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Electronic Supplementary Information for

Fluorescent Sensing for Amines with Ultralow Detection Limit Based on Conjugated Porous Polymers

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Experimental section

Materials

All chemical reagents were purchased from commercial sources (Aldrich, Alfa Aesar, Strem Energy Chemical and Adamas) and were, unless otherwise noted. 1,4-bis(1H-pyrazol-4-yl) benzothiadiazole (M1)[S1], 1,4-bis(1H-pyrazol-4-yl)benzene (M2)[S2], 4,7-Dibenzenebenzothiadiazole (M3)[S3], P1[S1] and P2[S1] were prepared according to reported literatures. All reactions and manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques.

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a 600 MHz BRUKER ARX600 spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. UV-vis absorption spectra were recorded using a SPECORD 200 PLUS (analytikjena, Germany) diode-array spectrophotometer equipped with an integrating sphere. Emission experiments were carried out on a HITACHI F-7000 FL spectrofluorometer. Fourier transform infrared (FT-IR) measurement was carried out using a BRUKER ALPHA spectrophotometer with polymers dispersed in pressed KBr disks or polymers dispersed in deionized water.

Synthesis template of compound 1,4-bis(1-trityl-1H-pyrazol-4-yl) benzothiadiazole (2) and 1,4-bis(1-trityl-1H-pyrazol-4-yl) benzene (3)

The process is a classic Suzuki coupling reaction. Add 4,7-dibromobenzothiadiazole (1 g, 3.4 mmol) or 4,7-dibromobenzene (1g, 4.24 mmol), 1-trityl-1H-pyrazol-4-ylboronate pinacol ester (3.26 g, 7.48 mmol), K_2CO_3 (4.37 g, 31.64 mmol) and 1,2-dimethoxyethane (80 mL) to a 250mL two-neck flask filled with nitrogen, and then add $Pd(PPh_3)_4$ (90.42 mg, 0.078 mmol) after degassing for half an hour, the mixture solution was then heated to 80 °C and stirred for 18h. After the reaction is complete, the solvent was removed in vacuo and extracted with dichloromethane, collected the organic phase, dried over $MgSO_4$ and concentrated to yield 1,4-bis(1-trityl-1H-pyrazol-4-yl) benzothiadiazole (2 g, 80 %) as a yellow solid and 1,4-bis(1-trityl-1H-pyrazol-4-yl) benzene (2.7 g, 91 %).

1,4-bis(1-trityl-1H-pyrazol-4-yl) benzothiadiazole (2): ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm)=8.43 (m, 4H; PzH), 7.70 (m, 2 H; ArH), 7.40-7.20 (m, 30 H; C_6H_5).

1,4-bis(1-trityl-1H-pyrazol-4-yl) benzene (3): ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm)=7.90 (d, 2H), 7.65 (d, 2 H), 7.39 (s, 4 H), 7.31-7.35 (m, 18 H), 7.18-7.20 (m, 12 H).

Synthesis template of compound 1,4-bis(1H-pyrazol-4-yl) benzothiadiazole (M1) and 1,4-bis(1H-pyrazol-4-yl) benzene (M2)

1,4-bis(1-trityl-1H-pyrazol-4-yl) benzothiadiazole (2) (0.3 g, 0.4 mmol) or 1,4-bis(1-trityl-1H-pyrazol-4-yl) benzene (3) (2.7g, 4 mmol) was dispersed in methanol and dichloromethane solution (3:2 vol., 23 mL), after trifluoroacetic acid (TFA, 6 mL, 80.78 mmol) was added, the mixture was heated to 70 °C reflux for 18 h. After the reaction is complete, the solvent was removed in vacuo. Then the solid was washed with toluene, chloroform, water, methanol and diethyl ether (3 mL each) to yield yellow solid (0.09 g, 86 %) or white solid (0.64 g, 78 %). Then the solid was dispersed in water and neutralize with 2M NaOH and adjust pH to 5. After filtration and drying, the final product is obtained.

