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## PAPER

# Controlled self-assembly and photovoltaic characteristics of porphyrin derivatives on a silicon surface at solid–liquid interfaces†

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Two *meso*-tetraphenylporphyrin (H<sub>2</sub>TPP) derivatives with different central metal ions, namely ZnTPP, CuTPP, were synthesized, and characterized by a series of spectroscopic methods. Their self-assembly behaviors in mixed solvents without surfactant were systematically investigated. The morphology of the thus produced nanoarchitectures could be efficiently controlled. Nanoslices can be manufactured when a volume of cyclohexane is involved, octahedrons can be produced when a mixed solvent of chloroform and isopropanol is employed, while four-leaf clover-shaped structures can be produced with a large volume of methanol injected. The nanostructures have been characterized by electronic absorption, scanning electron microscopy (SEM) and photoelectric conversion techniques. The internal structures of the nanostructures are well described by XRD. The nanostructures exhibit a power conversion under illumination intensity of 2.3 mW cm<sup>−2</sup>. The present result appears to represent an effort toward controlling the morphology of self-assembled nanostructures of porphyrin derivatives *via* synthesis through introduction of metal–ligand and solvent interaction. Nevertheless, the fundamental study will be helpful to understand photoinduced energy/charge transport in an organic interface and this might also serve as promising building blocks for nanoscale power sources for potential application in solar energy technologies and organic electronics and optoelectronics.

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## Introduction

Molecular aggregation chemistry has attracted considerable attention. The rapid development of this field has promoted the understanding of the concepts and strategies of design of molecular aggregations.<sup>1–3</sup> Organic molecular aggregations have attracted extensive attention recently due to their high-performance and promising applications in low-cost micro-electronics, such as active matrix displays, phototransistors, memory arrays, organic lasers, solar cells, and gas sensors.<sup>4–6</sup> However, due to the uncontrollability of intermolecular interactions and complexities of the self-assembly process, morphology control of organic micro/nanostructures is still a great challenge.<sup>7–10</sup> Tremendous attempts have been made to grow and assemble ordered nanostructures of various organic

functional materials. One strategy is a “top-down” method, such as lithography, for the fabrication of arrays of organic materials. This method is difficult to apply to fragile organic materials, especially for single crystals of small molecules. The other strategy employs the “bottom-up” process, typically self-assembly methods, to directly grow and align nanostructures on substrates at low cost. The self-assembly of nanostructure aggregates from organic building blocks *via* a “bottom-up” strategy has attracted considerable attention due to their wide applications in diverse fields. To date, a variety of organic nanostructures have been formulated through various self-assembly protocols, including organogelation, interfacial assembly, molecular recognition, reprecipitation, evaporation, electrospinning, surfactant-assisted self-assembly.<sup>11–14</sup> Among various organic building blocks,  $\pi$ -conjugated molecules are considered to be ideal units for nanofabrication. This is ascribed to their rigid and planar molecular skeleton, inherent aromatic electronic features, tunable spectroscopic and photochemical properties. These inherent features endow them with nice assembly properties, and make them promising candidates for the fabrication of advanced functional nanomaterials, which might initiate fertile opportunities for nanoscience and technology, soft matter, and biological science.<sup>15–18</sup> As one of the most distinguished  $\pi$ -conjugated molecules, porphyrins have

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received particular attention for the construction of diverse nanoassemblies.<sup>19–26</sup> Their advantages are their flexible and tunable molecular structures in terms of chemical modification. At the same time, porphyrins are typical organic semiconductors with advantages such as good stability in air and high thermal and chemical stability, they also show well-known biocompatibility and excellent electronic properties. However, there are few reports on the intrinsic optoelectrical behavior of porphyrin nanomaterials because of the complicated synthesis and the difficulty in crystal growth. Correspondingly, the exploration of the optical and electrical properties of porphyrin aggregations based on high-quality nano/microstructures prepared by a low-cost process could be an alternative way to further discern the intrinsic properties of these materials. To approach this scientific target, organic crystals are good candidates because of their purity, small number of defects, and long-range order, which are ideal for analyzing the intrinsic properties of organic semiconductors and probing the carrier transport property as a function of molecular arrangements, for instance, the charge-transport anisotropy.<sup>10,27–29</sup>

In the present paper, we describe the self-assembly properties of two typical porphyrins ZnTPP and CuTPP (Fig. 1A). Comparative studies of the self-assembly behavior of ZnTPP and CuTPP reveal that introduction of different coordinated ions into the porphyrin central hole or the solvent leads to the formation of nanostructures with different morphologies, indicating the effect of a synergistic interplay among non-covalent interactions such as  $\pi$ - $\pi$  interaction, hydrogen bonds and metal-ligand coordination bonding in controlling and tuning the morphology of self-assembled nanostructures of porphyrin compounds. And a top-contact configuration technique was designed to probe the transport of micrometer- and nanometer-sized organic crystals.

