

FEATURE ARTICLE



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Kinetic trapping – a strategy for directing the self-assembly of unique functional nanostructures

Yun Yan,^{*a} Jianbin Huang^a and Ben Zhong Tang^{*b}

Supramolecular self-assembly into various nano- or microscopic structures based on non-covalent interactions between molecules has been recognized as a very efficient approach that leads to functional materials. Since most non-covalent interactions are relatively weak and form and break without significant activation barriers, the thermodynamic equilibrium of many supramolecular systems can be easily influenced by processing pathways that allow the system to stay in a kinetically trapped state. Thus far, kinetic traps have been found to be very important in producing more elaborate structural and functional diversity of self-assembled systems. In this review, we try to summarize the approaches that can produce kinetically trapped self-assemblies based on examples made by us. We focus on the following subjects: (1) supramolecular pathway dependent self-assembly, including kinetically trapped self-assemblies facilitated by host–guest chemistry, coordination chemistry, and electrostatic interactions; (2) physical processing pathway dependent self-assembly, including solvent quality controlled self-assembly, evaporation induced self-assembly and crystallization induced self-assembly.

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^a Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

E-mail: yunyan@pku.edu.cn

^b Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration & Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk

1. Introduction

Molecular self-assembly is the oriented association of molecules into nano- or microscopic structures *via* noncovalent interactions.¹ The history of molecular self-assembly can be dated back to the beginning of the last century when McBain declared the formation of colloidal clusters in the solution of surfactants in 1913.² The name ‘micelles’ was given to these



Yun Yan

Yun Yan earned her PhD degree from Peking University in 2003. She conducted her postdoctoral work at Bayreuth University (Germany, with professor Heinz Hoffmann) and Wageningen University (the Netherlands, with professor Martien A. Cohen Stuart). She joined Peking University in 2008. She was selected into the New Century Training Program for the Talents by the State Education Commission of China in 2009, was awarded “Outstanding Young

Professor of Colloid Science of China” in 2013, and is the winner of Outstanding Youth Science Foundation, Natural Science Foundation of China (NSFC, 2014). Her interest is solution based functional molecular self-assemblies. Currently, she is a visiting scientist in Professor Ben Zhong Tang’s group in HKUST.



Jianbin Huang

Jianbin Huang obtained his bachelor’s (1987), master’s (1990), and PhD (1993) degree all at Peking University, China. After a postdoctoral study at the same university, he was nominated as an associate professor in 1995, as a full professor in 2001, and was awarded “Outstanding Young Scientist of China” in 2004. His main research interests include soft self-assembly of amphiphiles and one dimension nanomaterials that are synthesized using soft

templates. He is currently the senior editor of *Soft Matter*, and also the board editor of *Langmuir*.

clusters by Hartley in 1936 and has been popularized since then.³ The era of ‘micelles’ lasted until the first artificial vesicle was reported by Kunitake in 1977 using a synthetic double-chained amphiphile mimicking lipids in nature.⁴ In the last two decades, molecular self-assembly has attracted worldwide attention and has become one of the most important approaches leading to novel structures beyond chemistry.⁵ Currently, it is considered as the cradle for advanced functional materials.⁶ Whitesides *et al.*¹ and Lehn *et al.*⁷ have done pioneering work in this regard.

Up to date, diversified molecular self-assemblies have been created *via* various strategies, such as amphiphilic self-assembly driven by the quality of solvent,⁸ layer-by-layer⁹ or polyion complex self-assembly¹⁰ driven by charge interaction, and other ordered molecular arrangements driven by the combined effects of a set of noncovalent interactions.^{11–14} In general, the noncovalent interactions involved in molecular self-assembly include hydrogen bonding,¹⁴ hydrophobic effects,¹³ van der Waals forces,¹³ coordination interactions,¹⁵ ionic interactions,¹⁶ halogen bonding,¹⁷ *etc.* The role of noncovalent interactions in the molecular self-assemblies is similar to that of covalent bonds in molecules.¹⁸ Since the noncovalent interactions are usually much weaker than the covalent ones, materials based on molecular self-assemblies are readily influenced by external stimuli.¹⁹ For this reason, molecular self-assembly has become an important approach beyond synthetic chemistry to create new materials.^{20–23}

Molecular building blocks play determinative roles in the final self-assembled structures. Israelachvili *et al.* have deduced the relationship between the organized structure and the geometry of amphiphiles in aqueous media, which is well-known as the molecular packing parameter.²⁴ Under the guidance of this principle, tremendous efforts have been devoted to the design and synthesis of various molecules or supramolecules to achieve desired functional materials. A number of excellent reviews



Ben Zhong Tang

Ben Zhong Tang received his PhD degree from Kyoto University in 1988. He conducted his post-doctoral work at the University of Toronto and worked as a senior scientist in Neos Co., Ltd. He joined HKUST in 1994 and was promoted to Chair Professor in 2008. He is interested in the creation of new molecules with novel structures and unique properties. He received a Natural Science Award from the Chinese Government in 2007 and was

elected to the Chinese Academy of Sciences in 2009. He is serving as News Contributor to Noteworthy Chemistry (ACS) and Editor-in-Chiefs of Materials Chemistry Frontiers (RSC) and Polymer Chemistry Series (RSC).

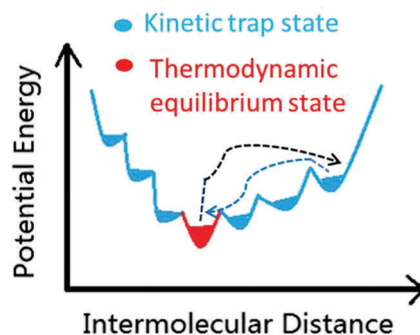


Fig. 1 Energy landscape of kinetic traps *versus* thermodynamic equilibrium states. The arrows demonstrate that transition between the kinetic traps and the thermodynamic equilibrium state is possible under appropriate external stimuli, which lays down the fundamentals for responsive materials.

focusing on individual self-assembled structures or specific type of building blocks can be found.^{25–34}

However, most recently, kinetic factors have been found to be very crucial in determining the self-assembled structures and their functions, which is especially true for self-assembling systems involving multiple noncovalent interactions or bulky molecules.^{18,35–40} In the former systems, compromise or competition between different interactions can lead the self-assembled structure to a kinetically trapped state rather than to a thermodynamic equilibrium state,^{37,41–44} whereas in the latter systems, the kinetics strongly affect the mode of molecular packing, so that different pathways often lead to self-assembled structures with distinct morphology and functions. Usually, fast processes result in kinetic traps while slow ones lead to thermal equilibrium. The kinetic trap possesses higher potential energy,⁴⁵ but the energy barrier between the kinetic trap and the thermal equilibrium state is not very high (often several kT). Therefore, it is possible to switch between these two energy states (Fig. 1), which allows the fabrication of responsive or adaptive materials.¹⁹

Many advanced biological functions only emerge from kinetically trapped structures. As an example, blood platelets may develop many branches and irregular shapes to form a blood clot when the tissue suffers a cut.^{46,47} It is crystal clear that kinetic control not only endows advanced functions to the molecular self-assembly, but also allows us to march closer to the mysterious world of life. For this reason, various self-assembled strategies related to kinetic issues have been proposed, such as catassembly,⁴⁸ fueled molecular self-assembly,⁴⁹ non-equilibrium self-assembly,⁵⁰ and dissipative self-assembly,⁵¹ *etc.* However, compared with the huge volume of literature on the spontaneous formation of various molecular self-assemblies, the literature on systematic summarization of kinetic or pathway controlled self-assembly is relatively small and is still case dependent.^{36,37,52} In this feature article, we try to sketch the method adopted by us.

Usually, high temperature, low concentration and a long time-course favor the thermal dynamic state, whereas the opposite leads to kinetically trapped states. However, these physical parameters are often intertwined together to drive

the self-assembly formation. Thereby, in this review, we would like to outline the kinetic control over molecular self-assemblies according to the arts that are employed, namely (1) supramolecular approaches, which include host-guest chemistry, coordination chemistry, and ionic self-assembly, and (2) physical processing approaches, including solvent quality control, evaporation and crystallization. Each art is demonstrated with representative examples made by us, and some examples from other groups are borrowed in case of necessity.