^{13}C{^{1}H} NMR of 1,4-bis(1H-pyrazol-4-yl) benzothiadiazole (M1)：^{1}H NMR (600 MHz, d_6-DMSO): δ (ppm)=8.53 (s, 4 H; PzH), 8.01 (s, 2 H; ArH). ^{13}C NMR (150 MHz, d_6-DMSO): δ (ppm)=153.0, 133.2, 125.3, 123.5, 117.8.

^{13}C{^{1}H} NMR of 1,4-bis(1H-pyrazol-4-yl) benzene (M2): ^{1}H NMR (600 MHz, d_6-DMSO): δ (ppm)=8.06 (s, 4 H; PzH), 7.58 (s, 4 H; ArH). ^{13}C NMR (150 MHz, d_6-DMSO): δ (ppm)= 121.9, 126.3, 131.3, 137.0.

Synthesis template of P1 and P2.

M1 (240 mg, 0.89 mmol) or M2 (250 mg, 1.19 mmol) was added to a dry two-neck bottle filled with nitrogen and cyanuric chloride (110 mg, 0.6 mmol) was then quickly added. Dry THF (tetrahydrofuran, 100 mL, anhydrous) was added as solvent and N, N-diisopropylethylamine (460 mg, 3.60 mmol) was added as a weak base. The mixture was heated to 80 °C and stirred for 24h. The solid product was obtained by suction filtration and washed with DI water, ethanol and dichloromethane, respectively, and dried in air (yellow or white solid, 240 mg for P1 and 200 mg for P2, 80% for P1 and 67% for P2).

^{13}C{^{1}H} NMR of P1: ^{13}C solid-state NMR (150 MHz): δ (ppm)=160.5, 150.1, 142.9, 120.1.

^{13}C{^{1}H} NMR of P2: ^{13}C solid-state NMR (150 MHz): δ (ppm)=141.8, 134.1, 127.9, 124.9, 122.9, 120.3.

Supplementary Figures

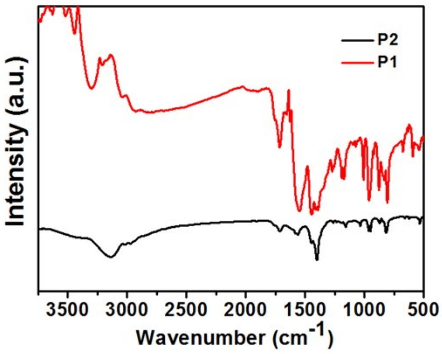


Fig. S1. Infrared absorption spectra of P1 and P2.

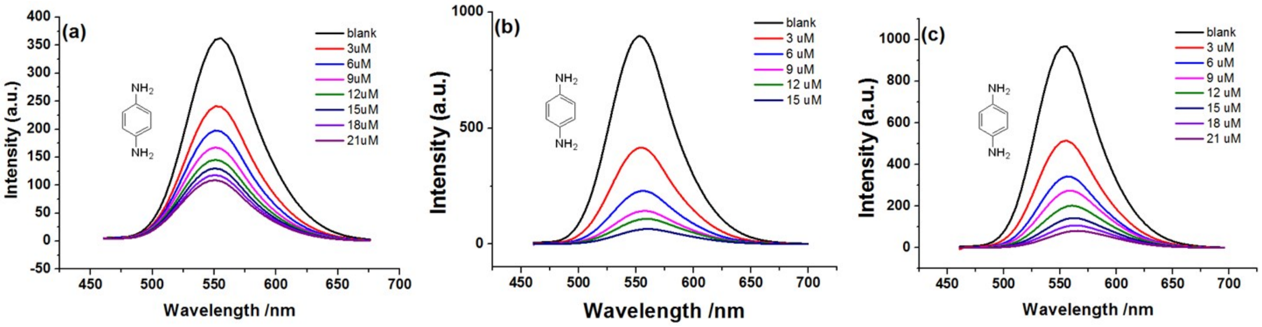
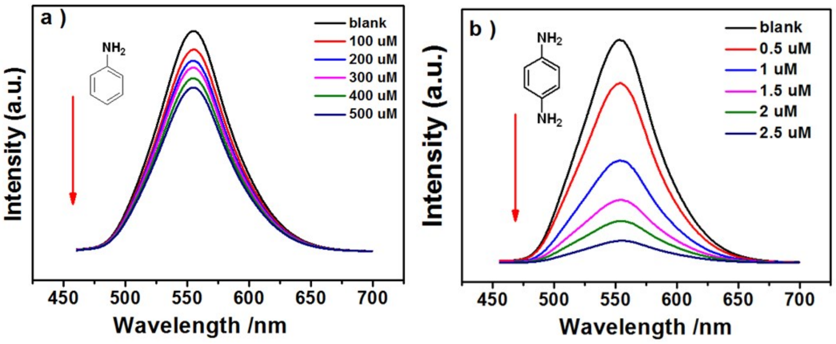


