treated by sonication for 5 s with shaking, and stored in the incubator at 25 °C for 12 h. And then, the isolated TPE-4Br plates were incubated in IPA-toluene mixture (V/V = 2:1), and the mixtures were allowed to stand for 10 min.

Synthesis of TPE-4Br plate dependent ribbons. The TPE-4Br plates were formed in *p*-xylene/IPA mixture as mentioned above. And then, the isolated TPE-4Br plates were incubated in IPA-acetone mixture (V/V = 1:1 or 2:1), and the mixtures were allowed to stand for 10 min.

4.2.3. Characterization.

The morphologies and sizes of the samples were examined using field-emission scanning electron microscopy (FESEM, JEOL 7600F) at an acceleration voltage of 5 kV. Prior to analysis, the samples were coated with a thin gold layer using an Edwards Sputter Coater. TEM images were obtained using a JEOL JEM-2100 electron microscope at an accelerating voltage of 200 kV. One drop of the as-prepared colloidal dispersion was deposited on a carbon-coated copper grid, and dried under high vacuum. The X-ray diffraction (XRD) patterns were measured by Bruker D8 Advance Powder with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). We operated in the 2θ range from 5 to 40° , by using the samples spin-coated on the surface of a quartz substrate. The single crystal XRD parameter of TPE-4Br/toluene nanorod was obtained by Bruker Kappa CCD Diffractometer. The single crystal images with growth directions were obtained by Bruker Smart APEXII SC-XRD. Thermogravimetric analysis (TGA) curve was obtained using a TGA Q500 thermogravimetry analyzer. The optical images were obtained Olympus BX51 optical microscope, and the fluorescent images were measured by using the Olympus BX51 optical microscope with 350 nm UV radiation. The Raman studies were measured under ambient conditions by using 488 nm excitation with integration time of 10 s. IR spectra were taken on a FTIR Perkin Elmer Frontier. For the UV-vis absorption spectra, the sample were dropped on a quartz wafer and tested by UV-vis-NIR Lambda 950.

4.3. Results and Discussion

4.3.1. Morphology of TPE-4Br crystals depend on the solvents

Tetrakis(4-bromophenyl)ethylene, abbreviated as TPE-4Br or TBTPE, was widely used as an intermediate to synthesize complex AIE molecules.^{33, 43} It was reported that the TPE-4Br could form inclusion crystals with different solvent molecules.⁴⁴ But they didn't provide the crystal morphologies. In this work, we first prepare TPE-4Br crystals in different systems by using the classical LLIP method.⁴⁵ In a typical experiment, TPE-4Br was dissolved in good solvent to give a near saturated solution in vial. Then, the IPA was slowly added into the solution to form an interface between stock solution and IPA. The vial was kept for a few minutes without mechanical agitation. After that the mixture was sonicated. Finally, the mixture was incubated for nucleation and growth. The TPE-4Br plates formed at IPA and 3-methylpyridine or *p*-xylene interface (Figure 4.8a, b). When the TPE-4Br grown in IPA-dioxane mixture, the prism-like crystals were obtained (Figure 4.8d). However, the TPE-4Br favors to crystallize wires at toluene or CCl₄ systems. (Figure 1c, f). If the TPE-4Br molecules aggregated between acetone and IPA solution, both of ribbons and wires formed during crystallization (Figure 4.8e). This dependence of TPE-4Br crystal morphologies on the solvent indicated the effects of the embedded solvents.

Figure 4.8. TPE-4Br crystals formed at interfaces between different solvent molecules and IPA solutions. (a) The TPE-4Br/3-methylpyridine plates. (b) The TPE-4Br/*p*-xylene plates. (c) The TPE-4Br/toluene wires. (d) The TPE-4Br/dioxane prism-like crystals. (e) The TPE-4Br/Acetone wires and ribbons. (f) The TPE-4Br/ CCl_4 wires.

4.3.2. Identification the crystals and solvents by XRD and TGA

The TGA demonstrated that all of the TPE-4Br crystals were incorporated solvent molecules (Figure 4.9). The TPE-4Br/3-methylpyridine plates contained 17.26% (*w/w*) 3-methylpyridine, which the molar ratio of TPE-4Br: 3-methylpyridine was about 3:2 (Figure 4.9a). TPE-4Br/*p*-xylene plates had 13.54% *p*-xylene (Figure 4.9b), and the molar ratio of TPE-4Br/*p*-xylene was same to the 1:1 TPE-4Br inclusion crystal recrystallized in *p*-xylene solution.⁴⁴ It indicated that the TPE-4Br plates contained rich solvents. In comparison with the plates, the TPE-4Br wires had small amount of solvents incorporation (2.33% for toluene rod and 0.2% for CCl_4 rods), as shown in Figure c, f. Whereas the TPE-4Br/*p*-xylene ratio was about 1:6. The TPE-4Br/dioxane prism-like structures contained 7.54% dioxane ($n_{\text{TPE-4Br}}: n_{\text{dioxane}} = 2:3$). It is worth noting that the weight loss curve decreases sharply at 162.8, 209.1, and 313.6 °C, corresponding to derivate weight change. Based on the TGA data of TPE-4Br (Figure 4.21 in

appendix), the 313.6 °C peak was contributed the TPE-4Br. Thus, the mass loss of the first two intervals belongs to solvent molecules, indicating that the acetone has two different embed modes, which conformed to two different morphologies (ribbons and wires). The TGA data and SEM images proved that the solvents were embedded in crystals and tuned the arrangement of host molecules.

The powder XRD patterns has been carried out to study the TPE crystals (Figure 4.22 in appendix). The XRD pattern of *p*-xylene-rich plates can be index to the primitive orthorhombic phase.⁴⁴ The crystal phase of acetone embed TPE-4Br crystals can be well-indexed to the orthorhombic system.⁴⁴ In addition, the XRD demonstrated that the rods formed at toluene/IPA interface has primitive monoclinic phase. Whereas, the XRD pattern of CCl₄ wires is similar to the toluene wires, which belong to monoclinic crystal system. The XRD patterns of TPE-4Br crystals formed in 3-methylpyridine and dioxane systems shown in the Figure 4.22. But there are no relevant crystal data to match them, which the parameters and crystal system need to further test the single crystal XRD and analyze the data.

