

## Self-assembly and properties of low-dimensional nanomaterials based on $\pi$ -conjugated organic molecules\*

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*Abstract:* Building supramolecular architectures with well-defined shapes and functions is of great importance in materials science, nanochemistry, and biomimetic chemistry. In recent years, we have devoted much effort to the construction of well-defined supramolecular structures through noncovalent forces such as hydrogen bonding,  $\pi$ -stacking, metal–ligand bonds, and hydrophilic and hydrophobic interactions, with the aid of functional building blocks. The morphologies and their physical properties were studied, and new methods for the construction of one-dimensional nanoscale structures have been developed. In this review, we summarize our recent studies on the design and synthesis of the supramolecular systems, as well as the physical properties of nanoscale structures.

*Keywords:* self-assembly; supramolecular architectures; low dimension; properties; methods.

### INTRODUCTION

One of the most fascinating subjects in areas such as materials science, nanochemistry, and biomimetic chemistry is concerned with the creation of supramolecular architectures with well-defined shapes and functions. Both covalent and noncovalent chemistry play important roles in this creativity. Self-assembly of molecules through noncovalent forces including hydrogen bonding,  $\pi$ -stacking, metal–ligand bonds, hydrophilic and hydrophobic interactions, and van der Waals forces has great potential for creating well-defined supramolecular structures. Much effort has been devoted to mimicking the molecular architectures of functional assemblies, including nanoscopic DNA and proteins to macroscopic viruses and bacteria, and much success has been gained in the design of a variety of artificial supramolecular architectures of different sizes, shapes, and functions [1–6].

The design and self-assembly of organic molecules to form functional suprastructures is the main goal of supramolecular chemistry. During the past decades, the control of the size, shape, and crystal structure of solid-state materials has become one of the most highly energized research areas for understanding their profound impact on chemical and physical properties [7–9]. Self-assembly of nanometer-sized building blocks into ordered architectures at interfaces is believed to be an appropriate approach for efficient preparation of long-range ordered molecular aggregates, creating possible im-

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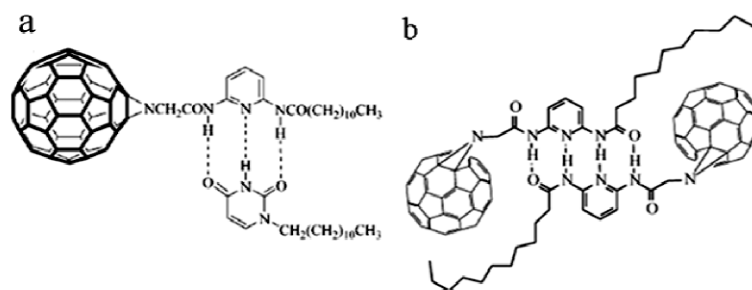
portant materials with novel properties [10–12]. Hence, in the construction of self-assembly building blocks, purposeful design and the introduction of functional groups play an essential role.

In recent years, our laboratory has designed and constructed many targeted supramolecular structures with the aid of functional building blocks, such as [60]fullerene, perylenebisimides, porphyrins, and so on. [60]Fullerene and its derivatives are well-known novel electropool  $\pi$ -systems and three-dimensional acceptors that have been widely studied for the construction of the third dimension of efficient electron-transfer model systems [13–16]. Perylene bisimides, with outstanding chemical, thermal, and photochemical stability, have been extensively studied as organic semiconductors in electronic and optical applications [17–24]. Porphyrins have remarkable photo-, catalytic-, electro-, and biochemical properties, and the self-assembly of porphyrin derivatives has attracted considerable attention in recent years [25–28]. The introduction of molecular recognition motifs into these building blocks, such as hydrogen bonding,  $\pi$ – $\pi$  stacking, electrostatic interactions, and metal–ligand bonds, offers an easy way to access well-defined arrays with novel photo- and electronic properties [29–34]. In this paper, we summarize our studies on self-assembly systems in the past few years, and focus on the design and properties of the functional assembly systems. As a matter of fact, in the construction of supramolecular systems, many kinds of weak interactions cooperate and coordinate to give rise to subtle structures. Usually, we focus on the leading interaction. In the first part of the review, hydrogen-bonding assemblies are the subject of our discussion. In the second part,  $\pi$ – $\pi$  stacking supramolecular systems are discussed. In the third part, the interactions of hydrophilic and hydrophobic in the self-assemblies are studied. In the fourth part, we focus on functional assemblies constructed by the weak interactions of metal–ligand. And in the fifth part, novel methods for construction of one-dimensional nanoscale structures are discussed.

## HYDROGEN-BONDING ASSEMBLIES

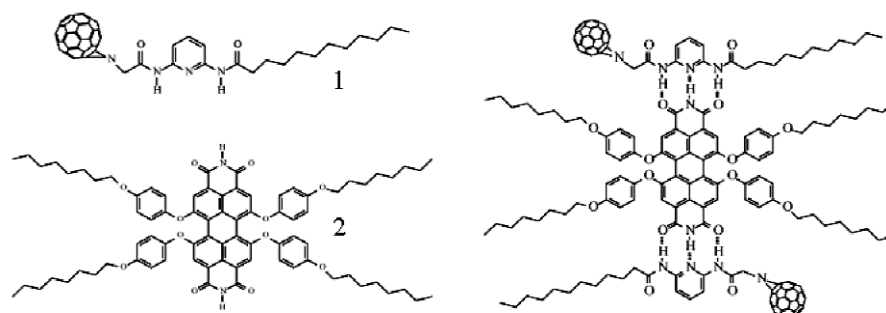
Control of hydrogen bonding, because of its directionality and specificity, has attracted much attention for the design of various molecular assemblies [35–38]. Well-defined nanosized aggregates should be very useful for the development of novel functional materials and nanoelectronic devices. Meanwhile, energy- and electron-transfer processes have also been investigated in the assembled supramolecular systems, through the interaction of hydrogen bonds [39,40]. Hydrogen bonding is one of the most promising methods to fabricate a controllable molecular array and shape for efficient intermolecular energy and electron transfer between donor and acceptor units [41].

[60]Fullerene has low reorganization energy in electron processes, which leads to a significant acceleration of the charge-separation step and effective deceleration of the energy-wasting charge-recombination step [42–47], and thus offers the promise of applications as excellent photoelectric materials. As mentioned above, hydrogen bonds provide an efficient way to build molecular arrays with efficient intermolecular energy and electron transfer between donor and acceptor units. Much effort has been put into designing the self-assemblies of fullerene derivatives by hydrogen bonds into zero-, one-, and three-dimensional supramolecular architectures. Guldi [48] and Hummelen [49] reported, respectively, the synthesis and photophysical properties of the first quadruple hydrogen-bonded fullerene dimer. Soon thereafter, we reported two assemblies of supramolecules, as shown in Fig. 1, based on [60]fullerene with three-centered intermolecular hydrogen-bonding bonds, and attempted to analyze the influences of the different structure features on the interactions and stability of molecular aggregates [50,51]. Well-defined supramolecular ball-like structures were constructed in our work, which could be of interest for the construction of three-dimensional nanomaterials for future applications as photoelectric devices.

