Our research progress in heteroaggregation and homoaggregation of organic π-conjugated systems

Xin Deng1 | Xiaohui Yu1 | Jinchong Xiao1 | Qichun Zhang2

1 College of Chemistry and Environmental Science, Key Laboratory of Chemical Biology of Hebei Province, Key Laboratory of Medicinal Chemistry and Molecular Diagnosis, Ministry of Education, Hebei University, Baoding, P. R. China
2 Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong, P. R. China

Correspondence
Jinchong Xiao, College of Chemistry and Environmental Science, Key Laboratory of Chemical Biology of Hebei Province, Key Laboratory of Medicinal Chemistry and Molecular Diagnosis, Ministry of Education, Hebei University, Baoding 071002, P. R. China.
Email: jcxiaoicas@163.com
Qichun Zhang, Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong, SAR 999077, P. R. China.
Email: qiczhang@cityu.edu.hk

Abstract
Construction of crystalline homo/heteroaggregation at micro/nanometer level from organic π-conjugated systems is of great importance because the controllable morphologies (i.e., size, shape, and dimension) could provide diverse optoelectronic properties for different applications in the electrooptical devices. In this review, we summarize our recent progress in the self-assembly of micro/nanostructures of organic π-conjugated molecules via the heteroaggregation and homoaggregation strategies. We also discuss various factors (i.e., temperature, solvents, and surfactants) that affect the aggregation process through a surfactant-assisted reprecipitation method. Moreover, their physical properties and possible applications in electronics and biofields are illustrated.

KEYWORDS
arene, hetero/homoaggregation, organic device, photophysics, self-assembly

INTRODUCTION
The construction of controllable micro/nanostructures has attracted a lot of researchers’ interests due to their unusual properties different from their bulk forms and the possibility to be used as an important platform to unveil the regularity of fundamental science and potential technological applications.[1–4] The possible electrooptic devices with micro/nanostructures as active elements usually include photovoltaic cells, memories, laser, field-effect transistors (FETs), light-emitting diodes (LEDs) and displays, and logic circuits.[5–11] Compared with traditional electronics on the basis of inorganic materials, including silicon and gallium arsenide, the devices prepared from organic counterparts (especially for organic π-systems) have promising advantages, including low temperature processing, high flexibility, low cost, and so on.[12–15] Since mechanical flexibility of devices is very important owing to the potential preparation of the collapsible integrated circuits without sacrificing the optoelectronic properties, the composition, shape, size, surface modification, driving force, and the orientation of organic micro/nanoaggregates affect their optoelectronic properties to a significant extent. Thus, understanding these factors would give us a strong support to design new micro/nanostructures with desirable properties.

Organic micro/nanoaggregates can be divided into two types: homoaggregates and heteroaggregates. Homoaggregates are the particles fabricated from single component, while heteroaggregates are constructed from two or more different compounds. The research of homoaggregates mainly focuses on the size, shape, stacking modes, and electrical/optical properties.[16–18] In addition to these studies,
heteroaggregates also concentrate on the heterointeractions between different molecules as well as how the ratio and stacking modes of different molecules affect the performance of the as-prepared particles.\textsuperscript{[19–21]} Currently, the study on heteroaggregates is becoming more and more attractive due to the increasing opportunities to modulate the performance of the as-prepared materials.

Since the classical polycyclic aromatic hydrocarbons (PAHs), such as anthracene,\textsuperscript{[22]} pyrene,\textsuperscript{[23]} tetracene (TC),\textsuperscript{[24]} perylene,\textsuperscript{[25]} naphthalene diimides,\textsuperscript{[26]} perylene diimides,\textsuperscript{[27]} benzo[ghi]perylene,\textsuperscript{[28]} and fluorinated aromatics,\textsuperscript{[29]} have been widely employed as photoluminescent materials or n/p-type carrier-transfer compounds in diverse devices, it is our research interest in developing novel PAHs with diverse molecular structures as well as their micro/nanoaggregates, and further understanding their structure-property relationships. Besides, the replacement of sp$^2$ carbons of PAHs with heteroatoms (i.e., N, O, P) would create a new type of materials (namely, heteroacenes or heteroarenes) as important active elements in diverse organic electronics.\textsuperscript{[30–32]} Especially, the self-assembled micro/nanoarchitectures of PAHs and the potential applications in photovoltaic devices and biofields have attracted many researchers’ interests.\textsuperscript{[33–40]}

Herein, we systematically summarize our research advances on these compounds and will discuss them according to following parts: (1) Heteroaggregation. As one promising heteroaggregation platform, organic micro/nanocrystals have been demonstrated as an important model with definite growth direction, negligible defects, and the possibility to display diverse physical properties. Thus, deep understanding of these factors would further provide us some important guidelines to design and optimize novel organic semiconducting materials. In addition, since the different methods to prepare organic cocrystals might provide various aggregation morphologies with variable physical properties, some important fabrication strategies will also be introduced. And (2) homoaggregation. Developing new compounds and investigating their homoaggregation are always important and interesting. In this part, the fabrication and the related property studies of our novel PAHs-based homoaggregation are discussed. Finally, the summary and outlook of these topics are provided in the conclusion part.

