

Electronic Supplementary Information

Chalcogen–substitution modulated supramolecular chirality and gas sensing properties in perylenediimides

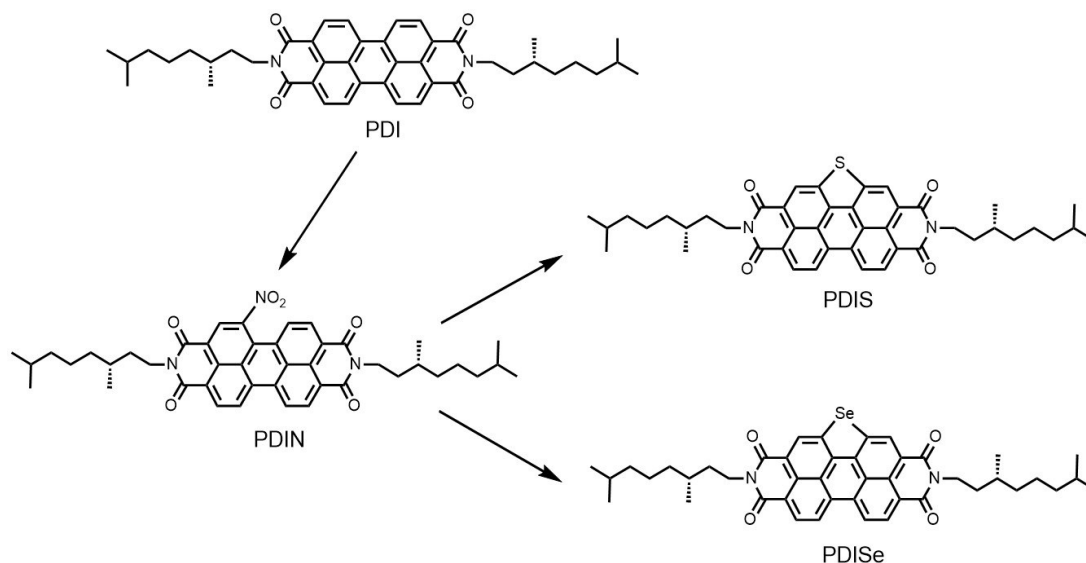
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Experimental

1. Synthesis and characterization of PDI, PDIS and PDISE



N, N'-bis((s)-(-)-3,7-dimethyloctyl)perylene-3,4:9,10-tetracarboxydiimide (PDI)

3,4,9,10-Prelenetetracarboxylic dianhydride (0.5 g, 1.27 mmol), *s*-(-)-3,6-dimethyl-heptylamine (0.73 g, 5.08 mmol)¹ and imidazole (6 g) were stirred at 180 °C under argon atmosphere for 4 h. The mixture was cooled to room temperature, then added ethanol (50 mL) and 2 M HCl (90 mL). The mixture was next allowed to stir overnight. The red precipitate was collected by filtration, followed by washing with water and drying under vacuum. The crude product was then purified by chromatographed on silica (chloroform) to afford the red product PDI (0.61 g, 71%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.62 (d, J = 8.0 Hz, 4 H), 8.52 (d, J = 8.0 Hz, 4 H), 4.22 (m, 4 H), 1.76 (m, 2 H), 1.60 (m, 4 H), 1.53 (m, 2 H), 1.30 (m, 18 H), 0.87 (t, 12 H). MS (MALDI-TOF): calcd for C₄₄H₅₀N₂O₄, 670.38 m/z, found 670.18. Anal. Calcd for C₄₄H₅₀N₂O₄: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.89; H, 7.42; N, 4.33.

N, N'-bis((s)-(-)-3,7-dimethyloctyl)-1-nitroperylene-3,4:9,10-tetracarboxydiimide (PDIN).²

A solution of PDI (1 g, 1.49 mmol) in CH₂Cl₂ was cooled in ice bath. Then a diluted solution of fuming nitric acid (3 mL) in CH₂Cl₂ (5 mL) was added by drop over a period of 15 min. The reaction mixture was stirred at 0 °C for additional 2 h. Next, the cooled mixture was poured into methanol and the precipitate was collected by vacuum filtration, washed with water, dried and purified by column chromatography on silica gel (petroleum ether / CH₂Cl₂, 1:1 v/v) to afford a dark red solid PDIN (0.60 g, 56%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.80 (m, 1 H), 8.73 (m, 4 H), 8.62 (m, 1 H), 8.26 (m, 1 H), 4.24 (m, 4 H), 2.22 (m, 1 H), 2.07 (m, 2 H), 1.75 (m, 3 H), 1.52 (m, 2 H)

,1.26 (m, 18 H), 0.87 (t, 12 H). MS (MALDI-TOF): calcd for C₄₄H₄₉N₃O₆, 715.36 m/z, found 715.25. Anal. Calcd for C₄₄H₄₉N₃O₆: C, 73.82; H, 6.90; N, 5.87. Found: C, 73.89; H, 6.78; N, 5.86.