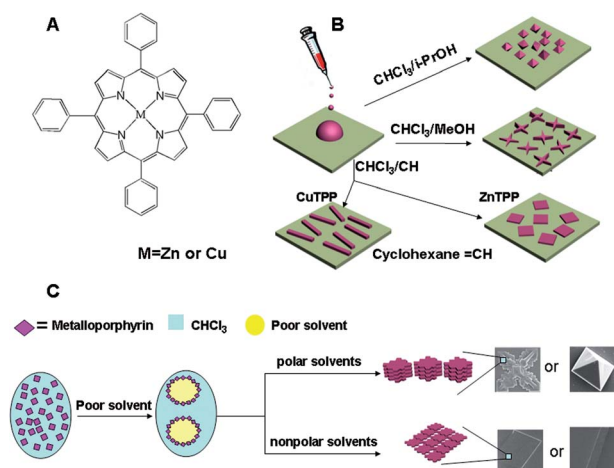


Fig. 1 Chemical structure of ZnTPP and CuTPP (A), schematic illustration for the controlled assembly of ZnTPP and CuTPP supramolecular nanostructures (B) and the proposed self-assembled mechanism for the formation of such ordered aggregation in different solvents (C).

## Experimental section

### Experimental materials

The compounds of zinc *meso*-tetraphenylporphyrin (ZnTPP) and copper *meso*-tetraphenylporphyrin (CuTPP) were prepared as described previously.<sup>30</sup> (as depicted in Fig. S1†) Chloroform, cyclohexane, isopropyl alcohol and other reagents were purchased from commercial suppliers and used without further purification.

### Preparation of porphyrin nanostructures

The porphyrin nanostructure is obtained based on the following steps. Firstly, the porphyrin compound is dissolved into chloroform in  $10^{-6}$  mol L<sup>-1</sup>, and then the porphyrin chloroform solution is dispersed into a volume of another solvent and subsequently mixed with a microinjector. After being ultrasonicated for 10 min, the samples were cast onto a substrate under 20 °C. Substrates used in the present study were successively cleaned with pure water, acetone, and methanol. After the solvent was evaporated, the designed porphyrin nanostructures were obtained.

### Characterization of porphyrin nanostructures

The sizes and morphologies of the porphyrin nanostructures were characterized by using scanning electron microscopy (SEM, S-4800, Japan Hitachi) operating at 5.0 kV. The samples were sputtered with platinum before detection to enhance the electrical conductivity. The morphologies of samples were also characterized by using a polarized optical microscope equipped with a charge-coupled device camera (Panasonic Super Dynamic II WVCP460). Optical images were obtained with an Olympus BX51. The X-ray diffraction measurement was carried out on a Rigaku D/max-2500 X-ray diffractometer. IR spectra were recorded on an EQUINOX 55 Fourier transformation infra-red spectrometer with KBr pellets. UV-vis spectroscopy (UV-1601PC, SHIMADZU) was used to characterize the optical absorbance of the porphyrin nanostructures.

### Field-effect transistor (FET) device fabrication, characterization and photo-responsivity measurement

The FET devices were fabricated by drop-casting of solutions of porphyrin nanostructure on 500 nm-thick thermally oxidized SiO<sub>2</sub> layer substrates. Drain and source electrodes (~50 nm) were deposited on the single crystals by thermal evaporation with an organic ribbon as a shadow mask. Then, the organic ribbon was removed to obtain a gap between the source and drain electrodes. Electrical transport properties were measured under vacuum by using a semiconductor analyzer (Keithley4200). For the photo-responsivity measurement, the FET devices of porphyrin microcrystal were tested with white light stimulation (optical power of 2.3 mW cm<sup>-2</sup>), and the photocurrent responses depending on the gate voltages were recorded.

