

Electronic Supplementary Information for

Effect of stereoisomerism of alkyl chain on the gas sensing
properties based on perylene dyes

Chunli Li,^b Haiyan Zhai,^a Xiaotian Liu^c, Weiguang Zhang^a and Yongwei Huang^{*a}

^a *Medical College, Henan University, Kaifeng 475004, China*

^b *Key Laboratory for Special Functional Materials of Ministry of Education,
Henan University, Kaifeng 475004, China*

^c *College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China.*

1. Synthesis of OT, ROT and SOT

***N, N'*-bis(*n*-dodecyl)-1,7-di(1-Octyn-3-ol) perylene-3,4:9,10-tetracarboxyldiimide (OT)**

N, N'-bis(*n*-dodecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxyldiimide (100 mg, 0.11 mmol), 1-Octyn-3-ol (85.56 mg, 0.68 mmol), [Pd(PPh₃)₄] (13 mg, 0.01 mmol), CuI (2.2 mg, 0.01 mmol) were stirred in a mixture of 13.5 mL of triethylamine and 13.5 mL of THF for 14 h at 53 °C under argon atmosphere. The mix was cooled to room temperature and diluted with CH₂Cl₂. The organic layer was extracted with water washing to neutral, dried with Na₂SO₄, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (methanol/CHCl₃, 2:98) to yield the brown product 60 mg (56%). ¹H-NMR (CDCl₃, 400MHz) δ (ppm): 0.3~2.37 (m, 68 H), 4.07~5.15 (m, 8 H), 8.17~8.92 (m, 4 H), 9.67~9.69 (d, *J* = 8.0, 2 H). MS (MALDI-TOF): calcd for C₆₄H₈₂N₂O₆, 974.62 m/z, found 974.31. Anal. Calcd for C₆₄H₈₂N₂O₆: C, 78.81; H, 8.47; N, 2.87. Found: C, 78.65; H, 8.96; N, 2.91.

***N, N'*-bis(*n*-dodecyl)-1,7-di(*R*)-1-Octyn-3-ol) perylene-3,4:9,10-tetracarboxyldiimide (ROT)**

N, N'-bis(*n*-dodecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxyldiimide (200 mg, 0.23 mmol), (*R*)-1-octyn-3-ol (125 mg, 0.95 mmol), [Pd(PPh₃)₄] (26 mg, 0.02 mmol), CuI (4.3 mg, 0.02 mmol) were stirred in a mixture of 13.5 mL of triethylamine and 13.5 mL of THF for 14 h at 53 °C under argon atmosphere. The mix was cooled to room temperature and diluted with CH₂Cl₂. The organic layer was extracted with water washing to neutral, dried with Na₂SO₄, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (methanol/CHCl₃, 2:98) to yield the brown product 140 mg (63%). ¹H-NMR (CDCl₃, 400MHz) δ (ppm): 0.3~2.60 (m, 68 H), 4.07~5.17 (m, 8 H), 8.37~9.02 (m, 4 H), 9.91~9.92 (d, *J* = 8.0, 2 H). MS (MALDI-TOF): calcd for C₆₄H₈₂N₂O₆, 974.62 m/z, found 974.41. Anal. Calcd for C₆₄H₈₂N₂O₆: C, 78.81; H, 8.47; N, 2.87. Found: C, 78.75; H, 8.66; N, 2.71.

***N, N'*-bis(*n*-dodecyl)-1,7-di(*S*)-1-Octyn-3-ol) perylene-3,4:9,10-tetracarboxyldiimide (SOT)**

N, N'-bis(*n*-dodecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxyldiimide (200 mg, 0.23 mmol), (*S*)-1-octyn-3-ol (125 mg, 0.95 mmol), [Pd(PPh₃)₄] (26 mg, 0.02 mmol), CuI (4.3 mg, 0.02 mmol) were stirred in a mixture of 13.5 mL of triethylamine and 13.5 mL of THF for 14 h at 53 °C under argon atmosphere. The mix was cooled to room temperature and diluted with CH₂Cl₂. The organic layer was extracted with water washing to neutral, dried with Na₂SO₄, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (methanol/CHCl₃, 2:98) to yield the brown product 163 mg (73%). ¹H-NMR (CDCl₃, 400MHz) δ (ppm): 0.2~2.34 (m, 68 H), 4.09~5.17 (m, 8 H), 8.12~8.86 (m, 4 H), 9.65~9.69 (d, *J* = 7.8, 2 H). MS (MALDI-TOF): calcd for C₆₄H₈₂N₂O₆, 974.62 m/z, found 974.61. Anal. Calcd for C₆₄H₈₂N₂O₆: C, 78.81; H, 8.47; N, 2.87. Found: C, 78.89; H, 8.42; N, 2.68.