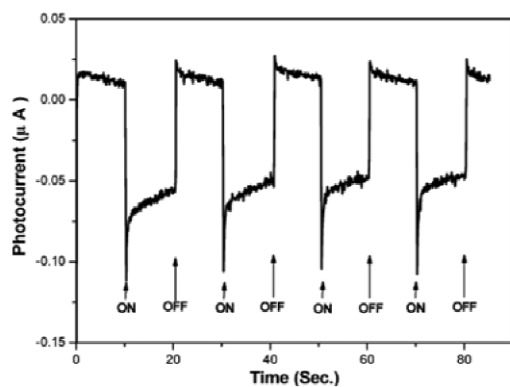


**Fig. 1** Structure of the self-assemblies.

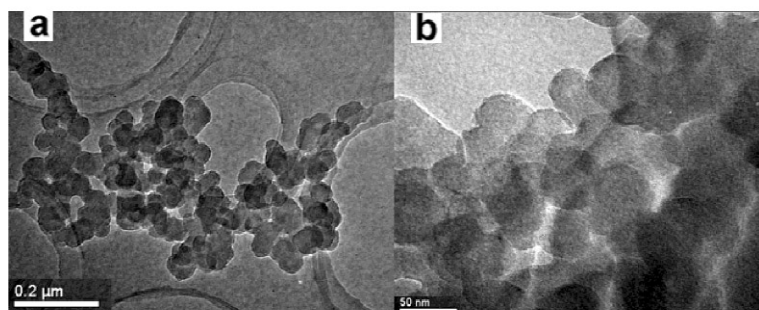
In the construction of suprastructures, functionalization is the main goal. Many organic systems have been developed which exhibit reasonable light-harvesting efficiencies, and many of them show the ability of the energy and electron transfer. These systems provide effective means to convert photons to electrons [52–54]. Usually, these dyads could be constructed by composing a donor and an acceptor which could be used as artificial light-energy harvesting systems [55], the donor and the acceptor are mostly linked in a covalent way. [60]Fullerene has been widely utilized as a three-dimensional electron acceptor, while porphyrins and pyrene are used as donors. In our previous work, hydrogen-bonding supramolecular assemblies containing [60]fullerene have been constructed, to explore the expected outstanding physical and chemical properties. In order to improve the optical and electronic properties of the supramolecular assemblies, a novel self-assembly of [60]fullerene derivative **1** as acceptor and perylene bisimide **2** as donor was designed and characterized (Fig. 2) [56]. The response of on-and-off cycling of the **1**·**2** film is prompt and reproducible, and the photocurrent stability is rather good in the system during the monitored time, as indicated in Fig. 3. The ball-like suprastructure (Fig. 4), assembled through hydrogen-bond and  $\pi$ – $\pi$  stacking, could be of importance for future studies on three-dimensional nanomaterials applied in the field of photoelectric devices. In the following research, in order to further study the photo-electron devices and investigate some good candidates, pyrene was chosen as an electron donor complexed with [60]fullerene acceptor [57]. A barbituric acid-substituted [60]fullerene derivative **3** and dipyrrenemethyl-substituted melamine **4** were designed and used to build a supramolecular system through hydrogen bond in organic solvent, and the possible self-assembled structures are shown in Fig. 5. Nanoparticles and nanorods could be fabricated by a self-assembly process, by virtue of hydrogen-bonding and  $\pi$ – $\pi$  stacking interactions. Importantly, self-assembled **3**·**4** film could produce a steady and prompt cathodic photocurrent response (Fig. 6). The new supramolecular system can be expected to find potential applications in photovoltaic solar cells.



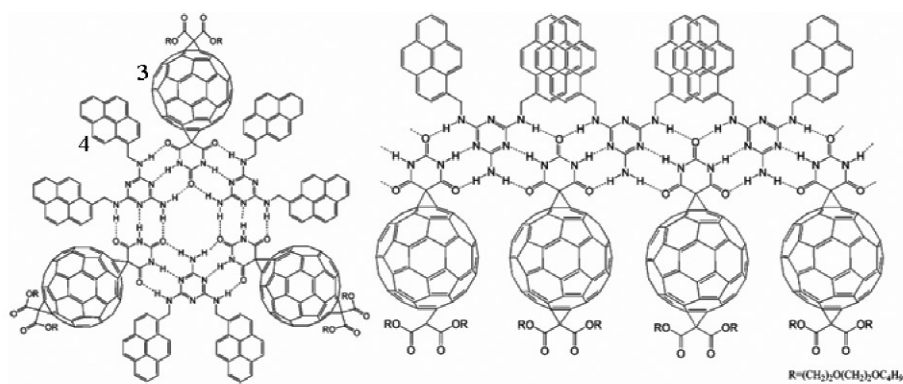
**Fig. 2** Suprastructure of self-assembly of [60]fullerene derivative **1** with perylene bisimide **2** by hydrogen bonding.



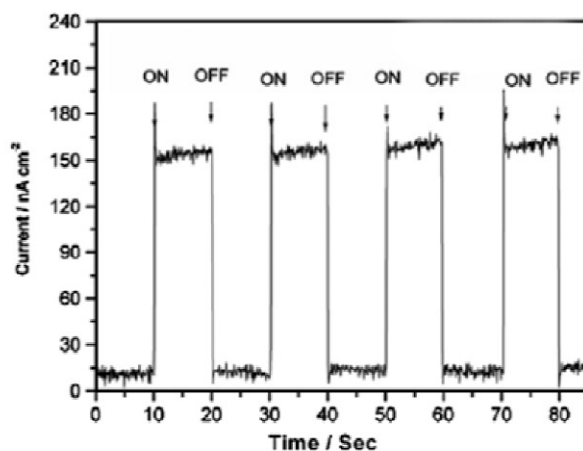
**Fig. 3** Time dependence of the photocurrent response of the self-assembly film ([1]:[2] = 2:1).