## Results and discussion

### Scanning electron microscopy

Self-assembly of ZnTPP and CuTPP at room temperature under different solvent conditions produced a range of microscale

structures. Representative SEM images obtained with different solvents are shown in Fig. 2. When the two compounds were prepared in  $\text{CHCl}_3$ -i-PrOH (v/v 1 : 1) respectively, octahedral nanostructures were obtained (Fig. 2A and D). The diameters of the octahedrons were from 7 to 18  $\mu\text{m}$ . When injecting a small volume of solution of these two compounds dissolved in  $\text{CHCl}_3$  into methanol, different nanostructures were obtained. As can be seen from Fig. 2C and F, the two compounds can aggregate to produce four-leaf clover-shaped structures with *ca.* 20–30  $\mu\text{m}$  length and 3–6  $\mu\text{m}$  width. Fig. S3 of the ESI† shows SEM images of the clovers after different reaction times. The images show that four-leaf clover-shaped morphology is already established after only 5 min, with nascent square clovers. Surprisingly, the deposition of the two compounds in a mixed solvent of  $\text{CHCl}_3$ -cyclohexane (v/v, 1 : 1) leads to the formation of nanoslices and nanorods, depending mainly on the intermolecular  $\pi$ - $\pi$  interaction in cooperation with the van der Waals interaction. The growth of ZnTPP molecules formed slices with *ca.* 10–20  $\mu\text{m}$  width and 10–20  $\mu\text{m}$  length (Fig. 2B). Nanorods were obtained for CuTPP (Fig. 2E). The length of the rods was longer than 20  $\mu\text{m}$ . The diameter of the rods was 0.7–2  $\mu\text{m}$ . According to the difference in the volatility of the solvents such as methanol and isopropanol, we could find that the self-assembly process was elongated with the decrease in the volatility, leading to the two porphyrin molecules to form different aggregate structures, for example, four-leaf clover-shaped nanostructures in methanol and octahedral nanostructures in isopropanol. The fluorescent images showed the vivid red color of the four-leaf clover-shaped nanostructures of ZnTPP molecules, which corresponds to its emission spectra. While CuTPP has no emission spectra (Fig. S4†). Compared with the four-leaf clover-shaped structures formed in a mixed solvent of chloroform and methanol, the nanoslices and nanorods were formed in the nonpolar solvents, which indicated that the polarity of the solvents also played an important role in the formation of self-assembled

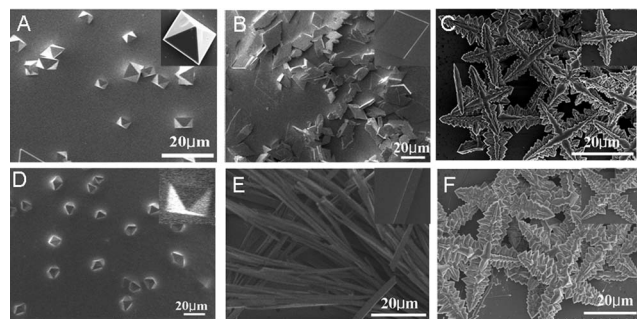


Fig. 2 SEM images of nanostructures of compounds ZnTPP and CuTPP at 20 °C. (A) Octahedrons formed from compound ZnTPP in  $\text{CHCl}_3$ -i-PrOH (v/v 1 : 1). (B) Nanoslices formed from compound ZnTPP in  $\text{CHCl}_3$ -cyclohexane (v/v 1 : 1). (C) Four-leaf clover-shaped structures formed from compound ZnTPP in  $\text{CHCl}_3$ -MeOH (v/v 1 : 1). (D) Octahedrons formed from compound CuTPP in  $\text{CHCl}_3$ -i-PrOH (v/v 1 : 1). (E) Nanorods formed from compound CuTPP in  $\text{CHCl}_3$ -cyclohexane (v/v 1 : 1). (F) Four-leaf clover-shaped structures formed from compound CuTPP in  $\text{CHCl}_3$ -MeOH (v/v 1 : 1) (the insets of panels show the corresponding amplified images).

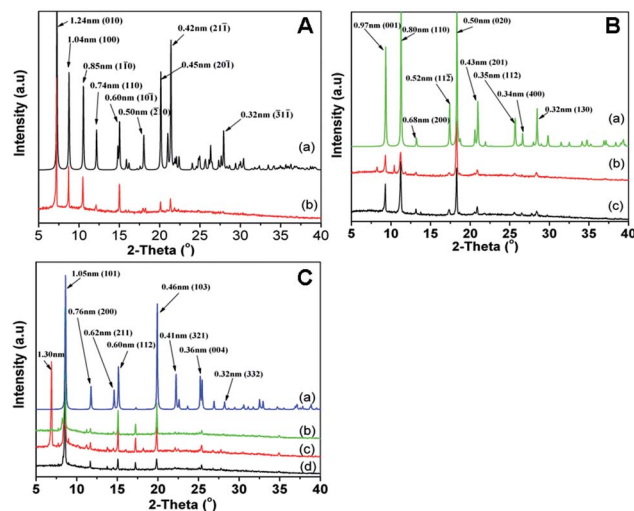


Fig. 3 (A) XRD patterns of self-assembled ZnTPP: simulated pattern from the published crystal structure data (CCDC, Refcode ZZZTAY02) (a), nanoslices (b); (B) XRD patterns of self-assembled ZnTPP: simulated pattern from the published crystal structure data (CCDC, Refcode ZNTPOR03) (a), octahedrons (b), four-leaf clover-shaped (c); and (C) XRD patterns of self-assembled CuTPP: simulated pattern from the published crystal structure data (CCDC, Refcode CUTPOR) (a), octahedrons (b), nanorods (c), four-leaf clover-shaped (d).