Figure 4.9. TGA of TPE-4Br crystals. (a) The TPE-4Br/3-methylpyridine plates. (b) The TPE-4Br/*p*-xylene plates. (c) The TPE-4Br/toluene wires. (d) The TPE-4Br/dioxane prism-like crystals. (e) The TPE-4Br/Acetone ribbons and wires. (f) The TPE-4Br/CCl₄ wires.

4.3.3. The stability of TPE-4Br crystals

These crystals have smooth surface under SEM characterization (Figure. 4.8, 4.10a, d). All of TPE-4Br crystals were stable in their mother liquor due to the equilibrium of the embedded solvent molecules in plates and the solvent molecules in solution. When the TPE-4Br/toluene wires were isolated and redispersed in IPA, the wires were still smooth (Figure 4.10e). The XRD shown that the wires after purification 1 time by IPA (600 μ L) were similar to the original TPE-4Br/toluene wires (Figure 4.23 in appendix). In addition, there was no structural change even the rods were exposed to air for 2 h (Figure 4.10f).

On the other hand, if the TPE-4Br plates leave the mother liquor (*p*-xylene/IPA), the plates have smooth surface (Figure 4.10a). However, when the plates were purified by IPA, the edge became bulged, and parts of plates were dissolved by IPA and recrystallized to allow out-of-plane growth, which formed additional structures on the side of plates (Figure 4.10b). The TGA shows that the plates contained 13.54% *p*-xylene (w/w, Figure 4.9b), which decreased to 12.85% after one round of purification (Figure 4.23 in Appendix). The plates were not stable when exposed to air condition for 2h, and the plates were collapsed and many pores appeared on the plates surface (Figure 4.10c). The stabilities of TPE-4Br crystals in air condition and IPA solution indicated that the wires are relative more stable than plates.

Figure 4. 10. The stability of TPE-4Br crystals. SEM images of (a) TPE-4Br/*p*-xylene plates, (b) the TPE-4Br plates were purified 1 time by IPA. (c) The plates were exposed to air for 2 h. (d) TPE-4Br/toluene wires. (e) The wires were purified 1 time by IPA. (f) The wires were exposed to air for 2 h.

In addition, the *p*-xylene-rich plates underwent severe crushed or even structural change in IPA solution than exposed to air. It indicated that entropy increases faster when solvent (*p*-xylene) molecules are mixed with to IPA solution than when they are in contact with air molecules because of much less in number. Thus, we believe that the desolvation is key factor of pore formation. Thus, the IPA molecules could facilitate the incorporation solvent molecules leave the organic crystals.

4.3.4. Strategy for crystal transformation

However, it is difficult to control the strian in air condition. The recrystallization of TPE-4Br in IPA solution provided a good case to effective tune the morphology by using solvent molecules. If we utilize another solvent molecules to directional induce recrystallization of solvate, the structural transformation will become controllable. It means that the crystal structure can be continuously controlled before collapse by desolvation. Here, the synthetic

handle of solvent exchange can be used to regulate the removal and incorporation of solvent molecules to reconstruct the crystal, leading to crystal transformation.

Therefore, the *p*-xylene-rich plates were served as sacrificial templates for further transformation. In the following step, an IPA solution with a certain amount acetone or toluene was used to transformative solution, which has the ability to recrystallize TPE-4Br plates to generate rods or wires. To reduce the dissolution rate of the TPE-4Br plates during crystal transformation, we introduced a saturated supernatant of TPE-4Br wires formed from the toluene/IPA or acetone/IPA mixture. In these two systems, the role of *p*-xylene was to protect the plates, and IPA accelerated the desolvation. The introduced toluene and acetone prevented degradation and promoted crystal transformation.

Figure 4.11. (a, c) The optical images of TPE-4Br microrod arrays. (b, d) The fluorescent images, corresponding to the optical images of (a, c), respectively. The luminescence was excited under 350 nm.

Therefore, the *p*-xylene-rich TPE-4Br plates were prepared as mentioned above (Figure 4.7b,

4.8b, 4.10a), whereas the length of plates is about 190 μm and the average width of plates is 156 μm (Figure 4.12 a-c). Then the plates were isolated and then immersed in IPA-acetone mixture ($V/V = 1:1$ or $2:1$). The dendritic ribbons scattered from the center were appeared on the plates after crystal transformation. But some ribbons or wires were random distributed on the plate surface (Figure 4.25, 4.26). However, the *p*-xylene-rich plates obtained in 1:1 IPA-*p*-xylene mixture could transform to microrod arrays when incubated in an IPA-toluene mixture ($V/V = 2:1$), as shown in Figure 4.7 c and 4.11. For the toluene wires, the average length and width is 144 μm and 6 μm , respectively. After crystal transformation, the length of newly formed rods on the plate is about 20 μm , and the width of the rods is 4 μm , which the size of rods on the plates is much lower than the pure toluene wires.

Figure 4.12. (a) Optical image of TPE-4Br/*p*-xylene plates. The statistics of the (b) length and (c) width of the plates in (a). (d) Optical image of TPE-4Br/toluene wires. The statistics of the (e) length and (f) width of the wires in (d). (g) Optical image of microrod arrays. The statistics of the (h) length and (i) width of the rods in (g).

width of the wires in (d). (g) SEM image of microrod arrays. The statistics of the (h) length and (i) width of the rods from the microrod arrays in (g).

