

Supporting Information for

Selective Detection of TNT and Picric Acid by
Conjugated Polymer Film Sensors with Donor-Acceptor
Architecture

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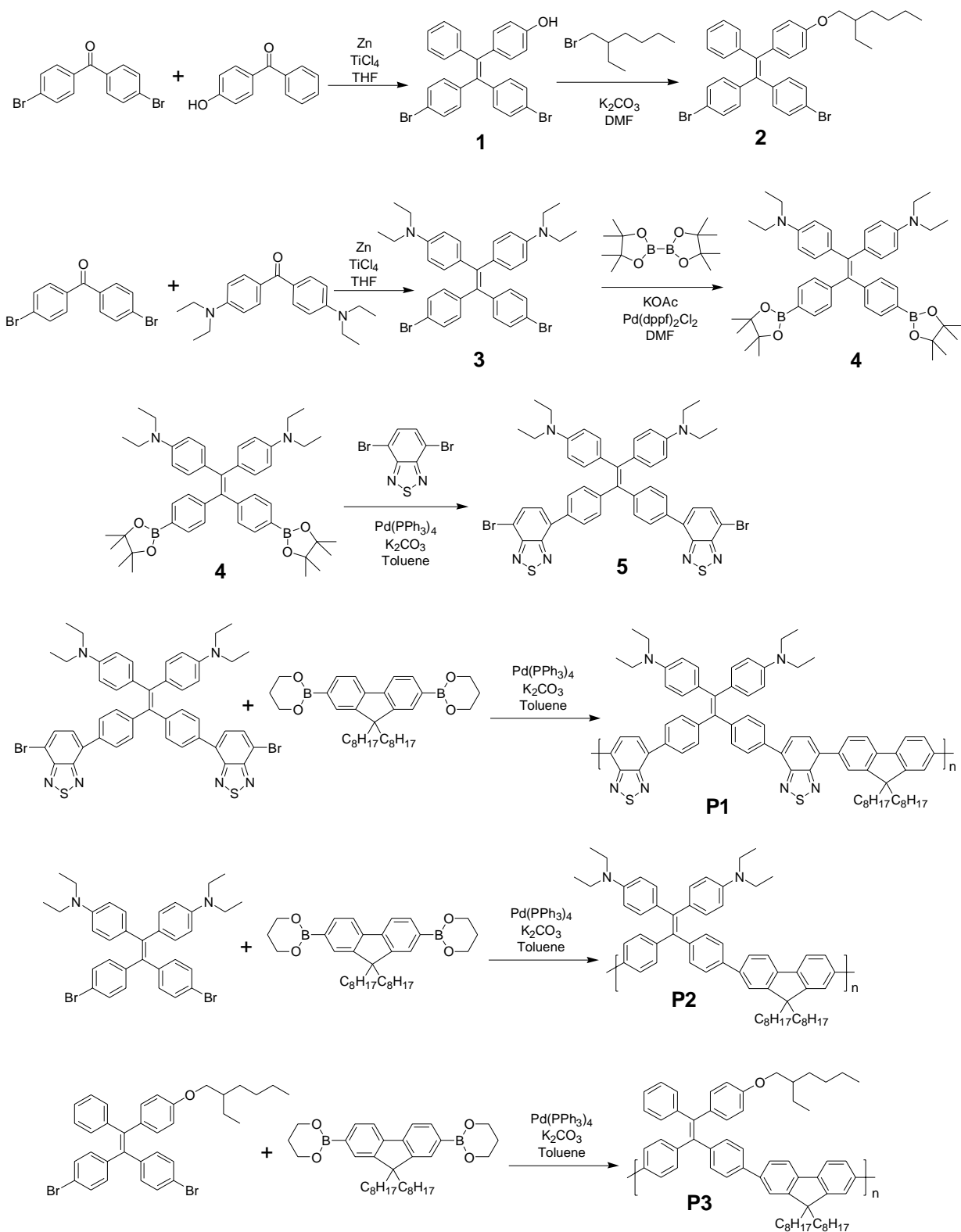
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General Information