nanostructures. As suggested by the XRD analysis below, Zn–O coordination bonding interactions between the hydroxyl oxygen and zinc center of the molecule also dominates the intermolecular interaction of the porphyrinato zinc compound. At the end of this section, the morphology of aggregates formed from the two porphyrin compounds clearly shows dependence on the solvent since different solvent molecules with different volatility and polarity can compete for specific intermolecular interaction moieties and therefore alter both the thermodynamics of the intermolecular interactions and the kinetics of the assembly process during nano-material formation. It should also be mentioned that assembly temperature produces a remarkable influence on the assembly structure as well, owing to the effect on the evaporation rate. Low temperature is helpful for smooth and complete nanostructures, while high temperature promotes the formation of uneven rough nanostructures (Fig. S5–S7†). Further studies are underway to investigate what other morphologies can be obtained with different combinations of porphyrin and coordinated metals.

### X-ray diffraction patterns of the aggregates

The internal structure of the self-assembled nanostructures of these two compounds was investigated by XRD analysis. Fig. 3 shows the XRD patterns and the proposed structural models. As shown in Fig. 3A and B, to ascertain the molecular self-assembly mode, we have searched the published crystal structures of zinc *meso*-tetraphenylporphyrin and have theoretically simulated the XRD pattern as shown in Fig. 3A(a) and B(a). It can be found that all of the peaks in the XRD pattern of self-assembled ZnTPP in the form of nanoslices can be indexed well according to the



simulated pattern from the crystal structure obtained by Scheidt *et al.*<sup>31</sup> (CCDC Refcode: ZZZTAY02) and the self-assembled nanostructures in the forms of octahedrons and four-leaf clover-shaped can be indexed well according to the simulated pattern from the crystal structure obtained by Zhu *et al.*<sup>32</sup> (CCDC, Refcode: ZNTPOR03). Therefore, it can be concluded that the slices structure has the same crystal structure as the crystal structure described by Scheidt *et al.*<sup>31</sup> and the octahedrons and four-leaf clover-shaped structures have the same crystal structure as the crystal structure described by Zhu *et al.*<sup>32</sup>

Fig. 3A. The XRD pattern of self-assembled nanoslices of ZnTPP in cyclohexane shows two peaks at 1.24 and 1.04 nm in the low-angle region and seven peaks at 0.85, 0.74, 0.60, 0.50, 0.45, 0.42 and 0.32 nm in the wide-angle region. As shown in Fig. S8 in the ESI,<sup>†</sup> a unit cell consisting of porphyrinato zinc molecules of ZnTPP with cell parameters of  $a = 1.04$ ,  $b = 1.24$ , and  $c = 0.64$  nm can be concluded on the basis of this XRD result as well as the single-crystal molecular structure size of this compound. It is worth noting that the XRD pattern of the nanoslice presents another refraction at 0.32 nm, which is attributed to the stacking distance between tetrapyrrole cores of neighboring porphyrin molecules along the direction perpendicular to the tetrapyrrole rings.<sup>33,34</sup> (Fig. S11A, ESI<sup>†</sup>). As shown in Fig. 3B, in the low angle range, the XRD diagram of the octahedrons and four-leaf clover-shaped structures formed from ZnTPP shows a well-defined refraction peak at  $2\theta = 9.35^\circ$  (corresponding to 0.97 nm), which is ascribed to the refraction from the (001) plane. Similar to the X-ray diffraction of nanoslices formed in cyclohexane (Fig. S9, ESI<sup>†</sup>). Octahedrons and four-leaf clover-shaped nanostructures formed in methanol and isopropanol also present a refraction at 0.32 nm in the wide angle region, corresponding to the porphyrin–porphyrin stacking distance (Fig. S11B, ESI<sup>†</sup>).

In comparison with the XRD pattern between Fig. 3A and B for the same compound ZnTPP formed in methanol, isopropanol or cyclohexane reveals their different molecular packing diagram, clearly indicating the effect of the solvent on the system and dimension size of the self-assembled nanostructure. In the slice model, the zinc atom at the center of ZnTPP is four-coordinated to four pyrrole nitrogens of the porphyrin core, while in the forms of octahedrons or four-leaf clover-shape, the zinc atom is five-coordinated to four pyrrole

nitrogens of the porphyrin core and to one oxygen atom. The observation of relatively increased distance along the 001 plane for octahedrons and four-leaf clover-shaped structures implies the stronger intermolecular core–core interaction along this direction due to the additionally introduced Zn–O coordination bond. Due to the different coordination patterns observed in the ZnTPP micro-particles, the morphology dependent optical properties in the present case imply an effect of both the reaction temperature, the central metal ion and solvent component on the intermolecular stacking.

