

Electronic supplementary information

How Does the Interplay between Bromine Substitution at Bay Area and Bulky Substituents at Imide Position Influence the Photophysical Properties of Perylene Diimides?

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Experimental Section

Chemicals and Solvents. Aminopropyl Isobutyl POSS (Hybrid Plastics, AM0265, $\geq 97\%$), dodecylamine (J&K chemical Ltd, $\geq 99.0\%$), perylene-3,4,9,10-tetracarboxylic dianhydride (J&K chemical Ltd, $\geq 98.0\%$), imidazole (J&K Chemical Ltd, $\geq 99\%$), 1,2-dichlorobenzene (ODCB, J&K Chemical Ltd, anhydrous, 99%), bromine (J&K Chemical Ltd, $\geq 99.0\%$), and other organic solvents (purchased from J&K Chemical Ltd if not noted otherwise) were used as received without further purification. PTCDA_{Br} was prepared according to the literature.^{S1}

Instrumentation. The NMR spectra were measured on a Bruker 400 MHz NMR spectrometer with deuterated chloroform (CDCl₃, J&K Chemical Ltd, ≥ 99.8 D%) as solvent. The ¹H NMR spectra were referenced to the residual proton impurities in the CDCl₃ at δ 7.27 ppm. The ¹³C NMR spectra were referenced to CDCl₃ at δ 77.00 ppm. The FT-IR spectra were recorded on Nicolet 5700 FT-IR in which KBr pellets were used for powder sample. UV-Vis spectra were recorded on a Lambda 35 (Perkin Elmer) spectrophotometer. The excitation and emission spectra of the samples were investigated on a FP-6600 steady-state fluorescence spectrophotometer. All the measurements were carried out at room temperature in ambient air (unless stated otherwise) and the analysis range was 200-800 nm with a resolution of 1 nm. Except for the self-assembly studies using hexanol as solvent, the spectra were obtained in chloroform. UV-Vis absorption spectra in solid state were tested on UV-Vis Lambda 950. The concave attachment was fully filled with samples and the testing range is from 300-800 nm. Solid-state steady-state fluorescence spectra and fluorescence quantum yield measurements were performed on a JASCO FP-6600 spectrofluorimeter equipped with a 60 mm diameter integrating sphere accessory and corresponding software.

One-dimensional (1D) WAXD powder pattern was obtained at room temperature with a Rigaku MultiFlex 2 kW tube-anode X-ray (Cu K α radiation) generator coupled to a diffractometer. The samples were scanned at a 1 °C/min scanning rate. SEM images were obtained on S-4800 (HITACHI, Japan). Sample preparation was achieved by dropping the dispersion of compound **4** in ethanol on aluminum foil. Quantum chemical calculation was performed by the method of density functional theory (DFT) using Gaussian 09 package. The optimized geometries of molecular structures of compounds **2** and **4** were achieved by adopting B3LYP method with 6-31G** basic set via energy minimization.

Synthesis of POSS-PDI_{Br}-POSS **4.** POSS-PDI_{Br}-POSS (**4**) was prepared from condensation of POSS-NH₂ and PTCDA_{Br} in a protocol modified from previous reports (Scheme S1).^{S2} Briefly, POSS-NH₂ (4.54 g, 5.2 mmol), PTCDA_{Br} (1.44 g, 2.6 mmol), imidazole (9.2 g) and 10 mL ODCB were placed in a round bottom flask fitted with a reflux condenser. Under an argon atmosphere, the mixture was heated in an oil bath at 160 °C with vigorous stirring for 6 h. It was then cooled and dispersed in 70 mL of 2 N HCl overnight and the precipitate formed was filtered and washed with water to remove excess amine. Then the crude compound was purified using column chromatography with hexane: ethyl acetate (25:1, v/v) to afford 4.77 g (yield 80%). FT-IR (KBr) 3431, 2950, 2879, 1702, 1664, 1590, 1466, 1394, 1333, 1227, 1100, 1025, 835, 809, 757, 563 and 482 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 9.51 (d, 2H), 8.94 (s, 2H), 8.73 (d, 2H), 4.23 (m, 4H), 1.85 (m, 16H), 0.96 (t, 84H), 0.73 to 0.6 (m, 32 H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 161.9, 138.3, 132.8, 129.4, 126.8, 122.8, 120.9, 43.1, 25.3, 23.6, 22.2, 21.1, 9.5.