Fig. S2. Sensing of 1,4-phenylenediamine by P1 (0.2 mg/mL) in (a) aqueous, (b) absolute ethanol and (c) acetonitrile.



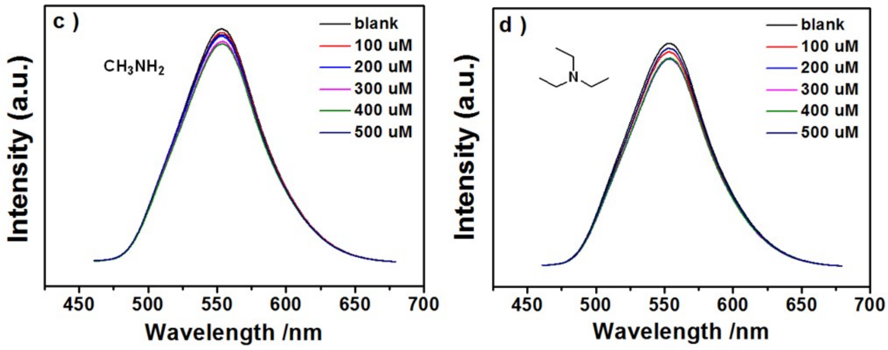


Fig. S3. Fluorescence sensing of M1 in aqueous dispersion (0.2 mg/mL) for (a) aniline, (b) 1,4-phenylenediamine, (c) methylamine, (d) triethylamine (excitation at 435 nm).