2. Methods

UV-vis adsorption spectra were recorded on Perkin-Elmer Lambda 950 UV-vis spectroscopy. ^1H NMR was acquired using a Bruker 400 MHz NMR spectrometer. The X-ray diffraction patterns of these OT, ROT and SOT films were determined on a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The surface morphologies of thin film from THF solutions ($0.5 \text{ mg}\cdot\text{mL}^{-1}$) on Si substrates were observed on a Nanoscope IIIa Atomic Force Microscopy (AFM) in tapping mode. CD measurements were conducted on a JASCOJ-810 spectrometer at room temperature. In the process of measuring CD spectra, the film on the quartz plate was placed perpendicular to the light path and continuously rotated within the film plane, using a custom-built attachment to avoid possible linear dichroism (LD) in the films. The film thickness was examined by KLa-Ten Alpha-step D-120 stylus profiler. OT, ROT and SOT devices were fabricated as shown below. Firstly, highly doped *n*-type Si (100) wafers ($< 0.004 \text{ } \Omega \text{ cm}$) were used as substrates, and a 500 nm SiO_2 layer (capacitance per unit area $C_i = 7.5 \text{ nF cm}^{-2}$) as a gate dielectric was thermally grown onto the Si substrates. These wafers were cleaned in piranha solution, a 7:3 mixture of H_2SO_4 and H_2O_2 , rinsed with deionized water, and then dried by N_2 stream. Then, the THF solutions of OT, ROT and SOT were transferred to Si/ SiO_2 substrates by spin-coating, followed drying in air, and the semiconductor film as sensitive layer was obtained. Finally, drain and source electrodes for current (I)-time (t) measurement were fabricated by vapor depositing Au ($5 \times 10^{-5} \text{ Torr}$, 0.5 \AA/s , $\sim 50 \text{ nm}$ thick) onto films with a shadow mask to obtain devices with a channel width of $0.5\text{-}1 \text{ } \mu\text{m}$ and length of 5 mm . The device was put into the test chamber having a volume of 2 L . The current variations were recorded at $25 \text{ }^\circ\text{C}$ in vacuum with a Keithley 4200-SCS system until the current reached a steady value. Then a certain amount of hydrazine was injected into the test chamber. The response was defined as the ration of I/I_0 , where I and I_0 represented the current flowing through films on exposure to hydrazine vapor and in vacuum, respectively.

2. Supporting Figures

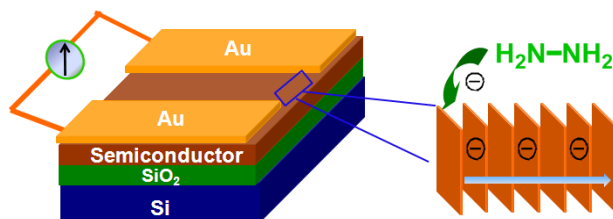


Fig. S1 Schematic for the electron transport along the long-axis of OT, ROT and SOT films in hydrazine vapor.

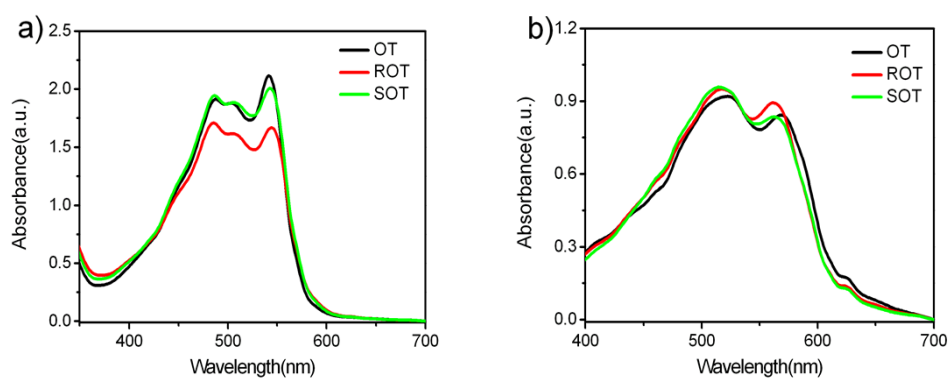


Fig. S2 Normalized UV-vis spectra of OT, ROT and SOT (a) in THF solution and (b) in films.

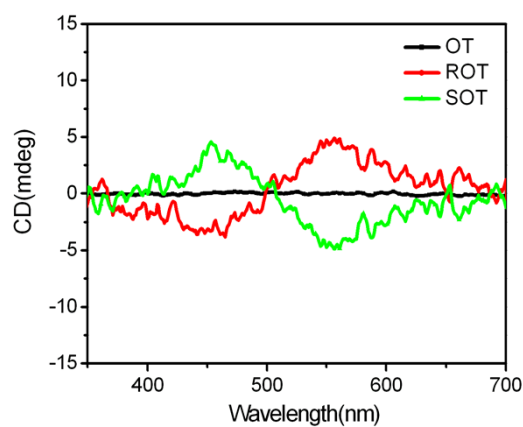


Fig. S3 The CD spectra for OT, ROT and SOT films.