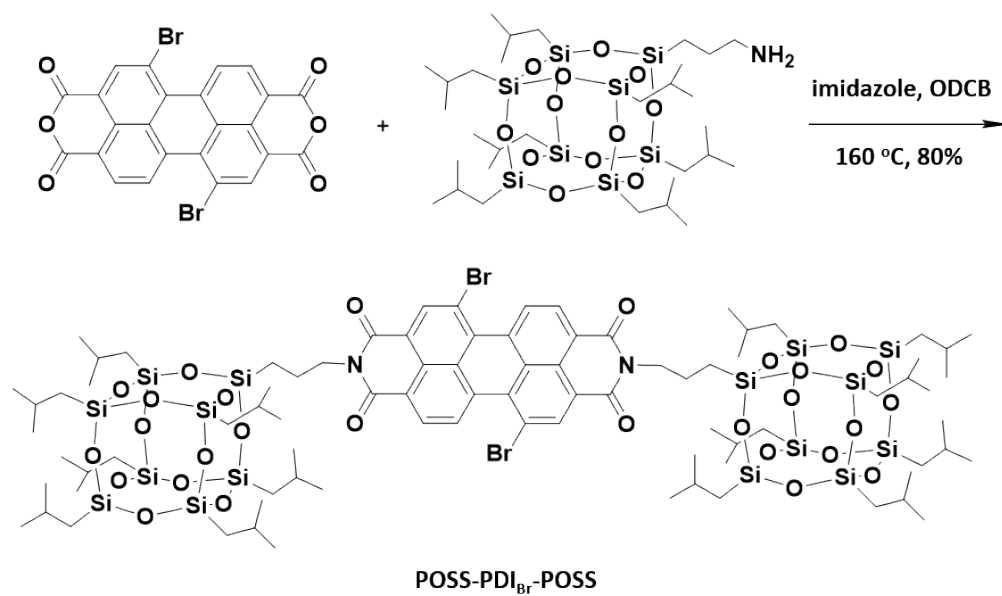
Crystal Growth and Characterization. The crystals of **4** were made by first dissolving a small amount of **4** in chloroform, then a large amount of methanol (which is poor solvent for **4**)

was carefully laid on top without disturbing the interface. The mixture was left to stand for a period of two weeks. Needle like crystals of the two samples were formed and settled at the bottom of the mixture. It could be easily separated and subsequently washed with clean methanol.

A single crystal of **4** with dimensions of 0.14 mm × 0.16 mm × 0.60 mm mounted on glass fibers for crystal structure analyses. Measurements of the compound was conducted on a Bruker Smart Apex CCD diffractometer with a graphite-monochromatic Mo K α radiation ($\lambda=0.071073$ nm) at 213 (2) K. The structure was solved by direct methods and refined on F2 with the SHELX-97 program. All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms were generated geometrically.

To calculate the parameters of the crystal structure. Firstly, we transform the twisted perylene planar to the planar in according to N-N axis as part of the planar. And then the longitudinal offset (l), transverse offset (t), interplanar spacing (d) and the rotational angle (α) were measured directly from the data of the crystal unit cell lattice parameters obtained from single crystal X-ray diffraction experiments.