**HETEROAGGREGATION**

**Cocrystals**

Organic cocrystals can be regarded as a unique and important category among organic materials and are usually obtained from two or more molecules via intermolecular weak interactions, including charge transfer interactions, π–π over-lapping, hydrogen bonds, and halogen bonds. Compared with single-component crystals, cocrystals present unpredicted and promising photochemical characteristic through synergistic effects. In addition, these materials exhibit tailored luminescence, multiphase, controllable size and morphology, and easy processability, which can miniaturize the devices and boost their development. The discovery of organic cocrystals can be dated back to 1844.\textsuperscript{[41]} The classical charge transfer complexes of tetraphiafulvalene or perylene and 7,7,8,8-tetracyanoquinodimethane were prepared, exhibiting high conductivity over a wide range of temperature in the 1970s.\textsuperscript{[42,43]} Subsequently, lots of groups focus on the construction, investigating their magnetic, optical, and electronic properties and testing the potential applications, including ferroelectrics, photovoltaic behavior, nonlinear optics, optical waveguide, luminescent response, and pharmaceutics.\textsuperscript{[33–35,44,45]}

Figure 1 lists a few representative acceptors and donors for the construction of cocrystals. Among these molecules, the planar coronene, in which one benzene ring surrounds with six benzene units, is a highly symmetric (D$_{6h}$) arene and has been widely selected as a model and the building unit for the construction of cocrystals and high conjugated molecules. In 2004, Siegrist et al. prepared the black needles of coronene-TCNQ,\textsuperscript{[46]} and the single crystal X-ray analysis suggested that the π-stacking distance between coronene and TCNQ in the sandwiched structure is 3.3 Å and the Child’s law mobility is about 0.3 cm$^2$ V$^{-1}$ s$^{-1}$. In 2015, the micro-rods of coronene-TCNQ cocrystals were fabricated and the FETs based on the as-prepared coronene-TCNQ microrod present an n-type behavior with a small threshold voltage of 0.7 V, $I_{on}/I_{off}$ ratio of 1 $\times$ 10$^5$, and the mobility of 0.02 cm$^2$ V$^{-1}$ s$^{-1}$, which is superior to the results of the similar device based on TCNQ.\textsuperscript{[47]} Beyond TCNQ as a coformer, other substituted TCNQs can also interact with coronene to form the charge transfer complexes.\textsuperscript{[48–52]} For example, owing to its lower LUMO (lowest unoccupied molecular orbital) energy level, F4TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) has been demonstrated to display a stronger electron-withdrawing ability than TCNQ. Moreover, the fluorine atom is beneficial to optimize and improve the mobility of organic field-effect transistors (OFETs). In 2015, the micro-rods of F4TCNQ cocrystals were prepared, exhibiting high conductivity over a wide range of temperature and showing excellent electronic properties compared to the similar TCNQ-based device.\textsuperscript{[48–52]}
stabilize the resulting cocrystals through the formation of intermolecular H···F weak bonds. In 2016, Kataeva and coworkers used two different methods (solution processing and vapor deposition) to prepare two charge transfer complexes of coronene-F4TCNQ with the different stoichiometry of 1:1:1 (solvated with acetonitrile) and 2:1[51] where, in the former cocrystals[49] coronene and F4TCNQ alternatively pack on each other to form the mixed-stacking columns and acetonitrile molecules locate at the channels between columns, while in the latter packing structure, two coronene molecules and one F4TCNQ molecule stack on each other with a face-to-face model.

In 2016, our group also reprepared the coronene-F4TCNQ cocrystals that was synthesized before by Yoshida et al.[40] (Figure 2), and both adopt triclinic space groups. The former exhibits an intermolecular distance of 3.24 Å between coronene and F4TCNQ, and the latter has the distance of 3.33 Å, suggesting the occurrence of strong π-overlapping. However, the inserted xylene in the latter complex leads to the increase of the interplanar distance (Figure 2).[53] The FETs based on individual single cocrystals exhibit the saturated electron mobility of 0.2 cm$^2$/Vs for the former, being close to the datum of pentacene (0.2 cm$^2$/Vs)[15] and the negligible transport behavior for the latter due to the loosen stacking and the blocking of electron transport caused the inserted xylene. As we know, both energy levels of LUMO and HOMO (highest occupied molecular orbital) of the cocrystals are mostly relevant to the energy levels of acceptor LUMO and donor HOMO, respectively. Thus, the electronic properties of the cocrystals can be controlled by proper molecular design with different LUMO of the acceptor and HOMO of the donor. Coronene has a HOMO energy level of −5.9 eV, while F4TCNQ has a LUMO energy level of −5.24 eV, being more negative than TCNQ (−4.23 eV).[54] In addition, the intramolecular H···F interaction is beneficial to stabilize the stacking pattern of the cocrystals. Consequently, coronene-F4TCNQ displays higher electron transport response than coronene-TCNQ.[47]

When TCNQ or its derivates were replaced by 1,2,4,5-tetracyanobenzene (TCNB, LUMO: −3.92 eV),[55] new cocrystals coronene-TCN were obtained via the solvent evaporation under ambient atmosphere (Figure 3) in 2017,[56] and their structure adopts the monoclinic space group (Cc) confirmed by single crystal X-ray analysis. More interestingly, when the crystals were heated from 30 to 42°C, then to 52, 54, and 68°C with a heating rate of 30°C/min, the initial cocrystals displayed a self-healing behavior during phase transition. In the cooling process, the similar phenomena were also observed. The single-crystal X-ray analysis of the crystals in two different phases indicated that during the phase transition, some certain molecular stacking columns had to flip and caused internal stress inside crystals. The cocrystals could release this stress through the crystal splitting at the same time. After the phase transition was completed, the split part came back and self-healed to become one single crystal again.