4.3.5. Solvent exchange during crystal transformation

The TGA of *p*-xylene-rich plates contained a lot of *p*-xylene (13.54%) around 91°C (Figure 4.9b). After transformation, the TGA of microrod arrays shown that the weight loss was 1.45% at about 190°C (Figure 4.13), which was approximate the toluene loss in TPE-4Br/toluene wires (Figure 4.9c, 2.33% solvent loss). Thus, the *p*-xylene is lost as toluene is included during the crystal transformation.

Figure 4.13. TGA of TPE-4Br microrod arrays after crystal transformation.

4.3.6. Temporal evolution during crystal transformation

We captured the intermediates during crystal transformation, as shown in Figure 4.14. At 1 min, the plates generated many tetrahedral holes in the plates (Figure 4.14a). The holes are

inverse pyramids with tetrahedral cross-section. With the transformation going on, the rods extended in length, which were parallel with each (Figure 4.14b). Finally, the microrod arrays were formed. There are some irregular rods on the plates because the crystal transformation too fast (10 min).

Figure 4.14. SEM images of the crystal transformation from plate to microrod arrays. (a) $t = 1$; (b) 3; (c) 10 min.

4.3.7. Effect of solvent molecules on luminescence of TPE-4Br crystals

The phenomenon of crystal luminescence has been explored. In the ultraviolet-visible (UV-vis) absorption spectra (Figure 4.15a), all of the TPE-4Br crystals were tested in solid state, which have absorption between 365 nm and 379 nm. The absorption plates shift to lower wavelength range (< 370 nm), while the absorption of wires shift to lower energy with longer wavelengths.

Figure 4.15. (a) Absorption and (b) fluorescence spectra of TPE-4Br crystals.

Based on the absorption, a 350 nm UV lamp were employed to excite the TPE-4Br crystals. The fluorescence of TPE-4Br crystal all the crystals shown blue emission (Figure 4.16). However, the fluorescence spectra proved that the TPE-4Br crystals have different emission (Figure 4.15b). The fluorescence emission of plates still shifts to higher energy at lower wavelength and the emission of wires shift to higher wavelength, which correspond to the absorption of the TPE-4Br crystals.

Figure 4.16. Optical and fluorescent images of TPE-4Br crystals. The optical images of (a) the TPE-4Br/3-methylpyridine plates, (b) the TPE-4Br/*p*-xylene plates, (c) the TPE-4Br/toluene wires. The fluorescent images of (d-f) correspond to (a-c), respectively. The optical images of the (g) TPE-4Br/dioxane prism-like crystals, (e) the TPE-4Br/acetone and wires, and (f) the TPE-4Br/CCl₄ wires. The fluorescent images of (j-i) correspond to (g-i), respectively.

The crystal transformation was accompanied by the luminescence changes. The maximum fluorescence emission peak is 438 nm. But the maximum fluorescence emission peak shifted to 449 nm after crystal transformation (Figure 17). The main reason for the luminescence change may be caused by the difference of embedded solvent molecules in the TPE-4Br crystals. A possible explanation is that polar molecules lead to the absorption and emission red shifts.⁴⁶⁻⁴⁸ Thus, the maximum absorption peak and emission peak of toluene wires and the microrod arrays are stronger than those of the plates.

Based on the experiment, we found that the intensity of AIE crystals became weak during transformation or weathering (Figure 4.27 in appendix). The possible underlying reason is that the degree of aggregation affects the intensity. The AIE crystals show strong luminescence because the restriction of intramolecular motions in solid state. Thus, the more the aggregation, the higher luminescent intensity. However, when the structural change (desolvation or transformation), the degree of aggregation decrease, and thus diminish luminescence.

Figure 4.17. (a) Absorption and (b) fluorescence spectra of (i) TPE-4Br/*p*-xylene plates, (ii) TPE-

4Br/toluene wires, (iii) microrod arrays via crystal transformation, and TPE-4Br/*p*-xylene plates were immersed in IPA solution for 10 min.

4.3.8. Characterization by Raman and IR spectra

In the Raman spectra, the major peaks at 741, 834, 1012, 1071, 1128, 1180, 1317, 1585 and 3066 cm^{-1} are characteristic TPE-4Br band, which were observed in all samples (Figure 4.18). Whereas, the group 1 shown ring deformation modes, and group 3 was assigned C–H out-of-plane bending.⁴⁹ The peak at 1028 cm^{-1} can be assigned to the ring-breathing mode.⁵⁰ The band at 3066 cm^{-1} was origin form C–H stretching vibrational modes.⁴⁹

The IR spectra of toluene wires shown one strong peak at 523 cm^{-1} , which can be assigned x sensitive of toluene.^{51, 52} In the *p*-xylene-rich wires, the bands at 2919 cm^{-1} was originated from CH₃ asym. stretching vibrational modes of *p*-xylene.⁴⁹ After crystal transformation, the main peak of *p*-xylene disappeared and toluene peak (527 cm^{-1}) shown in the spectrum of the microrod arrays. Thus, the Raman spectra demonstrated that the crystal transformation.

Figure 4.18. Raman spectra of (I) TPE-4Br powder, (II) TPE-4Br/*p*-xylene plates, (III) TPE-4Br/toluene wires, and (IV) microrod arrays.

Besides the characteristic TPE-4Br bands at 736, 1008, 1071, 1393, 1483, 1582, 3025, 3047 and 3079 cm⁻¹ (Figure 4.19), the (Infrared) IR spectra of the TPE-4Br plates showed two peaks at 1513 and 2915 cm⁻¹, which can be ascribed to *p*-xylene (Figure 4.19III).⁵³ The 1513 cm⁻¹ was denoted strong ring-mode and the 2915 cm⁻¹ belong to C–H stretches of the alkyl. The 2927 cm⁻¹ in the IR spectrum of wires was assigned to the C–H stretches of the alkyl (Figure 4.19 II), which was consistent with the literature.⁵⁴

Figure 4.19. IR spectra of TPE-4Br crystals. (I) TPE-4Br powder, (II) TPE-4Br/toluene wires, (III) TPE-4Br/*p*-xylene plates, and (IV) microrod arrays.

