Supporting Information

Host-Guest Chemistry of Giant Molecular Shape Amphiphiles Based on POSS−PDI Conjugates

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Materials.

Perylene, pyrene and anthracene were obtained from MACKLIN. TCM and MeOH were obtained from Sinopharm(Shanghai). The solvents or chemicals were commercially available and used directly.

Sample preparation.

Compound **PPP** was prepared according to the reported methods[1].

The films were prepared through drop-casting from 10 ul corresponding $CHCl_3$ solutions and the **PPP** concentration in $CHCl_3$ was 5×10^{-3} M.

Crystals of the **PPP**/pyrene and **PPP**/perylene were grown by slowly evaporating the solvent of a 1:4 **PPP**/perylene $CHCl_3$ solution and a 1:8 **PPP**/pyrene $CHCl_3$ solution (**Figure. S2**). Since **PPP** itself is crystalline, to prevent the crystallization of pristine

PPP, excess amounts of the guest molecules were used in the solutions. A higher equivalent of pyrene was used to prepare the **PPP**/pyrene crystals because of the lower K_{AD} of pyrene to **PPP**.

Equipment and Experiments.

Solution Nuclear Magnetic Resonance (NMR) Spectroscopy.

All ^{1}H NMR spectra were acquired in $CDCl_3$ (Adamas, 99.8% D) using a AVANCE III 600 NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.26 ppm. The concentration of **PPP** was fixed at 4.16 mM in all solutions.

Fluorescence Spectroscopy.

Fluorescence emission spectra were carried out on a fluorescence spectrophotometer (JASCO FP-6600). The dilute solution spectra were recorded in 2mm quartz cuvette and the concentration of **PPP** in $CHCl_3$ is 0.84 mM. The sample for film fluorescence emission spectra experiments were prepared by drop casting 10 ul $CHCl_3$ solution on quartz glass and the **PPP** concentration in $CHCl_3$ was 5×10^{-3} M.

X-ray Diffraction.

The crystallographic structure of the **PPP**/pyrene crystal was obtained with X-ray diffraction (XRD, Bruker APEX II, Cu K_α radiation). The pristine **PPP** and **PPP**/guest complexes powders were obtained by drying the $CHCl_3$ solutions of **PPP** and the **PPP**/guest mixtures, respectively. To obtain the needel-like crystal for the measurement of 2D XRD patterns, the cocrystal was prepared by slow evaporation of a 0.4 wt% **PPP**

$CHCl_3$ solution that contains 4 equivalent perylene or 8 equivalent pyrene in methanol (MeOH) atmosphere. The volume of MeOH is twice of chloroform solution. The 2D XRD patterns of the **PPP** and **PPP**/pyrene cocrystal were obtained by recording the XRD signal while rotating a needle crystal of **PPP** or **PPP**/pyrene.

Fluorescence microscope.

Fluorescence microscope images (excited at 530 - 550 nm) were recorded by (Olympus BX-51).

Computer Simulation.

Cerius2 program assisted the construction of molecular packing model and crystallographic simulation. Initial model was built based on the unit cell parameters calculated from the experimental results. X-ray diffraction (XRD) patterns can be simulated from this model and will be compared by the experimental data.

Additional characterization data.

Supplementary Figures

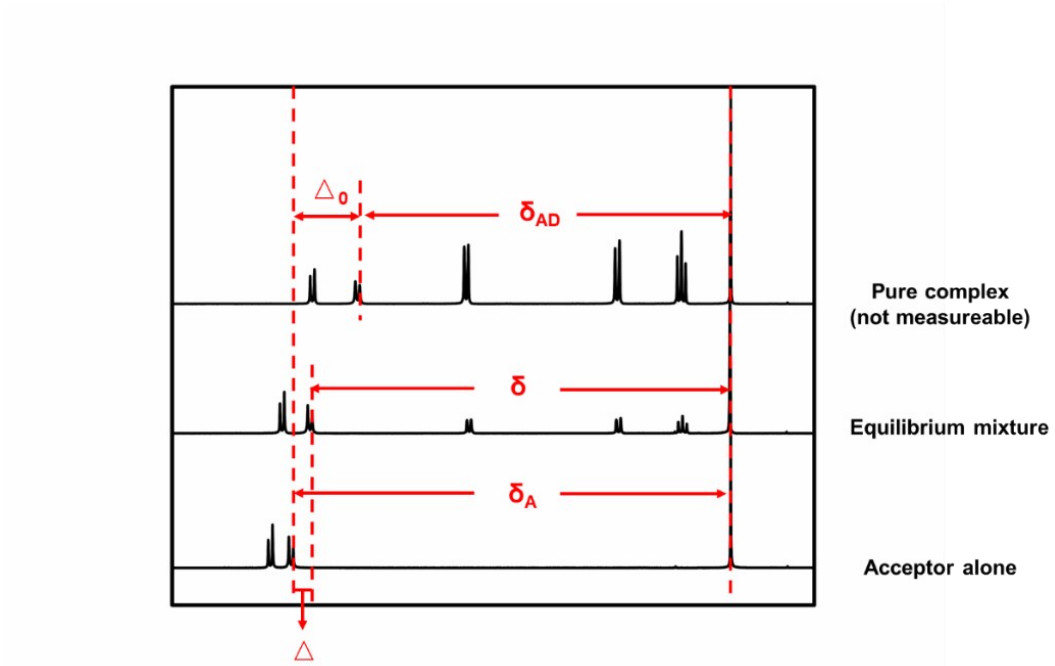

Figure S1. The graphic symbol of △, $\triangle_0$.