As shown in Fig. 3C, similar to the nanostructures formed from ZnTPP, the XRD diagrams of the nanostructures formed from CuTPP show analogous diffraction peaks in the low and wide angle range, indicating almost the same molecular stacking mode in the aggregates of octahedrons or four-leaf clover-shaped structures. They are indexed well according to the simulated pattern from the crystal structure obtained by Fleischer *et al.*<sup>35</sup> (CCDC, Refcode: CUTPOR). It can be concluded that the octahedrons and four-leaf clover-shaped structures formed from CuTPP have the same self-assembly form with the crystal structure described by Fleischer *et al.*<sup>35</sup> The copper atom at the center of CuTPP is four-coordinated to four pyrrole nitrogens of the porphyrin core (Fig. S10<sup>†</sup>). The XRD pattern shows eight peaks at 1.05, 0.76, 0.62, 0.60, 0.46, 0.41, 0.36, and 0.32 nm. Compared with the XRD pattern of the aggregates of octahedrons or four-leaf clover-shaped structures, it also reveals their different molecular packing diagram (Fig. S11C, ESI<sup>†</sup>). The XRD pattern shows an extended peak at 1.31 nm. Similar to the aggregates of ZnTPP, a diffraction peak of the three aggregates at 0.32 nm, corresponding to the stacking distance between neighboring molecules in the direction parallel to the tetrapyrrole rings, was also observed.

### UV-Vis spectroscopy

Extensive studies have revealed that discrimination between the H *versus* J porphyrin–porphyrin stacking modes can be easily achieved by electronic absorption spectroscopic examination.<sup>34,36</sup> Fig. 4A and B display the electronic absorption spectra of compounds ZnTPP and CuTPP dissolved in  $\text{CHCl}_3$  and their self-assembled nanostructures formed in mixed solvent  $\text{CHCl}_3$ –cyclohexane (v/v, 1 : 1), respectively. For the purpose of comparative studies, the electronic absorption spectra of metal free analogue  $\text{H}_2\text{TPP}$  in  $\text{CHCl}_3$  is shown in Fig. S2.<sup>†</sup> The metal-free porphyrin  $\text{H}_2\text{TPP}$  shows a typical non-aggregate molecular electronic absorption spectrum with the Soret band at 417 nm and Q absorption bands at 515, 549, 589, and 645 nm. Upon complexation with the coordinate zinc and copper ion, the increase in the molecular symmetry induces a change in the electronic absorption spectrum from typical features for metal-free *meso*-tetraphenylporphyrin to those for typical porphyrinato metal species. Fig. 4A (black line) shows the electronic absorption spectrum of typical non-aggregated metal porphyrin species ZnTPP in chloroform with a strong sharp Soret band at 422 nm and two weak Q absorptions at 553 and 595 nm. Fig. 4B (black line) shows the electronic absorption spectrum of typical non-aggregated metal porphyrin species CuTPP in chloroform

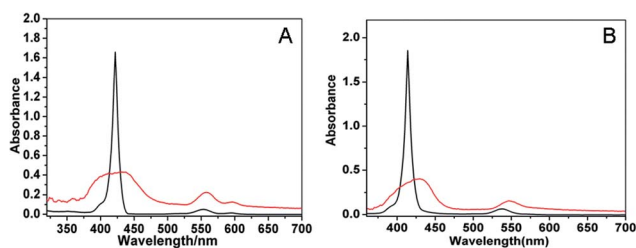


Fig. 4 (A) UV-visible absorption spectra of ZnTPP in  $\text{CHCl}_3$  (black line), nanoslices aggregates (red line); (B) UV-visible absorption spectra of CuTPP in  $\text{CHCl}_3$  (black line), nanorods aggregates (red line) the spectra are normalized at the Soret band for comparison.

with a strong sharp Soret band at 414 nm and one weak Q absorption at 538 nm. The UV-vis spectra of the aggregated species were significantly different from the spectra of the corresponding porphyrin solutions. When dispersed in cyclohexane, the peaks are significantly broadened and a red shift of the Soret band (with the porphyrin Q bands remained unchanged or slightly red-shifted, respectively). These observations indicate that cyclohexane interacted with the porphyrin units, and suggest J-type (edge-to-edge) interaction in the nanostructures, revealing the effect of a synergistic interplay among noncovalent interactions including  $\pi$ - $\pi$  interaction and metal-ligand coordination on controlling and tuning the molecular packing conformation of the corresponding self-assembled aggregates.<sup>23,31</sup>