4.3.9. The mechanism of crystal transformation

The XRD pattern shown that the *p*-xylene-rich plate had *primitive orthorhombic* system, which was similar to the previous report.⁴⁴ From the single XRD, the long axis of plate was [100] direction. The single crystal XRD has been carried out to measure the single toluene wire, which has *primitive monoclinic* phase, with unit cell parameters: $a = 20.38 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 23.85 \text{ \AA}$, and $\beta = 92.09^\circ$. The single crystal XRD also provided the information about the growth directions of the crystal facets (Figure 4.20 a, b). Thus, we found that the rod favor to grow along the growth direction of [010] and the lattice distance of d_{010} of the rod is $9.72 \text{ \AA}$. The other two sides of wire are (100) and (001) facets, the lattice distance of [100] and [001]

are 20.38 Å and 23.85 Å (Figure 4.20d). However, the surface of plate is (001) facet, which the lattice distance is 23.47 Å. The plate has two growth direction, the lateral and longitudinal directions. Whereas, the longitudinal growth direction of plate is [100] with the $d_{100} = 8.76$, and the lattice distance of lateral growth direction [010] is $d_{100} = 14.94$ (Figure 4.20c). Thus, the lattice matching (9.8% mismatch) between the [100] of *orthorhombic* plate and [010] of *monoclinic* rod leads to epitaxial growth of ordered microrod arrays on the plate. On the other hand, the the lattice mismatching rate between [100] direction of the rod and the [010] direction of plate is 26.69% (Figure 4.20). It is expected that such poor lattice matching would generate high strain, preventing conformal coating of one on the other. Thus, the high strain gives raise to island growth. The lattice matching between the (001) facet of the orthorhombic plate ($d_{001} = 23.47$ Å) and the (001) facet of the monoclinic rod ($d_{001} = 23.85$ Å) leads to rod stick to the plate and grow at the [010] direction of rod.

Figure 4.20. The optical images of (a) TPE-4Br/*p*-xylene plate and (b) TPE-4Br/toluene wire, which were captured during single crystal characterization. (c, d) The crystal lattice matching between plate and wire. (e, f) Schematic diagram of crystal transformation.

4.4. Conclusion

In this work, we have studied the dependence of crystal shapes (plates, prism-like structures or wires) and luminescence of crystals on the initial solvent. Based on the understanding solvent effect, we employed the solvent exchange method to synthesize complex TPE-4Br crystals. Thus, the *p*-xylene-rich TPE-4Br plate could transform to microrod arrays by the exchanging

of embedded solvent molecules (*p*-xylene) with toluene molecules. The crystal transformation was accompanied by the luminescence changes because of the polar solvent effect. The good lattice matching between the TPE-4Br plates and the emerging rods allows the epitaxial growth of TPE-4Br rods on the plates. Based on the understanding of solvent effect on morphologies and emission, we believe that our strategy will provide a new window for designing complex organic crystals and tuning the emission, which is promising to develop many organic photoelectric device applications.

4.5. Appendix

Figures

Figure 4.21. TGA of TPE-4Br powder.

Figure 4.22. XRD of powder and TPE-4Br crystals. (a) The TPE-4Br/3-methylpyridine plates. (b) The TPE-4Br/p-xylene plates. (c) The TPE-4Br/toluene wires. (d) The TPE-4Br/dioxane prism-like structures. (e) The TPE-4Br/acetone wires and ribbons. (f) The TPE-4Br/ CCl_4 wires.

Figure 4.23. XRD of TPE-4Br/toluene wires and the wires were purified 1 time by IPA.

Figure 4.24. TGA of TPE-4Br/p-xylene plates, which were purified one time by IPA.

Figure 4.25. The SEM images of dendritic ribbons were obtained when the plates incubated in an IPA-acetone mixture ($V/V = 1:1$). (c) The optical image of dendritic ribbons. (d) The fluorescent image was obtained under 350 nm ultraviolet radiation.

Figure 4.26. The SEM images of dendritic ribbons were obtained when the plates incubated in an IPA-acetone mixture ($V/V = 2:1$). (c) The optical image of dendritic ribbons. (d) The fluorescent image was obtained under 350 nm ultraviolet radiation.

Figure 4.27. (a) Fluorescence spectra of (i) TPE-4Br/*p*-xylene plates, (ii) microrod arrays. (b) Fluorescence spectra of (i) TPE-4Br/*p*-xylene plates, (ii) TPE-4Br/*p*-xylene plates were purified 1 time by IPA.

Reference

1. Birks, J. B., Photophysics of Aromatic Molecules. *Wiley, London* **1970**.
2. Menon, A.; Galvin, M.; Walz, K. A.; Rothberg, L. *Synthetic Met.* **2004**, *141* (1-2), 197-202.
3. Belletête, M.; Bouchard, J.; Leclerc, M.; Durocher, G. *Macromolecules* **2005**, *38* (3), 880-887.
4. Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107* (4), 1339-1386.
5. Hong, Y.; Lam, J. W.; Tang, B. Z. *Chem. Commun.* **2009**, (29), 4332-4353.
6. Hong, Y.; Lam, J. W.; Tang, B. Z. *Chem. Soc. Rev.* **2011**, *40* (11), 5361-5388.
7. Mei, J.; Hong, Y.; Lam, J. W.; Qin, A.; Tang, Y.; Tang, B. Z. *Adv. Mater.* **2014**, *26* (31), 5429-5479.
8. Feng, G.; Liu, B. *Acc. Chem. Res.* **2018**, *51* (6), 1404-1414.
9. Mei, J.; Leung, N. L.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. *Chem. Rev.* **2015**, *115* (21), 11718-11940.
10. Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265* (5173), 765-768.
11. Klymchenko, A. S. *Acc. Chem. Res.* **2017**, *50* (2), 366-375.
12. Sandanayaka, A. S.; Yoshida, K.; Inoue, M.; Qin, C.; Goushi, K.; Ribierre, J. C.; Matsushima, T.; Adachi, C. *Adv. Opt. Mater.* **2016**, *4* (6), 834-839.
13. Wang, C.; Li, Z. *Mater. Chem. Front.* **2017**, *1* (11), 2174-2194.
14. Ye, H.; Liu, G.; Liu, S.; Casanova, D.; Ye, X.; Tao, X.; Zhang, Q.; Xiong, Q. *Angew. Chem. Int. Edit.* **2018**, *57* (7), 1928-1932.
15. Hu, Q.; Gao, M.; Feng, G.; Liu, B. *Angew. Chem. Int. Edit.* **2014**, *53* (51), 14225-14229.
16. Gu, X.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. *Biomaterials* **2017**, *146*, 115-135.
17. Leung, C. W. T.; Hong, Y.; Chen, S.; Zhao, E.; Lam, J. W. Y.; Tang, B. Z. *J. Am.*