**Fig. 4** (a) TEM images of assemblies ([1]:[2] = 2:1). (b) High magnification of the TEM image.

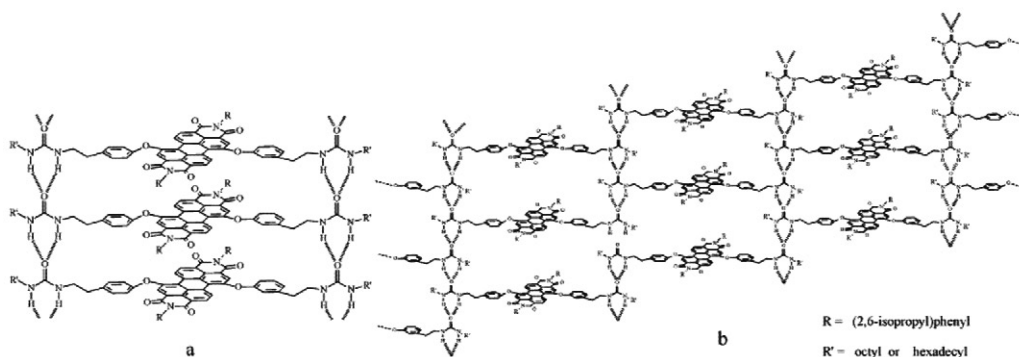


**Fig. 5** Possible structure arrangements of self-assembled supramolecular system.

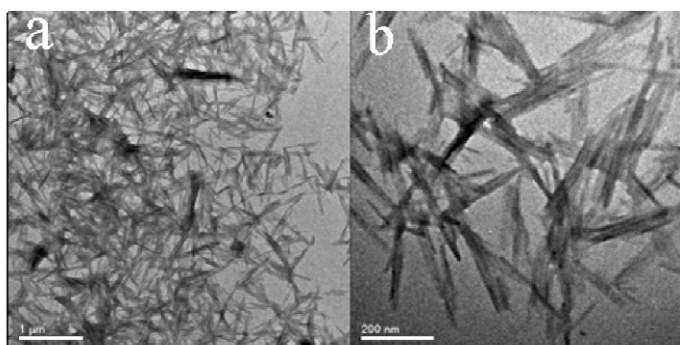


**Fig. 6.** Time dependence of the photocurrent generation of the self-assembled film ([3]:[4] = 1:1) upon the irradiation of  $70 \text{ mW cm}^{-2}$  white light in  $0.5 \text{ M KCl}$  solution.

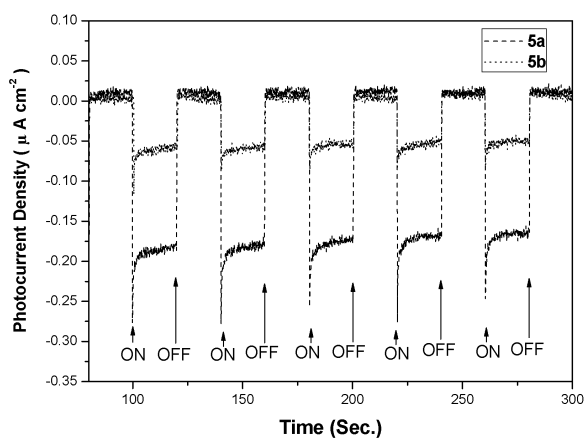
Previously, we discussed the functional supramolecular self-assemblies containing a donor (perylene bisimide or perylene derivative) and an acceptor ([60]fullerene derivative), and studied the intermolecular energy and electron transfer between donor and acceptor units bonding through hydrogen bond, which may indicate the potential application in photo-electron devices. Otherwise, we also constructed bis-urea compounds with perylene bisimides that self-assemble into well-defined nanoscale structures: supramolecular systems of a perylene derivative **5** that self-assemble into nanoscale rods (Fig. 8) [58], and a system of a perylene derivative containing double components, bis(2,6-diacylaminopyridine) units **6** and a perylene bisimide **7**, that self-assemble into well-defined long fibers. Both the systems assemble through three-centered intermolecular hydrogen-bonding interactions together with  $\pi$ - $\pi$  stacking interactions of perylene rings, as shown in Figs. 7 and 10, respectively. The photocurrent measurements showed that the self-assembled films of **5** could produce steady and rapid anodic photocurrent responses (Fig. 9), while a steady cathodic photocurrent response was detected in the self-assembled **6**·**7** film (Fig. 11). This constitutes a first study of the photoinduced electron-transfer property of self-assemblies on the basis of the hydrogen-bond-induced nanostructure system. Therefore, these perylene bisimides modified with three-centered hydrogen-bond units, with the capability for self-assembly through hydrogen bonds, are promising candidates for inclusion in photoelectric devices based on organic semiconducting layers.



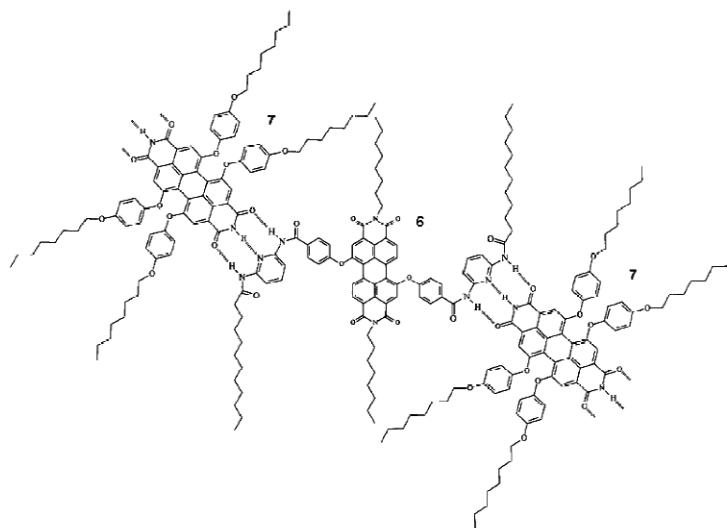
**Fig. 7** Possible suprastructure arrangements of **5**.



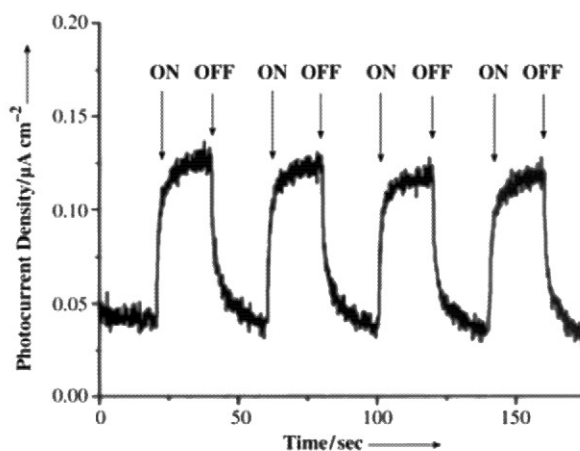
**Fig. 8** (a) TEM images of self-assembled **5a** in *p*-xylene. (b) High magnification of TEM image.



**Fig. 9** Time dependence of the photocurrent responses of the self-assembled **5a** and **5b** films upon irradiation by  $100 \text{ mW cm}^{-2}$  white light in  $0.5 \text{ M KCl}$  solution.



