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). H_2SO_4 (95-98%), Silica gel (>80%, 200-300), Chloroform (>99%), K_2CO_3 (>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_3CN. For 1D XRD patterns, a Rigaku MultiFlex 2 kW tube-anode X-ray (Cu Kα 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)-perylene-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 ℃. The unreacted triethylene glycol was removed by extraction with chloroform and water. Rotary evaporation was used again to remove chloroform at 50 ℃. 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 = 12Hz, 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.

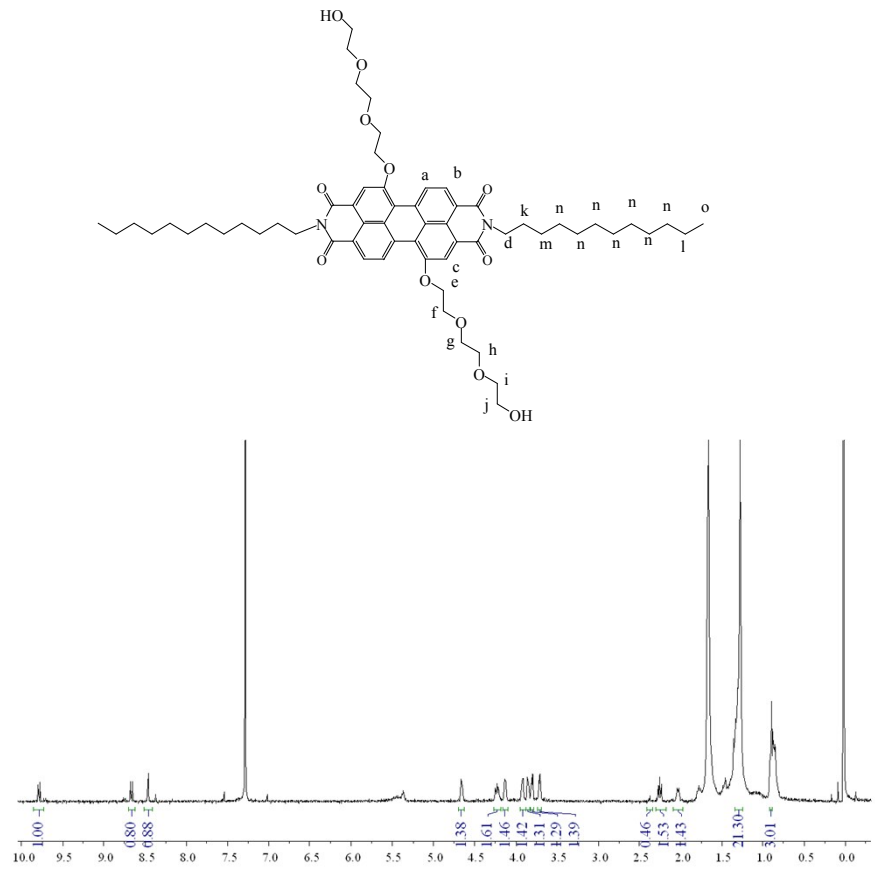

Fig. S1 ^{1}H NMR spectrum of 1,7-TEG-PDI-C_{12} in $CDCl_3$.

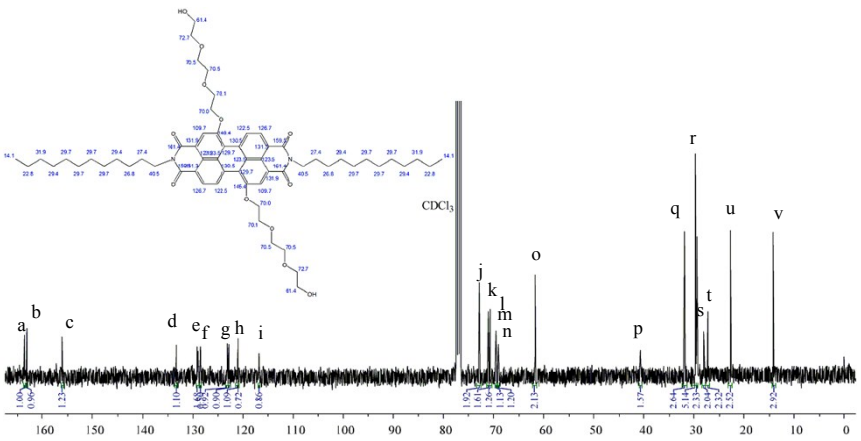

Fig. S2 ^{13}C NMR spectrum of 1,7-TEG-PDI-C_{12} in $CDCl_3$.

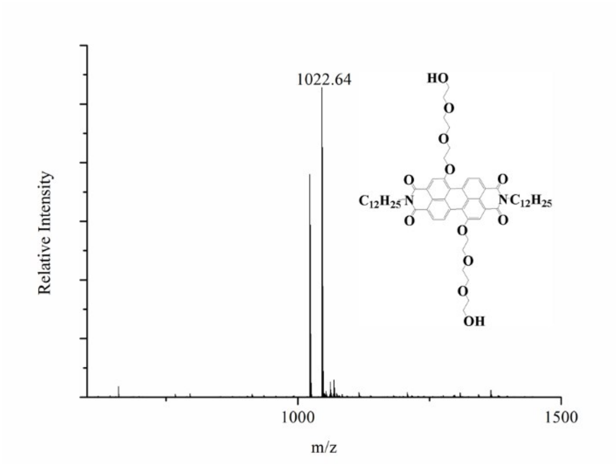

Fig. S3 MALDI-TOF-MS spectrum of 1,7-TEG-PDI-C_{12}**.**

Reference

(S1). L. Fan, Y. Xu and H. Tian, *Tetrahedron lett*., 2005, **46**, 4443-4447.

(S2). F. Würthner, V. Stepanenko, Z. Chen, C. R. Saha-Möller, N. Kocher and D. Stalke, *J. Org. Chem.*, 2004, **69**, 7933-7939.