^1H and ^{13}C NMR spectra were recorded at 298 K obtained with a Bruke Avance 300 NMR spectrometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by GPC on a Waters 410 instrument with polystyrene as standards and THF as eluent. MALDI-TOF was measured by a Bruker Daltonics Flex analysis system. UV-Vis absorption spectra were recorded by a Perkin-Elmer Lambda35 UV/vis spectrometer. PL spectra were recorded with a Perkin-Elmer LS50B spectrofluorometer. Cyclic voltammetry was conducted on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system at a scan rate of 100 mV/s with an three-electrode cell in 0.1 M anhydrous and argon-saturated solution of tetrabutylammonium tetrafluoborate (Bu_4NBF_4) in DCM. A glass carbon disk was used as working electrode with a platinum electrode as the counter electrode and a Ag/AgCl electrode as reference electrode. The absolute PL quantum efficiencies of the solid samples were obtained on a quantum yield measurement system (C9920-02, Hamamatsu Photonics K. K., Japan).

Synthesis Procedures



Scheme S1. Synthetic procedures for monomers and polymers

1: Under an Ar atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with zinc dust (6.40 g, 100 mmol) and THF (80 mL). After the mixture was cooled to -5 °C, TiCl₄ (5.44 mL, 50 mmol) was slowly added to the mixture by a syringe under temperature of 10 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at reflux for 2.5 h. The mixture was again cooled to -5 °C, charged with pyridine (0.50 mL, 6 mmol) and stirred for 10 min. Then to the mixture 20 mL of a THF solution of 4,4'-bisbromobenzophenone (3.40 g, 10 mmol) and (4-hydroxyphenyl)(phenyl)methanone (1.98 g, 10 mmol) was added slowly. The resulting mixture was refluxed overnight. The reaction was quenched with 10% K₂CO₃ aqueous solution and extracted with DCM. The organic layer was collected and concentrated. The crude product was purified by silica gel column using gradient eluent from hexane to DCM/hexane (1:1 by volume). A yellow solid was obtained in 30.1% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.25(d, J=8.4Hz, 2H), 7.22 (d, J=8.4Hz, 2H), 7.12 (t, J=3.3Hz, 3H), 6.99(m, 2H), 6.86(m, 6H), 6.59 (d, J=8.4Hz, 2H), 4.64 (s, 1H). ¹³C NMR (CDCl₃): δ (ppm) 143.1, 142.3, 141.7, 137.5, 135.5, 132.6, 131.1, 130.9, 127.8, 126.8, 120.4, 114.8. MALDI-TOF (*m/z*): 505.0 [M⁺]

2: In a flask equipped with a magnetic stirrer, K₂CO₃ (17.0 g, 100 mmol), 3-bromoheptane (5.37 g, 10 mmol, 4.71 ml) and **1** (5.06 g, 10 mmol) with 20 ml DMF was added at room temperature. The mixture was heated to reflux and stirred for 24 h. After cooled to ambient temperature, the reaction mixture was extracted with DCM and washed with saturated brines. Then the product was dried over Na₂SO₄, and isolated and purified by silica gel chromatography using chloroform/hexane (1:1 v/v) as elute. The resulting product was obtained in 90.1% yield, 5.56 g. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.25(d, J=8.4Hz, 2H), 7.22 (d, J=8.4Hz, 2H), 7.12 (t, J=3.3Hz, 3H), 7.02(m, 2H), 6.89(m, 6H), 6.67(d, 8.4Hz, 2H), 3.80(d, J=5.6Hz, 2H), 1.70 (m, 1H), 1.33(m, 8H), 0.93(t, J=7.2, 6H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 158.1, 142.6, 137.3, 132.3, 131.4, 130.1, 120.4, 119.9, 113.8, 76.9, 70.4, 39.4, 30.1, 22.9, 14.0, 11.2. MALDI-TOF (*m/z*): 616.1 [M⁺]

3: Compound **3** was synthesized by the same process like compound **1** as mentioned above. A yellow solid was obtained in 58.6% yield. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.22(d, J=7.5Hz, 4H), 6.90(d, J=7.8Hz, 4H), 6.85(d, J=8.4Hz, 4H), 6.41(d, J=9.0Hz, 4H), 3.31(q, J=9.0Hz, 8H), 1.12(t, J=6.6Hz, 12H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 133.2, 130.7, 110.7, 77.3, 44.1, 12.6. MALDI-TOF (*m/z*): 630.1 [M⁺]