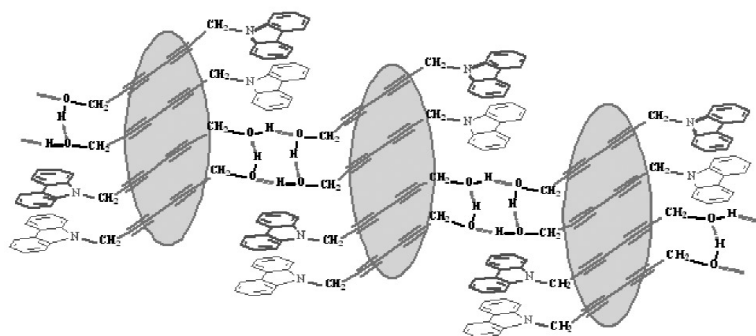
**Fig. 10** Suprastructure of the self-assembly of **6** with **7**.



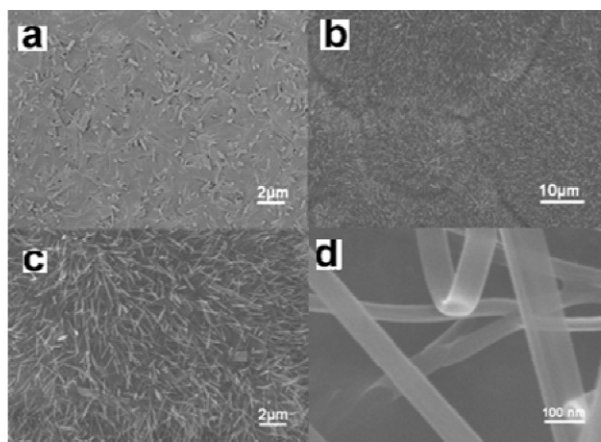
**Fig. 11** Time dependence of the photocurrent response of the self-assembled 6·7 film upon the irradiation of  $32 \text{ mW cm}^{-2}$  white light in  $0.5 \text{ M KCl}$  solution ( $[6]:[7] = 1:2$  in  $\text{CHCl}_3$ ).

### CONSTRUCTION OF $\pi$ - $\pi$ STACKING ASSEMBLIES

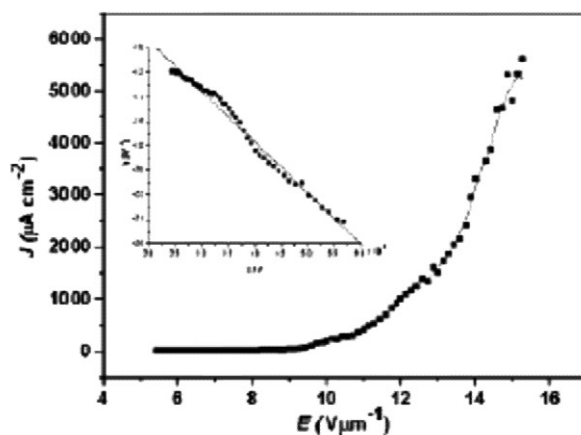
Much effort has been devoted to synthesizing low-dimensional structures of conjugated polymers in view of their extraordinary optical and electronic properties [61–64]. The self-assembly of a conjugated polymer for forming different morphology is currently attracting considerable attention [65–67]. The self-assembly of organic molecules with the assistance of noncovalent forces, such as hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions, which lead the orientations of molecules in an ordered style, provides an efficient method for creating nanoscopic and mesoscopic structures. We sought to develop a complementary strategy for self-polymerization and self-assembly to produce new aggregate nanostructures of a conjugated polymer. Two key conditions are required for the direct formation of polymer aggregate nanostructures by the mentioned associated effect: (i) the monomer is able to undergo self-polymerization by UV light; (ii) the self-polymerization polymer could be self-assembled by noncovalent forces. Accordingly, we designed a small molecule 6-carbazol-9-ylhexa-2,4-diy-1-ol (CYDIOL) containing diacetylene units which could be self-polymerized by UV light [60]. We suggest that the CYDIOL molecules possess the capability for forming low-dimensional nanostructures by the associated effects of self-polymerization and self-assembly (Fig. 12). Our study has shown that the association of self-polymerization and self-assembly induces the production of well-defined polydiacetylene nanowires which show excellent field-emission properties (Figs. 13 and 14). Our work presents a new concept for fabricating conducting polymer nanowires, and it may have great potential for further applications of fabri-



**Fig. 12** Probable self-assembly suprastructure arrangements of CYDIOL.



**Fig. 13** Self-assembled nanostructures on copper foils: (a) without polymerization process (b) and (c) large area of ordered polydiacetylene nanowires (d) with some entangled polydiacetylene nanowires.



**Fig. 14** Field-emission  $J$ - $E$  curves of the polyCYDIOL nanowires. The inset shows the Fowler–Nordheim plot.

cating supramolecular materials-based conducting polymers for various fields, such as sensors, optical materials, and nanotips in field-emission devices.

In the study of supramolecular materials, larger macrocyclic aromatic molecules such as hexabenzocoronene [68,69] have received much attention due to their stronger  $\pi$ - $\pi$  stacking ability and improved emission behavior. A series of molecules with polycyclic aromatic structures was designed and studied in our laboratory (Fig. 15). We first find that introduction of  $\pi$ -rich or  $\pi$ -poor heterocycles significantly affects not only the physical properties of the perylene-3,4:9,10-tetracarboxylic acid diimides (PTIs) but also the molecular self-assembly behavior [70]. The  $\pi$ -rich **8** was able to self-assemble into one-dimensional nanostructures as a result of strong  $\pi$ - $\pi$  stacking (Fig. 16), while the  $\pi$ -poor **9** lacked the one-dimensional self-assembly capability. These findings offer us the potential to control the self-assembly capability of the  $\pi$ -conjugated perylene core through decoration with  $N$ -heterocycles, and also the way to control the aggregate structures further by tuning of the solvents. In the study of larger macrocyclic aromatic molecules, another novel compound with an enlarged aromatic system carbazole-coronenediimide-carbazole triad (CPC) was designed and synthesized by routine methodology [71]. The molecule is able to self-aggregate into unique sandwich diamond-like structures in saturated chloroform solution; in further self-assembly, it can form diamond structures with holes as shown in



Fig. 17.  $\pi$ - $\pi$  Stacking was supposed to be the main interaction of the self-assembling process. What is more, CPC emits fluorescence faintly in polar solvents ( $\text{CH}_2\text{Cl}_2$  or tetrahydrofuran) but intensively in aggregates, which may permit the potential application in construction of optical devices.

