Supplementary information for

Ionic Self-assembled Derivatives of Perylenetetracarboxylic Dianhydride: Facile Synthesis, Morphology and Structures

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1. Packing Behavior of PTCT-DOAB-1

Fig. S5 shows the XRD patterns of PTCT-DOAB-1. The peaks at s = 1.89, 3.78, 5.65 have a position ratio of 1:2:3. The peaks at s = 2.78, 5.65, 8.38 also have a position ratio of 1:2:3. The peaks at s = 2.0-3.0 can be usually attributed to crystallized alkyl chains. We can conclude that two set of layered structures exist in the as-prepared complex. Some molecules form layered structure with a layer spacing of about 4.67 nm, in which alkyl chains are crystallized. The others form another layered structure with a layer spacing of about 3.17nm, in which alkyl chains assume random coils. Through recrystallization in ethanol/water or toluene/acetone binary solvent, PTCT-DOAB can form one ordered layered structure, PTCT-DOAB-2 or PTCT-DOAB-3.

2. Results and discussion of PTCT-DHAB

The morphology of as-prepared PTCT-DHAB-1 and PTCT-DHAB-2 are similar with that of as-prepared PTCT-DOAB-1 and PTCT-DOAB-2, respectively, see Fig. S6 and S7. In the case of PTCT-DHAB aggregation in toluene/acetone binary solvent (PTCT-DHAB-3), needle-like aggregates were also obtained, but the length is much longer than that of PTCT-DOAB and PTCT-DHAB-2, up to 200μm (Fig. S8). This may reveal that PTCT-DHAB is easier to aggregate along 1D direction than PTCT-DOAB because of the weaker solvophobic effect of shorter alky chains. Then we perform the assembly of PTCT-DHAB by slow

evaporation of toluene. As expected, ultralong aggregates were fabricated (PTCT-DHAB-4, Fig. 4).

Fig. S9 shows the XRD curves of PTCT-DHAB, which are quite different from that of PTCT-DOAB. For PTCT-DHAB-1, PTCT-DHAB-2 and PTCT-DHAB-4, three distinct scatterings were observed (position ratio 1:2:3) at lower angles and no other peaks, which are similar to that of PTCT-DOAB-3, indicating of a highly ordered layer structure with interlayer spacing of 3.21 nm, 3.21 nm and 3.49 nm, respectively. While PTCT-DHAB-3 shows similar XRD patterns with PTCT-DOAB-2, except that the Bragg peaks that correspond to the (00*l*) reflections have shifted to a larger angle. The corresponding long period is 4.14 nm, about 0.36 nm shorter than that of PTCT-DOAB-2. This is because the alkyl C16 chain is shorter than the C18 chain. The shortened value of long period equals the longitude offset difference between C16 and C18 chain. So the similar packing model can be expected.

In the case of PTCT-DHAB having the same chromophores with PTCT-DOAB, the electronic properties of them are essentially the same, so the spectra are similar in the shape and the maxima wavelengths. Differences in the alkyl side chain length have only small effect on the absorption and emission spectra, as shown in Fig. S10.

The images in Fig. S11 show the liquid crystal texture of PTCT-DHAB in the sample prepared by casting its ethanol solution.