4: Compound **3** (3.16 g, 5 mmol), bis(pinacolato)diboron (3.05 g, 12 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (0.245 g, 0.3 mmol) and potassium acetate (2.94g, 30mmol) were dissolved in 10 mL of dry DMF. The solution was purged with nitrogen for 20 min, and then heated with stirring at 100 °C for 20 hours. The cooled mixture was extracted with DCM, and the extract was washed with saturated brine and then dried over Na₂SO₄. The obtained crude product was purified by silica gel chromatography using chloroform/hexane (1:1 v/v) as elute. The product was obtained in 68.5% yield, 2.49 g. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.520(d, J=8.0Hz, 4H), 7.04(d, J=8.0Hz, 4H), 6.86(d, J=8.4Hz, 4H), 6.38 (d, J=8.8Hz, 4H), 3.28(q, J=7.2Hz, 8H), 1.31 (s, 24H), 1.12(t, J=7.2Hz, 12H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 148.6, 146.4, 132.8, 110.7, 83.5, 76.9, 44.1, 24.9, 12.6. MALDI-TOF (*m/z*): 726.4 [M⁺]

5: A mixture of **4** (0.726 g, 1 mmol) and 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.882 g, 3 mmol), K₂CO₃ (2.0 g, 15mmol), toluene (10 mL), and water (2 mL) was carefully degassed before and after Pd(PPh₃)₄ (0.112 g, 0.1 mmol) was added. The reaction mixture was stirred at 100°C under nitrogen atmosphere for 24 hours. After the reaction was cooled to ambient temperature, the mixture was poured to 100ml distilled water, then extracted with DCM. The organic layer was collected, dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with CH₂Cl₂/hexane (2:3, v:v) to afford BT-TPE-BT as red solid (0.473 g, 52.5%). ¹H NMR (300 MHz, CDCl₃): δ 7.89(d, J=6.0Hz, 2H), 7.73(d, J=9.0Hz, 4H), 7.57(d, J=6.0Hz, 2H), 7.28(d, J=9.0Hz, 4H), 6.98(d, J=6.0Hz, 4H), 6.45(d, J=8.1Hz, 4H), 3.30(m, 8H), 1.12(t, J=6.6Hz, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 153.1, 146.1, 133.3, 132.2, 132.1, 130.9, 128.4, 127.7, 112.4, 112.4, 110.8, 77.0, 44.2, 12.6. MALDI-TOF (*m/z*): 898.1 [M⁺]

General Polymerization Procedure.

In a 50 mL flask of flame-drying, 1.0 mmol of monomer, (9,9-dioctyl-fluorene-2,7-diyl) bis(1,3,2-dioxaborinane) (0.558g, 1.0 mmol), Pd(PPh₃)₄ (0.006 g, 0.005 mmol) were dissolved in 6 mL of degassed toluene and 2 mL of 2M aqueous Potassium carbonate. The reaction mixture was vigorously stirred at 100 °C for 48h. After the reaction was finished, the polymer was purified by precipitation in methanol and air-dried overnight.

P1: Following the general polymerization procedure, compound **5** was reacted for 48 hours with yield: 90 %.

¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.06-7.86(m, 14H), 7.34(br, 4H), 7.04(m, 4H), 6.47 (br, 4H), 3.32 (br, 8H), 2.1 (m, 4H), 1.26 (m, 12H), 1.12 (m, 24H), 0.77 (m, 6H). GPC: Mn=5.54×10⁴ g/mol, PDI=3.30

P2: Following the general polymerization procedure, compound **3** was reacted for 48 hours with yield: 70 %.

¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.72(m, 2H), 7.55(m, 8H), 7.21(m, 4H), 6.99(d, J=8.4Hz, 4H), 6.47(m, J=8.4Hz, 4H), 3.32 (br, 8H), 2.00 (br, 4H), 1.13 (m, 12H), 1.04(m, 24H), 0.81 (br, 6H). GPC: Mn = 1.60×10⁴ g/mol, PDI = 1.73.

P3: Following the general polymerization procedure, compound **2** was reacted for 48 hours with yield: 75 %.

¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.72(m, 3H), 7.58-7.44(m, 9H), 7.20-7.15(m, 9H), 7.02(d, J=5.1Hz, 2H), 6.70(d, J=5.1Hz, 2H), 3.73 (m, 2H), 1.93 (s, 4H), 1.68(m, 1H), 1.55-1.30 (m, 8H), 1.16(br, 4H), 1.04(m, 16H), 0.92(m, 6H), 0.78 (t, J=4.2Hz, 6H), 0.67 (br, 4H). GPC: Mn=1.63×10⁴ g/mol, PDI=1.92

Film Preparation and Fluorescence Measurement

The film thickness was determined by step profiler. A linear relationship of optical density (OD) with thickness was established and this allows the film thickness to be measured by OD.^[2]

In the experiment of fluorescence responses to explosives in aqueous phase, the film was adhered to one innerside of a quartz cell filled with 5 ml deionized water. Fluorescence measurement was carried out by adding small aliquots of explosives solution. The spectra were recorded when the fluorescence intensity kept being stable after injecting the analytes into the cell.^[3]

The fluorescence response of the polymer films to the vapors of nitro-containing aromatics was ascertained by inserting the prepared films into quartz cuvette at RT containing solid analytes and cotton gauze, which prevents the direct contact of the silica film with the analyte and helps to maintain a constant saturated vapor pressure. Polymer film was placed in the quartz cuvette and fluorescence spectra were measured after exposing the film for a specific interval time.^[4]

Experimental Data:

Table S1. Photophysical and HOMO, LUMO data of **P1-P3**.

	Solution			Film			HOMO	LUMO
	λ_{\max} (nm)	λ_{PL} (nm)	Φ_{PL} (%)	λ_{\max} (nm)	λ_{PL} (nm)	Φ_{PL} (%)	(eV)	(eV)
P1	317,468	545	0.50	327,493	665	6.9	-4.91	-2.92
P2	337,390	418	0.69	338,390	550	13.0	-4.90	-2.23
P3	358	419	0.53	362	501	43.9	-5.42	-2.39

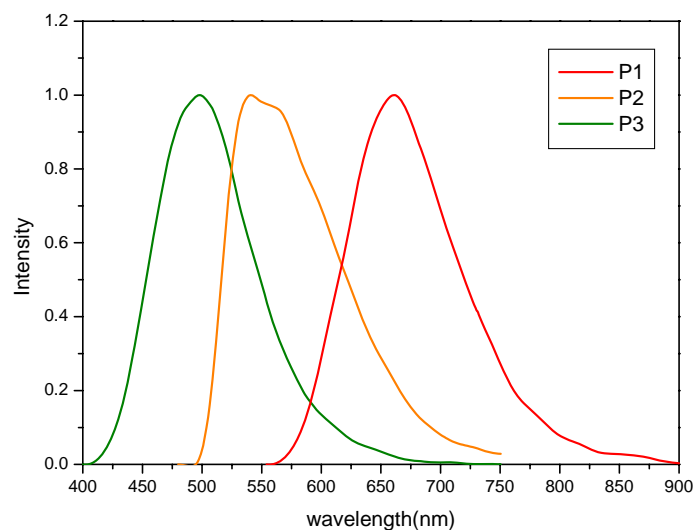


Figure S1. Normalized Photoluminescence spectra of **P1**, **P2** and **P3** in thin solid film