Crystal data for **4**: C₈₆H₁₄₄Br₂N₂O₂₈Si₁₆, $M = 2263.28$, triclinic, $a = 1.11$ nm, $b = 2.16$ nm, $c = 2.43$ nm, $\alpha = 92.6^\circ$, $\beta = 99.0^\circ$, $\gamma = 90.6^\circ$, $V = 5773.2$ Å³, $T = 213$ K, space group P-1, $Z = 2$, $\mu_{(\text{MoK}\alpha)} = 0.258$ mm⁻¹, 40710 reflections measured, 24993 independent reflections ($R_{\text{int}} = 0.0556$). The final R_I values were 0.0902 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2464 ($I > 2\sigma(I)$). The final R_I values were 0.1705 (all data). The final $wR(F^2)$ values were 0.2991 (all data). The goodness of fit on F^2 was 0.946.



Scheme S1 Synthetic scheme for POSS-PDI_{Br}-POSS (4).

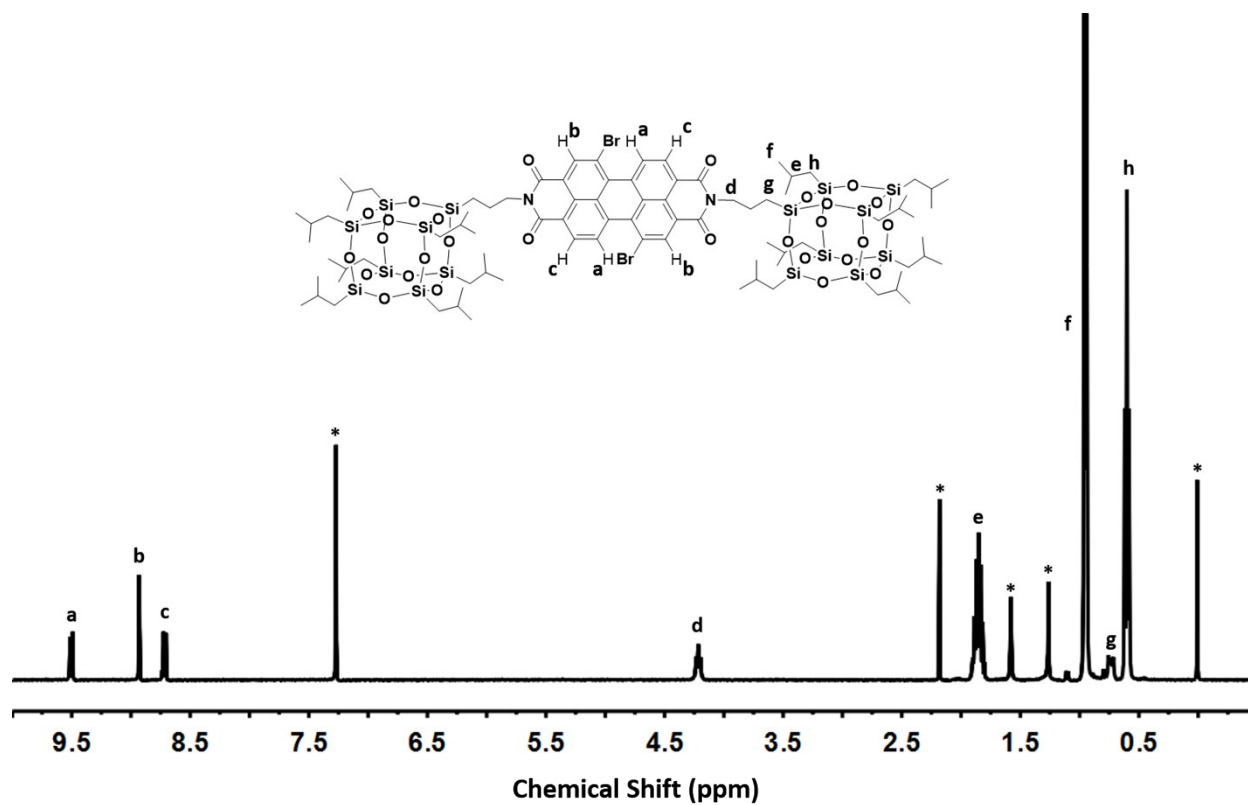


Fig. S1 ¹H NMR spectrum of POSS-PDI_{Br}-POSS (4) in CDCl₃.