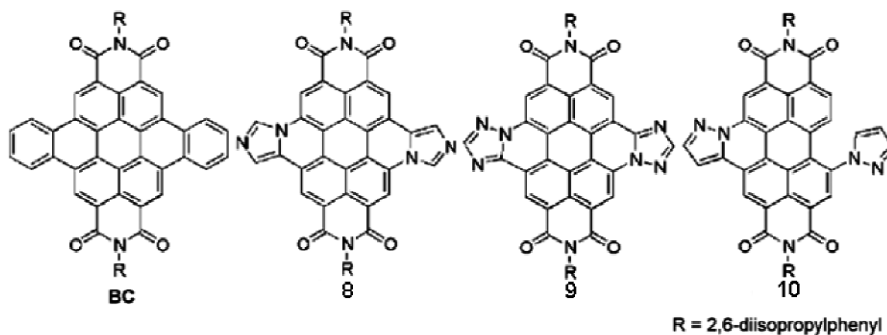


Fig. 15 Chemical structure of PTI derivatives.

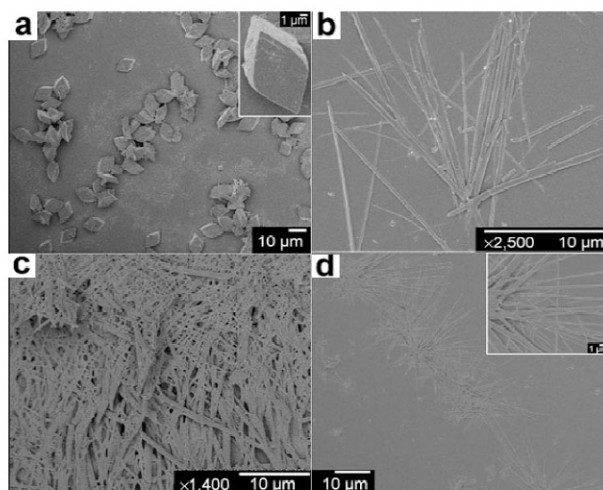


Fig. 16 SEM images of **8**: (a) rhombic structures precipitated from  $\text{CH}_3\text{CN}$ , together with nanofibers (gold stained) cast from (b)  $\text{CH}_3\text{CN}$ ; (c) pyridine; and (d) a nanofiber network from an *n*-hexane/pyridine mixture.

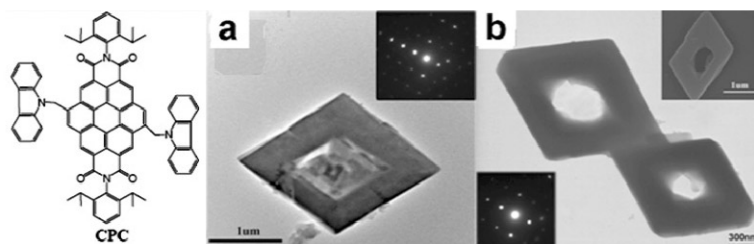
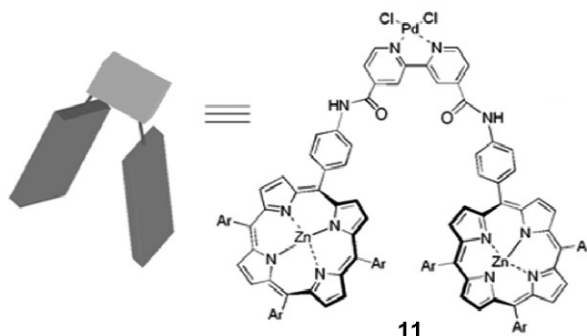


Fig. 17 Chemical structure of CPC and TEM images of CPC nanostructures with different morphologies. (a) TEM image of sandwich diamond, inset: electron diffraction image. (b) TEM image of diamond with hole obtained after the diamond was sonicated; upper inset: SEM image; bottom inset: electron diffraction image.

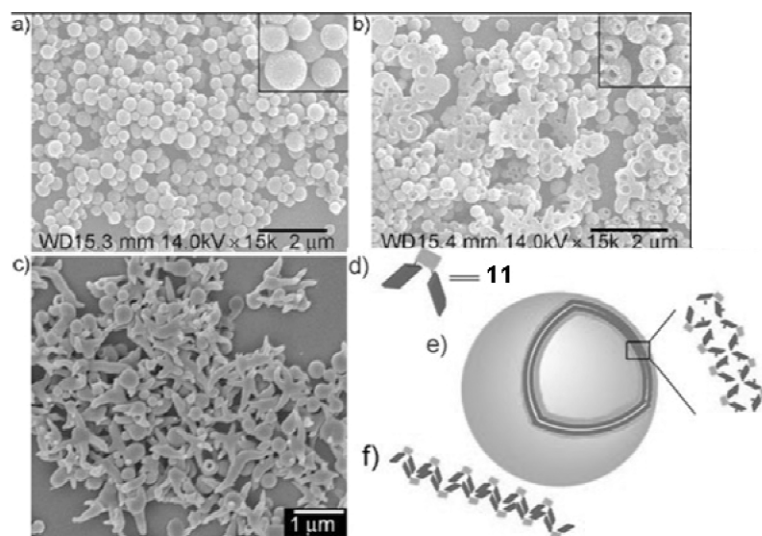
## ASSEMBLIES LEADING BY HYDROPHILIC AND HYDROPHOBIC INTERACTIONS

The self-assembly of amphiphilic molecules has attracted special attention for a long time, not only for its importance in theoretical studies, but also for its crucial role in biological systems and daily life. Usually, amphiphilic molecules contain hydrophilic and hydrophobic parts at the same time. Because of the different solubility of the hydrophilic and hydrophobic parts, the amphiphilic molecules tend to self-assemble into well-defined structures, and the morphologies may differ in hydrophilic and hydrophobic solvents, to an extent that even the control over specific shapes, dimensions, and pattern formation of supramolecular organization becomes possible. Our laboratory has designed many amphiphilic molecules which have been constructed into functional supramolecular structures.

Various efforts have been made to prepare inorganic and organic hollow capsules, because this kind of nanoscale structure displays unique structural, optical, and surface properties that may lead to a wide range of applications, such as capsule agents for drug delivery, filters, coatings, chemical catalysis, or templates for functional architectural composite materials [72,73]. Porphyrins have remarkable photo-, catalytic-, electro-, and biochemical properties, therefore, the self-assembly of porphyrin derivatives has attracted considerable attention in recent years, especially for the amphiphilic porphyrins, which have been exploited in the preparation of simple micelles, fibers, and vesicles [74–76]. We designed a new V-sharp amphiphilic zinc porphyrin derivative **11**, as shown in Fig. 18, which could self-assemble into vesicles with a diameter of 200 nm [77]. These vesicles could be controlled to assemble into hollow capsules and worm-like structures, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirmed the controllable process (Fig. 19). The different amphiphilic properties of the porphyrin moiety and bipyridine-Pd unit in a mixed chloroform/methanol solvent, and the coordination of methanol to zinc porphyrin molecules were the driving forces for formation of vesicles with multi-bilayer structure.