2. Supramolecular approaches leading to kinetically trapped self-assembly

2.1 Host-guest chemistry facilitated self-assembly

Host-guest chemistry has been widely employed in constructing self-assembled supramolecular structures, where a guest molecule can be sheltered in the cavity of a host to form a host-guest complex.^{27,53} So far many macrocyclic compounds, such as cyclodextrins (CD),^{27,33} crown ethers,⁵⁴ calixarenes,⁵³ cucurbiturils, pillarenes,⁵⁵ cyclotrimeratrylenes, cryptophanes, carcerands, and foldamers,³² have been found to act as hosts which can accommodate different guests. In most cases, formation of a host-guest complex is utilized to construct smart materials.⁵⁶ However, in some cases, host-guest chemistry can be employed to control the kinetics of molecular self-assembly. In the following we show some examples made by us.

2.1.1 Cyclodextrin catalyzed self-assembly. Cyclodextrins are classical hosts that have been well-studied in the past.^{27,33,57–63} They are truncated doughnut ring-shaped structures formed by six, seven, or eight D-glucopyranose (C₆H₁₀O₅) units (named as α -, β -, and γ -CD, respectively) linked by α -1,4-glycoside bonds. Because the hydrophobic CH₂ groups are located in the cavity of CDs whereas the hydrophilic OH groups are located on the exterior, the host-guest interaction between CDs and a guest often results in enhanced solubility of the guest. Therefore, introducing CD to an amphiphilic system may generate strong competition between hydrophilic and hydrophobic effects. This property was employed by us to slow down the aggregation or precipitation of some strongly hydrophobic molecules.

For instance, the amphiphilic terthiophene compound TTC4L quickly precipitates at acidic pH which ends in an amorphous structure.⁶⁴ However, in the presence of β -CD, the precipitation process can be retarded and a well-defined microsphere is formed (Fig. 2). Surprisingly, the microspheres are found to be composed of only TTC4L where β -CD is absent.

XRD measurements revealed that the TTC4L molecules are packed in an orderly manner to form a lamellar structure. ¹HNMR experiments revealed that before acidification, the terthiophene group of TTC4L partly enters the cavity of β -CD which results in the formation of a hydrophilic host-guest complex of TTC4L@ β -CD. Upon acidification, the equilibrium of TTC4L + β -CD \leftrightarrow TTC4L@ β -CD shifts toward the left to release TTC4L. Since this process takes time, the concentration of TTC4L remains at a low level which allows TTC4L molecules to steadily assemble into an ordered structure (Fig. 2). In this example, the self-assembly of TTC4L allows the whole chain of TTC4L to escape from water, whereas the 1:1 host-guest complex of TTC4L@ β -CD only shelters part of the hydrophobic chain of TTC4L. As a result, TTC4L escapes from the cavity of β -CD when acidified. In this way, β -CD slows down the aggregation kinetics, which allows TTC4L molecules to pack steadily into well-defined microspheres rather than forming amorphous precipitates. In this sense, β -CD acts as a ‘catalyst’ that helps TTC4L to self-assemble. Such a catalyst that facilitates the assembly of molecules was proposed by Tian *et al.* as a ‘catassembler’.⁴⁸ Similarly, Li *et al.* also reported a case of host-guest chemistry catalyzed self-assembly. They found that upon complexation with an amphiphile, the cucurbit[*n*]uril can self-assemble into nanocrystals, yet the amphiphile is released when the nanocrystals of cucurbit[*n*]uril are formed.⁶⁵

2.1.2 Host-guest chemistry facilitated self-assembly of cyclodextrins. Although cyclodextrins are often employed as an efficient host to change the hydrophilicity of the guest, they can also self-assemble in water.^{66,67} However, their self-assembly is rather ill-defined and hasn't attracted enough attention. Considering that the self-assembling process of CDs is actually a compromise between the entropy favored thermal motion and the enthalpy favored intermolecular hydrogen bonding, we expect that reducing their thermal motion would lead to better self-assembly. To this end, we constructed channel type dimers of β -CD using host-guest chemistry: the classical surfactant sodium dodecyl sulfate (SDS) was allowed to complex with β -CD at a molar ratio of 1:2 to form the SDS@2 β -CD building block.^{68,69} This successfully resulted in well-defined vesicles, multiwalled microtubes, and lamellae with increasing concentration from 5% to 30% (Fig. 3A). Since the extending length of the chain of SDS is about 1.2 nm, whereas the height of one β -CD is about 0.79 nm, the chain of SDS is completely buried in the hydrophobic channel formed by two β -CDs. Thus, the entity that directly participates in the self-assembling process is the channel type dimer of β -CD. It is noticed that this family

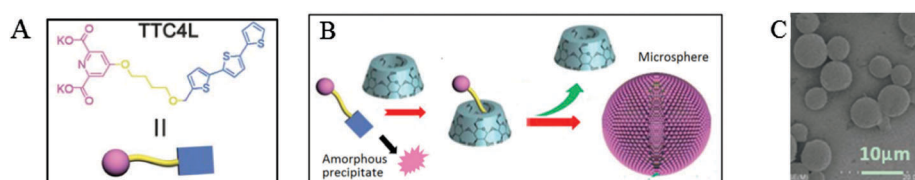


Fig. 2 β -CD catalyzed self-assembly of TTC4L. (A) Structure of TTC4L; (B) schematic illustration of the self-assembly of TTC4L catalyzed by β -CD; (C) SEM image of the microspheres self-assembled from TTC4L. Copyright © 2012 Royal Society of Chemistry.

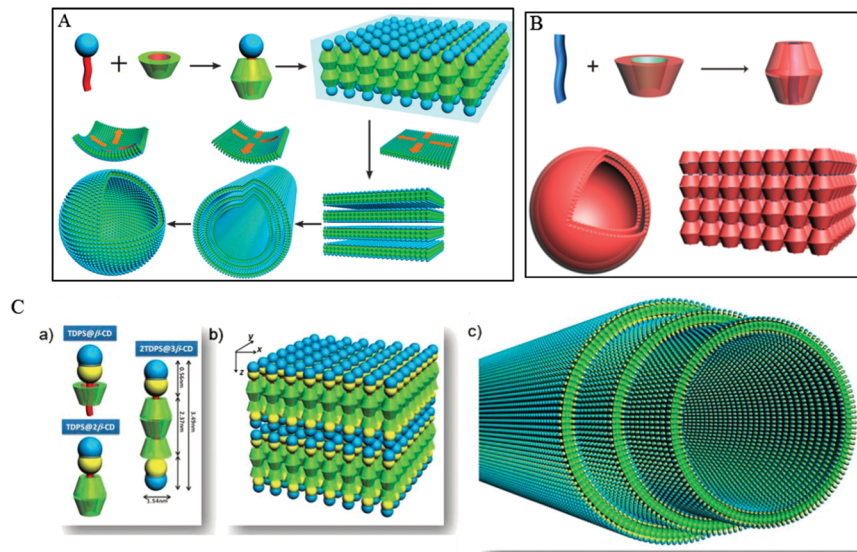


Fig. 3 Schematic illustration of the host-guest chemistry facilitated self-assembly of β -CD. (A–C) Are the self-assemblies facilitated by SDS, dodecane, and TDPS, respectively. Copyright © 2012 Royal Society of Chemistry.

of self-assembled structures is exclusively driven by hydrogen bonding. The electrostatic repulsion triggered by the anionic head of SDS mainly affects the critical aggregation concentration (CAC). As the anionic SDS is replaced with the nonionic surfactant Tween 20, vesicles are found again, but the CAC is decreased to 0.01% (0.03 mM).⁷⁰ Furthermore, as the head-tail structured SDS or Tween 20 is replaced by pure hydrocarbons, such as dodecane or decane, vesicles and lamellar structures are still found in the low and high concentration regime, respectively (Fig. 3B).^{71,72} Because the whole alkane chain is sheltered in the channel formed by two β -CDs, the apparent building blocks for the alkane@ 2β -CD vesicles are only the channel type dimer of β -CD, where no interactions between the alkanes exist. Such a fact clearly demonstrates that the host-guest complexation with alkanes only facilitates the self-assembly of β -CD. It strongly supports the picture proposed by us: the increased mass of the building block reduces their thermal motion, thus hydrogen bonding becomes dominant over the thermal motion. Actually, the discoveries of Liu⁷³ and Hao's⁷⁴ group are also in good agreement with the scenario proposed by us, especially the observation of vesicles by Liu *et al.* in phosphate modified γ -CD solution.⁷³ This suggests that the self-assembly of CDs needs additional 'help', while the host-guest chemistry can offer a facile assistance by slowing down their diffusion. However, it should be pointed out that the guests surely have an influence on the self-assembled structure. For instance, by using a zwitterionic surfactant TDPS (tetradecyl dimethylammonium propane sulfonate) which has a longer alkyl chain, the complexing ratio with β -CD can be 1 : 1.5, so that diamond shaped structures and flexible nanofibers are formed in the low and high concentration regimes, respectively (Fig. 3C).⁷⁵

Because the self-assembly of CDs facilitated by host-guest interaction is simply driven by hydrogen bonding, temperature responsiveness can be expected. For instance, the vesicles and

microtubes formed by SDS@ 2β CD can be reversibly transformed into each other upon changing the temperature,⁷⁶ whereas the SDS@ 2β CD microtubes can be used to thermo-reversibly assemble colloidal spheres.⁷⁷ In this approach, the co-assembly of spherical colloids and SDS@ 2β CD microtubes yields a library of dynamic colloid-in-tube structures including helices, zigzags (Fig. 4), while de-assembly can be achieved simply by heating the system.