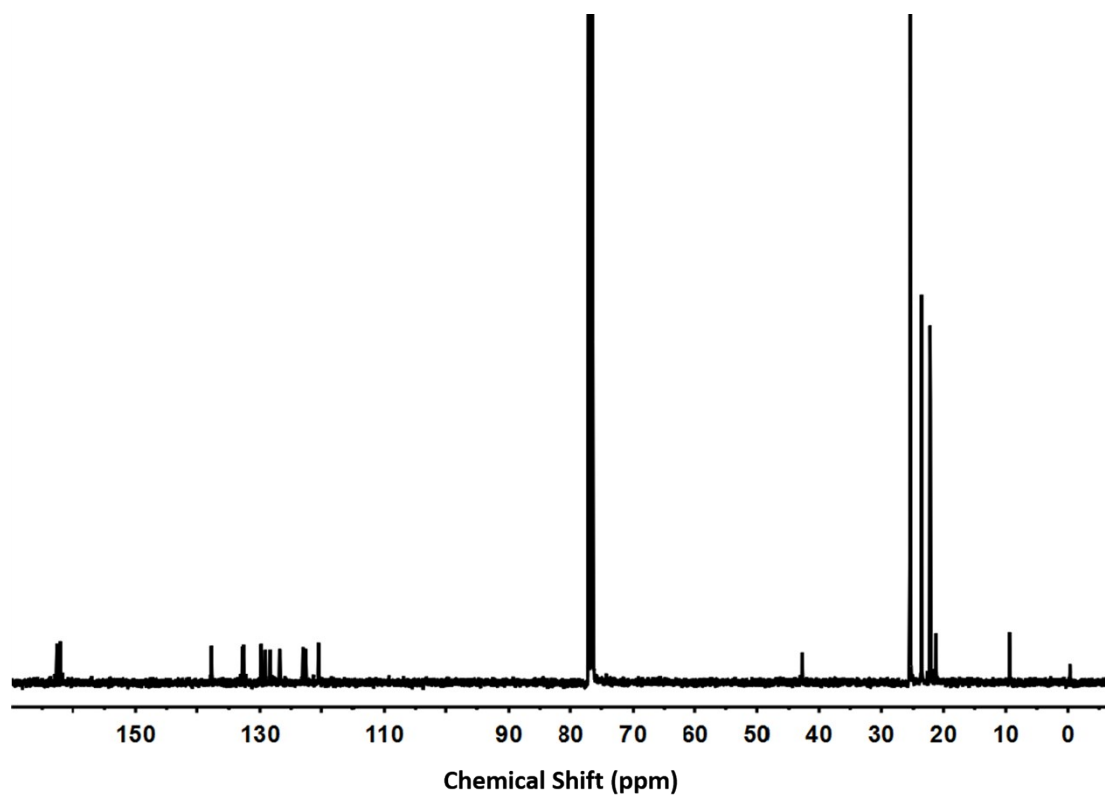


Fig. S2 ^{13}C NMR spectrum of POSS-PDI_{Br}-POSS (**4**) in CDCl_3 .