- Chem. Soc.* **2012**, *135* (1), 62-65.
18. Qian, J.; Tang, B. Z. *Chem* **2017**, *3* (1), 56-91.
 19. Liu, Y.; Mu, C.; Jiang, K.; Zhao, J.; Li, Y.; Zhang, L.; Li, Z.; Lai, J. Y. L.; Hu, H.; Ma, T. *Adv. Mater.* **2015**, *27* (6), 1015-1020.
 20. Dong, Y.; Lam, J. W.; Qin, A.; Liu, J.; Li, Z.; Tang, B. Z.; Sun, J.; Kwok, H. S. *Appl. Phys. Lett.* **2007**, *91* (1), 011111.
 21. Chen, L.; Jiang, Y.; Nie, H.; Lu, P.; Sung, H. H.; Williams, I. D.; Kwok, H. S.; Huang, F.; Qin, A.; Zhao, Z. *Adv. Funct. Mater.* **2014**, *24* (23), 3621-3630.
 22. Li, H.; Chi, Z.; Xu, B.; Zhang, X.; Li, X.; Liu, S.; Zhang, Y.; Xu, J. *J. Mater. Chem.* **2011**, *21* (11), 3760-3767.
 23. Meher, N.; Iyer, P. K. *Angew. Chem. Int. Edit.* **2018**, *130* (28), 8624-8628.
 24. Liao, S. H.; Jhuo, H. J.; Cheng, Y. S.; Chen, S. A. *Adv. Mater.* **2013**, *25* (34), 4766-4771.
 25. Qin, W.; Lam, J. W.; Yang, Z.; Chen, S.; Liang, G.; Zhao, W.; Kwok, H. S.; Tang, B. Z. *Chem. Commun.* **2015**, *51* (34), 7321-7324.
 26. Luo, J.; Xie, Z.; Lam, J. W.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D. *Chem. Commun.* **2001**, (18), 1740-1741.
 27. Tang, B. Z.; Zhan, X.; Yu, G.; Lee, P. P. S.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2001**, *11* (12), 2974-2978.
 28. Wang, M.; Zhang, G.; Zhang, D.; Zhu, D.; Tang, B. Z. *J. Mater. Chem.* **2010**, *20* (10), 1858-1867.
 29. Vyas, V. S.; Banerjee, M.; Rathore, R. *Tetrahedron Lett.* **2009**, *50* (45), 6159-6162.
 30. Shustova, N. B.; McCarthy, B. D.; Dinca, M. *J. Am. Chem. Soc.* **2011**, *133* (50), 20126-20129.
 31. Shustova, N. B.; Cozzolino, A. F.; Dincă, M. *J. Am. Chem. Soc.* **2012**, *134* (48), 19596-

- 19599.
32. Hu, R.; Leung, N. L. C.; Tang, B. Z. *Chem. Soc. Rev.* **2014**, *43* (13), 4494-4562.
 33. Xu, Y.; Nagai, A.; Jiang, D. *Chem. Commun.* **2013**, *49* (16), 1591-1593.
 34. Xu, Y.; Chen, L.; Guo, Z.; Nagai, A.; Jiang, D. *J. Am. Chem. Soc.* **2011**, *133* (44), 17622-17625.
 35. Chandrasekaran, Y.; Venkatramaiah, N.; Patil, S. *Chem. Eur. J.* **2016**, *22* (15), 5288-5294.
 36. Shao, A.; Xie, Y.; Zhu, S.; Guo, Z.; Zhu, S.; Guo, J.; Shi, P.; James, T. D.; Tian, H.; Zhu, W. H. *Angew. Chem. Int. Edit.* **2015**, *54* (25), 7275-7280.
 37. An, B.-K.; Gihm, S. H.; Chung, J. W.; Park, C. R.; Kwon, S.-K.; Park, S. Y. *J. Am. Chem. Soc.* **2009**, *131* (11), 3950-3957.
 38. Chen, Q.; Wang, J.-X.; Yang, F.; Zhou, D.; Bian, N.; Zhang, X.-J.; Yan, C.-G.; Han, B.-H. *J. Mater. Chem.* **2011**, *21* (35), 13554-13560.
 39. Hinoue, T.; Miyata, M.; Hisaki, I.; Tohnai, N. *Angew. Chem. Int. Edit.* **2012**, *51* (1), 155-158.
 40. Wang, Y.; Zhang, G.; Zhang, W.; Wang, X.; Wu, Y.; Liang, T.; Hao, X.; Fu, H.; Zhao, Y.; Zhang, D. *Small* **2016**, *12* (47), 6554-6561.
 41. Hasell, T.; Culshaw, J. L.; Chong, S. Y.; Schmidtman, M.; Little, M. A.; Jelfs, K. E.; Pyzer-Knapp, E. O.; Shepherd, H.; Adams, D. J.; Day, G. M. *J. Am. Chem. Soc.* **2014**, *136* (4), 1438-1448.
 42. Lei, Y.; Wang, S.; Lai, Z.; Yao, X.; Zhao, Y.; Zhang, H.; Chen, H. *Nanoscale* **2019**, *11* (18), 8692-8698.
 43. Su, Y.; Wang, Y.; Li, X.; Li, X.; Wang, R. *ACS Appl. Mater. Inter.* **2016**, *8* (29), 18904-18911.
 44. Tanaka, K.; Fujimoto, D.; Oeser, T.; Irngartinger, H.; Toda, F. *Chem. Commun.* **2000**,