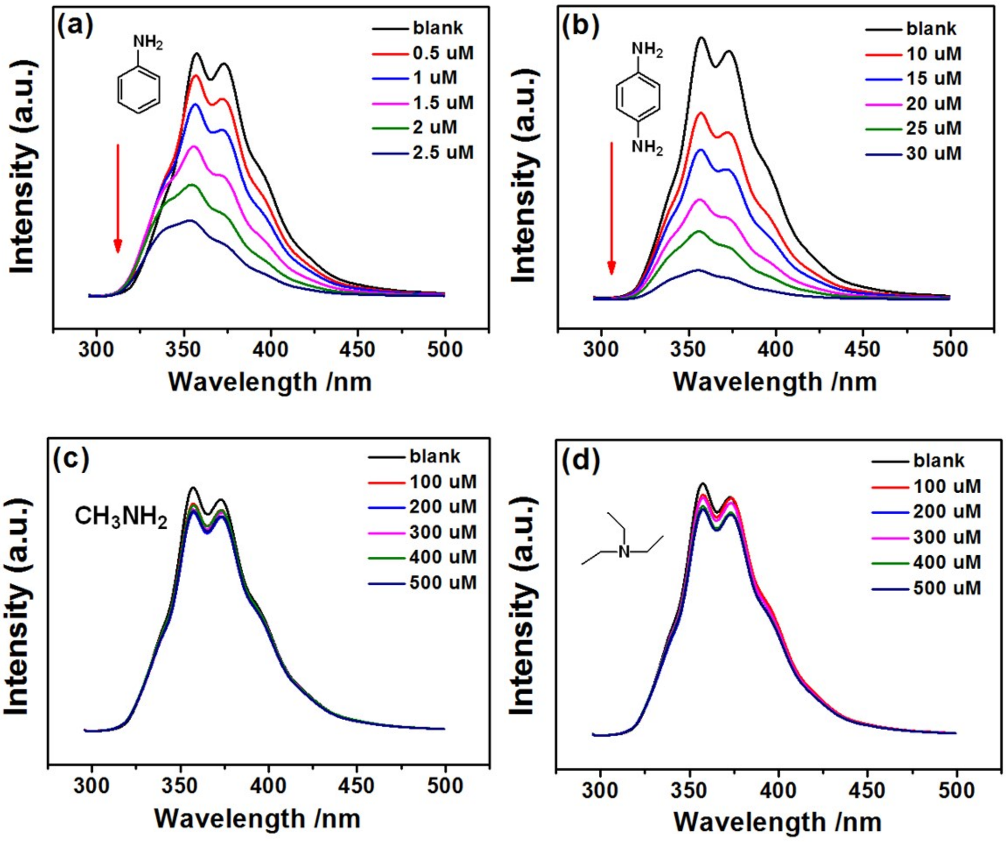


Fig. S4. Fluorescence sensing of M2 in aqueous dispersion (0.2 mg/mL) for (a) aniline, (b) 1,4-phenylenediamine, (c) methylamine, (d) triethylamine (excitation at 285 nm).

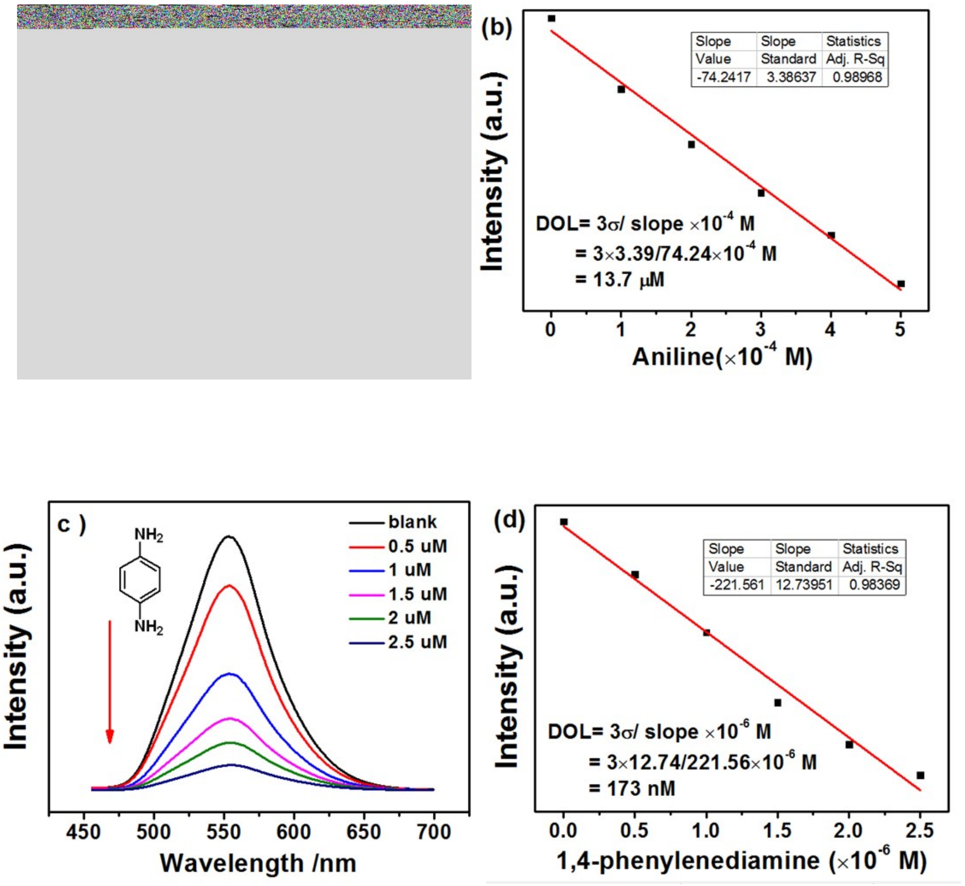
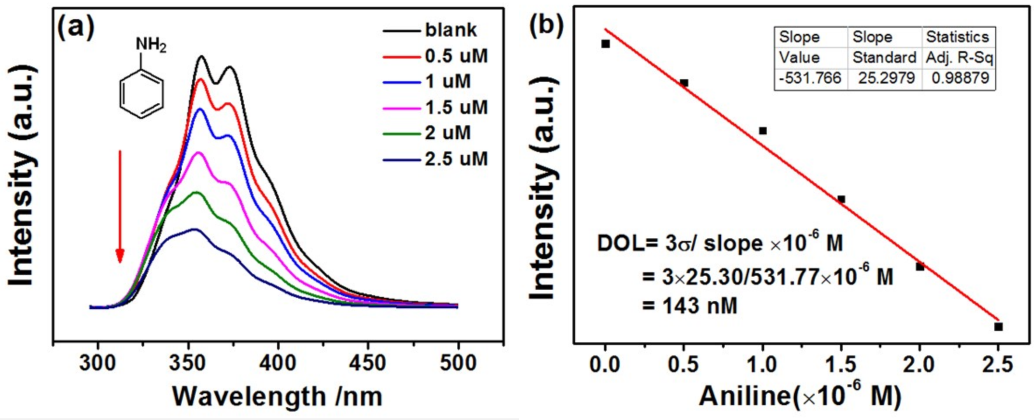