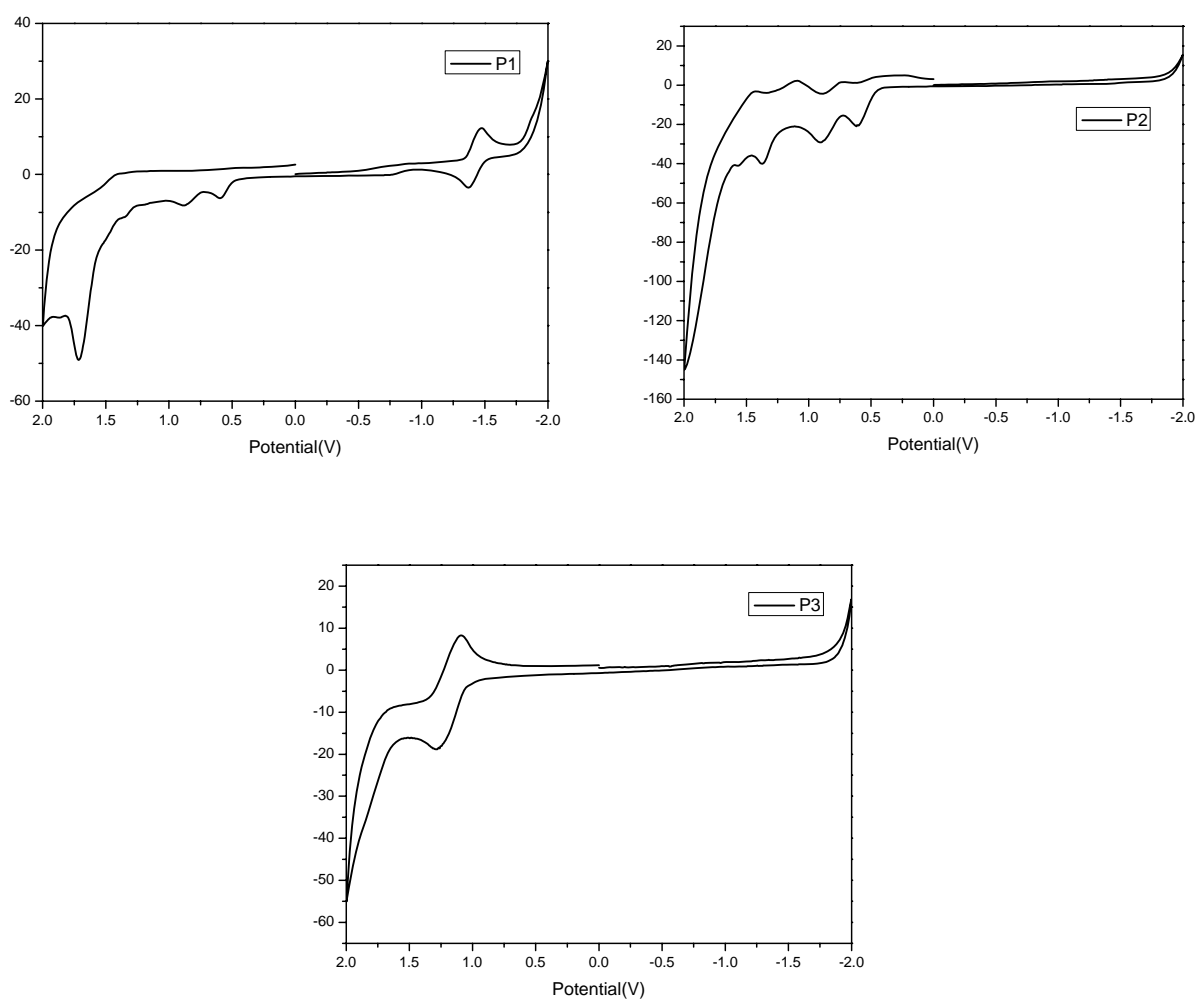


Figure S2. Cyclic voltammogram behaviors of **P1–P3** in dichloromethane.

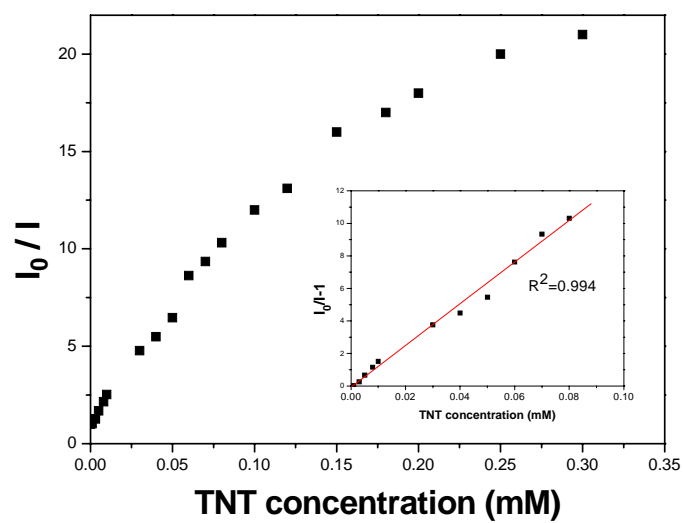


Figure S3. Quenching efficiencies of the **P1** film in the presence of different concentrations of TNT in aqueous phase. Inset is the Stern-Volmer plot.