Continuing on this research direction, if TCNB was replaced with naphthalenetetracarboxylic diimide (NDI), coronene and NDI could not only form binary cocrystals in dichloromethane solution but also yield ternary cocrystals in THF solution (Figure 4).[57] Based on the density functional theory calculation, the Mulliken charge of coronene is 0.0388 and a pined to dipole moment is 2.37 D, indicating the charge transfer from coronene to NDI in the ground state. These cocrystals are one family member of smart stimulus-responsive materials, which display visible mechanochromic luminescent. In our research, we found that the fluorescence of these cocrystals is very sensitive to the mechanical forces, including smearing, grinding, and pressing, which can be used as security papers, mecanoso- and sensor and information displays. More importantly, the introduction of THF in ternary cocrystals (NDI-coronene)-THF can effectively impair the intermolecular interaction, leading to a sparse molecular network likewise. The escape and capture of THF molecules create high-contrast and reproducible nonvolatile haptic memory. Such phenomenon was also reported by Lei and Hu et al.,[58] where the grayish-green binary perylene-TCNB microrod could be completely transformed into red crystals (perylene-TCNB)-2THF, along with the crystal bending, when the microrod was exposed to THF vapor; while the red microrod could return back to grayish-green quickly when it is exposed to air. Coronene was also demonstrated to form cocrystals with other acceptors (i.e., PTCDI (3,4,9,10-tetracarboxylic-3,4,9,10-diimides), HAT(CN)$_6$ (3,4,5,8,9,12-hexazatriphenylene-hexacarbonitrile).[59–61]

The as-prepared materials displayed diverse properties, such as p-type, n-type, and ambipolar behaviors.
Figure 4  
(A) Chemical structures of donor (Coronene), acceptor (NDI), and tetrahydrofuran (THF) molecules, as well as the digital images of ternary cocrystal (NCT) taken under daylight and 365 nm UV irradiation. (B) Fluorescence images of the optical memory device with the reversible MCL behavior for NCD film (powder coated on a weighing paper). (C) Diagram of the transformation of molecular packing in the lattice under multistimuli: (i) Binary cocrystal of NDI-Coronene. Prepared from CH2Cl2; (ii) ternary cocrystal of NCT prepared from THF; (iii) DA complex (NCD) after escape of THF; and (iv) NCD complex with external pressure. Reproduced with permission: Copyright 2020, Wiley-VCH.

Besides strong acceptors, these conjugated molecular donors, such as anthracene (Ant) and coronene (Cor), could also form cocrystals with weak acceptors (i.e., octafluoronaphthalene (OFN)). It is widely known that suppressing the singlet-triplet conversion in organic electroluminescent materials is very challenging to tailor their optical properties. In 2018, we presented a promising strategy to address this through introducing molecular barriers to these conjugated lattices, where the donors anthracene and coronene have the optical energy gaps of $\sim 3.10$ and $2.76$ eV, while the weak-fluorescent acceptor OFN has a higher HOMO-LUMO gap of $\sim 3.78$ eV. The introduction of OFN can effectively inhibit electron exchange and intermolecular interaction among the fluorophores, being propitious to intersystem crossing. As shown in Figure 5, OFN molecules intercalate into the periodic packed structures of coronene and anthracene, which significantly reduces intermolecular interaction between neighboring PAH molecules and their electron exchange, resulting in the loss of triplet states. Thus, the as-prepared coronene-OFN and anthracene-OFN crystals have the quantum yields of $100 \pm 13\%$ and $100 \pm 5\%$, respectively, which are higher than the data of $5 \pm 5\%$ and $81 \pm 5\%$ in the pristine crystals, indicating that the as-formed cocrystals possess enhanced bright luminescence compared with OFN and the PAH chromophores.

Beyond anthracene and coronene, the intercalation of OFN as a molecular barrier into the packed structures of perylene (bandgap: 2.76 eV) and TC (bandgap: 2.56 eV) also hinders the electron coupling and intermolecular interaction. Generally, if the size of the high fluorescence cocrystals decreases to micro/nanoscales, these materials might have potential applications in bioimaging fields. Recently, we fabricated well-ordered heteroaggregates between weak-fluorescent OFN and other PAHs (Figure 6). Since OFN has been demonstrated to enhance the photoluminescence of coronene through total isolation of coronene molecules in space, it is logical to consider that it should also display the similar in the cocrystal of OFN-perylene. Upon the addition of PAHs THF solution into water containing biocompatible surfactant P123, perylene (Per), perylene-OFN, coronene, and coronene-OFN self-assemble into square sheets, particles, rods, uniform rods, respectively, at micro and nano scale. More importantly, the as-prepared nanoaggregates possess enhanced quantum yields, cellular permeability, less cytotoxicity, and cell imaging response.