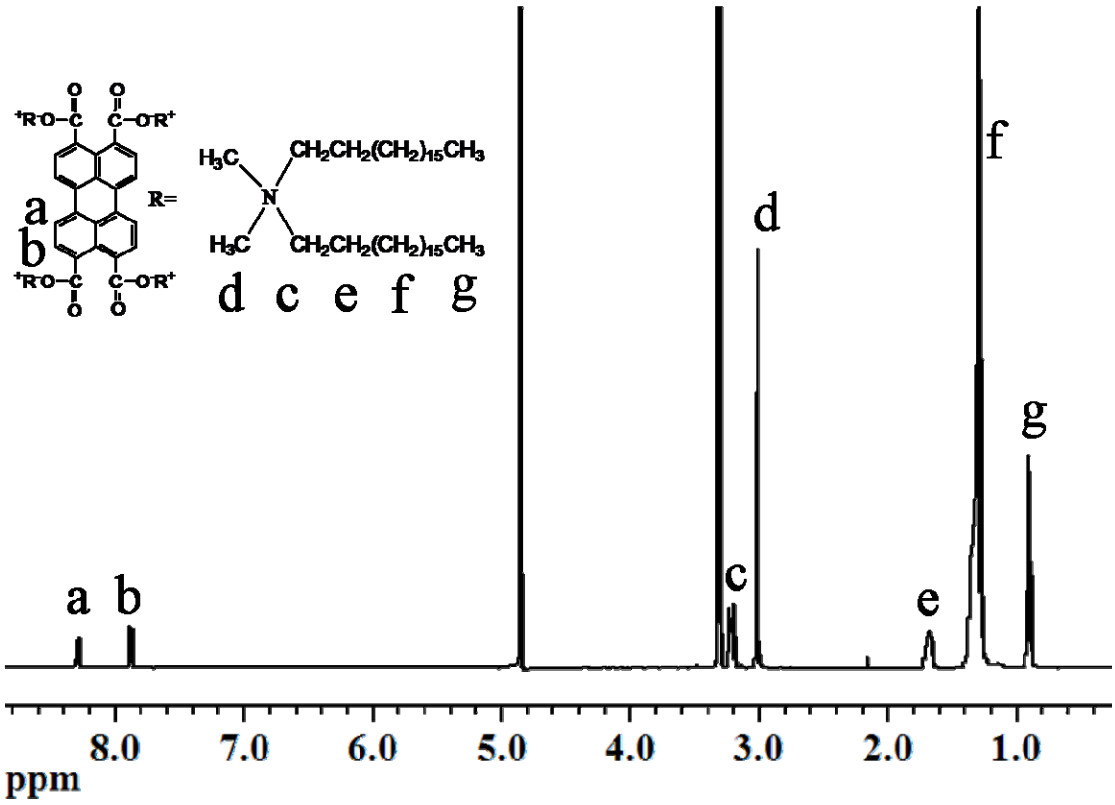

Fig. S1 ^{1}H-NMR spectra of PTCT-DOAB.

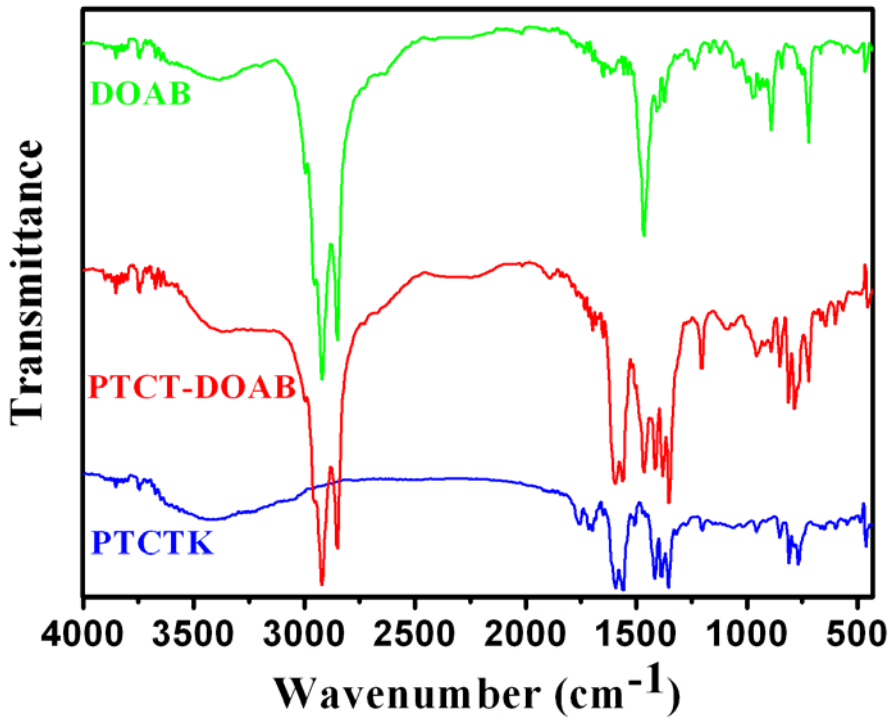

Fig. S2 FTIR spectra of PTCT-DOAB.