- (5), 413-414.
45. Miyazawa, K.; Kuwasaki, Y.; Obayashi, A.; Kuwabara, M. *J. Mater. Res.* **2002**, *17* (1), 83-88.
 46. Hudson, B. S.; Kohler, B. E. *J. Chem. Phys.* **1973**, *59* (9), 4984-5002.
 47. Hudson, B. S.; Kohler, B. E.; Schulten, K. *Excited states* **1982**, 6, 1-95.
 48. Andersson, P. O.; Gillbro, T.; Ferguson, L.; Cogdell, R. J. *Photochem. Photobiol.* **1991**, *54* (3), 353-360.
 49. Bai, Y.; Yu, Z.; Liu, R.; Li, N.; Yan, S.; Yang, K.; Liu, B.; Wei, D.; Wang, L. *Sci. Rep.* **2017**, *7* (1), 5321.
 50. Materny, A.; Chen, T.; Schmitt, M.; Siebert, T.; Vierheilig, A.; Engel, V.; Kiefer, W. *Appl. Phys. B* **2000**, *71* (3), 299-317.
 51. Gustafsson, M. *Lund Reports in Atomic Physics* **1996**, **1-45**.
 52. Ortiz-Rivera, W.; Pacheco-Londoño, L. C.; Hernández-Rivera, S. P. *Sens. Imaging: Int. J.* **2010**, *11* (3), 131-145.
 53. Smith, B. C. *Spectroscopy* **2016**, *31* (5), 36-39.
 54. McMurry, J., Organic chemistry. Ninth edition/Hybrid edition. ed.; *Cengage Learning: Boston, MA, USA*, **2016**.

Chapter 5. Conclusion and Future Works

5.1. Conclusion

In this thesis, we have done a series of works to solve the problem of difficult for controlling molecular crystals at micro- or nanoscale by proposing a new method, understanding the mechanism and developing the generality for complex micro- nano-architectures of organic/molecular crystals.

In **Chapter 2**, we have developed the complex C₆₀ mesh networks via crystal transformation from the hexagonal plates by the removal and incorporation of co-solvents molecules. The change of solvent environment is the key factor for destabilization of C₆₀ plates, and subsequent growth of nanorods. The well-defined nanorod arrays was resulting in the lattice mismatching between the *fcc* plate and the *hcp* rod. The unconventional role of solvent molecules opens a new window for preparing complex organic/molecular crystals.

Thus, a new synthetic handle of solvent exchange has been put forward for creating complex nanostructures of organic crystals (**Chapter 3**). Based on the understanding the mechanism of solvent exchange during crystal transformation, the two core mechanistic questions have been addressed: 1) The effect of different solvent molecules; 2) The driving force and critical factors of exchange. The thermodynamic driving force is the relative stability of crystals in the different solvent environment. Whereas, the entropy drives CCl₄ losing and favorable stabilization energy of the rods promotes inclusion of *m*-xylene. The rates of desolvation, C₆₀ dissolution, and recrystallization are attributed to the critical factors. Therefore, with mitigated driving force in solution phase, desolvation could be avoided to structural collapse, but exchange leads to crystal transformation to mesh networks. Actually, the CCl₄ and *m*-xylene have symmetrical roles in the system, which the CCl₄ can transform the xylene-rich rods to the orthogonal plates that have an overall rod shape.

The solvent exchange method has demonstrated to have generality. Firstly, the C₆₀/ferrocene mesh networks were obtained by crystal transformation from the *fcc* C₆₀/ferrocene plates. In addition, the rhombic C₆₀·trichlorobenzene plates could be transformed to rhombic nanomeshes by solvent exchange. Conversion was not limited to C₆₀ crystals, C₇₀ meshes were converted from C₇₀ cubes by incubation in the transformative solution.

Interestingly, this method was not only applied to molecular crystals (C₆₀ or C₇₀), but also to the organic crystals (such as AIE crystals). The TPE-4Br organic crystal has been demonstrated to form different shapes (plates, prism-like structures or wires) by tuning the solvent (**Chapter 4**). Upon exchanging the incorporated solvent molecules, the *p*-xylene-rich TPE-4Br plate can undergo crystal transformation to microrod arrays, which was accompanied by the luminescence changes.

Considering the wide variety of solvate crystals in the literature, our new synthetic handle and the understanding of mechanism provides a platform for designing sophisticated crystal morphologies.

5.2. Future Works

Based on the understanding the mechanism of the new synthetic, several complex micro- or nano-architectures have been prepared. However, many organic crystals still can be explored. Here, we will introduce the general guidelines. The first principle is to choose solvates. Generally speaking, the non-planar organic molecules easy to form co-crystals with solvent molecules due to the available spaces. Other organic molecules have strong π - π interaction favor to form solvates. Thus, the candidate of non-planar organic molecule can be designed and synthesized. Then, we can search the solvate crystals from Cambridge Crystallographic Data Centre (CCDC). When we choose one organic molecule, the different morphologies should be obtained when different solvent molecules were incorporated inside the crystals. Then, we use one solvents to fill the space to maximize the extent of solvent incorporation. Then a high concentration of another solvent was used as the transformative solution, to provide a larger driving force to exchange for the embedded solvent. To reduce the dissolution rate of the crystals during crystal transformation, we introduce a saturated supernatant of another solvent incorporated crystals as a modified transformative solution. Thus, the template can be transformed rather than dissolved.

Besides, the rational synthesis of complex nanostructures with specific topographies need to investigate the properties for promising application.