Although OFN can easily form cocrystals with soluble PAHs in solution, it is very challenge to insert OFN molecules into the PAH matrices with poor solubility. Thus, how to grow organic cocrystals with solubility-mismatched ingredients, in which one of them has a poor solubility, is a notorious topic. Very recently, we developed a fascinating strategy (namely, liquid-assisted-grinding coassembly) to address this issue, where TC and OFN were chosen as model compounds.

Figure 5  
(A) Schematic of the electronic energies in the periodic cocrystalline structure. The blue arrows indicate the transition of the singlet emission. The orange arrows indicate singlet trapping via SSA. (B) Ant--OFN, Ant, Cor--OFN, and Cor absorptions in the crystal morphology. (C) PL spectra of the studied cocrystals and pristine crystals at 325 nm CW photoexcitation. (D) Time-resolved PL spectra of the studied cocrystals and pristine crystals using a 355 nm 5 ns-pulsed photoexcitation. The lifetimes refer to multiple decay components. [\tau] represents the average lifetime. Reproduced with permission: Copyright 2018, Wiley-VCH.
FIGURE 6 Cocrystallization schemes of Per/OFN MW (A) and Cor/OFN MW (B) and corresponding photos. The corresponding photographs of the five as-prepared powders (OFN crystals, Per MS, Per/OFN MW, Cor MW, and Cor/OFN MW) and the patterned “NTU” as well as their aqueous dispersions (can be considered as all-water dispersed fluorescent inks) under daylight (C) and 365 nm UV lamp on (D). Reproduced with permission: Copyright 2019, Springer Nature[63]

FIGURE 7 Illustrations of the ACQ effect of TC and the preparation of target TC-OFN cocrystals. The PLQYs of the TC solution (THF as a solvent, concentration: 0.1 mg mL$^{-1}$) and solid TC as well as the solubilities (in THF) of TC and OFN are indicated (left). Comparison between the common solution-processing method and the current LAGC strategy is illustrated (right). Preparation of target TC-OFN cocrystals using a TC/OFN ratio of 1:4 (right-top) compared with the cases of 1:2 (right-middle) and 1:1 (right-bottom), among which the 1:4 ratio is the optimal condition toward pure TC-OFN. Photos of the resultant pure TC-OFN powders in gram scale are shown. The schematic morphologies of different crystals (TC crystals in orange, OFN crystals in gray, and TC-OFN cocrystals in green) as well as their molecular stacking modes are also indicated, and the CCDC numbers of the TC crystal, OFN crystal, and TC-OFN cocrystal are 1,502,159, 177,726, and 1,990,854, respectively. Reproduced with permission: Copyright 2020, ACS[64]

(Figure 7).[64] This method has several advantages: (1) gram-scale preparation; (2) the simple and short grinding to retard the oxidation of unstable TC; (3) the highly green-emissive cocrystals with the quantum yield up to 13.75%; and (4) the aqueous cocrystal inks for luminescent paintings and ultra-transparent flexible films.

In another research, we found that the charge transfer complexes between pyrene and F4TCNQ/1TNCNQ/TCNQ could form through slowly evaporating their chloroform solutions. The structural analyses of the as-obtained single crystals suggest that all the crystals adopt the monoclinic system with different unit cell parameters (Figure 8).[65] All charge transfer complexes show weak ferromagnetic properties at room temperature, where pyrene–F4TCNQ complex is the strongest one with the saturation magnetization of $5.6 \times 10^{-3}$ emu/g, representing $4.8 \times 10^{-4}$ μB magnetic moment in every pyrene-F4TCNQ unit. This might be caused by three factors: (1) the spin density is apparent for the strongest charge-transfer system pyrene-F4TCNQ; (2) the shortest mean distance (0.328 nm) between molecular layers in pyrene-F4TCNQ makes it more easy for charge transfer; and (3) the calculated charge transfer value of 0.183 for pyrene-F4TCNQ does contribute to the magnetism. More interestingly, pyrene–F4TCNQ complexes have been demonstrated to display Cotton–Mouton response as well as the anisotropic magnetoelectric coupling effect.

To systematically examine the regulatory effects of acceptors on the cocrystals, a novel TMIQ (diindolodiazapentacene 8,8,18,18-tetramethyl-8,18-dihydropinololo[1,2,3-fg]indolo[3′,2′,1′:8,1]quinolino[2,3-b]jacridine) has been prepared and used it as a donor to complex with the commercially available benzoquin-o-analogs with different electron-withdrawing abilities (p-chloranil, CA; p-fluoranil, FA; tetracyanoquinodimethane, TCNQ) to afford cocrystals TMCA, TMFA, and TMTQ, respectively (Figure 9).[66] The DFT calculations indicate that TMIQ exhibits the HOMO energy level of $–4.82$ eV and FA possesses a LUMO energy level of $–4.50$ eV. In comparison, the resulted cocrystal TMFA shows the lower HOMO level of $–5.03$ eV and the elevated LUMO level of $–3.7$ eV, respectively. Meanwhile, a narrow bandgap of 1.6 eV is observed. All the results suggest that ππ charge transfer from TMIQ to FA occurs, leading to the rearrangement of the electron cloud and the formation of new hybridized orbitals. Similar findings are found for TMCA and TMTQ. To test their charge transport behaviors, the organic FET devices based on the cocrystals are constructed, and the results suggest that the devices based on a TMFA microrod present a hole-transport mobility of 0.54 cm$^2$/Vs, the devices based on TMCA display the solely hole transport of 0.11

