Electronic supplementary information

Concentration-Dependent Self-Assembly Structures of An Amphiphilic Perylene Diimide with tri(Ethylene Glycol) Substituents at Bay Positions

Xin Wang,1, # Ting Zeng,1, # Mohamed Nourrein,1 Bo-Han Lai,2 Kaiwen Shen,1 Chien-Lung Wang,2, # Bin Sun,1, * Meifang Zhu, 1, *

1 State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, and Center for Advanced Low-dimension Materials, Donghua University, 201620, Shanghai, P. R. China

2 Department of Applied Chemistry, National Chiao Tung University, 1001 Ta Hsueh Road, Hsin-Chu, 30010, Taiwan.

E-mail: sunbin@dhu.edu.cn; kclwang@nctu.edu.tw; zmf@dhu.edu.cn

#: These authors contribute equally to the work.

Experimental Section

Materials and Sample Preparations. 3,4,9,10-Perylenetetracarboxylic dianhydride (>99.9%) and dodecylamine (>99.9%) were purchased from Aldrich. Iodine (>98.0%), Bromine (>99.5%), 18-crown 6-ether (>99.0%) were obtained from J&K Chemical (China). H₂SO₄ (95-98%), Silica gel (>80%, 200-300), Chloroform (>99%), K₂CO₃ (>99.0%), triethylene glycol were purchased from Sinopharm Chemical Reagent Co., LTD (Shanghai, China).
**General Measurement and Characterization.** UV-Vis experiment was carried out by the PerkinElmer Lambda 35 spectrophotometer with the change of the concentration. Fluorescence spectra were obtained on JASCO FP-6600. The cyclic voltammetry (CV) data were analyzed by a electrode system with platinum electrode served as the working electrode and saturated calomel electrode (SCE) as the reference electrode, while acetonitrile solution of 0.1M TBAPF$_6$ as the electrolyte and 10$^{-2}$ M desired compound dissolved in CH$_3$CN. For 1D XRD patterns, a Rigaku MultiFlex 2 kW tube-anode X-ray (Cu Ka radiation) generator coupled to a diffractometer were used at room temperature, and the sample was scanned with 1°/min scanning rate. Transmission Electron Microscopy (TEM) observations were performed on a JEOL JEM-2010 transmission electron microscope with an accelerating voltage of 160 kV and a Gatan-831 CCD camera. The photographs of the self-assembled morphologies were observed by BX-51 polarizing microscope (polarized light and natural light) and Japan HITACHI field emission scanning electron microscope(SEM), model S-4800. FTIR data were performed by US Thermo Fisher Nicolet iN 10 MX.

**Synthesis and Characterization of N,N′-bis(n-dodecyl)-1,7-di(triethylene glycol)-perylen-3,4,9,10-tetracarboxyl-diimide (1,7-TEG-PDI-C$_{12}$)**

N,N′-bis(n-dodecyl)-1,7-dibromo-perylene-3,4,9,10-tetracarboxyl-diimide$^{1,2}$ (100 mg, 0.11 mmol) was dissolved in 25 mL THF and stirred at room temperature for 1 hour. Then, potassium carbonate (60.8 mg, 0.44 mmol), 18-crown-6-ether (116.30 mg, 0.44 mmol) and triethylene glycol (0.06594 mL, 0.495 mmol) were added and stirred at room temperature for two hours. THF was removed by rotary evaporation at 50 °C. The unreacted triethylene glycol was removed by extraction with chloroform and water. Rotary evaporation was used again to remove chloroform at 50 °C. The crude product was purified by column chromatography (chloroform/methanol = 200/3, v/v, $R_f = 0.40$) to give a fuchsia solid (92.48mg, 80%). Vacuum oven was used to obtain dry product.

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 9.77 (d, $J = 12$ Hz, 2H), 9.44 (d, $J = 12$ Hz, 2H), 8.46 (s, 2H), 4.66 (d, 2H), 4.23 (d, $J = 8$ Hz, 4H), 4.13 (s, 4H), 3.91 –3.86 (m, $J = 8$ Hz, 4H), 3.81 (m, $J = 8$ Hz, 4H), 3.71 (m, $J = 8$ Hz, 4H), 2.26 (m, 4H), 2.04 (m, 4H), 1.27 (s, 32H), 0.88 (t, $J = 6.7$ Hz, 6H); MALDI-TOF MS (m/z): C$_{60}$H$_{82}$O$_{12}$N$_2$ 1022.59 (calcd), 1022.64 (measured). $^{13}$C NMR (400 MHz,CDCl$_3$) δ (ppm) 163, 164, 156, 133, 130, 128, 123, 122, 121, 120, 117, 72, 71, 70, 69.5, 69, 62, 41, 32, 30, 29, 28, 27, 23, 14.
Fig. S1  $^1$H NMR spectrum of 1,7-TEG-PDI-$\text{C}_12$ in CDCl$_3$.

Fig. S2  $^{13}$C NMR spectrum of 1,7-TEG-PDI-$\text{C}_12$ in CDCl$_3$. 
Fig. S3  MALDI-TOF-MS spectrum of 1,7-TEG-PDI-C_{12}.

Reference