Formula of POSS-PDI_{Br}-POSS: C₈₆H₁₄₄Br₂N₂O₂₈Si₁₆Na

Calcd.: 2281.45

Found: 2281.45

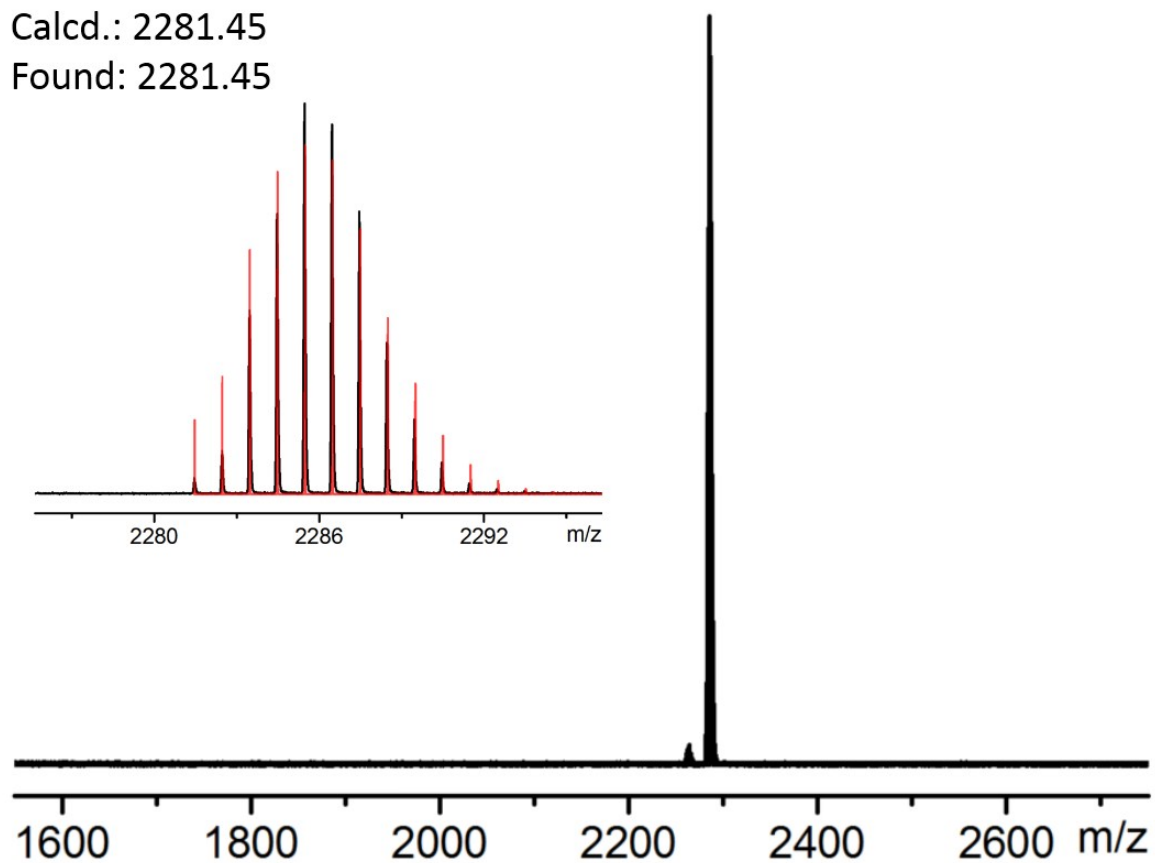


Fig. S3 MALDI-TOF-MS spectrum of POSS-PDI_{Br}-POSS (**4**). The inset shows the zoom-in view of the peak (black line) which matches well with the simulated spectrum (red line).