2.1.3 Host-guest chemistry facilitated self-assembly deformation. The kinetic trap of self-assembly in its deformation process remains challenging since usually the energy in the deformation process is downhill so that it can hardly stop midway. However, in an appropriate situation, host-guest chemistry is able to lock the deformation. For instance, we designed a pseudo-sugar surfactant C4AG which bears an azobenzene group in the hydrophobic portion. This molecule on its own can self-assemble into a double helix in water,⁷⁸ but forms

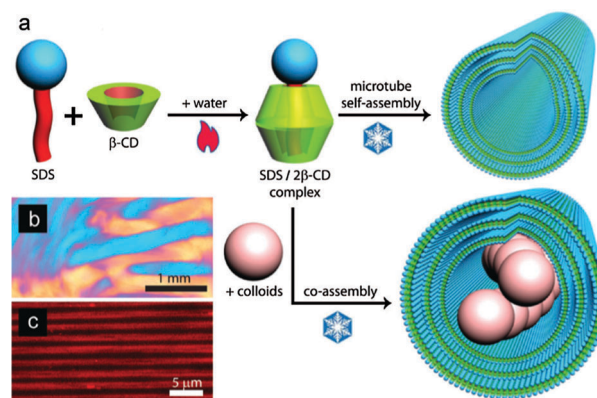


Fig. 4 Thermo-reversible co-assembly of microtubes and colloids.⁷⁷ Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

vesicles upon complexation with β -CD at a molar ratio of 1:2.⁷⁹ C4AG@2 β -CD is the basic building block in the vesicle, similar to what we observed in the alkane@2 β -CD or SDS@2 β -CD systems. Before UV irradiation, the azobenzene group of C4AG in its *trans*-form is able to form a host-guest complex with β -CD. When subjected to UV irradiation, the *trans*-azobenzene group changes to the *cis*-form so that it slips out of β -CD. However, the butyl group attached to the azobenzene group is still sheltered in the cavity of β -CD, while the latter stays on the vesicle surface *via* hydrogen bonding. As a result, the *cis*-C4AG@ β -CD further self-assembles into a helix on the vesicle, just like the development of cilia from the surface of bacteria (Fig. 5). Most interestingly, the cilia disappear under visible light, but they reoccur once subjected to UV irradiation. This process can be reversibly switched many times. Since the material that forms the cilia is extracted from the original C4AG@2 β -CD vesicle, the development of cilia triggers the release of the loaded drug. Thereby, the photo-switchable cilia represent a novel photogated controlled release system. It was noticed that the bacteria-like vesicles can be finally transformed into double helices if we prolong the irradiation time. This means that the bacteria-like vesicles are the kinetically trapped state in the process of vesicle to double helix transition. Compared with many photoresponsive systems, the unique kinetic trap allows the use of deformed vesicles to achieve controlled release. This is in clear contrast with the often employed thorough breaking of carriers when releasing systems are designed. The host-guest chemistry of β -CD, together with the intermolecular hydrogen bonding, plays a crucial role in the kinetic trap of the deformed self-assembly of C4AG@2 β -CD vesicles.

2.1.4 Host-guest chemistry enabled equilibrium shift of self-assembly. Usually, molecular self-assembly ends up at a thermodynamic equilibrium, where the self-assembled structure and the macroscopic phase behaviours are well-defined. However, the equilibrium can be easily shifted to a new state with the help of host-guest chemistry. An elegant example was presented by Jiang *et al.* where β -CD is found to have a

buffering effect in the biased mixed system of cationic and anionic surfactants.^{80,81} Regardless of the starting molar ratio, addition of β -CD always shifts the original equilibrium toward charge-neutral mixing, which is accompanied by the transition of micelles into vesicles and an increase of the macroscopic turbidity (Fig. 6).⁸⁰ The reason is that the excess component can always be complexed by β -CD. This selective binding shifts the molar ratio toward 1:1 which results in the self-assembly transition. Interestingly, this shift can be recovered by addition of enzymes, since α -amylase can decompose the cyclodextrins, which thus release the surfactants into the bulk system. This elegant change was employed to construct enzyme responsive surfaces, micelles, and vesicles⁸² (Fig. 6).

2.2 Ionic interaction triggered kinetically trapped self-assembly

The ionic interaction has emerged as an important driving force for the fabrication of molecular self-assemblies,^{83–85} especially the polyion complex (PIC) assemblies formed in water by pairs of oppositely charged polyelectrolytes, such as polyion complex micelles^{10,85–91} and vesicles,^{92–94} layer-by-layer assembled films^{95–97} and capsules.^{98–102} This is also the case when one of the polyelectrolytes is replaced by reversible or “soft” coordination polymers, namely, supramolecular chains in which organic bisligands and transition metal ions alternate in a regular fashion.^{103–106} In this case, kinetically trapped structures of the dynamic coordination polymers can be formed in the ionic self-assemblies which enhance the functional performance of the coordination polymers.

2.2.1 Kinetically trapped suprapolymeric structure. Reversible coordination polymers have emerged as a novel family of functional materials which enable solution processed and stimuli responsive functions. However, one of the drawbacks of this category of polymers is their concentration and stoichiometry dependent structures,^{107,108} which make it difficult to maintain the material performance at a constant level. Fortunately, upon utilizing the charges at the coordination center to form ionic

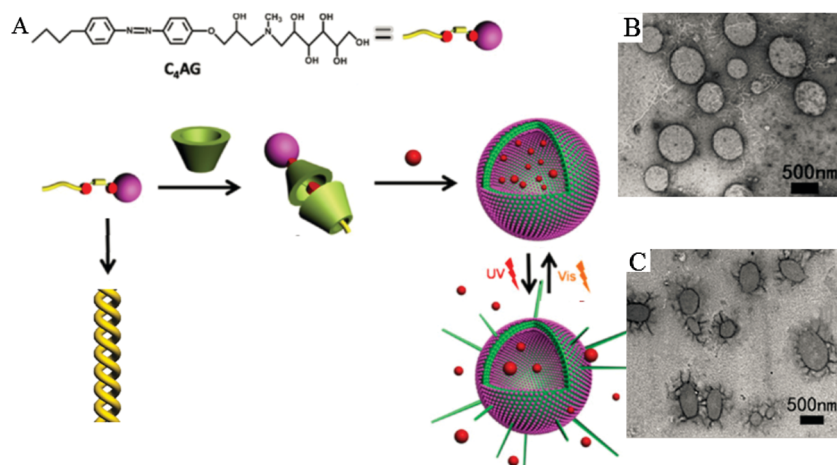


Fig. 5 (A) Illustration of the host-guest chemistry facilitated formation of bacteria-like vesicles and their photo-controllable release. (B and C) The original and the bacteria-like vesicles obtained before and after UV irradiation, respectively. Copyright © 2014, American Chemical Society.

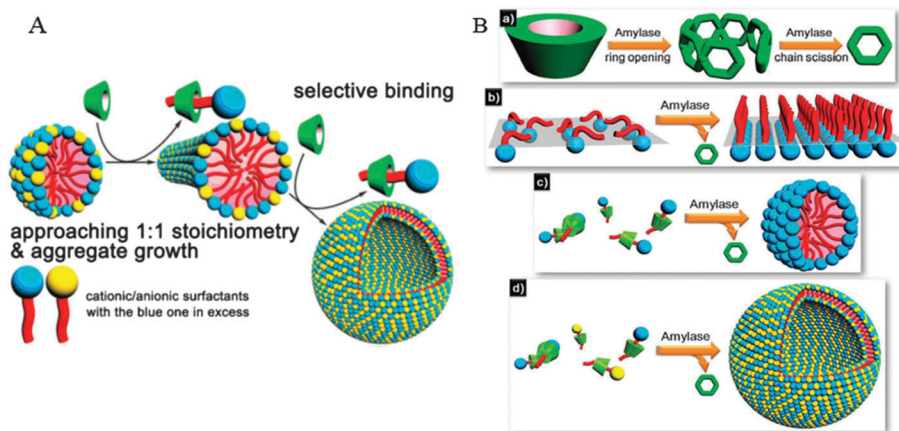


Fig. 6 (A) β -CD triggered shift of equilibrium in the self-assembled system of cationic/anionic surfactant mixed solution. (B) Degradation of β -CD by alpha-amylase (a), enzyme-triggered monolayer formation (b), enzyme-triggered micellization (c), and enzyme-triggered vesicle formation (d). Copyright © 2009, American Chemical Society, Copyright © 2012 Royal Society of Chemistry.

self-assembly,^{108,109} these shortcomings can be easily overcome with the formation of kinetically trapped polymeric structures.