FIGURE 8 Characterization of cocrystals. Crystal packing mode of pyrene–TCNQ (A) and pyrene–F4TCNQ, (B) (abbreviation: P-T and P-4F, respectively). (C) HRTEM of pyrene–F4TCNQ cocrystals. The inset is the image of SAED pattern of pyrene–F4TCNQ. (D) Solid state absorption spectra of pristine pyrene, F4TCNQ, and pyrene–F4TCNQ. Magnetic hysteresis loops of pyrene–TCNQ (E) and pyrene–F4TCNQ (F) at different temperatures. The down inset of (F) is temperature-dependent magnetization of pyrene–F4TCNQ. Reproduced with permission: Copyright 2018, ACS[65]
cm²/Vs, while TMTQ-based devices exhibit an electron-transport characteristic of 0.02 cm²/Vs, which is superior to the electron-transport performance of quinacridone (0.01 cm²/Vs).[15] All the findings infer that the cocrystals can provide more room to design and develop new optoelectronic materials.

Chemical reactions between micro/nanostructures

Besides the direct formation of cocrystals through solvent evaporation or grinding, the formation of cocrystals can also be realized through the chemical reaction between two different particles in water. In 2010, we first demonstrated that TTF (tetrathiafulvalene) microparticles and TCNQ microstructures could react each other in aqueous solution to form TTF-TCNQ nanowires (Figure 10),[67] confirmed by SEM images and the yellow-green-to-brown change in the solution color. The as-prepared semiconducting TTF-TCNQ nanowires can be employed as active elements in nonvolatile memory devices with the multiple write-read-erase-read cycles, indicating that the as-fabricated nanomaterials are stable.

Then, another aqueous chemical reaction between TCNQ particles and Ag nanoparticles was also explored in our group (Figure 11),[68] despite the fact that the Ag-TCNQ organic thin film was prepared by Benson et al. in 1982.[69] SEM and TEM images indicate that the diameter of the as-formed Ag-TCNQ nanowires is ca. 100 nm and their length is more than 10 μm, where their crystallinity was confirmed by the selected area electron diffraction pattern. The memory devices with Ag-TCNQ as active elements were fabricated, and the devices displayed the high conductivity and the low conductivity at different applied voltages. The devices can be conducted with at least 100 write-read-erase-read cycles, proving the high stability of these devices.

The concept to form new particles through chemical reactions can also be extended into the small molecule-to-polymer system and the metal-cation exchange of particles. For example, we demonstrated that the microrods of DBEDOT (2,5-dibromo-3,4-ethylenedioxythiophene) could be converted into PEDOT rods after heating for 4 h.[70]
In another research, Zn cations in the organic-inorganic hybrid spherical particles of \([\text{Zn(SPh)₂}]\)_n could be successfully exchanged in aqueous solution by Pb²⁺, Cd²⁺, and Hg²⁺ ions to form diverse particles, such as nanorods, pebble-like nanoparticles, and nanowires.\[^{[71]}\] This method was also adopted by other groups to prepare new organic micro/nanostructures.\[^{[72]}\]

**HOMOAGGREGATION**

Ordered micro/nanostructures (homoaggregation), assembled from single organic components, such as PAHs and heteroatom-modified PAHs, have also received considerable interests. The aggregated shape/size as well as the surface decoration of particles would offer an important platform to tune their physical properties. The main driving forces to form homoaggregation include different noncovalent interactions, such as electrostatic interaction, hydrogen bond, and π-π stacking. In general, the self-assembly methods can be divided into solution-processing, vapor-fabrication, and template-directed ways. Among all these methods, the surfactant-assisted precipitation method is widely used, along with changing the kinds of surfactants, organic π-systems, and the ratio of organic solvents/water. In this part, we will introduce the construction of micro/nano homoaggregation based on this strategy and investigate their potential applications.

As a classical organic semiconductor, 9,10-diphenylanthracene (DPA) is highly fluorescent and usually used as a standard to determine the fluorescence quantum yield. Moreover, DPA and its derivatives could be widely employed as active layers in many organic devices. Lee et al. found that when DPA/THF solutions with different concentrations were injected into the cetyltrimethyl ammonium bromide (CTAB)/H₂O solution, the ribbons with different sizes were formed (Figure 12).\[^{[73]}\] The FETs based on a single DPA nanoribbon display an average hole mobility of 0.16 cm² V⁻¹ s⁻¹. In 2011, we reinvestigated this molecule and found two new shapes (microoctahedron and nanosphere) in addition to rod and wire under the similar operation condition but using P123 (poly-(ethylene glycol)-block-poly(propylene glycol)-block-poly-(ethylene glycol) and PVP40T (polyvinylpyrrolidone, wt 40,000) to replace CTAB (Figure 13).\[^{[74]}\] The possible formation of this homoaggregation might be described as follows: DPA displays the different solubilities in THF and H₂O. When DPA/THF solution was added to water containing P123, CTAB, and SDS, the micro/nanostructures were formed via the dynamic growth process, where DPA molecules interact each other and the dipolar–dipolar interaction has a weak effect on DPA. In comparison, the formation of nanospheres might be caused by the strong interaction between the surfactant PVP and DPA, which affects the order self-aggregation.