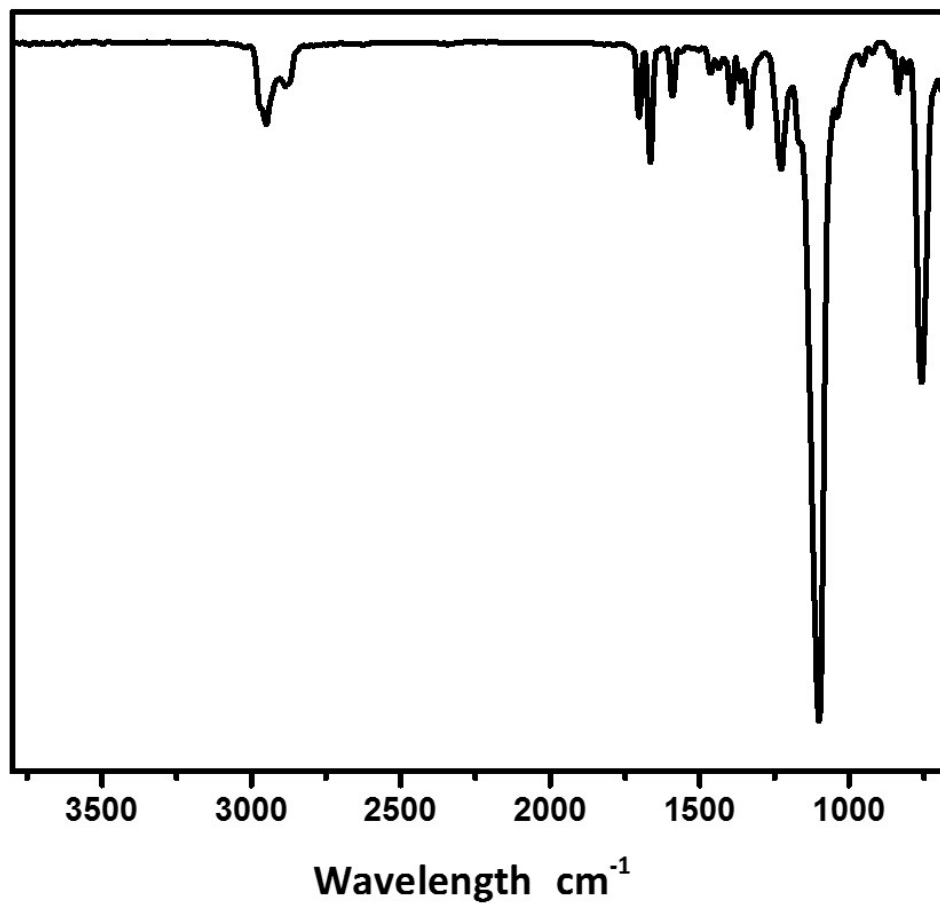


Fig. S4 FT-IR spectrum of POSS-PDI_{Br}-POSS (4).

