Electronic Supplementary Information for

Highly responsive hydrazine sensors based on donor-acceptor perylene diimides: impact of electron-donating groups

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1. Synthesis of PDI-PY, PDI-PI and PDI-HE

N,N′-(n-hexadecyl)-1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxyldiimide (PDI-PY).[1]

N,N'-(*n*-hexadecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic diimide (0.066 g, 0.066 mmol), pyrrolidine (2.23 g, 31.4 mmol) and dry K_2CO_3 (0.50 g , 3.60 mmol) was stirred under Ar for 24 h at 55 °C .Subsequently, the reaction mixture was poured into 15 mL of 10% HCl under stirring and extracted with methylene chloride (3×30 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting precipitate was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to yield green solid PDI-PY (34.4 mg, 53%). ^{1}H NMR (400 MHz，$CDCl_3$)，δ (ppm)：7.42-8.70 (m，6 H)，4.21 (m，4 H)，3.72 (m，4 H)，2.79 (m，8 H)，1.75(m，4 H)，1.30 (m，56 H)，0.87(m，6 H). ^{13}C NMR(100 MHz,$CDCl_3$)：δ (ppm) 167.7, 163.9, 146.3, 130.8, 129.8, 128.8, 126.5,123.6, 122.0, 121.6, 120.6, 119.0, 118.0,

77.3, 77.0, 76.7, 68.1, 65.5, 52.1, 40.5, 38.7, 29.7, 29.6, 29.3, 28.2, 25.7, 23.7, 22.6, 19.1, 14.1, 13.7, 10.9. MS (MALDI-TOF): calcd for $C_{64}H_{88}N_2O_4$, 976.68 m/z, found 976.9.

***N,N'*-(*n*-hexadecyl)-1,7-dipiperidinylperylene-3,4:9,10-tetracarboxyldiimide (PDI-PI).[2]**

N, N'-(*n*-hexadecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic diimide (0.066 g, 0.066 mmol), piperidine (2.67 g, 31.4 mmol) and dry K_2CO_3 (0.50 g , 3.60mmol) was stirred under Ar for 24 h at 55 °C. Subsequently, the reaction mixture was poured into 15 mL of 10% HCl under stirring and extracted with methylene chloride (3×30 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting precipitate was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to yield green solid **PDI-PI** (23.8 mg, 35%). ^{1}H NMR (400 MHz，$CDCl_3$)，δ (ppm)：7.50-9.66 (m，6 H)，4.21 (m，4 H)，3.33(m，4 H)，2.76(m，4 H)，1.73(m，12 H)，1.30(m，56 H)，0.86(m，6 H). ^{13}C NMR(100 MHz,$CDCl_3$)：δ (ppm) 162.6, 162.4, 161.5, 149.6, 134.1, 126.7, 122.4, 122.0, 121.5, 121.2, 119.7, 76.3, 76.2, 76.0, 75.6, 52.1, 51.6, 28.6, 28.5, 28.3, 26.2, 24.7, 21.6, 13.0. MS (MALDI-TOF): calcd for $C_{64}H_{92}N_4O_4$, 1004.71 m/z, found 1005.1.