For instance, the $\text{Zn-L}_2\text{EO}_4$ system forms small rings at low concentrations, whereas chains become dominating only at concentrations above 20 mM.¹⁰⁷ Since each coordination center carries 2 elementary negative charges, ionic interaction occurs when the block polyelectrolyte $\text{PMVP}_{41}\text{-PEO}_{204}$ carrying positive charges is added. At the charge balancing ratio, polyion complex

micelles can be formed (Fig. 7a).¹¹⁰ It is striking to find that the small rings can automatically transform into linear chains as a result of the increased local concentration. Thus, the sizes of the PIC micelles remain constant no matter what concentration of $\text{Zn-L}_2\text{EO}_4$ was employed. Such a strategy is applicable to other ionic self-assembly of reversible coordination polymers, too.^{111–114}

With this principle, the emission of europium in aqueous media was successfully enhanced (Fig. 7b).^{115–117} Before ionic

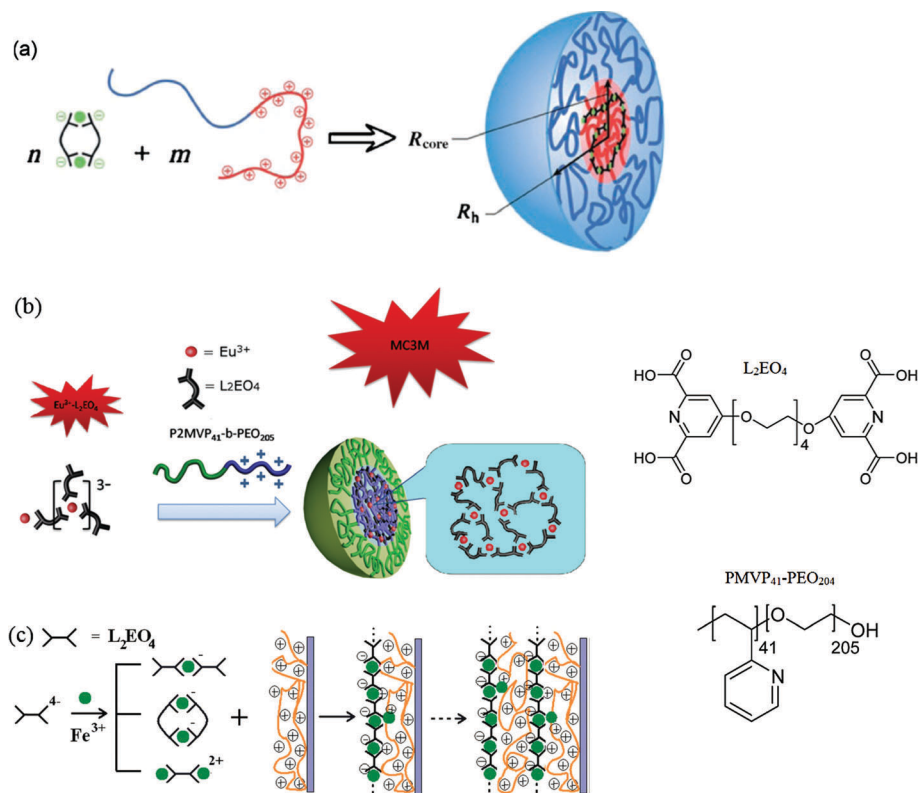


Fig. 7 Kinetically trapped suprapolymer in ionic self-assembly. (a) Kinetic trap of the suprapolymer of $\text{Zn-L}_2\text{EO}_4$ using the ionic interaction with $\text{PMVP}_{41}\text{-PEO}_{204}$. (b) Kinetic trap of $\text{Eu-L}_2\text{EO}_4$. (c) Kinetic trap of the $\text{Fe(III)-L}_2\text{EO}_4$ suprapolymers at different starting feed ratios. Copyright (a) © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Copyright (b and c) © 2012 Royal Society of Chemistry.

assembly formation, the coordination complexes of $\text{Eu-L}_2\text{EO}_4$ alone are oligomers which have many ends allowing the partially coordinated europium exposed to water. This results in significant quenching of the emission of europium. However, in the presence of oppositely charged polyelectrolytes, the local concentration of the coordination complexes is greatly enhanced, so that they transform into polymeric structures and simultaneously induce the formation of PIC micelles. This effectively decreases the number of europium–water coordination bonds, which leads to the enhancement of fluorescence emission.

Kinetic trapping of the degree of polymerization for reversible coordination polymers not only occurs in the micellar core, but also in the layer-by-layer films and microcapsules.^{118,119} In this case, a leveling effect of the stoichiometric ratio is found. Usually, the degree of polymerization for dynamic coordination polymers is very sensitive to the stoichiometry. For instance, one can only expect small coordination complexes at the ratio deviate from 1:1 in the $\text{Fe(III)-L}_2\text{EO}_4$ solution. However, linear chains of 1:1 complexed $\text{Fe(III)-L}_2\text{EO}_4$ can always be formed in the layer-by-layer assembled film even at the $\text{Fe}^{3+}:\text{L}_2\text{EO}_4$ ratio in the feeding solution of 16:1 or 1:16.¹¹⁸ Unambiguously, the kinetic trap facilitated by ionic interaction is very useful in constructing self-assembled materials based on dynamically reversible coordination polymers (Fig. 7c).

2.2.2 Kinetically trapped self-assembled structure. Ionic interactions can also allow the formation of supramolecular self-assemblies *via* kinetic trap. The coordination complex of $\text{TPE-C}_4\text{-L}_2/\text{Ni}$ can self-assemble very slowly into a cocoon-like structure (Fig. 8).¹²⁰ This is because the coordination center carries negative charges, so that the ionic repulsion does not allow them to self-assemble easily. However, upon compensating the charges with $\text{PMVP}_{41}\text{-PEO}_{205}$, the cocoons can be transferred into long nanoladders as a result of charge compensation.¹²⁰ This is very similar to the formation of supramolecular polymers with ionic interaction, where the polymeric structure is kinetically trapped by the enhanced local concentration. Although examples of this kind have been scarce so far, we expect that this will be an effective approach to build hierarchical self-assembly on the basis of charged primary self-assembled structures.

2.2.3 Kinetically trapped charges in the PIC micelles. Usually, excess of one polyelectrolyte chain will result in less intact PIC self-assemblies since the excess charges are diffusely distributed in the whole structure, thus generating considerable repulsion.^{121,122} This is also the case in the PIC micelles made with $\text{Fe(III)-L}_2\text{EO}_4$ and $\text{PMVP}_{41}\text{-PEO}_{204}$. When these two components were mixed directly in water, excess $\text{Fe(III)-L}_2\text{EO}_4$ ($f > 0.5$) results in micelles with a negative zeta potential, indicating that some of the negatively charged $\text{Fe(III)-L}_2\text{EO}_4$ is located on the surface of the micellar corona.^{123,124} In this case, addition of positively charged rigid MEPE can link these negative charged micelles into fibrils, as illustrated in Fig. 9A.¹²⁴ In contrast, if the excess negative charges were achieved by reduction of the originally charge-neutral micelles, the charges can be kinetically trapped in the micellar core owing to the entanglement of $\text{Fe(III)-L}_2\text{EO}_4$ with the PMVP_{41} segments of $\text{PMVP}_{41}\text{-PEO}_{204}$. In this case, the rigid MEPEs may be taken