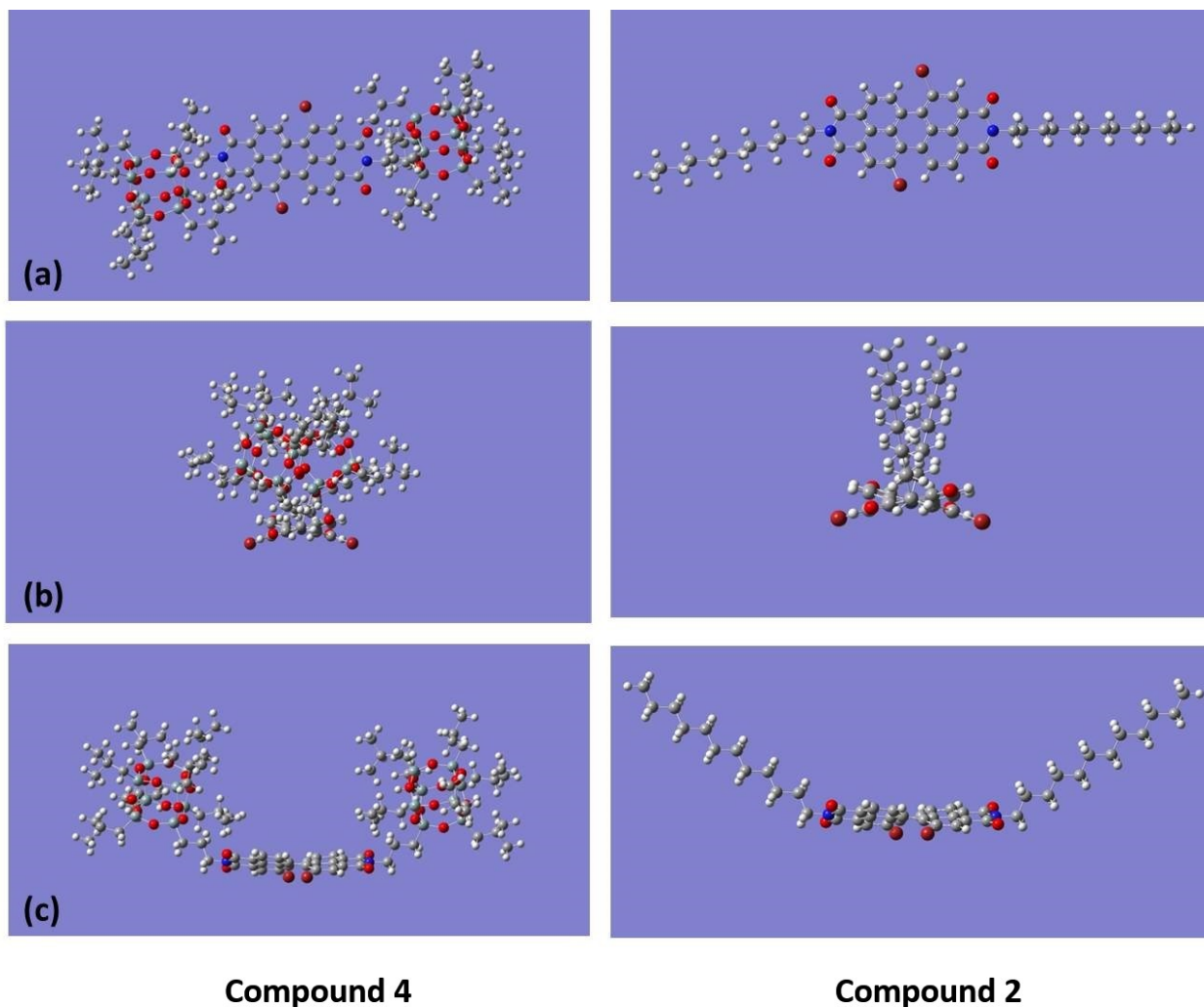


Fig. S5 Energy-minimized molecular models of compounds **2** and **4** obtained at B3LYP/6-31G** level: (a) the perylene plane, (b) view along the long axis (N-N axis), (c) view along the short axis.

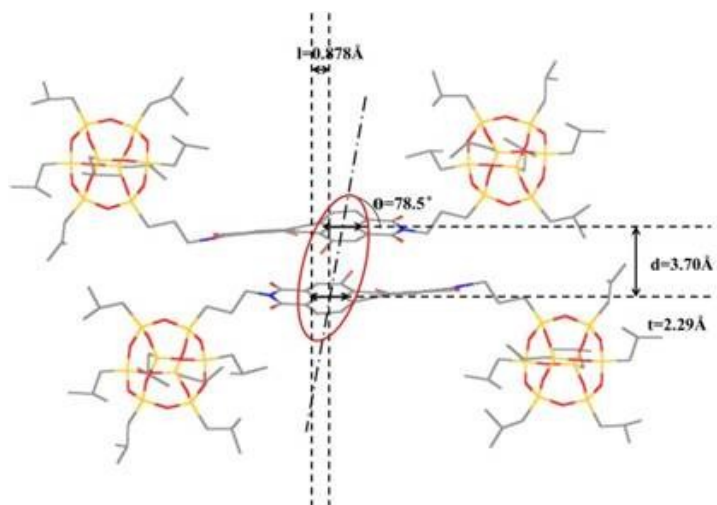


Fig. S6 Molecular model of the dimer of compound **4** as in the crystal. It shows that the packing of two naphthalene moieties has a tilting angle of 78.5° , which is close to face-to-face arrangement.

References

- (S1) R. K. Dubey, A. Efimov and H. Lemmetyinen, *Chem. Mater.*, 2010, **23**, 778-788.
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- (S3) L. M. Wangatia, B. Sun, T. Zeng, and M. F. Zhu, *Mater. Sci-Poland* **2015**, 33(1):113-121