Subsequently, by using the same reprecipitation method, both DBA (9,10-dibromoanthracene) and DCNA (9,10-dicyanoanthracene) nanowires were also acquired through the addition of their THF solution to P123-containing water solution.\[^{[75]}\] The TEM and SAED images suggested the crystalline nanowires. The photoconducting behaviors of the as-fabricated nanowires were investigated via photocurrent test in a photoelectrochemical cell with the structure of nanowire/rGO/SiO₂/Si, where the observed photocurrents in anodes are 0.21 and 1.10 μA at 120 mW cm⁻², respectively, implying that photo-induced charge transfer occurs.

As mentioned in the previous discussion, pyrene and its derivatives are important semiconductors and building blocks owing to their fascinating optical and electronic

---

**FIGURE 12**  SEM images of DPA nanostructures prepared by injecting (A) 0.1; (B) 0.3; (C) 0.4; (D) 0.5; and (E) 1 mL of 2×10⁻³ M DAP/THF solution into 5 mL of 1 mM CTAB aqueous solution. Reproduced with permission: Copyright 2008, ACS\[^{[73]}\]

**FIGURE 13**  FESEM images of different morphologies of DPA particles: (A) microoctahedrons, the insert is the magnified area; (B) microrods; (C) nanowires, the insert shows a typical nanowire; (D) nanospheres, the insert is a magnified area. Reproduced with permission: Copyright 2011, ACS\[^{[74]}\]
properties.\textsuperscript{[76,77]} Thus, pursuing and constructing novel pyrene-based derivatives is highly desirable. In 2011, our group serendipitously found that pyrene-4,5-dione could be converted into a novel yellow solid \textbf{BPF} (11-methylbenzo[\textit{d}]pyreno[4,5-b]furan, Figure 14) through reacting with 3-methylphenol promoted by trifluoromethanesulfonic acid.\textsuperscript{[78]} \textbf{BPF} could self-assemble into nanowires through classical reprecipitation method, where \textbf{BPF}/THF was added to aqueous solution containing P123 (Figure 15). More importantly, the electroluminescent performance with the nanowire-based film as an emitter is superior to that of the film prepared from drop-coating molecules.

Under the similar operation condition, we also employed the different substrates to prepare a series of pyrene/phenanthrene-annulated furan derivatives (Figure 16),\textsuperscript{[79]} where the introduction of bromo and methoxy groups is in favor of further selective functionalization. Molecule 3 can self-assemble into nanowires upon the addition of 3/THF solution to water containing CTAB. However, compound 5 could form nanorods and nanoparticles with the ratio of THF-H\textsubscript{2}O changing from 1:5, to 1:7, then to 1:11 (Figure 17). More recently, two new phenanthro[9,10-\textit{b}]benzofuran and pyreno[4,5-\textit{b}]benzofuran functionalized twistarenes 9 and 10 were also prepared, which emitted blue light in organic solvents. However, strong pure white light was observed in electroluminescent devices with 9 or 10 as active layers (Figure 18).\textsuperscript{[80]} We believe that the white electroluminescence might come from the intramolecular and intermolecular ordered aggregation, resulting in the generation of excimer in the densely packed films.

In 2013, we also prepared thiadiazole and selenadiazole-fused pyrene derivatives PyS and PySe through the condensation reaction between pyrene-4,5-diamine and thionyl chloride or selenium oxide (Figure 19).\textsuperscript{[81]} The structure analyses indicate that PyS shows a herringbone arrangement, while PySe adopts a sandwich-herringbone stacking. More strikingly, the former could form nanowires by using a simple
reprecipitation method and the latter yielded nanoquadran-
gles (Figure 20). Obviously, the aggregation morphologies
can be tuned through choosing different soft templates or
different chalcogen atoms.

Twistacenes, especially containing one or more pyrene
units at the terminal or in the middle part, represent
one of aesthetically fascinating PAHs. Since most of
them possess alluring optical and electronic properties,
they are widely chosen as active ingredient in vari-
ous organic devices. These compounds could also self-assemble into diverse aggregation morphologies. For
example, in 2014, we synthesized three novel diazatwist-
pentacenes \(9,11,14,16\)-tetraphenyl-1,6-dihydrobenzo[8,9]
triphenyleno[2,3-g]phthalazine (11), 9,16-diphenyl-11,14-
di(pyridin-2-yl)-1,6-dihydrobenzo[8,9] triphenyleno[2,3-
g]phthalazine (12), and 9,16-diphenyl-11,14-di(thien-2-
yl)-1,6-dihydrobenzo[8,9]triphenyleno-[2,3-g] phthalazine
(13) via [4+2] cycloadition reactions (Figure 21). The
single crystal analysis indicated that all molecules exhib-
ited the twisted configuration with the torsion angles of
21.52° for 11, 24.74° for 12, and 21.14° for 13. When
their THF solutions were added to water containing P123,
11–13 readily form microrods, nanoprisms, and nanobelts,
respectively (Figure 22). More interestingly, unlike their
THF solution with weak fluorescence, the self-assembly
micro/nanostructures of 11 and 12 exhibited the enhanced
fluorescence, known as the famous aggregation-induced
emission (AIE) effect. By comparison, the fluorescence of
the aggregation of 13 is weaker than that in THF, suggesting
the aggregation-caused quenching effect. These findings
indicate that the modification of different substituent not only
affects the optoelectronic properties, but also the promising
AIE response of self-assembly micro/nanostructures of 11 and 12 might be utilized as biosensors.