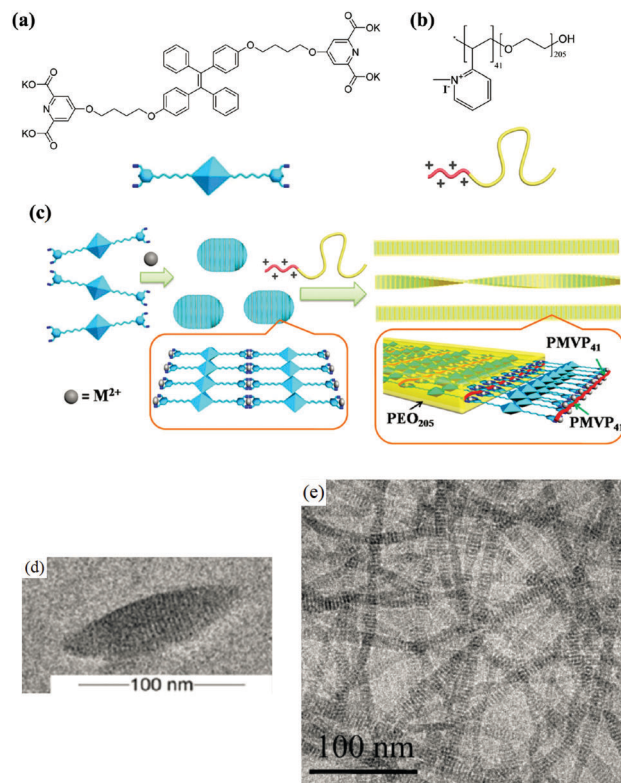


Fig. 8 The cocoons are transferred to nanoladders in ionic self-assembly. (a and b) Structure of $\text{TPE-C}_4\text{-L}_2$ and $\text{PMVP}_{41}\text{-PEO}_{204}$; (c) schematic illustration of the transition from cocoons to nanoladders; (d) and (e) cryo-TEM image of the cocoon and the nanoladder. Copyright © 2014, American Chemical Society.

into the core, which leads to core elongation, as demonstrated in Fig. 9B. Since the kinetically trapped excess charges are less diffusing and better confined in the micellar core, one can get a smart loading system that is able to selectively take up oppositely charged cargo (Fig. 9C).¹²⁵ Upon reduction, the core can expel the cargo, demonstrating the possibility of continuous shipping.¹²⁵

2.3 Coordination chemistry facilitated self-assembly

When coordinating groups are introduced to an amphiphile, coordination chemistry can be utilized to control the self-assembling behavior. The impact of coordination chemistry on the molecular self-assembly involves two aspects. On the one hand, coordination interaction is directional due to the requirement of the electron donation, which determines the arrangement of molecules around the metal ions. This affects the dynamic conformation of the molecules and thereby their self-assembling behavior. On the other hand, coordination interaction can compete with other noncovalent interactions, thus resulting in kinetically trapped structures. Thereby, coordination chemistry adds additional possibilities to control the structure of molecular self-assembly and the resultant material performance.

2.3.1 Coordination chemistry facilitated allosteric self-assembly. The conformation of an amphiphile can significantly affect its packing so that it is anticipated that kinetic locking of

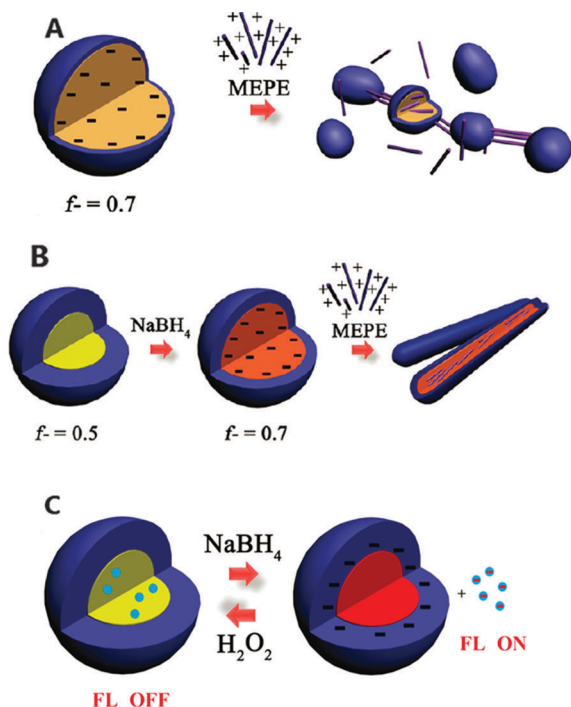


Fig. 9 Uptake and release of the micellar system. (A–C) Adapted with permission from ref. 126. (D) Adapted with permission from ref. 127. Copyright © 2012, American Chemical Society.

the conformation will lead to different self-assembled structures. For molecules with luminescent groups, the different packing will influence their emission. In coordinating assemblies, metal ions can be utilized to control the conformation of the ligand where it has to rearrange to satisfy the steric requirement. In the literature, this is called the ‘allosteric effect’,¹²⁸ a word borrowed from biology. However, in biology, the ‘allosteric effect’ generally refers to the fact that binding a ligand at one site of a protein^{129–131} or DNA^{132–134} modifies the performance at a distant site through conformational or dynamic changes. Similarly, we consider that the ‘allosteric effect’ in molecular self-assemblies should also relate to the change of function triggered by conformation. This was achieved when the coordinating amphiphile TTC4L was triggered to self-assemble with metal ions (Fig. 10).¹³⁵ TTC4L has a coordinating head which is linked to a terthiophene end group with a 1,4 oxy-butyl spacer. There is a twisting angle of 156° between the terthiophene plane and the butyl group for the energy minimized TTC4L. However, this angle, together with the planarity of the terthiophene group, changes upon binding to different metal ions. For instance, the twisting angle is changed to 116°, 149° and 134° upon coordinating with Ag⁺, Ca²⁺, and Pd²⁺, respectively. These different conformations allow TTC4L to pack adaptively, where the intermolecular distance between the terthiophene groups varies. Because the emission of terthiophene is highly dependent on the intermolecular separations, each self-assembled structure thus displays distinct emissions. For example, TTC4L–Ag self-assembled into microspheres with green emission, TTC4L–Ca formed microscopic flowers with

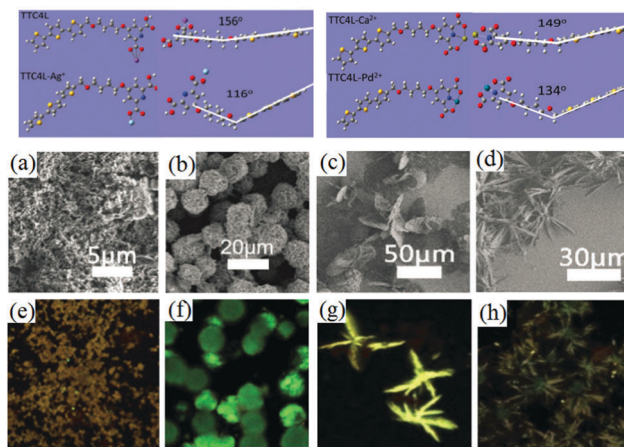


Fig. 10 Metal ion triggered conformational change of TTC4L and the resulting self-assembled structures with distinct emissions. (a–d) The SEM image for TTC4L, TTC4L–Ag, TTC4L–Ca, and TTC4L–Pd, respectively, (e–h) the CLSM image of (a–d). Copyright © 2016 Royal Society of Chemistry.

yellow emission, and TTC4L–Pd packed into star anises with yellow-green emission. Clearly, binding of metal ions at the hydrophilic head of TTC4L has triggered the change of emission performance of the terthiophene groups at the chain end through conformational changes. This is in high analogy with the allosteric effect of proteins or DNA, where binding a ligand at one site will result in functional changes at a remote site through conformational changes. The coordination chemistry facilitated allosteric self-assembly is expected to be an efficient approach to control the self-assembled structures and their functions.

2.3.2 Temperature dependent coordinating self-assembly.

Recently, amphiphilic molecules with multidentate coordinating sites are gaining increasing attention in the construction of molecular self-assemblies. Because it allows multimode coordination, temperature can play a very important role that dictates the final structures and the resultant function.

The coordinating amphiphile perylene tetracarboxylate (PTC) in Fig. 11 has a planar conjugated skeleton. At the lower temperature of 25 °C, the intermolecular coordination between PTC and Ni²⁺ leads to extension of the coordinating system along the long axis of PTC, which finally results in microbelts with lengths over several micrometers. However, PTC in this coordination mode is not planar, which is disadvantageous to minimize the energy of the system *via* π–π stacking. In contrast, at a higher temperature of 60 °C, the PTC–Ni undergoes intramolecular coordination. This results in PTC being in a much planar conformation thus facilitating their π–π stacking.¹³⁶ As a result, the PTC–Ni self-assemble into much shorter nanorods, which further self-assemble into microspheres to minimize the surface energy. XRD measurements revealed that the diffraction peaks for the microspheres are much sharper than that for the microbelt, confirming the presence of better molecular stacking in the microspheres. It is interesting to find that the microspheres can be used as effective adsorbents to remove dyes from water, whereas the one-dimensional microbelts display excellent conductivity.