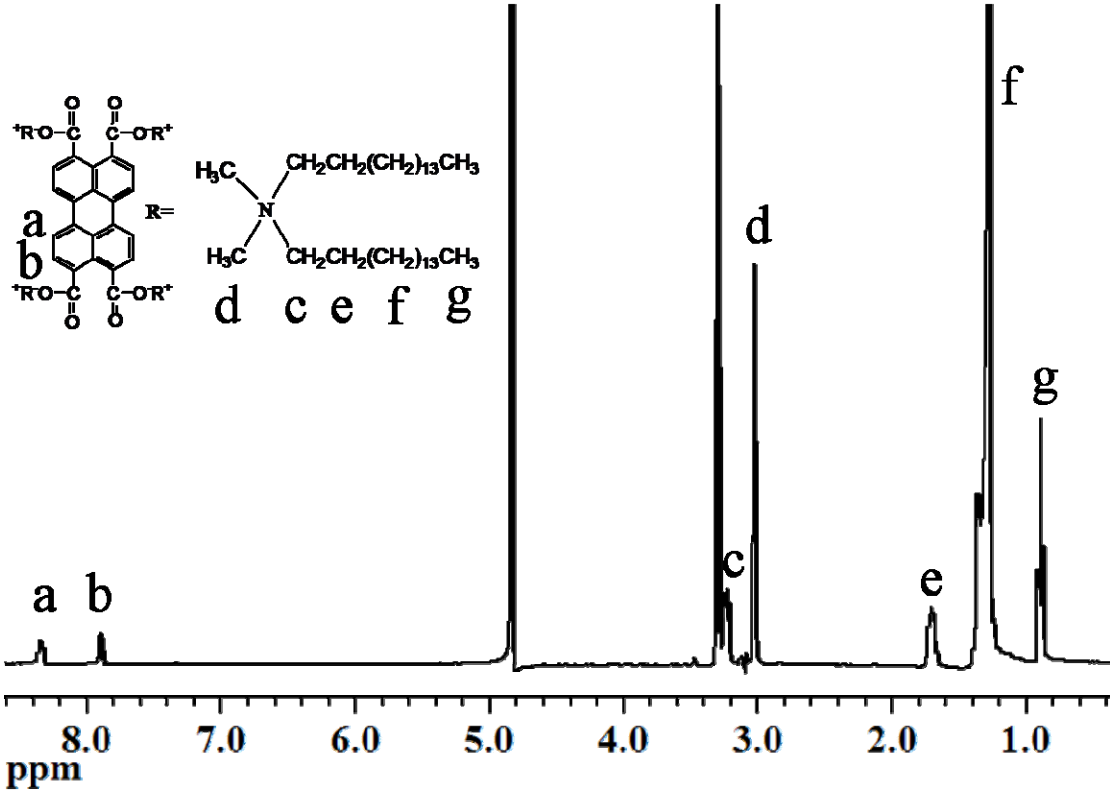

Fig. S3 ^{1}H-NMR spectra of PTCT-DHAB.

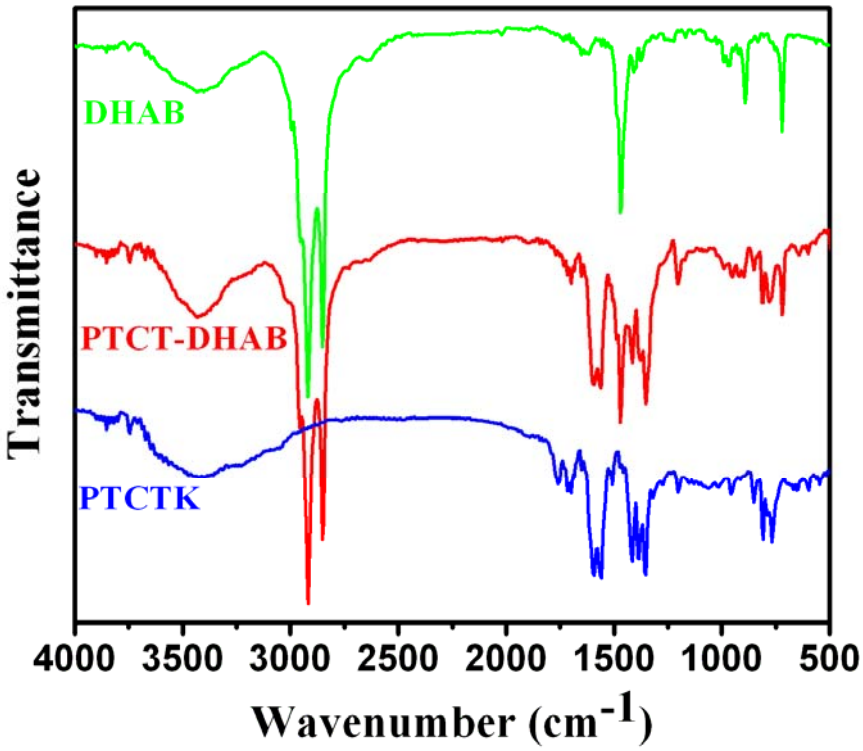

Fig. S4 FTIR spectra of PTCT-DHAB.