5.2.1. New morphologies for other organic crystals

In the chapter 4, we have reported that the AIE crystals (TPE-4Br plates) can be employed the solvent exchange method to prepare microrod arrays via crystal transformation. However, the tetraphenylethene (TPE) has many derivatives, which can form inclusion crystals with different solvent molecules.^{1 2} Tanaka *et al.* reported that many solvent molecules could embed into the achiral tetrakis(p-halophenyl)-ethylenes crystals during crystallization,² as shown in

Figure 5.1a. In addition, the molar ratio between TPE derivatives and solvent molecules provided in the Figure 5.1b. It indicated that these crystals contain more than one solvent molecule. Thus, it is hopeful that the host materials can form different morphologies.

a

b

Guest	2	3	4	5	6	7
MeOH	— ^b	—	—	—	—	2:3
Acetone	1:2 ^c (8)	—	2:1	—	—	1:2
Cyclohexanone	1:1	—	1:1	1:2 ^c	—	1:4
Ethyl acetate	—	—	—	—	—	1:1:H ₂ O (13)
THF	1:2 ^c (9)	1:2 ^c	1:1	1:2 ^c	—	1:4
Dioxane	1:1 ^c	1:1 ^c	2:1	1:2	1:2 ^c	1:4
DMF	—	1:1 ^c	1:1	1:2	—	1:2
Benzene	1:1 ^c	1:1 ^c	2:1	1:1 ^c	1:1	—
Toluene	1:1	—	2:1	—	—	—
<i>o</i> -Xylene	—	—	1:1	—	—	—
<i>m</i> -Xylene	—	—	—	—	—	—
<i>p</i> -Xylene	1:1 ^c (10)	1:1 ^c (11)	2:3 (12)	—	—	—
1-Methylnaphthalene	1:2	—	1:1 ^c	1:1	—	—
2-Methylnaphthalene	—	—	2:3 ^c	1:1	—	—
α -Picoline	—	—	1:1	—	—	1:4
β -Picoline	1:1	1:1 ^c	1:1	1:1 ^c	—	1:2
γ -Picoline	—	—	1:1	—	—	1:4

^a The host: guest ratio was determined by TG and NMR. ^b No inclusion occurred. ^c Chiral crystal.

Figure 5.1. (a) The molecule structures of achiral TPE and TPE derivatives. (b) The molar ratio of TPE derivate crystal/solvent. Printed from ref 2 with permission. Copyright © 2010 The Royal Society of Chemistry.

Preliminary attempts have shown that tetrakis (p-hydroxyphenyl) ethylene (TPE-4OH) have different morphologies when the crystals were slowly precipitated from the stock solution (Figure 5.2). The crystal formed in the acetone and 2,6-Lutidine have wire structures, and the TPE-4OH plates were obtained in the dioxane or ethyl acetate systems. In addition, the TPE-4OH formed the ribbon-like structures when crystallized in methanol solution. Thus, the TPE-4OH crystals were good templates to prepare complex structures by solvent exchange.

Figure 5.2. Optical images of TPE-4OH crystals. (a) TPE-4OH/acetone wires. (b-c) TPE-4OH/2,6-Lutidine wires. (d) TPE-4OH/dioxane plates. (e) TPE-4OH/ethyl acetate plates. (f) TPE-4OH/methanol ribbons.

The solvent inclusion crystals provide a precondition for further crystal transformation of organic crystals. The ethyl acetate-TPE-4OH plates could transform to nanorod arrays when incubated in an IPA-acetone mixture ($V/V = 2:1$), as shown in Figure 5.3 (a, b). So far, we only obtain the complex structures, the mechanism is not clear. Therefore, the lattice relationship still need to study in the future works.

Figure 5.3. (a) TPE-4OH plates. (b) TPE-4OH nanorod arrays.

It's worth noting that the organic crystal of 4,4-(Fluorene-9,9-diyl)diphenol could also form inclusion compounds.³ The 4,4-(Fluorene-9,9-diyl)diphenol crystal were obtained by

embedding a series of solvents, such as alcohols, amines, ketones, nitriles and other solvents (including dimethylformamide, dimethyl sulfoxide, dioxane dioxane). The category of solvent incorporated crystals and its molar ratio of organic material/solvent molecule were shown in Figure 5.3. Therefore, the 4,4-(Fluorene-9,9-diyl)diphenol crystals are good candidates for studying the structural transformation by tuning the solvent.

1 R = H

With alcohols:	Methanol (1 : 2), ethanol (1 : 2), propan-1-ol (1 : 1), butan-1-ol (2 : 1), butan-2-ol (1 : 1)
With amines:	<i>n</i> -Propylamine (1 : 1), <i>n</i> -octylamine (1 : 3), cyclopentylamine (1 : 1), <i>sec</i> -butylamine (1 : 1), pyrrolidine (1 : 2), morpholine (1 : 2), tri- <i>n</i> -propylamine (2 : 1), tri- <i>n</i> -butylamine (1 : 3), pyridine (1 : 1)
With ketones:	Acetone (1 : 1), cyclohexanone (1 : 2), 2-methyl-Cyclohexanone (1 : 1)
With nitriles:	Acetonitrile (1 : 1), propionitrile (1 : 1), butyronitrile
With others:	Dimethylformamide (1 : 1), dimethyl sulfoxide (1 : 1), dioxane (2 : 1)

^a The following solvents yielded no crystalline inclusion compounds: propane-1,2-diol, cyclopentanol, cyclohexanol, benzylamine, acetophenone, 3-methylcyclohexanone, 4-methylcyclohexanone, β -butyrolactone, γ -valerolactone, nitromethane, nitroethane, dichloromethane, benzene, toluene, xylenes, cyclohexane.

Figure 5.3. The chemical structure of 4, 4-(Fluorene-9, 9-diyl)diphenol and the inclusion solvent molecules of 4, 4-(Fluorene-9, 9-diyl)diphenol crystal.