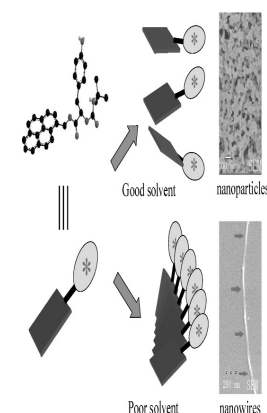


**Fig. 18** Chemical structure of compound **11**.



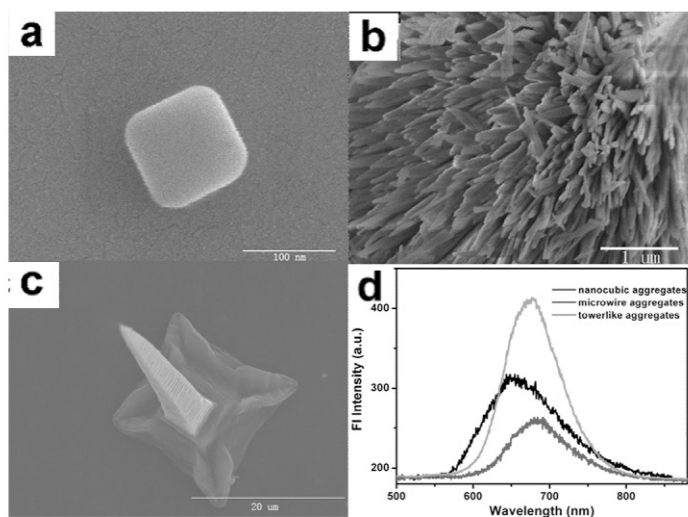
**Fig. 19** Morphology transition of the vesicle heated (a) at 60 °C (b) at 80 °C. (c) SEM image of worm-like aggregates of **11**. (d) Schematic representation of compound **11**. (e) Schematic representation (f) of compound **11** vesicle formed in methanol with a close-up of the vesicle membrane showing the proposed multilayer structure. The blue dots represent the ligated  $\text{CH}_3\text{OH}$ . (f) Schematic representation of an interdigitated bilayer structure.

The self-assembly of small molecules into a chiral supramolecular architecture on a nanoscale are also of great interest, due to their potential applications in studies of biological sensors, information storage technology, light energy conversion, and optical devices [79]. Many researches have been performed on incorporating chiral moieties [80,81] or achiral molecules [82,83] in self-assembling organic molecules with the objective of forming chiral supramolecular structures. In our laboratory, a chiral small-molecule *L*-{2-(4-hydroxy-phenyl)-1-[(pyren-1-ylmethyl)-carbamoyl]-ethyl}-carbamic acid *tert*-butyl ester (PLBT) was designed and synthesized, which could self-assemble into ball-like particles and helical nanowires with a perfect structure (Fig. 20) by employing different solvents [84]. The chiral molecule assembled through hydrophilic and hydrophobic interactions and  $\pi$ - $\pi$  stacking.

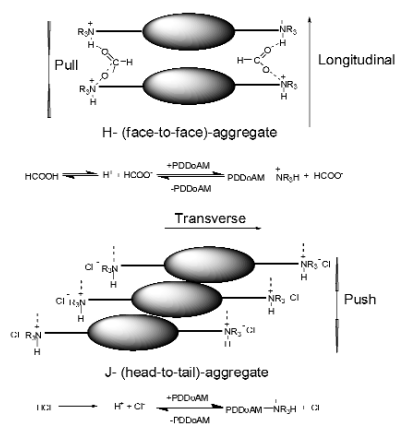


**Fig. 20** Structure of PLBT and schematic representation of self-assembly of compound PLBT.

In the construction of well-defined nanoscale structures, the specific orientations of the final self-assemblies and the dependences of their morphology and optical properties on assembled conditions deserve more attention. Much effort has been devoted to designing functional building blocks, such as oligo(phenylene vinylene) (OPV), porphyrins, and perylene tetracarboxylic diimide derivatives, for the excellent electric and optical properties. On our side, we constructed an amphiphilic perylene derivative **PDDoAM** possessing a hydrophobic core and cationic tails [85], which could be controllably constructed into nanocubic (zero-dimensional), micro-sheet aggregates (one-dimensional) and tower-like architectures (three-dimensional) (Fig. 21) [86]. We systemically studied the dependences of the morphology and orientation of water-soluble **PDDoAM** on the choice of acids (Fig. 22). Because of the variability and flexibility in materials synthesis and nanostructures preparation, the red emission fluorescent organic nano- and micromaterials (Fig. 21d) constructed by us may hold the higher potentials in biological labels, light-emitting diodes, and optical sensors.



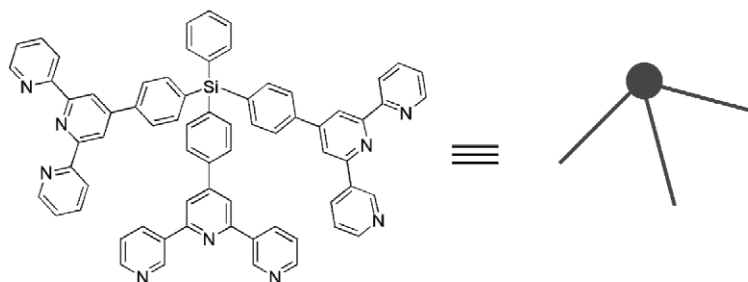
**Fig. 21** SEM images of **PDDoAM** aggregates formed during evaporation of HCOOH solution (a), HCl solution (b) by fast deposition method. (c) SEM images of **PDDoAM** aggregates formed during evaporation of HCOOH solution by slow deposition method. (d) Photomicrographs of **PDDoAM** aggregates formed during evaporation of HCOOH solution (the scale was 50  $\mu\text{m}$ ).



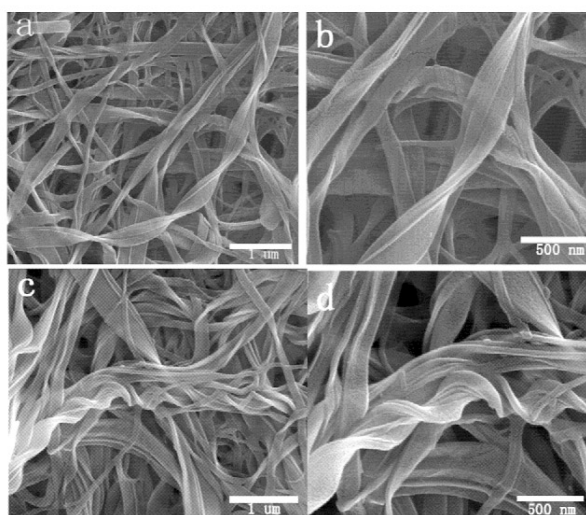
**Fig. 22** Proposed H-aggregate (left) and J-aggregate modules (right).