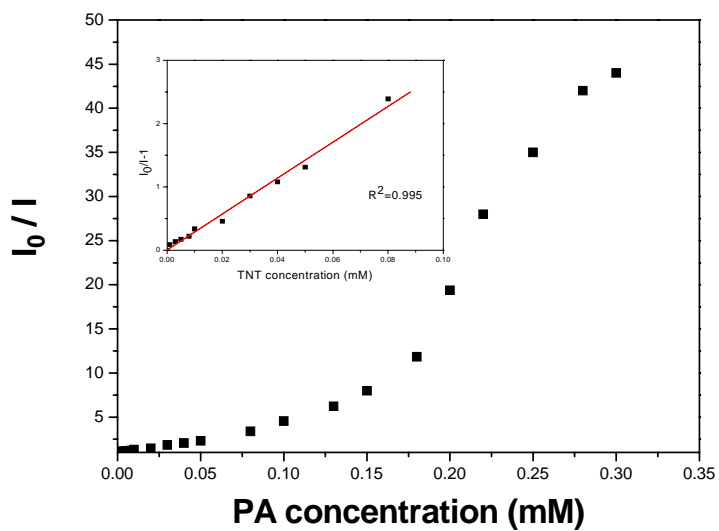


Figure S4. Quenching efficiencies of the **P3** film in the presence of different concentrations of PA in aqueous phase. Inset is the Stern-Volmer plot.

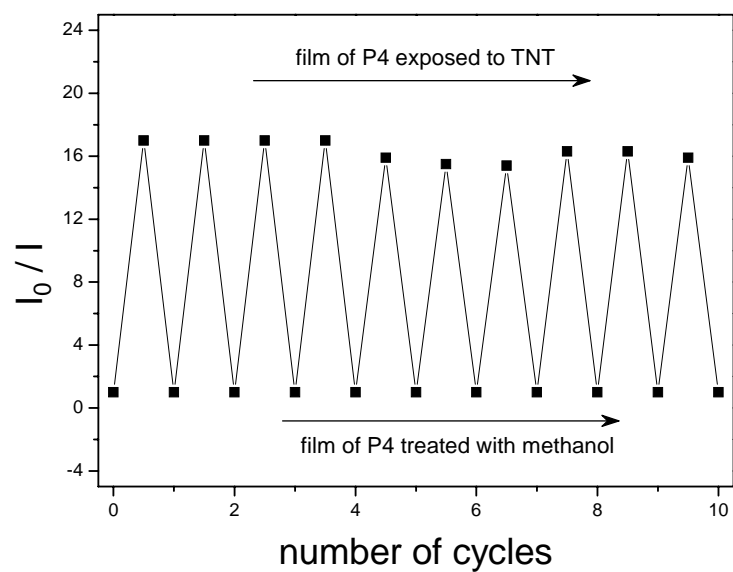


Figure S5. Reversibility of the response of the **P1** film to TNT. ($[TNT] = 0.2 \text{ mM}$)

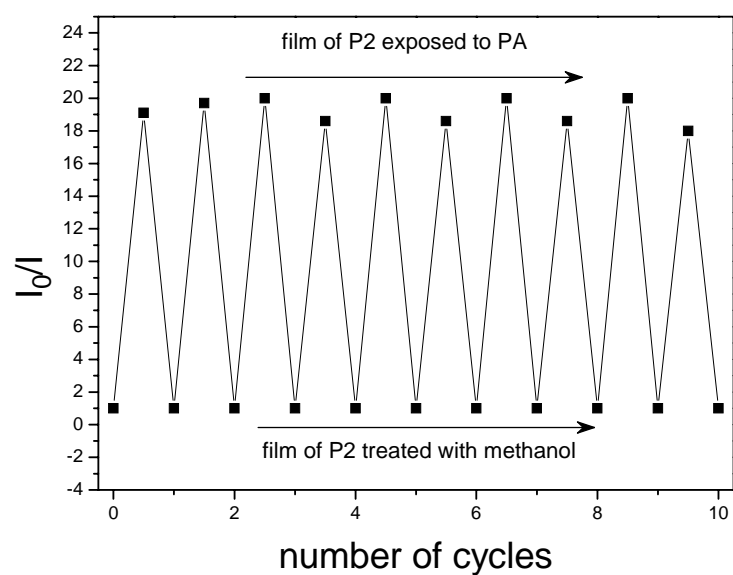


Figure S6. Reversibility of the response of the **P3** film to PA. ($[PA] = 0.2 \text{ mM}$)