### FT-IR spectra

The FT-IR spectra of ZnTPP and CuTPP in the formation of various aggregation are compared in Fig. S12, (ESI†). The similar features of the IR spectra of the self-assembled ZnTPP in various aggregates confirm the composition of the nanoslices, octahedrons and four-leaf clover-shaped structures from starting porphyrin compounds ZnTPP. Similar results could also be seen in the self-assembled CuTPP aggregates in Fig. S13.† The characteristic strong band around  $1630\text{ cm}^{-1}$ , due to the C=N stretching vibration of pyrrole, splits into two peaks indicating the formation of a Zn-N or Cu-N metal-ligand coordination.<sup>37</sup>

Based on all the above results, a possible mechanism for the formation of such ordered aggregation was proposed (Fig. 1C).

At first, the metalloporphyrins dissolved in chloroform formed the oligomer with J-type aggregates, which could be driven by the  $\pi$ - $\pi$  stacking between porphyrin cores. Subsequently, the oligomer further extended to form a supermolecular polymer in mixed solvents, which deposited as a film on the silicon substrate.

In the second stage, the polarity of the solvents played an important role in the formation of various aggregations.<sup>25,38,39</sup> In the nonpolar solvents such as cyclohexane, due to the enhanced hydrophobic interaction, the metalloporphyrins have a tendency to form an ordered array of nanoslices or nanorods, upon solvent evaporation. However, when the solvent was changed to methanol or isopropanol, the coordinating bonds and hydrogen bonds formed between metalloporphyrins and polar solvents caused the supermolecular structure to form octahedrons or four-leaf clover-shaped structures on the substrate. Although it is still very difficult to demonstrate the definite process for the formation of such different aggregates, there is no doubt that the polarity of the solvents plays an important role in the formation of ordered aggregates.

### Current-voltage characteristics

The single-crystalline nature of porphyrins indicates their high quality and potential use in devices and circuits. As an example, organic field-effect transistors of two porphyrin crystals were fabricated and tested. The nanoribbons were grown *in situ* on

the substrates by PVT<sup>29,40</sup> to avoid surface contamination and damage of the crystals during the mechanical transfer process for device fabrication and allow an intimate contact between the nanostructure and the octadecyltrichlorosilane (OTS)-modified  $\text{SiO}_2$  substrate to be established. Gold source and drain electrodes were fabricated on a single-crystal nanostructure by the “stamping technique”. A schematic diagram, representative optical images and a typical current voltage ( $I$ - $V$ ) plot of the two single crystalline columns are shown in Fig. 5. As shown in Fig. 5C and F, the highly reproducible, symmetrical  $I$ - $V$  characteristics of the devices suggest symmetrical contacts between the column and electrodes. The separate voltage regions were observed, with nearly ohmic  $I$ - $V$  dependence at low voltage indicating a space charge limited current in the crystal.<sup>41</sup> Moreover, it was interesting to note that the two devices exhibited similar semiconductor behavior, and even when higher voltages were applied to the devices until they broke, no switching phenomena were observed. The typical semiconductor behavior of the single crystalline products of nanoslices and nanorods suggested potential applications of the nanostructures of ZnTPP and CuTPP. To explore the reason for the photoresponse properties,  $I$ - $V$  curves of the two kinds of devices were also measured both in the dark and under white light illumination. The results further confirm that the two devices exhibit photoresponse characteristics. The photocurrent across the nanostructures increases under light illumination compared to the dark current, because the light illumination can excite electron-hole pairs in the porphyrin single crystal and result in an increase of the conductance.