## ASSEMBLIES CONSTRUCTED BY THE METAL–LIGAND INTERACTIONS

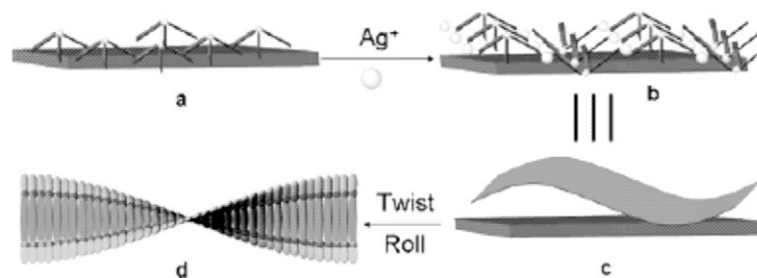
The coordination-driven motif offers an alternative to the biological motif allowing for unique design features in the assembly of discrete supramolecular species. The most important point is the greater directionality offered by metal–ligand coordinative bonding compared to weak electrostatic and  $\pi$ – $\pi$  stacking interactions or even hydrogen bonding [87]. Metal template strategies, using the coordination of d-metals to oligopolydentate ligands, lead to homopolymetallic helicates, ladder, grids, rings, cages, and knots [88]. On our side, we constructed a metal-directed self-assembly of perylene-tetracarboxylic diimide connected to ligand  $H_3L$  through different spacers, which provided the opportunity to elucidate the impact of the metal ions and spacers on the photophysical properties of perylene-tetracarboxylic diimide and on the nanostructure of these self-assembled photofunctional materials [89]. Moreover, the metal–ligand interactions play an important role in the chiral supramolecular system because of its high directionality [87]. As one of the most known coordination systems, successful assemblies of metal-oligopyridine helices from chiral ligands [90] have been well studied. We also constructed chiral supramolecular assemblies from a novel achiral tripodterpyridine ligand, in which three terpyridine components were introduced into respective sites of silicon core to form tripodal configuration (Fig. 23) [91]. And chiral coordination architectures were constructed by the self-assembly of the achiral tripod-ligand with silver(I) cations (Fig. 24), and the possible formation mechanism of the superhelix was exhibited in Fig. 25. An effective approach of designing ligands of specific configuration was to study the effect of “structure property” in the molecular recognition process.



**Fig. 23** Chemical structure of tripod-terpyridine ligand and the proposed “umbrella-shaped” module.



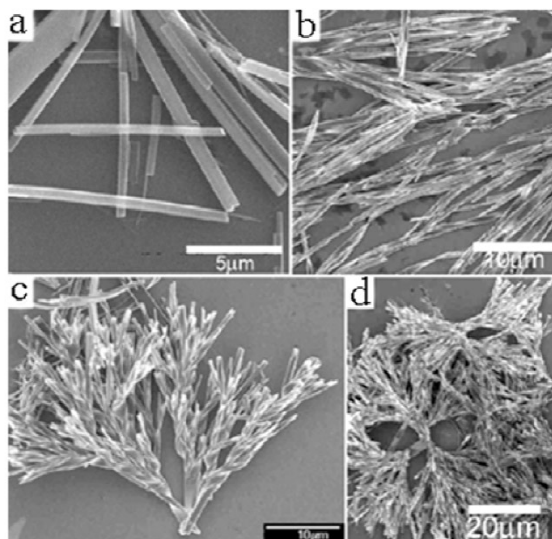
**Fig. 24** SEM (on Pt substrate) images of helical strips of  $[Ag_3L]$  in different views and magnitude.



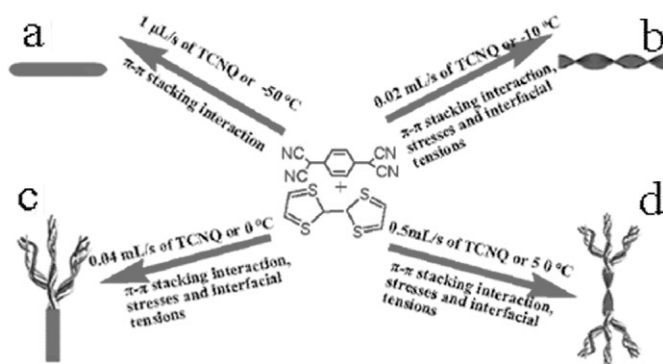
**Fig. 25** Proposed formation mechanism of the superhelix: free ligand molecules in dichloromethane (a), original flat strips with Ag (I) cations (b, c), and twisted strips induced by continuous tilt of coordination planes between ligand and Ag (I) cations (d).

### OTHER METHODS FOR CONSTRUCTION OF ONE-DIMENSIONAL NANOMATERIALS

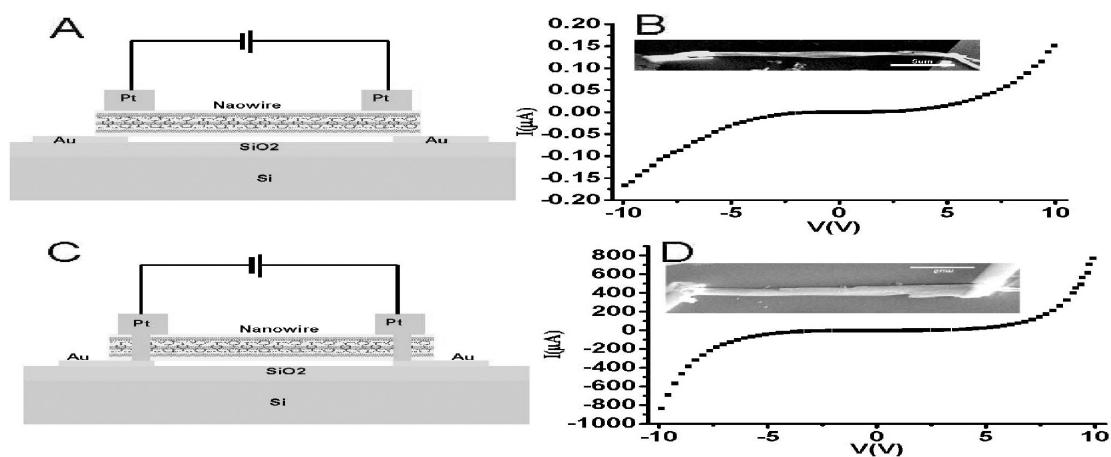
One-dimensional nanomaterials possess highly unusual physical properties. Despite great efforts and application of various methods, the synthesis of one-dimensional organic nanomaterials [92–97] remains poorly to be studied, and only a few successful examples have been reported [98]. However, we have developed a novel and generic technique to fabricate the controlled morphology-synthesis of organic molecular materials in restricted dimensions, with controlled size and shape [99,100]. In the following study, we controllably prepared straight nanowires to helical nanowires and complicated helical dendrite structures from charge-transfer complex tetrathiafulvalene -7,7',8,8'-tetracyanoquinodimethane (TTF-TCNQ) (Figs. 26 and 27) by two-phase methods in a creative way [101–103]. *I*-*V* measurements of an individual nanowire indicated that the TTF-TCNQ helical nanowire is conducting along the *b*-axis, with a conductivity of  $\sim 295 \text{ S cm}^{-1}$  (Fig. 28). The synthetic procedure offers a general approach for producing controlled organic conductor/semiconductor nanowires, and the technique has been applied to the synthesis of AgTCNQ/CuTCNQ nanowires in a two-phase system of acetonitrile/hexane in



**Fig. 26** SEM images of TTF-TCNQ complex morphologies as prepared at the drip rate of (a)  $1 \mu\text{l s}^{-1}$ , TTF-TCNQ nanowires; (b)  $0.02 \text{ ml s}^{-1}$ , TTF-TCNQ helical nanowires; (c)  $0.04 \text{ ml s}^{-1}$ , TTF-TCNQ helical dendrites; (d)  $0.5 \text{ ml s}^{-1}$ , TTF-TCNQ complicated helical dendrites.