Recently, we prepared another two heterotwistarenes
ADOP and ADOQ via nucleophilic substitution reaction
between 2,7-di-tert-butyl-9,14-diphenyldibenzo[de,qr]
tetracene-11,12-diol and 2,3-dichloropyrazine/2,3-
dichloroquinoxaline catalyzed by \(K_2CO_3\). As depicted
in Figure 23, ADOP shows a twisted structure with the
torsion angle of 37.21°. More specifically, it features a helix
twist with a trans-configuration arrangement. In comparison, ADOQ containing one more benzene ring at the terminal displays a reclining chair configuration and forms a slipped 1D stacking motif. In addition, the self-assembly behaviors of the as-synthesized materials were studied through the above-mentioned way (Figure 24). When the ratio of THF (containing ADOP) to water (containing CTAB) is changed from 1 to 1:7, then to 1:5, similar nanobelts are obtained. However, a large quantity of nanowires is 2 if the ratio is 1:11. When the ratio is 1:7, the diameter and length of nanowires decrease and no obvious regular morphology is observed for the ratio of 1:5.

We also found that coronene can self-assemble into nanostructures.[90] As shown in Figure 25, coronene nanowires were conveniently acquired by simple addition of its THF solution to water containing P123, and the diameters of 100–500 nm and the lengths of several micrometers to 150 μm. Note that similar nanowires were obtained when the surfactant of P123 was replaced with CTAB and SDS, indicating that the surfactants with neutral, positive ions, and negative ions show negligible effect on the aggregation morphologies. The SAED and XRD patterns infer that the as-formed nanowires are single crystals. Thereafter, a photoelectrochemical cell with one electrode containing the coronene nanowires/rGO/SiO2/Si structure was fabricated, exhibiting a steady anodic photocurrent of 1.64 μA cm⁻² upon irradiating with 350 W xenon lamp. In addition, the heterojunction LED was fabricated, indicating that the usage of coronene nanowires as the hole transport layer is beneficial for the formation of diodes with better performance than those with inorganic-based films.

Fluorescence cell imaging has been widely demonstrated as a promising platform to unveil the nucleus modification and diagnostic information. At present, the design and preparation of proper fluorescent biomaterials with high sensitivity and selectivity is of great value. Along this line,
we have synthesized a series of twistacene-modified dendrons TPPh, TTPy, OTPy, and TOPhP.[91] Subsequently, all of them can self-assemble into uniform nanoparticles upon injecting their THF solutions to pure water. The as-fabricated micro/nanostructures emit blue, cyan, green, and red light. The diameters are 60–200 nm for TPPh, 40–120 nm for TTPy, 150–500 nm for OTPy, and 76–300 nm for TOPhP, being consistent to those of hydrodynamic diameters (102, 204, 169, and 81 nm). Moreover, the desired nanoparticles exhibit good photostability with continuous irradiation for 60 s and low cytotoxicity measured by an MTT assay. The cellular imaging in vitro on the basis of the as-prepared nanoparticles was examined via confocal laser scanning microscope and red fluorescence PI was chosen as the nucleus-deposited dyes for TPPh, TTPy, OTPy and blue DAPI was chosen for TOPhP. As shown in Figure 26, TPPh nanoparticles, OTPy nanoparticles, and TOPhP nanoparticles are concentrated on the cytoplasmas of the HeLa cell and TTPy nanoparticles are dispersed on the membrane, which might be attributed to significant aggregation of TTPy, leading to the difficulty to penetrate into the membrane. Obviously, the nanoparticles can be deposited in special position of HeLa cells, which provides a promising platform to acquire the diagnostic and prognostic bioinformation for pathologists.

Pursuing stable materials with high photothermal conversion efficiency (PTCE) for near infrared photothermal cancer treatment is of great value but is a big challenge. We recently synthesized a perylene-diimide-based oligomer with NIR absorbance (Figure 27).[92] The as-prepared oligomer can self-assemble into nanoparticles upon the addition of the THF solution into pure water. More strikingly, the as-prepared nanoparticles exhibit excellent stability and biocompatibility, and the promising therapeutic effect with an ultrahigh PTCE of up to 79.8%. In addition, we also synthesized H-type bichromophoric perylenediimide Gemini,[93] which can self-assemble into various morphologies, including 1D (one-dimensional) helices, 2D (two-dimensional) rectangular nanocrystals, ultra-large microsheets, pyramid-type parallelograms, and nanoparticles by changing the operation condition.
CONCLUSION