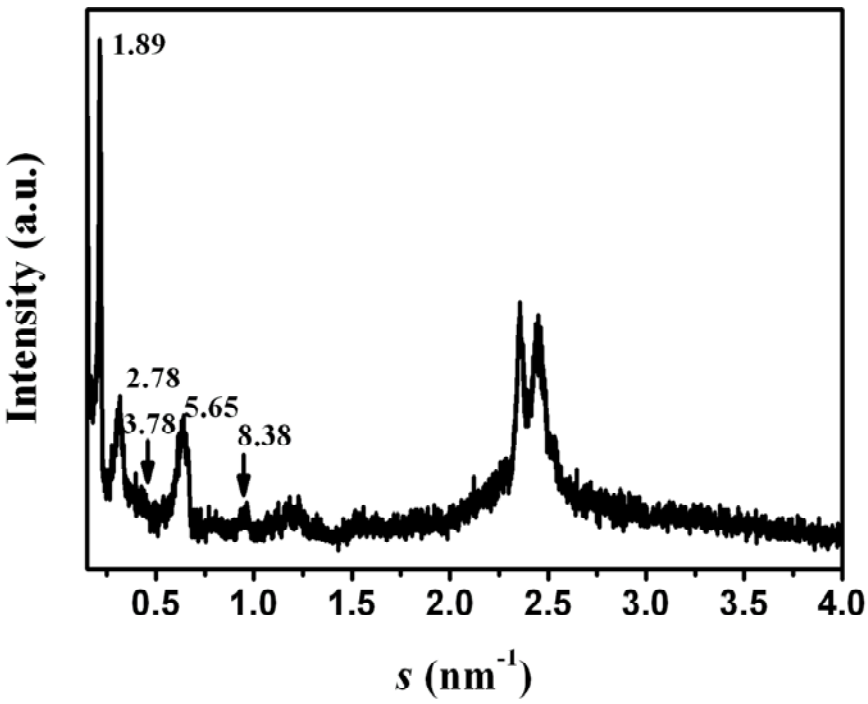

Fig. S5 X-ray diffraction patterns of PTCT-DOAB-1.