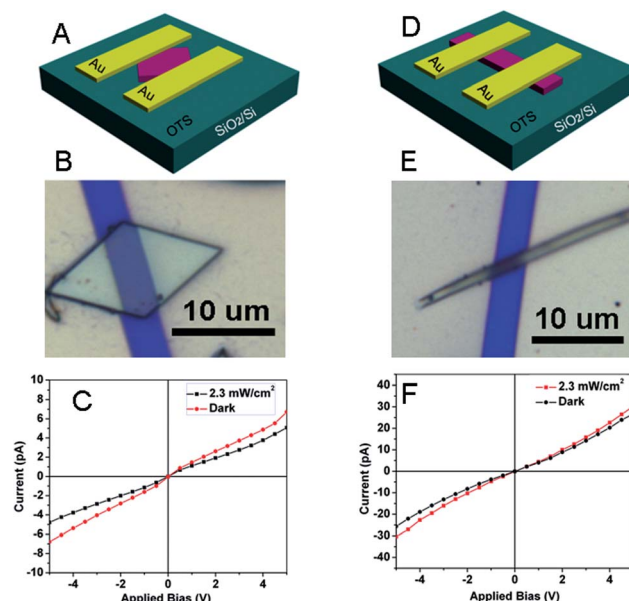


Fig. 5 (A and D) Schematic illustration of two kinds of single micrometer-sized porphyrin nanoslice or nanorod devices with top-contact. (B and E) Optical image of the device obtained with an individual single crystal. (C and F)  $I$ - $V$  curves of the single nanosheet-based device with top-contact in dark conditions and under light illumination.

## Conclusions

In summary, we synthesized and investigated the self-assembly properties of two porphyrin derivatives whose self-assembly can be controlled through exposure to different solvents. Comparative investigation results reveal that competition of intermolecular metal–ligand coordination bonding with the  $\pi$ – $\pi$  interaction between tetrapyrrole rings in tetrapyrrole molecules leads to a different molecular packing conformation and in turn a different self-assembled nanostructure morphology. A long-range  $\pi$ – $\pi$  interaction tended to gradually become dominating in the crystals, and this tendency was the reason that led to an assembly morphology transformation. In particular, the availability of the single crystal and molecular structure revealed by XRD analysis for both metal porphyrins renders it possible to investigate the formation mechanism and the molecular packing conformation of self-assembled nanostructures. Single crystal field-effect transistors based on individual micro/nanometer-sized slices/rods were fabricated and exhibited high performance. All these results suggested the significant roles of intermolecular interactions in the morphology control and potential applications in organic electronics.