In summary, we review our recent research progress in the self-assembly of hetero/homoaggregations of some organic π-systems via hydrogen bond, π-π stacking interaction, hydrophobic effect, and dipolar moment. We found that molecular structures, packing model, and operation conditions (i.e., temperature, the ratio of solvents, and templates) have crucial effects on the size, shape, and dimension of micro/nanostructures as well as their opto-electronic properties. The diverse physical properties of homo/heteroaggregation would provide more chances for the selective functionalization and the optimization of the device performance. Despite the great achievements in the construction of hetero/homoaggregations, some new challenges and prospective still need to be addressed as follows: (1) the creation of novel organic π-conjugated systems, especially for the single mirror enantiomers, is highly desirable; (2) the novel growth strategies would be very important to obtain the cocrysals with large-scale, low-cost, and ordered arrangement; and (3) it is urgent to diversify the potential applications and unveil the structure–property relationships.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21672051), the Natural Science Foundation of Hebei Province for Distinguished Young Scholar (B2017201072), the Natural Science Foundation of Hebei Province (B2020201044), Key Research Projects of Science and Technology Project of Hebei Education Department (ZD2020128), and the talent training project of Hebei Education and Technology Project of Hebei Education Department (B2020201044), Key Research Projects of Supramolecular Structure and Materials, Jilin University (sklssm2020041).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ORCID

Qichun Zhang https://orcid.org/0000-0003-1854-8659

1. J. Demarteau, A. Debuigne, C. Detrembleur, Chem. Rev. (2019), 119, 6906.
2. P. Wang, S. Lin, Z. Lin, M.D. Peeks, T.V. Voorhis, T.M. Swager, J. Am. Chem. Soc. (2018), 140, 10881.
3. J. Heinze, B.A. Frontana-Urbié, S. Ludwigs, Chem. Rev. (2010), 110, 4724.
4. H. Shen, Y.J. Li, Y.L. Li, Aggregate (2020), 1, 57.
5. I. Ratera, J. Vescianca, Chem. Soc. Rev. (2012), 41, 303.
6. P. Bujak, I. Kulszewicz-Bajer, M. Zagorska, V. Maurel, I. Wielgus, A. Prun, Chem. Soc. Rev. (2013), 42, 8895.
7. H. Zheng, Y. Li, H. Liu, Y. Li, Chem. Soc. Rev. (2011), 40, 4506.
8. Y. Guo, L. Xu, H. Liu, Y. Li, C. Chen, Y. Li, Adv. Mater. (2015), 27, 985.
9. S. Shao, L. Wang, Aggregate (2020), 1, 45.
10. J. Yang, M. Fang, Z. Li, Aggregate (2020), 1, 6.
11. X. Lou, Y. Yang, Aggregate (2020), 1, 19.
12. Y. Yang, L. Sun, C. Wang, F. Yang, X. Ren, X. Zhang, H. Dong, W. Hu, Chem. Soc. Rev. (2019), 48, 1492.
13. M. Chu, B. Qu, W. Zhang, Z. Zhou, X. Yang, Y. Yan, J. Yao, L. Li, Y. Zhao, ACS Appl. Mater. Interfaces (2018), 10, 42740.
14. J.F. Morin, J. Mater. Chem. C (2017), 5, 12298.
15. E.D. Głowiak, M. Irinia-Vladiu, M. Kaltenbrunner, I. Gąsiorowski, M.S. White, U. Monkowski, G. Romanazzi, G.P. Suranna, P. Mastro-
Xin Deng Yu received her bachelor’s degree from Hebei University. Currently, she is pursuing her master’s degree under the supervision of Professor Jinchong Xiao in Hebei University, mainly working on the synthesis and investigating the potential application of organic heteroarenes.

Xiaohui Yu received her bachelor’s degree from Hebei University. Now, she is pursuing her master’s degree under the supervision of Professor Jinchong Xiao in Hebei University, mainly working on the synthesis and investigating the potential application of organic chiral nanographenes.

Jinchong Xiao completed his PhD in 2007 under the supervision of Professor Yuliang Li at the Institute of Chemistry, Chinese Academy of Science, China. Then, he started to work as Assistant Professor at Hebei University. In July 2009, he joined Professor Qichun Zhang’s group as a Postdoctoral Fellow at Nanyang Technological University in Singapore. In August 2011, he returned to Hebei University and was promoted to Full Professor on November 2016. His research interests focus on the construction of functional organic materials, including acenes, heteroaromatics, and chiral nanographene materials, and the exploitation of their potential applications in organic electronics.
Qichun Zhang is a Professor at City University of Hong Kong, China. Before he moved to Hong Kong, he was an assistant Professor (01/2009–02/2014) and an associate professor with tenure (03/2014–08/2020) at Nanyang Technological University, Singapore. His research focuses on carbon-rich conjugated materials and their applications. Currently, he is an associate editor for *Journal of Solid State Chemistry*, and the advisory board member of *Materials Chemistry Frontiers*, *Chemistry—an Asian Journal*, *Journal of Materials Chemistry C*, *Aggregate*, and *Inorganic Chemistry Frontiers*. He is also a fellow of the Royal Society of Chemistry. He has published > 400 papers and 5 patents (H-index: 80).

**How to cite this article:** Deng X, Yu X, Xiao J, Zhang Q. Our research progress in heteroaggregation and homoaggregation of organic π-conjugated systems. *Aggregate*. 2021;2:e35. https://doi.org/10.1002/agt2.35