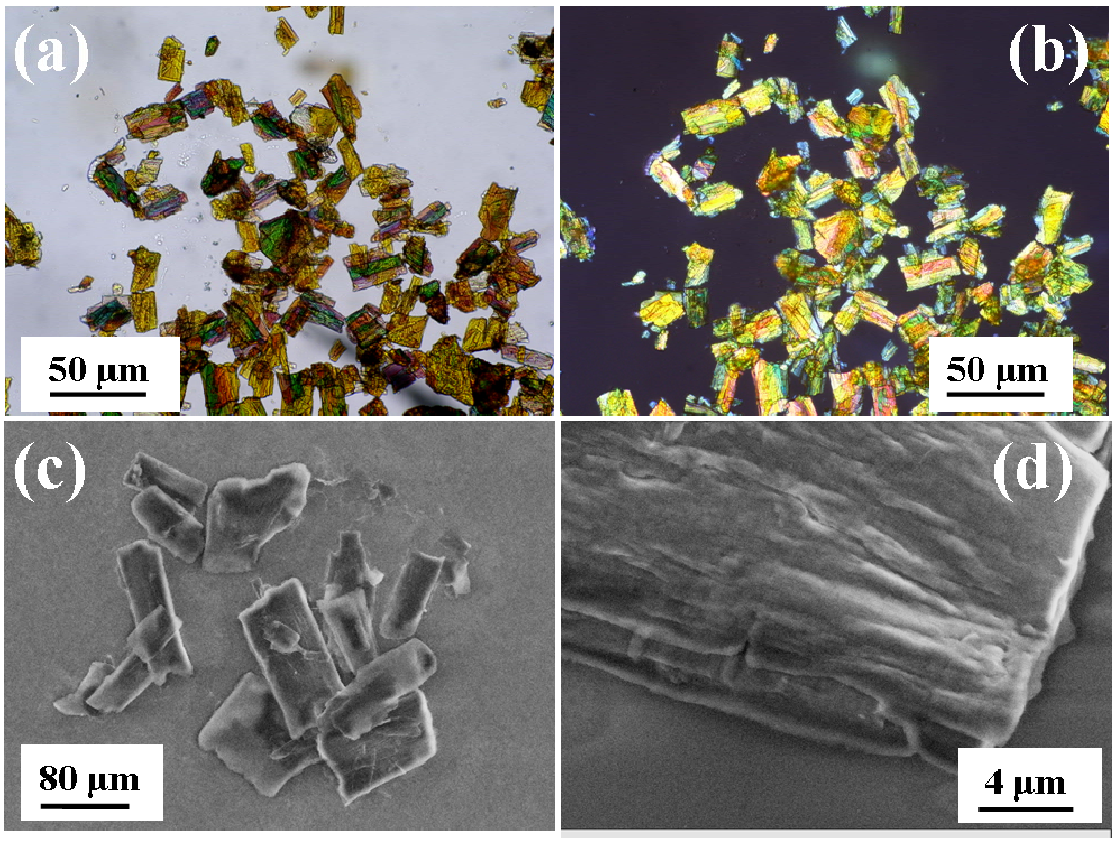

Fig. S6 Morphology of as-prepared PTCT-DHAB-1: (a) POM image, (b) POM image under crossed polarizers, (c) SEM image and (d) higher-magnification SEM image over an aggregate.

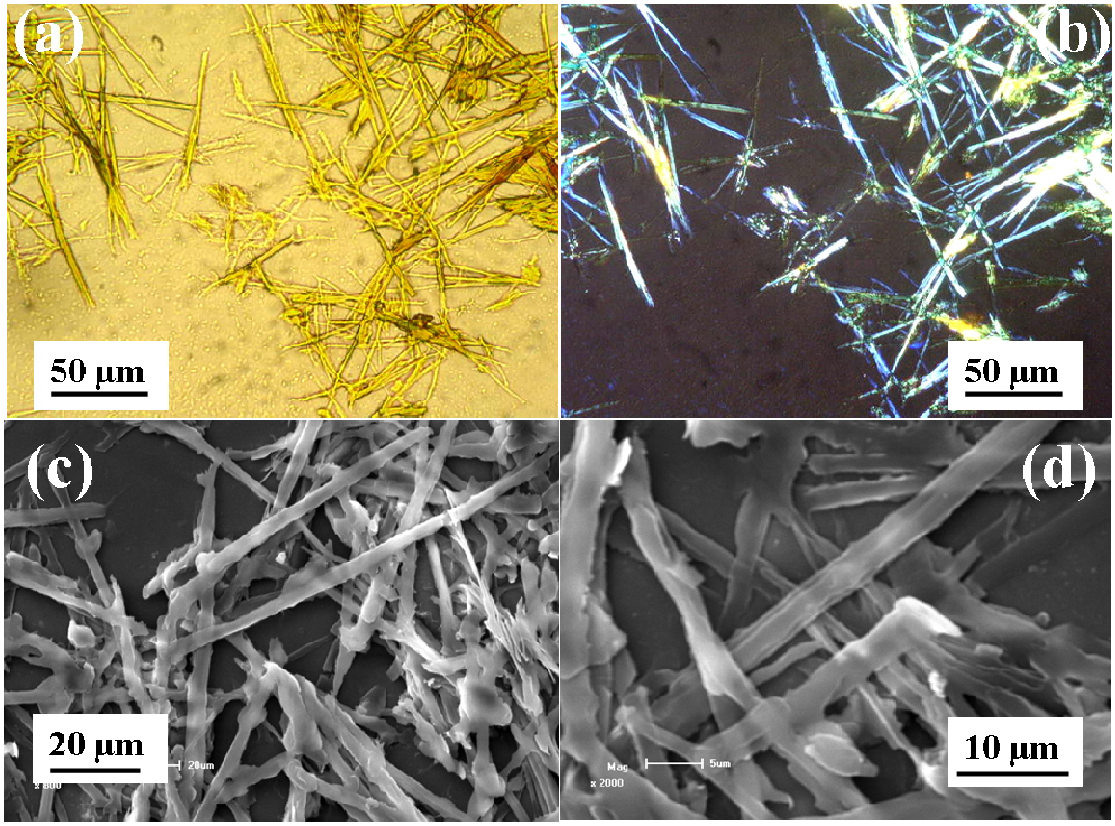

Fig. S7 Morphology of PTCT-DHAB-2 precipitated from ethanol solution with water: (a) POM image, (b) POM image under crossed polarizers, (c) and (d) SEM images.