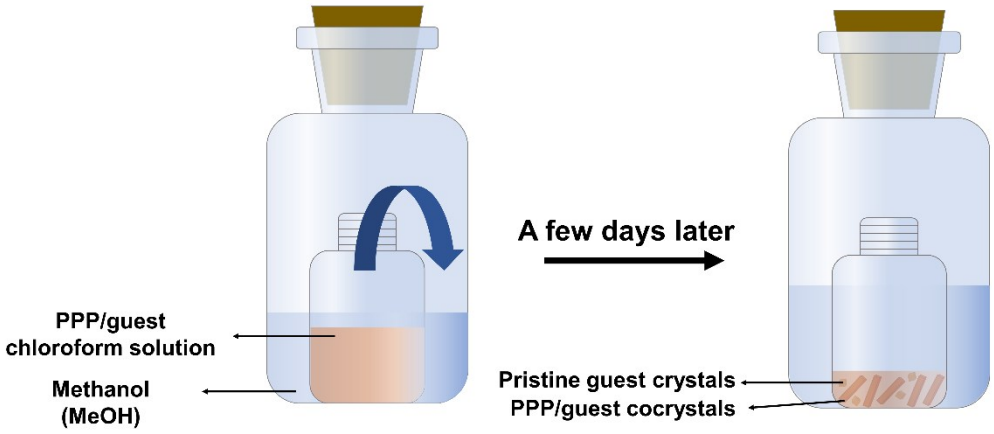

Figure S2. Illustration of the "slowly evaporating the solvent" cocrystal preparation method. Crystals of the **PPP**/pyrene and **PPP**/perylene mixtures were grown by slowly evaporating the solvent of a 1:4 **PPP**/perylene $CHCl_3$ solution and a 1:8 **PPP**/pyrene $CHCl_3$ solution. The concentration of PPP in $CHCl_3$ was 0.4 wt% and the volume of methanol is twice of chloroform solution.

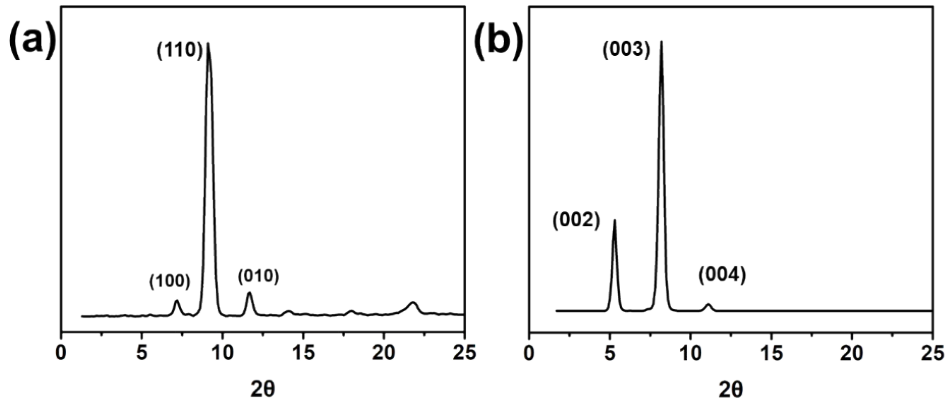

Figure S3. 1D pattern stemmed from the integral of the diffraction along (a) (hk0) and (b) (00l) in Figure 7a.