Fig. S5. (a) Fluorescence intensity responses of M1 in aqueous dispersion (0.2 mg/mL) after adding 100 μM aniline at each time (excitation at 435 nm) and (b) linear fit for the detection limit estimation of aniline sensing. (c) Fluorescence intensity responses of M1 in aqueous dispersion (0.2 mg/mL) after adding 0.5 μM 1,4-phenylenediamine at each time (excitation at 435 nm) and (d) linear fit for the detection limit estimation of 1,4-phenylenediamine sensing.



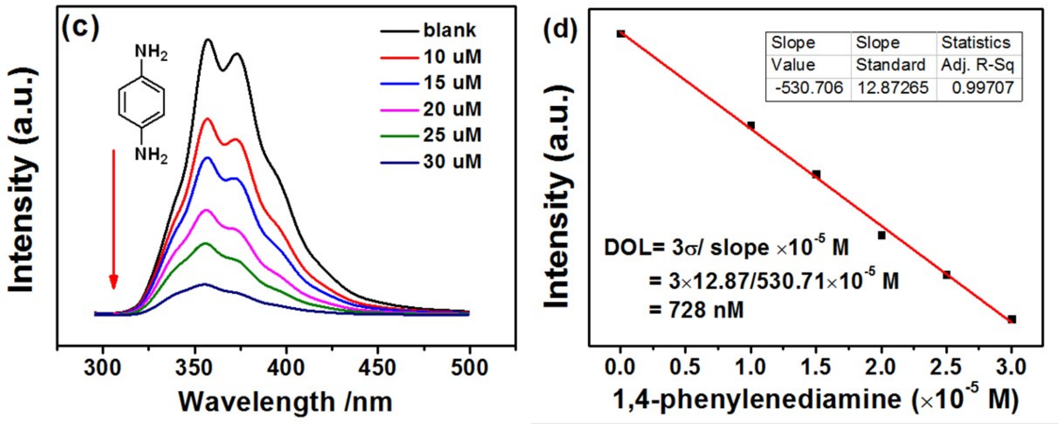


Fig. S6. (a) Fluorescence intensity responses of M2 in aqueous dispersion (0.2 mg/mL) after adding 0.5 μM aniline at each time (excitation at 285 nm) and (b) linear fit for the detection limit estimation of aniline sensing. (c) Fluorescence intensity responses of M2 in aqueous dispersion (0.2 mg/mL) after adding 10 μM 1,4-phenylenediamine at each time (excitation at 285 nm) and (d) linear fit for the detection limit estimation of 1,4-phenylenediamine sensing.