***N,N'*-(*n*-hexadecyl)-1,7-di(*n*-hexylamineperylene)-3,4:9,10-tetracarboxyldiimide (PDI-HE).[3]**

N, N'-(*n*-hexadecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic diimide (0.066 g, 0.066 mmol), *n*-hexylamine (3.17 g, 31.4 mmol) and dry K_2CO_3 (0.50 g , 3.60vmmol) was stirred under Ar for 24 h at 55 °C. Subsequently, the reaction mixture was poured into 15 mL of 10% HCl under stirring and extracted with chloroform (3×30 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting precipitate was purified by column chromatography on silica gel (eluent: petroleum ether/CH_2Cl_2, 1:9) to yield blue PDI-HE (24.6 mg, 36%). ^{1}H NMR (400 MHz，$CDCl_3$)，δ(ppm)：8.81(d，2 H)，7.50-9.66(m，6 H)，4.20 (m，4 H)，3.48(m，4 H)， 1.67-1.87 (m，4 H)，1.67-1.87 (m，4 H)，1.34-1.20 (m，64 H)，0.95(m，6 H)，0.87(m，6 H). ^{13}C NMR(100 MHz,$CDCl_3$)：δ (ppm) 162.5, 162.0, 144.6, 132.6, 128.5, 125.5, 121.2, 120.9, 120.1, 118.8, 116.5, 115.4, 76.3, 76.2, 76.0, 75.6, 43.5, 39.5, 28.6, 27.0, 21.5, 13.1, 13.0. MS (MALDI-TOF): calcd for $C_{68}H_{100}N_4O_4$, 1036.77 m/z, found 1036.89.

2. Supporting Figures

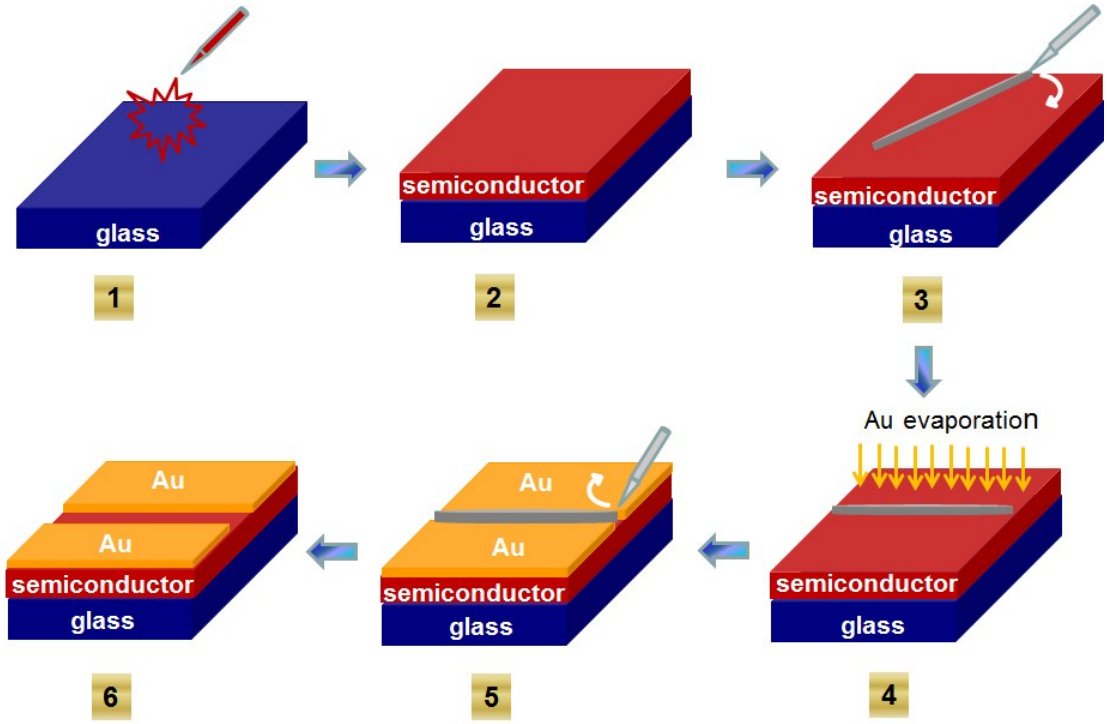

Fig. S1 Schematic diagram of device fabrication by using ‘‘organic ribbon mask’’ technique.