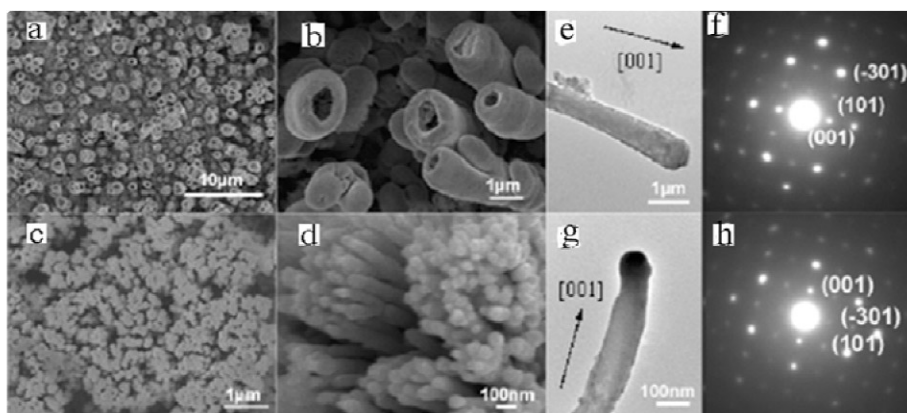
**Fig. 27** Shape control of TTF-TCNQ nanostructures: (a) TTF-TCNQ nanowires; (b) TTF-TCNQ helical nanowires; (c) TTF-TCNQ helical dendrites; (d) TTF-TCNQ complicated helical dendrites.



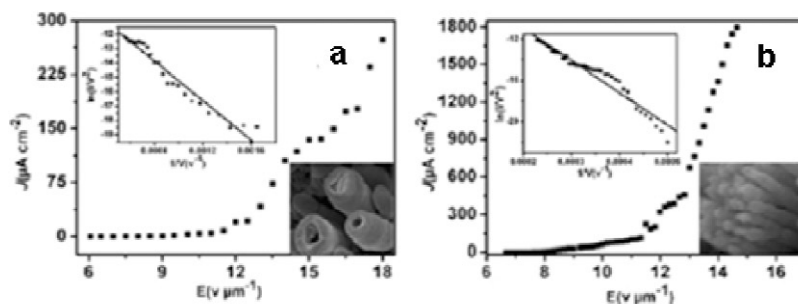
**Fig. 28** (a) Schematic diagram and SEM image of the device with contacts made on the side wall of the TTF-TCNQ helical nanowire; (b)  $I$ - $V$  characteristic of the corresponding nanowire in (a). (c) Schematic diagram and SEM image of the device with contacts made on the ends of the TTF-TCNQ helical nanowire (open ends were milled with FIB). (d)  $I$ - $V$  characteristic of the corresponding nanowires in (d).

our experiments. This approach should have an outstanding potential for ordered nano- and microscale architectures for advanced devices.

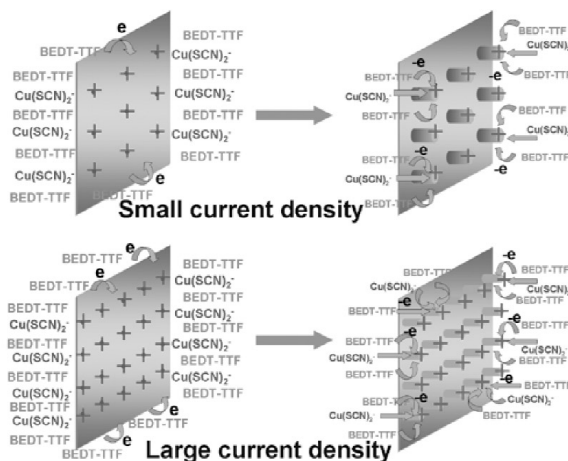
In the construction of one-dimensional nanoscale architectures, the controllability and order are always of high interest. In our experiments, we demonstrated a simple and convenient electrocrystallization approach, for fabricating the free-standing nanorod arrays in a large area of the organic charge-transfer complex of  $\kappa$ -(BEDT-TTF) $_2$ Cu(SCN) $_2$  supported on Pt foil and indium tin oxide (ITO) glass (Fig. 29), which showed an excellent field-emission property (Fig. 30). The morphologies of the  $\kappa$ -(BEDT-TTF) $_2$ Cu(SCN) $_2$  nanorod arrays can be controlled by adjusting the growth of current density as indicated by Fig. 31. These results suggest that these nanorod arrays could be useful in electron field emitters, and the fabricating approach should be indicative of potential applications in demonstrating efficient field-emission materials.



**Fig. 29** (a) Lower-magnification and (b) higher-magnification SEM images of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorods **c**. (c) Lower-magnification and (d) higher-magnification SEM images of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorods **d**. (e) TEM image and (f) SAED pattern of a typical  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorod **c**. (g) TEM image and (h) SAED pattern of a typical  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorod **d**.



**Fig. 30** (a) Field-emission  $J$ - $E$  curve of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorods **c**; the inset depicts the corresponding Fowler–Nordheim (FN) plots and the SEM image of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorods **c**. (b) Field-emission  $J$ - $E$  curve of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorods **d**; the inset depicts the corresponding Fowler–Nordheim (FN) plot and the SEM image of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorods **d**.



**Fig. 31** Possible formation process of the  $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$  nanorod arrays under different current densities.



## CONCLUSIONS

This review summarizes our recent progress in building functional supramolecular architectures. We have focused on the construction of well-defined zero-, one-, and three-dimensional supramolecular assemblies with optic, electronic, and field-emission properties, which may indicate the potential applications in the various fields, such as sensors, optical materials, biosensors, biolabels, and nanotips in field-emission devices. The report also demonstrates the interdependence of physical properties, molecular design, and supramolecular architecture, and offers pointers to potential opportunities in supramolecular design. The novel methods for controllable construction of one-dimensional nanoscale structures by self-polymerization show outstanding potential applications in nanoscience.

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