N,N'-bis((s)-(-)-3,7-dimethyloctyl)-[1,7-*b*:7',1'-*d*]thiophene-perylene-3,4:9,10-tetracarboxyldiimide (PDIS).²

Sulfur powder (8.74 mmol) was dissolved in *N*-methylpyrrolidone (NMP, 35 mL, 70 °C), then PDIN (624 mg, 0.874 mmol) was added under argon. The mixture was heated to 190 °C with vigorous stirring for 3 h until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into 1 L of 2 M HCl, then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether /CH₂Cl₂, 1:1 v/v) to give yellow-brown needle PDIS (318 mg, 52%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 9.30 (m, 2 H), 8.91 (m, 4 H), 4.33 (m, 4 H), 2.22 (m, 1 H), 2.02 (m, 2 H), 1.81 (m, 3 H), 1.52 (m, 2 H), 1.21 (m, 12 H), 1.08 (m, 6 H), 0.88 (t, 12 H). MS (MALDI-TOF): calcd for C₄₄H₄₈N₂O₄S, 700.33 m/z, found 700.12. Anal. Calcd for C₄₄H₄₈N₂O₄S: C, 75.40; H, 6.90; N, 4.00. Found: C, 75.10; H, 6.76; N, 3.92.

N,N'-bis((s)-(-)-3,7-dimethyloctyl)-[1,7-*b*:7',1'-*d*]selenophene-perylene-3,4:9,10-tetracarboxyldiimide (PDISe).³

Selenium (8.74 mmol) was dissolved in *N*-methylpyrrolidone (NMP, 35 mL, 70 °C), then PDIN (624 mg, 0.874 mmol) was added under argon. The mixture was heated to 190 °C with vigorous stirring for 3 h until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into 1 L of 2 M HCl, then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether /CH₂Cl₂, 1:1 v/v) to give yellow-brown needle PDISe (311 mg, 48%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.96 (m, 2 H), 8.84 (m, 4 H), 4.31 (m, 4 H), 2.22 (m, 1 H), 2.01 (m, 2 H), 1.80 (m, 3 H), 1.62 (m, 6 H), 1.40 (m, 6 H), 1.19 (m, 4 H), 1.08 (m, 4 H), 0.88 (t, 12 H). MS (MALDI-TOF): calcd for C₄₄H₄₈N₂O₄Se, 748.28 m/z, found 748.12. Anal. Calcd for C₄₄H₄₈N₂O₄Se: C, 70.67; H, 6.47; N, 3.75. Found: C, 70.36; H, 6.56; N, 3.83.

2. Methods

Circular dichroism (CD) measurements were conducted on a JASCOJ-810 spectrometer at room temperature. UV-vis adsorption spectra were recorded on Perkin-Elmer Lambda 950 UV-vis spectroscopy. SEM measurement was acquired using a field-emission scanning electron microscopy (Hitachi S-4800, 5 kV). ¹H NMR was acquired using a Bruker 400 MHz NMR spectrometer. PDI, PDIS and PDISe gas sensing devices were fabricated according to a published procedure with some modifications.⁴ Firstly, highly doped *n*-type Si (100) wafers (< 0.004 Ω cm) were used as substrates, and a 500 nm SiO₂ layer (capacitance per unit area C_i = 7.5 nF cm⁻²) as a gate dielectric was thermally grown onto the Si substrates. These wafers were cleaned in piranha solution, a 7:3 mixture

of H₂SO₄ and H₂O₂, rinsed with deionized water, and then dried by N₂ stream. Then, self-assembled PDI, PDIS and PDISE nanostructures were transferred to Si/SiO₂ substrates by drop-casting, followed drying in air, and nanowires or nanofibers as sensitive layer was obtained. Finally, drain and source electrodes for current (I)-time (t) measurement were fabricated by vapor depositing Au (5×10^{-5} Torr, 0.5 Å/s, ~50 nm thick) onto nanowires or nanofibers with a shadow mask to obtain devices with a channel width of 1-2 μm and length of 5 mm. The device was put into the test chamber having a volume of 1 L. The current variations were recorded at 25 °C in vacuum with a Keithley 4200-SCS system until the current reached a steady value. Then a certain amount of ammonia was injected into the test chamber. The response was defined as the ration of I/I₀, where I and I₀ represented the real-time and the initial current on exposure to ammonia vapor, respectively.