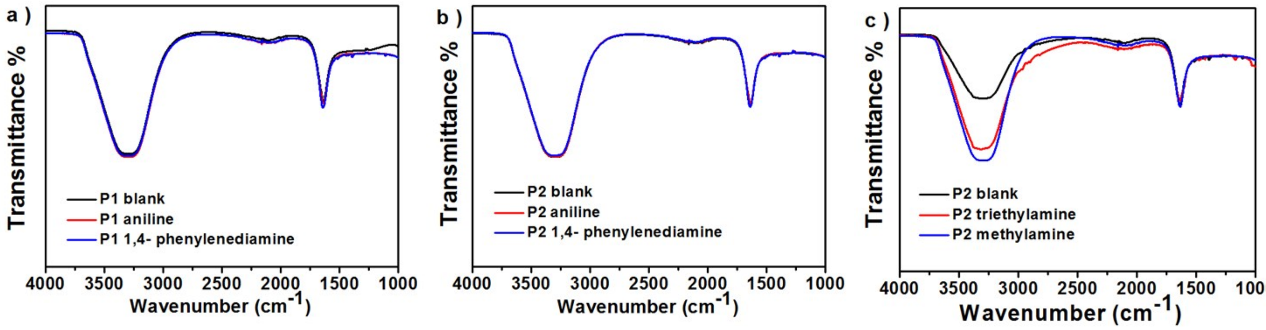


Fig. S7. (a) Fourier transform infrared spectra of P1 in aqueous dispersion and after adding aromatic amines. (b) Fourier transform infrared spectra of P2 in aqueous dispersion and after adding aromatic amines. (c) Fourier transform infrared spectra of P2 in aqueous dispersion and after adding aliphatic amines.

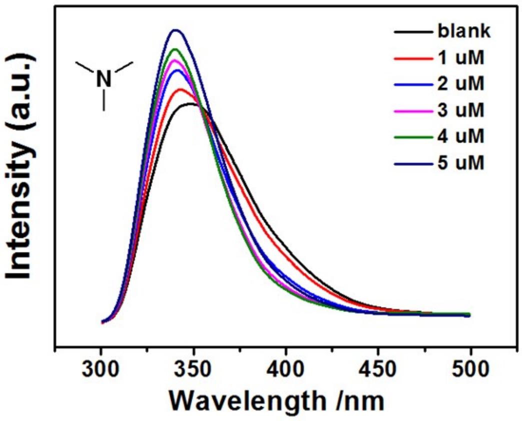


Fig. S8. The sensing performance of P2 on trimethylamine.

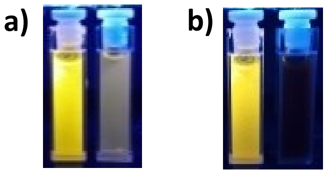


Fig. S9. (a) Fluorescence quenching of P1 during the process of aniline sensing. (b) Fluorescence quenching of P1 during the process of 1,4-phenylenediamine sensing.

References

[S1] J. Yu, X. Sun, X. Xu, C. Zhang, X. He, Applied Catalysis B: Environmental. 2019, **257** 117935-117944.

[S2] L. J. Kershaw Cook, R. Kearsey, J. V. Lamb, E. J. Pace and J. A. Gould, *Tetrahedron Lett.* 2016, **57**, 895-898.

[S3] Y. Xu, L. Ren, D. Dang, Y. Zhi, X. Wang, and L. Meng, Chem. Eur. J. 2018, **24**, 10383–10389.