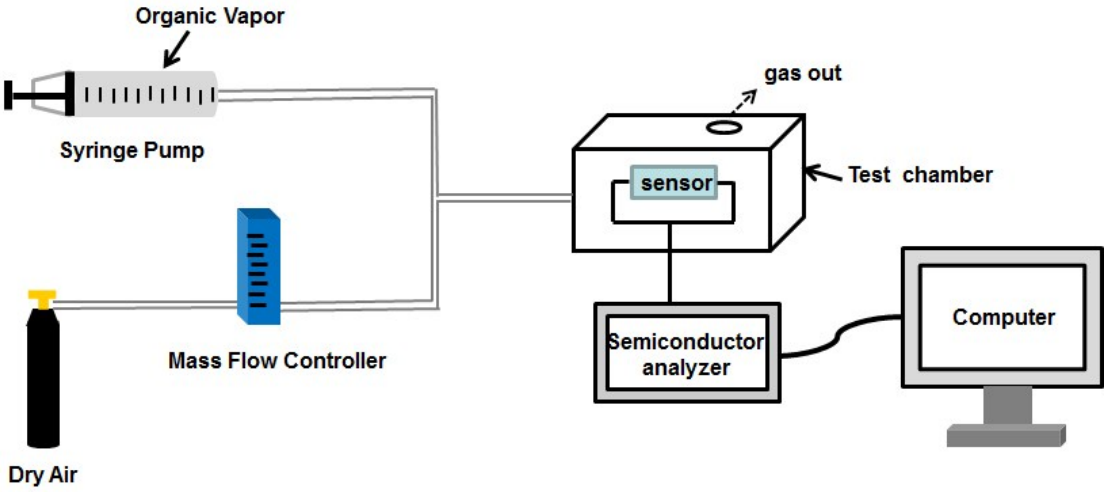

Fig. S2 Schematic diagram for the vapor sensing measurement system.

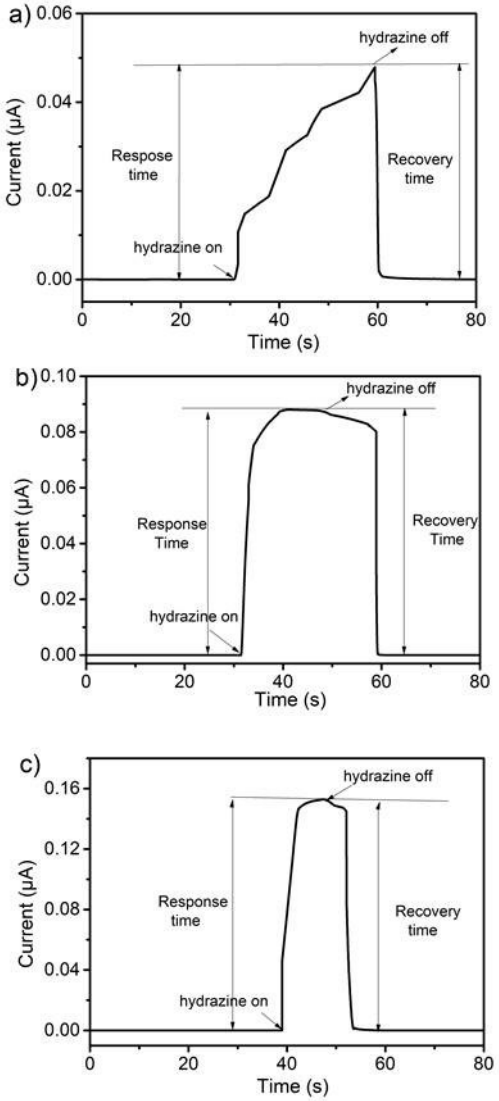

Fig. S3 Response and recovery time of the (a) PDI-PY, (b) PDI-PI and (c) PDI-HE devices.

References

1 A. Lukas, Y. Zhao, S. Miller and M. Wasielewski, *J. Phys. Chem. B*, 2002, **106**, 1299.

2 M. Planells, F. Céspedes-Guirao, L. Gonçalves, A. Sastre-Santos, F. Fernández-Lázaro, *J. Mater. Chem.*, 2009, **19**, 5818.

3 M. Ahrens, M. Tauber, M. Wasielewski, *J. Org. Chem.*, 2006, **71**, 2107.