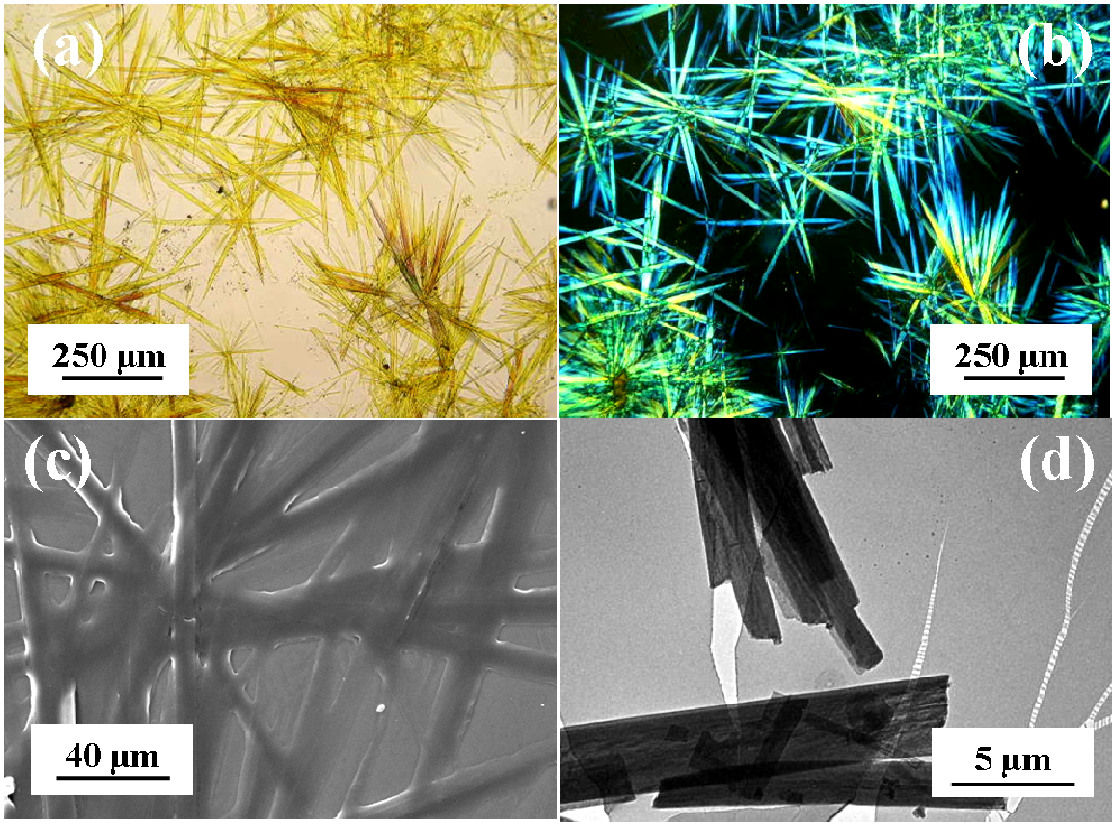

Fig. S8 Morphology of PTCT-DHAB-3 precipitated from toluene solution with acetone: (a) POM image, (b) POM image under crossed polarizers, (c) SEM image and (d) TEM image.