5.2.2. The heterojunction structures for photoelectric application

As we known, the heterojunction is an interface between two layers or regions of two different crystalline materials, which are n-type (donor doped) semiconductors and p-type (acceptor doped) semiconductors. The two kinds of materials with different band gaps are opposed to a homojunction. Thus, the electrons and holes can be transferred between the two semiconductors. The heterojunction can be used to photovoltaics and transistors.⁴⁻⁷ Generally, the heterojunction structure was fabricated by depositing two or more different semiconductor materials films on the substrates. In order to better integrate the junctions, we hope to combine the p-type and n-type materials by epitaxial growth, which can facilitate the electron transport. Previous work has reported that anthracene-1,2,4,5-tetracyanobenzene (TCNB) grown on the end of naphthalene-TCNB microtubes to form the microdumbbells by seeded-growth.⁸ Whereas the TCNB act as a n-type semiconductor in the Microdumbbells. Thus, if we can grow the TCNB on the AIE crystals (TPE-4Br act as a p-type semiconductor), the heterogeneous structure would have a promising application in multicolor fluorescent barcodes and photovoltaics. On the other hand, as a n-type semiconductor, the C₆₀ mesh networks can also grow with the TPE-4Br microrod arrays to for an interconnected heterojunction structure. More interesting heterojunction structures to be developed and applied in devices.

Previously reported that C₆₀ and C₇₀ could combine with meso-diphenyltetrathia[22]-annulene[2,1,2,1] (DPTTA) to form cocrystals. Whereas, the DPTTA acts as p-type semiconductor. Then, the materials based on organic donor-acceptor were used to prepare photovoltaic devices.⁹ Based on our previous method, the DPTTA and C₆₀ (or C₇₀) mixtures were dissolved in chlorobenzene, then added IPA to form crystals. Then the co-crystals were mixed with *m*-xylene-IPA solution. It was reported that $d_{centroid}$ in the C₆₀-DPTTA cocrystal was 10.02 Å.¹⁰ Thus, the good lattice matching between the *m*-xylene-rods (10.02 Å) and co-crystals plates leads to mesh networks or hierarchical structures. Then the transformed

structures were dripped on the Si/SiO₂ substrate. After the solvent evaporation, the crystal formed on the substrate. Afterward, aluminum (Al) was masked on one side of the crystal, and Au was evaporated on the other side. After that, the current density-voltage ($J-V$) of C₆₀-DPTTA cocrystals based device was characterized to obtain conversion efficiency. The cocrystals with a p-n junction donor-acceptor is promising for photovoltaic applications.

Reference

1. Tanaka, K.; Fujimoto, D.; Oeser, T.; Irngartinger, H.; Toda, F. *Chem. Commun.* **2000**, (5), 413-414.
2. Tanaka, K.; Fujimoto, D.; Altreuther, A.; Oeser, T.; Irngartinger, H.; Toda, F. *J. Chem. Soc. Perk. T. 2* **2000**, (10), 2115-2120.
3. Apel, S.; Nitsche, S.; Beketov, K.; Seichter, W.; Seidel, J.; Weber, E. *J. Chem. Soc. Perk. T. 2* **2001**, (7), 1212-1218.
4. Agbolaghi, S.; Charoughchi, S.; Aghapour, S.; Abbasi, F.; Bahadori, A.; Sarvari, R. *Solar Energy* **2018**, *170*, 138-150.
5. Pezeshki, A.; Shokouh, S. H. H.; Nazari, T.; Oh, K.; Im, S. *Adv. Mater.* **2016**, *28* (16), 3216-3222.
6. Shi, J.; Wang, H.; Song, D.; Tian, H.; Geng, Y.; Yan, D. *Adv. Funct. Mater.* **2007**, *17* (3), 397-400.
7. Tumbleston, J. R.; Collins, B. A.; Yang, L.; Stuart, A. C.; Gann, E.; Ma, W.; You, W.; Ade, H. *Nat. Photonics* **2014**, *8* (5), 385.
8. Lei, Y. L.; Liao, L. S.; Lee, S. T. *J. Am. Chem. Soc.* **2013**, *135* (10), 3744-3747.
9. Zhang, H.; Jiang, L.; Zhen, Y.; Zhang, J.; Han, G.; Zhang, X.; Fu, X.; Yi, Y.; Xu, W.; Dong, H. *Adv. Electron. Mater.* **2016**, *2* (6), 1500423.
10. Zhang, J., Tan, J., Ma, Z., Xu, W., Zhao, G., Geng, H., Di, C.; Hu, W.; Shuai Z.; Singh, K.; Zhu, D. *J. Am. Chem. Soc.* **2013**, *135* (2), 558-561.

List of Publications

1. **S. Wang** (co-first author), Y. Lei, Z. Lai, X. Yao, Y. Zhao, H. Zhang, H. Chen* Two-dimensional C₆₀ nano-mesh *via* crystal transformation. *Nanoscale* **2019**, *11* (18), 8692-8698.
2. **S. Wang**, Z. Lai, T. H. Tran, F. Han, D. Su, R. Wang, H. Zhang, H. Chen* Solvent exchange as a synthetic handle for controlling molecular crystals. *Carbon* **2019**, DOI: <https://doi.org/10.1016/j.carbon.2019.11.028>
3. **S. Wang**, H. Chen* Solvent exchange induced crystal transformation of AIE molecules accompanied by tuning emission. (manuscript under preparation)
4. J. Liu, **S. Wang**, K. Cai, Y. Li, Z. Liu, L. Liu, Y. Han, H. Wang, H. Han,* H. Chen* A New Type of Capping Agent in Nanoscience: Metal Cations. *Small* 2019, 1900444.
5. F. Han, R. Wang, Y. Feng, **S. Wang**, L. Liu, X. Li, Y. H, Chen. On demand synthesis of hollow fullerene nanostructures. *Nature Commun.* 2019, *10*, 1548