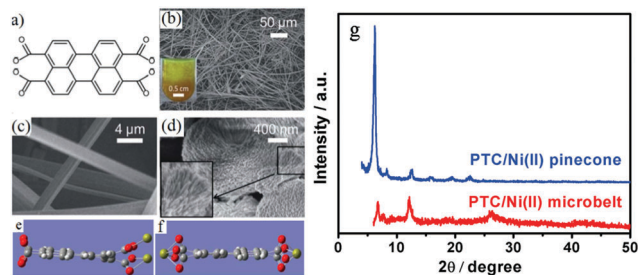


Fig. 11 (a) Scheme of the chemical structure of the perylene tetracarboxylate ion (PTC). SEM images of micro-belts (b and c) from a 1 mM PTC/2 mM Ni(II) mixture incubated at 25 °C for 24 h, and (d) pinecone structures from a 1 mM PTC/2 mM Ni(II) mixture incubated at 60 °C for 24 h. The insets in (b) and (d) are the photos of the yellow precipitates and the enlarged view of the selected section, respectively. (e) Is the molecular modeling of coordination that occurred at the PTC : Ni = 1 : 2 system at 25 °C; (f) is the modeling for the PTC : Ni = 1 : 2 system at 60 °C. (g) Is the XRD pattern of the PTC–Ni(II) microbelts (red line) and pinecone structures (blue line). Copyright (b and c) © 2014 Royal Society of Chemistry.

2.3.3 Concentration dependent self-assembly. Many coordination processes are reversible, especially those formed with carboxylate groups,^{103,137} which is in clear contrast with the inert coordination that behaves just like covalent bonding. The goodness of the reversible coordination allows the fabrication of responsive materials, especially self-healing hydrogels.^{138–142} On the other hand, the reversible coordination also facilitates the formation of dynamic self-assembled structures which highly depends on concentration. An elegant example can be found in the concentration dependent supramolecular network illustrated in Fig. 12a.¹⁴³ The planar tris-terpyridine ligand forms a bis-rhombus at high concentrations above 12 mg mL⁻¹ but a tetrahedron at low concentrations of less than 0.5 mg mL⁻¹. In between these two concentration regimes a mixture of the two self-assembled structures is formed. This observation opens an unexpected door to unusual chemical pathways under high dilution conditions. In a recent study in our lab, different concentration regimes were found to have drastic impact on the coordination stoichiometry between PTC and Ni, hence the self-assembled structures. This further resulted in a significant difference in a series of properties, such as conductivity, gas capture, and thermo-responsiveness.

Concentration dependent coordination is general for reversible coordination polymers, which is usually considered a drawback for their material process if no ionic interactions are introduced. However, this feature can also be employed in a positive way, such as in the promotion of the folding of polypeptides.¹⁴⁴ In the example shown in Fig. 12c, the polypeptide carries positive charges at acidic pH so that it forms random coils. Upon charge neutralization, such as addition of a base, a negatively charged polyelectrolyte (sodium polystyrene sulphate, PSS), or the reversible coordination polymer Zn–L₂EO₄, it tends to fold. However, perfect folding can only occur when the charges were neutralized with the dilute Zn–L₂EO₄ coordinating system. This is because at low concentrations, Zn–L₂EO₄ exists in the form of small rings, which can adjust their conformation aptly when complexed with the polypeptide through ionic interaction.

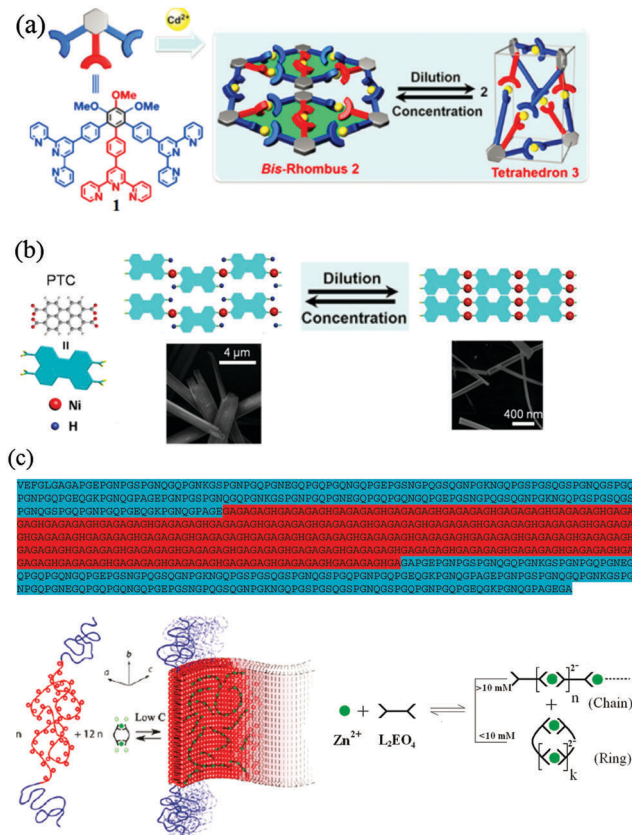


Fig. 12 (a) Self-assembly of tris-terpyridine building block **1** gives either a bis-rhombus **2** or a tetrahedral structure **3** depending on the concentration. (b) The schematic illustration of the possible molecular packing of PTC/Ni at high and low concentrations and the SEM images of the corresponding self-assembled structures. (c) Folding of polypeptide facilitated by the concentration dependence of the dynamic coordination polymer of Zn–L₂EO₄. Copyright (a) © 2014, American Chemical Society. Copyright (c) 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In this way, the folding of the polypeptide is not interfered. In contrast, the bulky PSS may entangle with the polypeptide, which interferes with the hydrogen bonding inside the polypeptide. As a result, disordered domains always exist. Nevertheless, we expect that the concentration dependent dynamic feature of coordination chemistry can be employed to facilitate self-assembly in an adaptive way.

3. Physical processing pathway dependent self-assembly

In addition to supramolecular approaches in the control of the kinetics of molecular self-assembly, the physical processes, such as solvent condition, evaporation, or crystallization, can also be very effective, especially for block copolymers or bulky molecules. Müller *et al.*¹⁴⁵ and Mai and Eisenberg⁸ have conducted excellent works in controlling the self-assembled structure of various block copolymers through solvent dependent pathways. On the other hand, Tang *et al.* found that the bulky propeller-shaped molecules often display physical processing

pathway dependent self-assembled structures and emissions. These molecules show negligible luminescence but strong fluorescence in the dry or self-assembled state. This is now well known as the AIE (aggregation induced emission) phenomenon.¹⁴⁶ In a fast process, the molecules can hardly arrange into spatially favored twisted conformations, so that they have a much more 'planar' topology and emit 'redder' lights, while in a slow process, they can take time to arrange into a much twisted conformation which gives out 'bluer' emission.^{147,148} Generally, the physical parameters that influence the self-assembled structure and emission of AIE fluorogens include solvent quality, evaporation or crystallization conditions.

3.1 Solvent quality facilitated self-assembly of AIE fluorogens

The solvent quality is a determinative factor that dictates the aggregating state of the 'solute'. In good solvents, the solute exists in the form of individual molecules, while with decreasing quality of the solvent, the 'solute' tends to aggregate. In a very poor solvent, the aggregation is very quick so that they have no time to orient and assemble, and thereby they form amorphous aggregates. In between the extremely good and poor quality, one can expect a slow aggregation of the 'solute', which allows the molecules to orient regularly. Thus, by manipulating the solvent quality one can control the kinetics of molecular self-assembly. For instance, the AIE fluorogen **1** forms nanoparticles in the 10/90 THF-water mixed solvent due to the fast aggregation, whereas it steadily self-assembles into helical nanofibers in 40/60 THF-water media (Fig. 13). In line with the different structures, the emission property also changes: the nanoparticles display a peak centered at 480 nm, whereas for the nanofibers the peak is blue shifted to 455 nm. This is because the AIE fluorogens self-assemble slowly in a better solvent (40/60 THF-water),

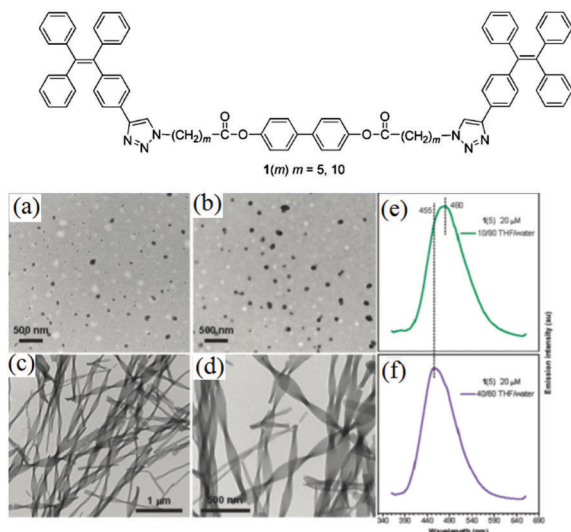


Fig. 13 TEM images for the nanoparticles of (a) **1** ($m = 5$), (b) **1** ($m = 10$) formed in 10/90 THF-water aqueous media and (c) and (d) the helical ribbons in 40/60 THF-water media upon standing for 6 h. (e and f) Normalized fluorescence spectra corresponding to the two systems with varied solvent composition. Copyright © 2012 Royal Society of Chemistry.