The theoretical calculation was performed using density functional theory (DFT) provided by the DMol3 code.⁵ The Perdew and Wang parameterization⁶ of the local exchange correlation energy are applied in the local spin density approximation (LSDA) to describe exchange and correlation. We expanded the all-electron spin-unrestricted Kohn-Sham wave functions in a local atomic orbital basis. In such double-numerical basis set polarization was described. All calculations were all-electron ones, and performed with the Extra-Fine mesh. Self-consistent field procedure was done with a convergence criterion of 10⁻⁵ a.u. on the energy and electron density.

3. Supporting Table and Figures

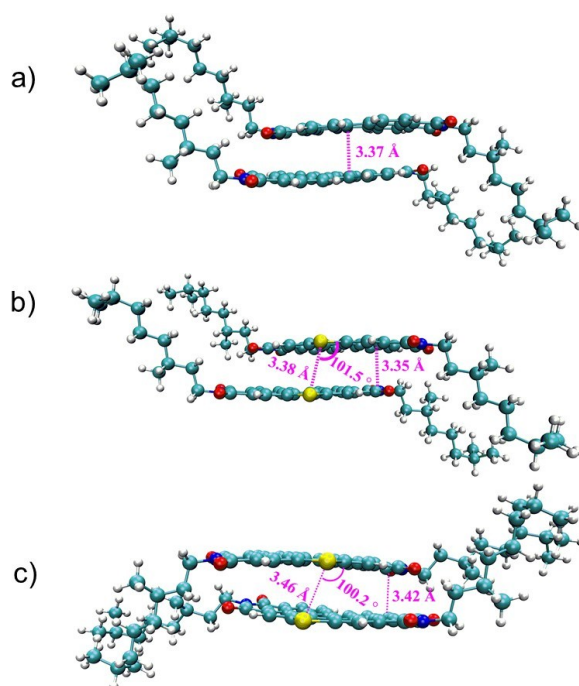


Fig. S1 The chalcogen-chalcogen distance, Lewis base angle and stacking distance for (a) PDI, (b) PDIS and (c) PDISE dimers.

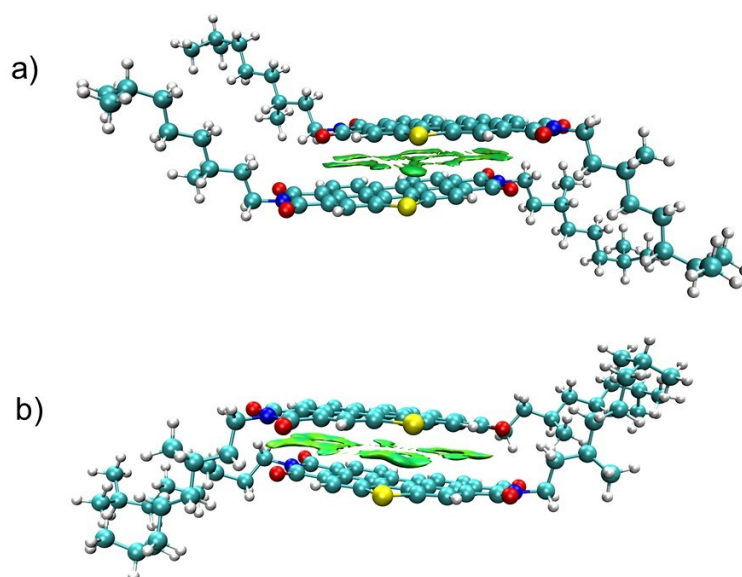


Fig. S2 Color-filled IGM maps of intermolecular interactions for (a) PDIS and (b) PDISe dimers. IGM isovalue $\delta g^{\text{inter}}(r) = 0.01$, the strength of interaction indicated by the color bar possessing the values of $\text{sign}(\lambda_2)\rho$ ranging from -0.05 to $+0.05$ a.u. Green denotes vdW dispersion interaction.

References

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