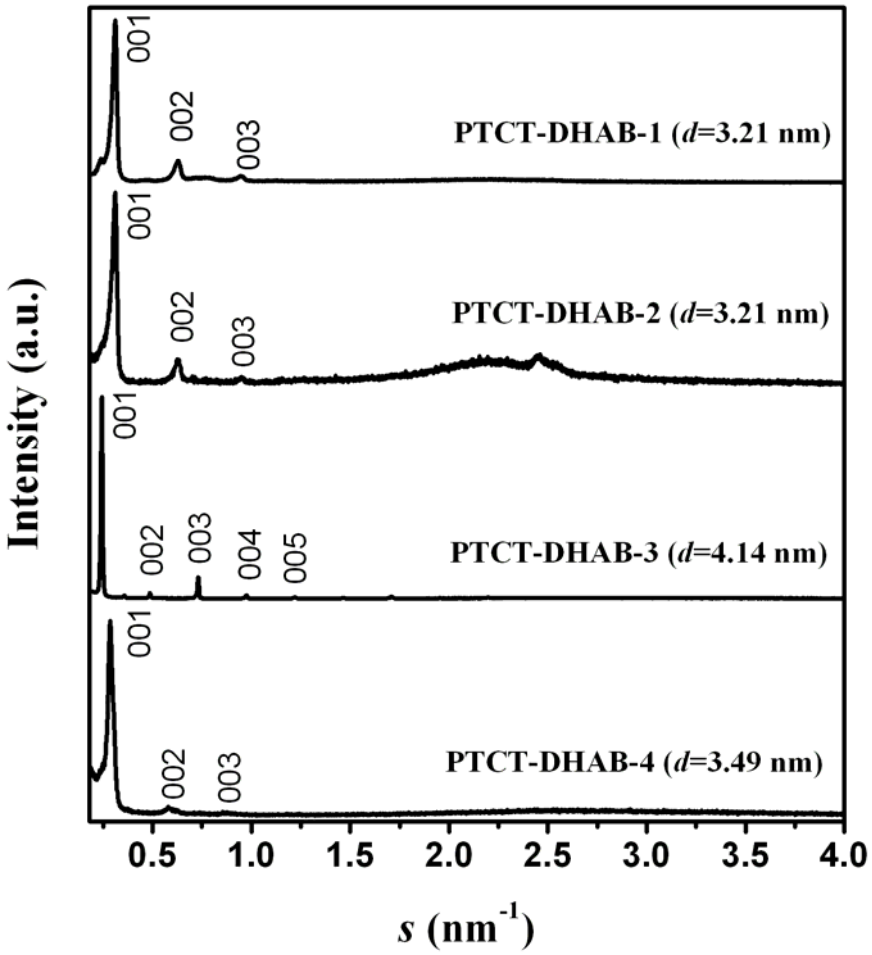

Fig. S9 X-ray diffraction patterns of PTCT-DHAB-1, PTCT-DHAB-2, PTCT-DHAB-3 and PTCT-DHAB-4. (Miller indices are used to assign the reflections; the traces are offset for clarity).

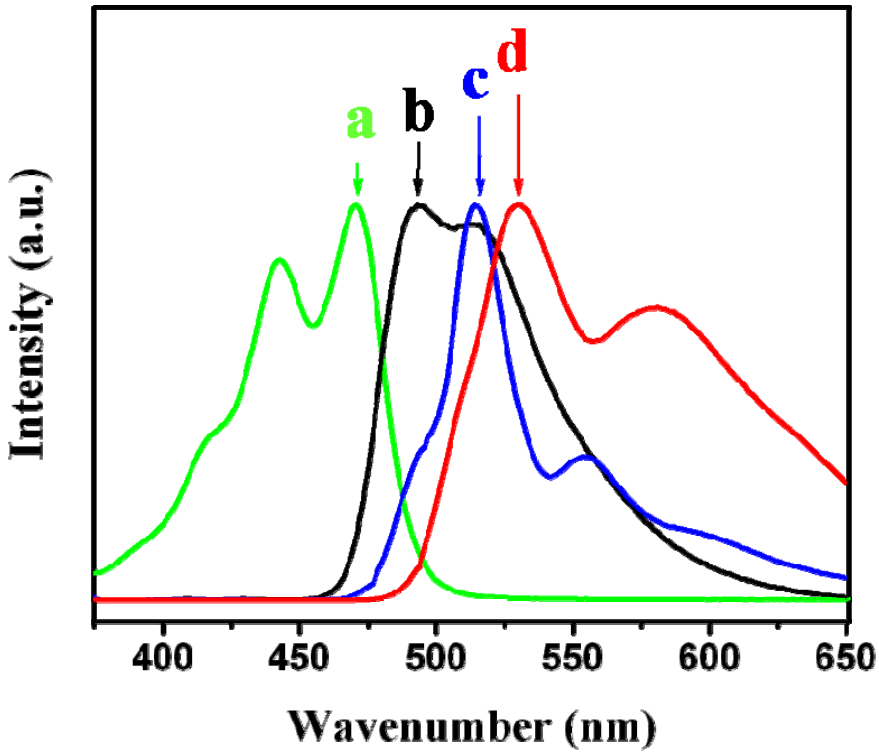

Fig. S10 UV-Vis absorption spectra (a), fluorescence spectra of ethanol solutions (b), fluorescence spectra of solid state for PTCT-DHAB-3 (c) and PTCT-DHAB-1 (d), the spectra are normalized.