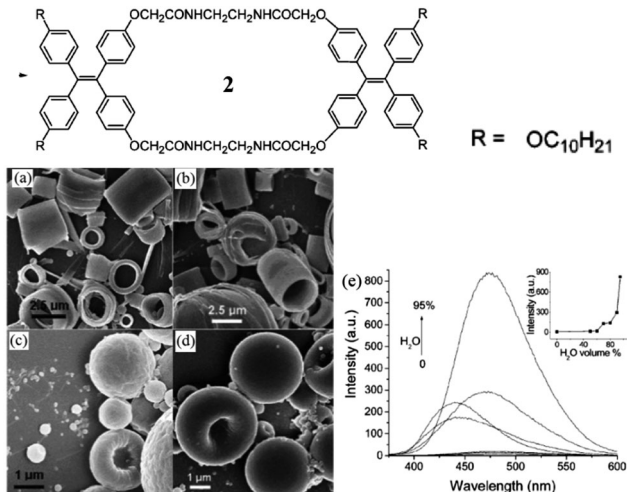


Fig. 14 SEM images for the self-assembled structure of **2** in THF-water media with water fractions of 70%, 80%, 90%, and 95%, respectively. Left is the variation of the fluorescence spectra with increasing water fraction. Copyright © 2012 Royal Society of Chemistry.

which allows them to adopt a twisted conformation to minimize the steric effect. In contrast, the molecules in a non-solvent environment (10/90 THF-water) aggregate quickly and the time scale is not sufficient to orient. As a result, the AIE fluorogens take a relatively planar conformation which produces a redder emission.

Most AIE dyes display such solvent dependent self-assembly and emission shift. For instance, the TPE amide macrocycle **2** can self-assemble into microtubes and hollow spheres in the THF/water environment as the water content is 70% and 95%, respectively (Fig. 14).¹⁴⁹ In between these two solvent compositions, such as the 80% and 90% water system, the hollow spheres coexist with the nanotubes. Meanwhile, the emission maximum is found to shift from 450 nm for the nanotubes to 470 nm for the hollow spheres. This is in line with the expectation: decreasing the solvent quality leads to faster aggregation where less twisting of the molecules occurs.

3.2 Natural evaporation facilitated self-assembly

Some AIE fluorogens don't easily self-assemble in the dispersed state, but well-defined supramolecular assemblies can be formed upon evaporation.^{150–154} For instance, upon slow evaporation of the THF/ethanol solution of BTPE, crystalline microfibers, which are several hundred microns in length and several microns in diameter, are formed.¹⁵⁵ The fibers can also grow on a quartz plate when the plate is immersed in the dye solution. After solvent evaporation, fibers with lengths up to several millimeters are readily formed, which can be observed even with naked eyes. The fibers can further self-assemble into thicker rods, as exemplified by the optical image shown in Fig. 15. The micro wires are highly luminescent, emitting an intense blue light upon photoexcitation with quantum yield of **1**, which enables construction of light-emitting diodes.

Evaporation also induces the self-assembly of chiral modified AIE molecules.^{38,40,41} Upon conjugation of sugar or amino groups with an AIE molecule, chiral AIE fluorogens can be fabricated.^{150–152,154}

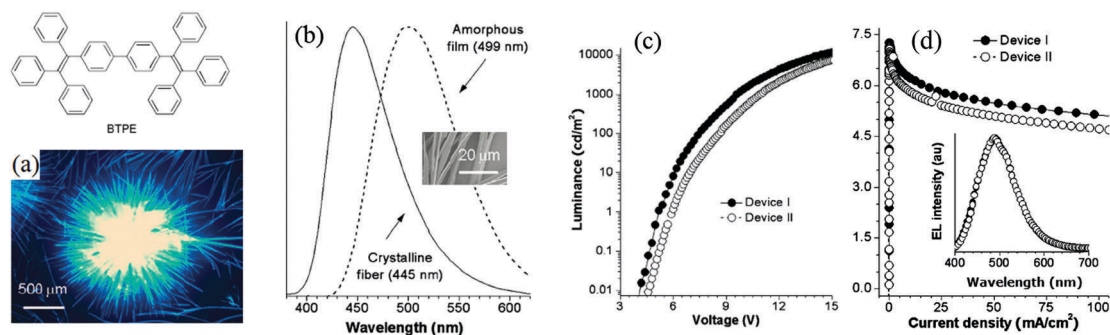


Fig. 15 (a) The intensively luminescent crystal fibers self-assembled from slow evaporation of the THF solution of BTPE. (b) The fluorescence spectra of the BTPE crystalline fiber and amorphous film. (c) The luminance vs. voltage and (d) current efficiency vs. current density in the BTPE-based multilayer light-emitting diodes with a device configuration of ITO/NPB/BTPE/TPBi/Alq3/LiF/AL. The (BTPE, Alq3) layers in devices I and II are (20 nm, 30 nm) and (40 nm, 10 nm) in thickness, respectively. The inset in (b) and (d) is the SEM image of the crystal fibers and the current density vs. emission wavelength, respectively. Copyright © 2010 Royal Society of Chemistry.

They are nonemissive in good solvents, but can slowly self-assemble into one-dimensional helical nanoribbons upon evaporation. Fig. 16 shows a typical evaporation induced helical ribbon formed with TPE-DVAL. The homogeneous solution of TPE-DVAL is CD silent, whereas the helical ribbons display a strong CD signal, suggesting the formation of helical ribbons have produced symmetry breaking structures. Indeed, the helical ribbons display circular polarized luminescence (CPL) behavior with an emission dissymmetry factor (g_{em}), which is defined as $g_{em} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the intensities of the left- and right-handed polarized emissions in the range of -3.5×10^{-3} to -5.2×10^{-3} , indicating that it is a promising candidate for high-tech applications.¹⁵⁰

3.3 Space confined evaporation facilitated self-assembly

Space confinement has a great impact on the evaporation induced self-assembly, just as it does for self-assembly in solutions.⁵² Compared with natural evaporation, the confined

space, such as in the channels of microfluids, has higher saturated vapor tension, which slows down the solvent evaporation process. This gives molecules enough time to reorient and self-assemble, thus leading to an enhanced packing order. For instance, the chiral AIE molecule **3** can always form helical nanofibers under different evaporation conditions. All these helical nanofibers are CD active. However, the efficiency of the CPL, generally evaluated by the emission dissymmetry factor g_{em} , is found to be extremely high (-0.32) in the micro-channels. In contrast, the g_{em} values for the same molecule under other evaporation processes are only -0.12 , -0.08 , and -0.17 – -0.13 , for the suspended aggregates, the film obtained by natural evaporation of its solution on a quartz substrate, and the solid dispersed in a polymer matrix, respectively (Fig. 17).¹⁵³ Since the g_{em} for organic molecules is often in the range of 10^{-5} – 10^{-2} , the value of -0.32 is two orders higher, which indicates that by controlling the kinetics of the self-assembly, one can achieve very promising optical materials that display excellent CPL properties.

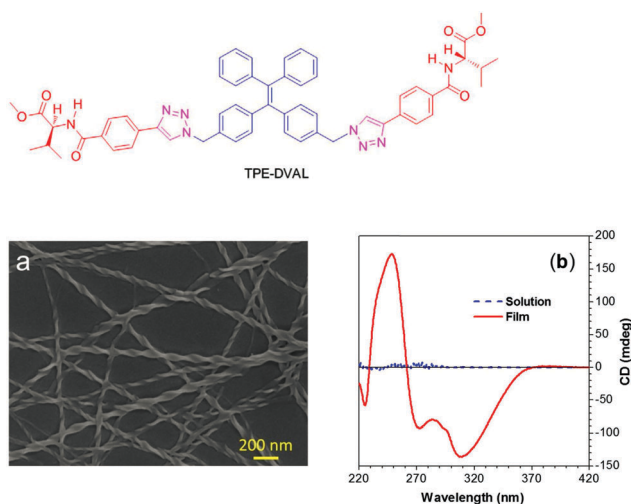


Fig. 16 Evaporation induced helical ribbon self-assembly of TPE-DPAL, which displays enhanced CPL behavior when the self-assembly occurs in the channels of the microfluid. Copyright © 2016 Nature Publishing Group.