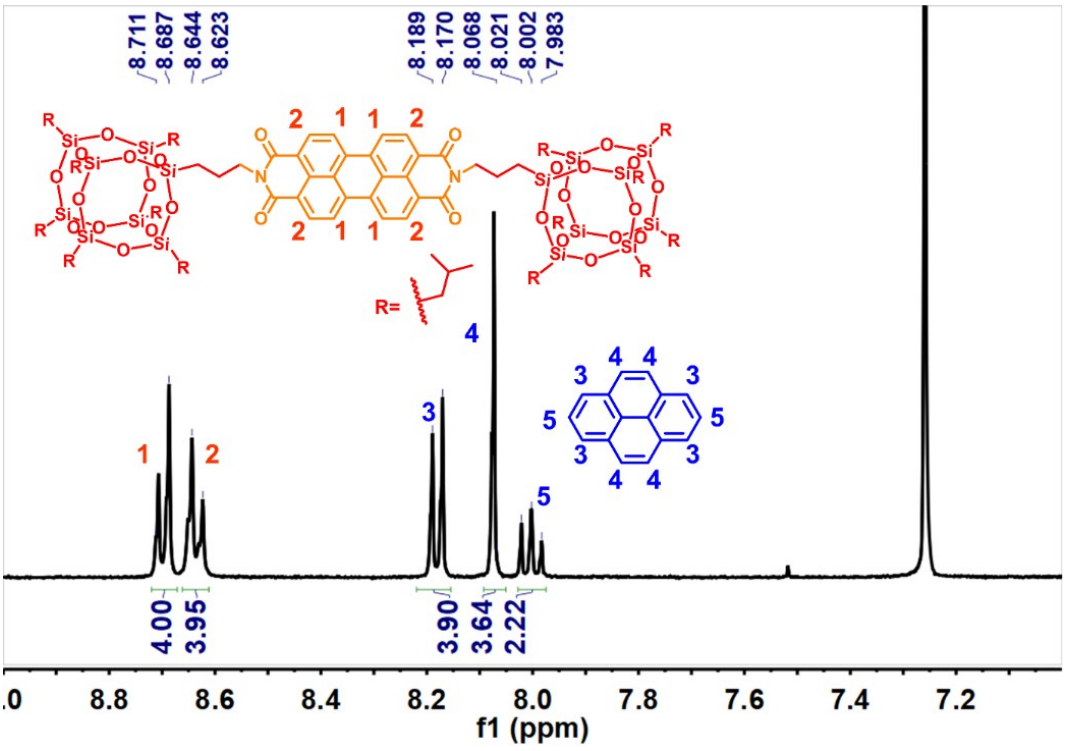

Figure S4. NMR spectra of (a) **PPP**/perylene cocrystal and (b) **PPP**/pyrene cocrystal.

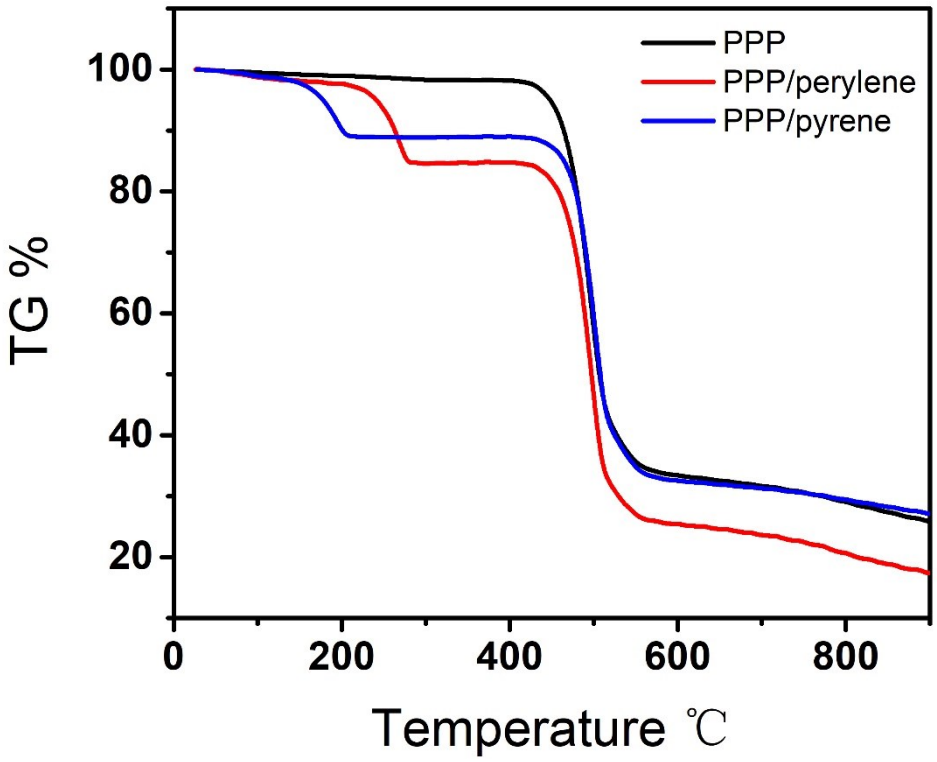

Figure S5. TGA curve of **PPP**, **PPP**/perylene and **PPP**/pyrene crystals. The sample was heated under nitrogen from 30 °C to 900 °C at a scanning rate of 10 °C/min with TGA (Perkin-Elmer).

Reference

1. Y. Shao, G.-Z. Yin, X. Ren, X. Zhang, J. Wang, K. Guo, X. Li, C. Wesdemiotis, W.-B. Zhang, S. Yang, M. Zhu and B. Sun, *RSC. Adv.*, 2017, **7**, 6530-6537.