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## References

- 1 S. A. DiBenedetto, A. Facchetti, M. A. Ratner and T. J. Marks, *Adv. Mater.*, 2009, **21**, 1407–1433.
- 2 Z. H. Nie, A. Petukhova and E. Kumacheva, *Nat. Nanotechnol.*, 2010, **5**, 15–25.
- 3 R. J. Warburton, *Nat. Mater.*, 2013, **12**, 483–493.
- 4 Q. H. Wang and M. C. Hersam, *Nat. Chem.*, 2009, **1**, 206–211.
- 5 M. Halik and A. Hirsch, *Adv. Mater.*, 2011, **23**, 2689–2695.
- 6 L. L. Li and E. W. G. Diau, *Chem. Soc. Rev.*, 2013, **42**, 291–304.
- 7 C. L. Wang, Y. L. Liu, Z. Y. Ji, E. J. Wang, R. J. Li, H. Jiang, Q. X. Tang, H. X. Li and W. P. Hu, *Chem. Mater.*, 2009, **21**, 2840–2845.
- 8 L. Jiang, Y. Y. Fu, H. X. Li and W. P. Hu, *J. Am. Chem. Soc.*, 2008, **130**, 3937–3941.
- 9 X. J. Zhang, X. H. Zhang, K. Zou, C. S. Lee and S. T. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 3527–3532.
- 10 R. J. Li, L. Jiang, Q. Meng, J. H. Gao, H. X. Li, Q. X. Tang, M. He, W. P. Hu, Y. Q. Liu and D. B. Zhu, *Adv. Mater.*, 2009, **21**, 4492–4495.
- 11 M. M. Smith, W. Edwards and D. K. Smith, *Chem. Sci.*, 2013, **4**, 671–676.
- 12 B. Li, A. V. Klekachev, M. Cantoro, C. Huyghebaert, A. Stesmans, I. Asselberghs, S. De Gendt and S. De Feyter, *Nanoscale*, 2013, **5**, 9640–9644.
- 13 C. M. Jager, T. Schmaltz, M. Novak, A. Khassanov, A. Vorobiev, M. Hennemann, A. Krause, H. Dietrich, D. Zahn, A. Hirsch, M. Halik and T. Clark, *J. Am. Chem. Soc.*, 2013, **135**, 4893–4900.
- 14 S. S. Babu, S. Prasanthkumar and A. Ajayaghosh, *Angew. Chem., Int. Ed.*, 2012, **51**, 1766–1776.
- 15 Z. J. Chen, A. Lohr, C. R. Saha-Moller and F. Wurthner, *Chem. Soc. Rev.*, 2009, **38**, 564–584.
- 16 H. Imahori, T. Umeyama, K. Kurotobi and Y. Takano, *Chem. Commun.*, 2012, **48**, 4032–4045.
- 17 J. M. Lim, P. Kim, M. C. Yoon, J. Sung, V. Dehm, Z. J. Chen, F. Wurthner and D. Kim, *Chem. Sci.*, 2013, **4**, 388–397.
- 18 L. Loots and L. J. Barbour, *Chem. Commun.*, 2013, **49**, 671–673.
- 19 L. Wang, Y. Chen, Y. Bian and J. Jiang, *J. Phys. Chem. C*, 2013, **117**, 17352–17359.
- 20 K. K. Ng, J. F. Lovell, A. Vedadi, T. Hajian and G. Zheng, *ACS Nano*, 2013, **7**, 3484–3490.
- 21 P. Guo, P. Chen and M. Liu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5336–5345.
- 22 C. M. Drain, A. Varotto and I. Radivojevic, *Chem. Rev.*, 2009, **109**, 1630–1658.
- 23 C. S. Huang, L. P. Wen, H. B. Liu, Y. L. Li, X. F. Liu, M. J. Yuan, J. Zhai, L. Jiang and D. B. Zhu, *Adv. Mater.*, 2009, **21**, 1721–1725.
- 24 Y. N. Gao, X. M. Zhang, C. Q. Ma, X. Y. Li and J. Z. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 17044–17052.
- 25 K. E. Martin, Z. C. Wang, T. Busani, R. M. Garcia, Z. Chen, Y. B. Jiang, Y. J. Song, J. L. Jacobsen, T. T. Vu, N. E. Schore, B. S. Swartzentruber, C. J. Medforth and J. A. Shelnutt, *J. Am. Chem. Soc.*, 2010, **132**, 8194–8201.
- 26 C. J. Medforth, Z. C. Wang, K. E. Martin, Y. J. Song, J. L. Jacobsen and J. A. Shelnutt, *Chem. Commun.*, 2009, 7261–7277.
- 27 H. L. Dong, S. D. Jiang, L. Jiang, Y. L. Liu, H. X. Li, W. P. Hu, E. J. Wang, S. K. Yan, Z. M. Wei, W. Xu and X. Gong, *J. Am. Chem. Soc.*, 2009, **131**, 17315–17320.
- 28 L. C. Palmer and S. I. Stupp, *Acc. Chem. Res.*, 2008, **41**, 1674–1684.
- 29 Y. J. Zhang, H. L. Dong, Q. X. Tang, S. Ferdous, F. Liu, S. C. B. Mannsfeld, W. P. Hu and A. L. Briseno, *J. Am. Chem. Soc.*, 2010, **132**, 11580–11584.
- 30 J. H. Cai, Y. J. Ye, J. W. Huang, H. C. Yu and L. N. Ji, *J. Sol-Gel Sci. Technol.*, 2012, **62**, 432–440.
- 31 W. R. Scheidt, J. U. Mondal, C. W. Eigenbrot, A. Adler, L. J. Radonovich and J. L. Hoard, *Inorg. Chem.*, 1986, **25**, 795–799.
- 32 W. J. Run, Z. A. Zhu, X. H. Bu, Z. H. Zhang, Y. Shao and Y. T. Chen, *Chin. J. Struct. Chem.*, 1998, **17**, 159–164.
- 33 M. Kimura, K. Wada, K. Ohta, K. Hanabusa, H. Shirai and N. Kobayashi, *J. Am. Chem. Soc.*, 2001, **123**, 2438–2439.
- 34 G. Lu, X. Zhang, X. Cai and J. Jiang, *J. Mater. Chem.*, 2009, **19**, 2417–2424.
- 35 E. B. Fleischer, C. K. Miller and L. E. Webb, *J. Am. Chem. Soc.*, 1964, **86**, 2342–2347.

- 36 X. Gong, T. Milic, C. Xu, J. D. Batteas and C. M. Drain, *J. Am. Chem. Soc.*, 2002, **124**, 14290–14291.
- 37 W. Sun, H. Wang, D. Qi, L. Wang, K. Wang, J. Kan, W. Li, Y. Chen and J. Jiang, *CrystEngComm*, 2012, **14**, 7780–7786.
- 38 X. D. Xu, J. Zhang, L. J. Chen, R. Guo, D. X. Wang and H. B. Yang, *Chem. Commun.*, 2012, **48**, 11223–11225.
- 39 X. Yang, X. Xu and H.-F. Ji, *J. Phys. Chem. B*, 2008, **112**, 7196–7202.
- 40 Q. Tang, H. Li, Y. Song, W. Xu, W. Hu, L. Jiang, Y. Liu, X. Wang and D. Zhu, *Adv. Mater.*, 2006, **18**, 3010–3014.
- 41 Z. Y. Ji, H. L. Dong, M. Liu and W. P. Hu, *Nano Res.*, 2009, **2**, 857–864.