3.4 Crystallization facilitated self-assembly

The formation of crystals can be viewed as the self-assembly of molecules into a highly ordered state. In appropriate cases, controlling the kinetics of crystallization can also lead to different molecular packing. A representative example can be found in the polymorphs of the racemic THP dyes **1**, **2**, and **3** (Fig. 18). They form fatter crystals at room temperature, whereas form narrower ones at 4 °C. The polymorphs obtained at different temperatures are attributed to the formation of different pairs of racemic THPs in the crystals. For the crystals formed at 4 °C, where the kinetic trap determines the potential energy, SS or RR pairs of the THPs are formed which further pack into narrower crystals, such as the structure of **1c**, **2c⁰**, **3b** and **3c**. However, at room temperature, the *S* and *R* forms don't have enough time to find their colleagues and thus form *RS* pairs. The conformations of these pairs are different, which further result in different crystal morphologies, and hence drastically different excitation and emission spectra. We expect

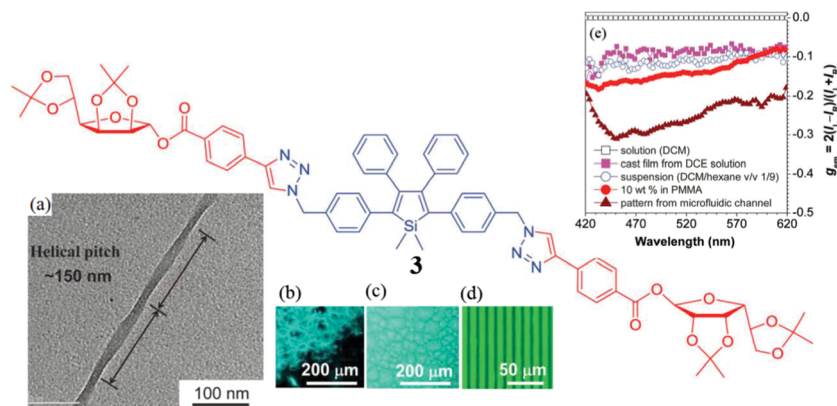


Fig. 17 (a) TEM image of the evaporation induced helical ribbons of **3**. (b–d) Fluorescence microscope images under UV excitation of **3**: (b) natural evaporation of DCE solution, (c) dispersion in the PMMA matrix (10 wt%), and (d) evaporation of DCM/toluene solution in microfluidic channels on quartz substrates. (e) Plots of the CPL dissymmetry factor g_{em} versus wavelength for **3** existing in different formats. Copyright © 2012 Royal Society of Chemistry.

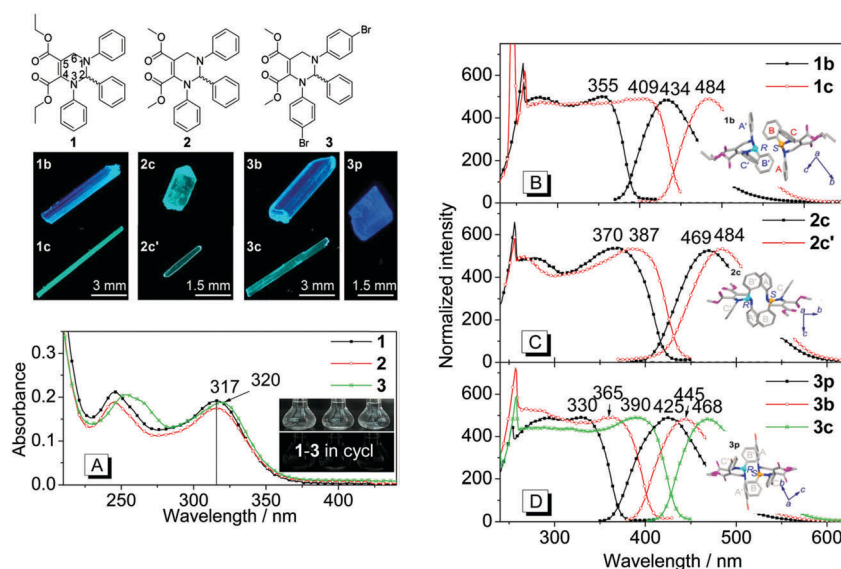


Fig. 18 Molecular structures of the racemic THPs **1–3** and their polymorphs under UV light (350 nm). **1b** and **1c** represent the blue- and cyan-fluorescence polymorphs of **1**; **2c** and **2c'** represent different cyan-fluorescence polymorphs of **2**; **3b**, **3c** and **3p** represent the blue-, cyan- and purple-fluorescence polymorphs of **3**, respectively. (A–D) Optical properties of THPs **1–3**. (A) Absorption spectra of **1–3** in cyclohexane solutions (1.0×10^{-5} M). (B–D) Excitation (left) and emission (right) spectra of the polymorphs of **1–3**, respectively. Excitation and emission spectra were detected by emission and excitation at the peak wavelengths marked in (B–D). Insets in (A) are THPs **1–3** in cyclohexane solutions under daylight (top) and UV light at 365 nm (bottom). The insets in (B–D) are the molecular packing modeling of **1b**, **2c** and **3p**. Copyright © 2015 Royal Society of Chemistry.

that such self-sorting crystallization can be a protocol to selectively fabricate desired functional materials.

4. Perspectives and conclusions

It is clear that the kinetically controlled supramolecular self-assemblies can provide elaborate structural and functional diversities when the equilibrium ones fail to do so. First of all, through controlling the kinetics of the self-assembling units, supramolecular systems can be entrapped in different states in the energy landscapes (Fig. 1). Switching between these states

allows fabrication of smart materials. Secondly, the kinetic control also makes it possible to capture molecular self-assembly in its deformation state, which enables mimicking biological behaviors occurring in nature. Thirdly, kinetic control allows generation of new self-assembled structures, which opens up an additional avenue toward materials science. These benefits are no doubt the important development of equilibrium supramolecular self-assembled systems, thus representing the new trend in the field of molecular self-assembly studies.

However, compared with the well-studied equilibrium molecular self-assemblies, the kinetically controlled self-assembly is still in its infancy. Because formation of the kinetically

controlled self-assembly requires rather specific conditions, it is difficult to generalize the protocols of fabrication. Despite these difficulties, it is crystal clear that both supramolecular approaches and physical processing pathways are effective in producing kinetic traps. In the case of supramolecular approaches, competition between different non-covalent interactions is the origin of the kinetic traps, whereas for the physical processing pathway approaches, many factors intertwine together, but they are generally effective for bulky molecules. Since there are diversified non-covalent interactions and rich physical processing possibilities in addition to those discussed in this article, the space for controlling the kinetically trapped supramolecular self-assemblies is really huge.

Among various possibilities, we expect that controlling the conformation of the self-assembling units can be a very attractive approach that leads to diversified supramolecular self-assemblies with distinct functions. It is gradually recognized that the molecular arrangement dictates the microstructure and the intermolecular interactions determine the material performance of a supramolecular self-assembling system. Because molecular conformation is the fundamental element that leads to diversified packing and interactions, control over it is expected to be a general rule that is applicable to various molecular self-assembling systems. Many of the examples given in this review actually are related to conformational changes, such as the allosteric self-assembly triggered by coordination chemistry, and the solvent or crystallization induced self-assembly of propeller-shaped AIE fluorogens. Even in the electrostatic self-assembly, the confinement of excess charges in the core of the PIC micelles is related to the entangled chain of the polyelectrolytes.

Furthermore, steric confinement of both the self-assembling units and the systems seems very effective in leading to kinetically trapped self-assemblies. The free motion of the molecules can be disturbed, which thus changes their pathway of assembly. The enhanced dissymmetry factor in the CPL performance is a convincing example. Since biological systems are all confined spaces, the self-assembly of biomolecules thus has to adapt to the local room. In this regard, creating confined spaces in the self-assembling process will be very challenging.

Most self-assembling systems in nature are in non-equilibrium states and evolution of the structure and functions occurs continuously this inspires us to believe that kinetically controlled self-assembly will lead the development of supramolecular materials. How to achieve control and how to establish such kinetically trapped systems are the main challenges facing us. With such prospects, it is our hope that this review will accelerate the advancement of the kinetically controlled supramolecular self-assemblies which possess novel and fascinating structures and properties, as well as innovative high-tech applications.

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