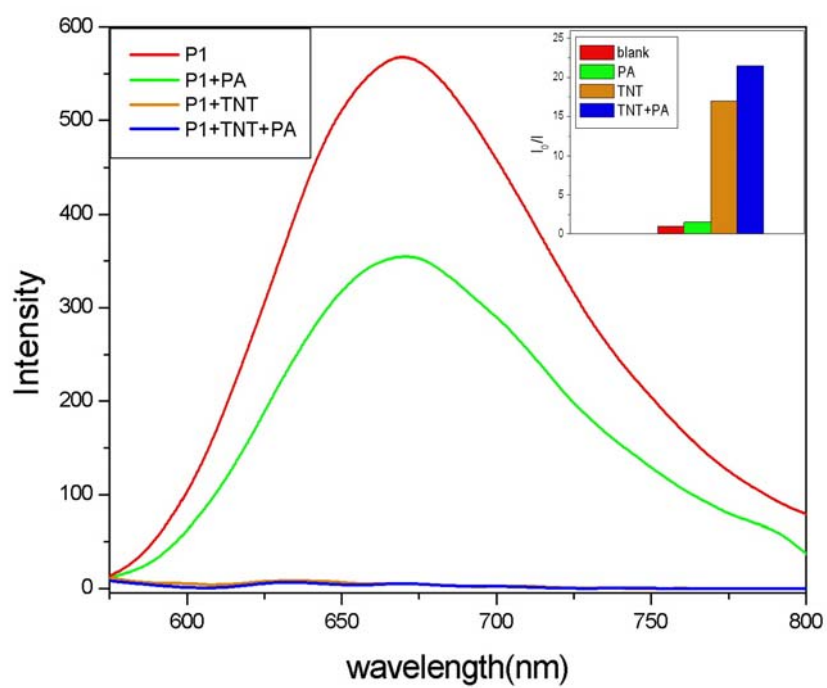


Figure S7. Fluorescence quenching measurement of **P1** thin film by TNT (0.2 mM) and/or PA (0.2 mM) in aqueous solution.

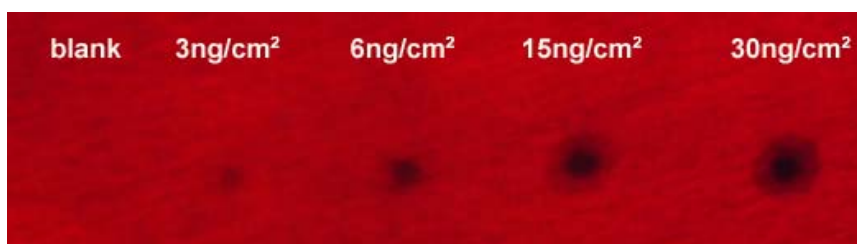


Figure S8. Fluorescence quenching of **P1** thin-film on filter paper by solid particulates of TNT with various concentrations.



Figure S9. Fluorescence quenching of **P2** thin-film on filter paper by solid particulates of TNT with various concentrations.

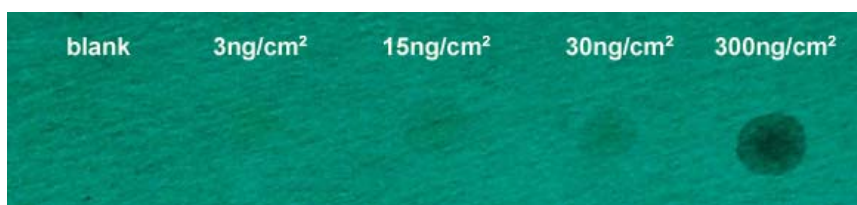


Figure S10. Fluorescence quenching of **P3** thin-film on filter paper by solid particulates of TNT with various concentrations.

Calculation Data:

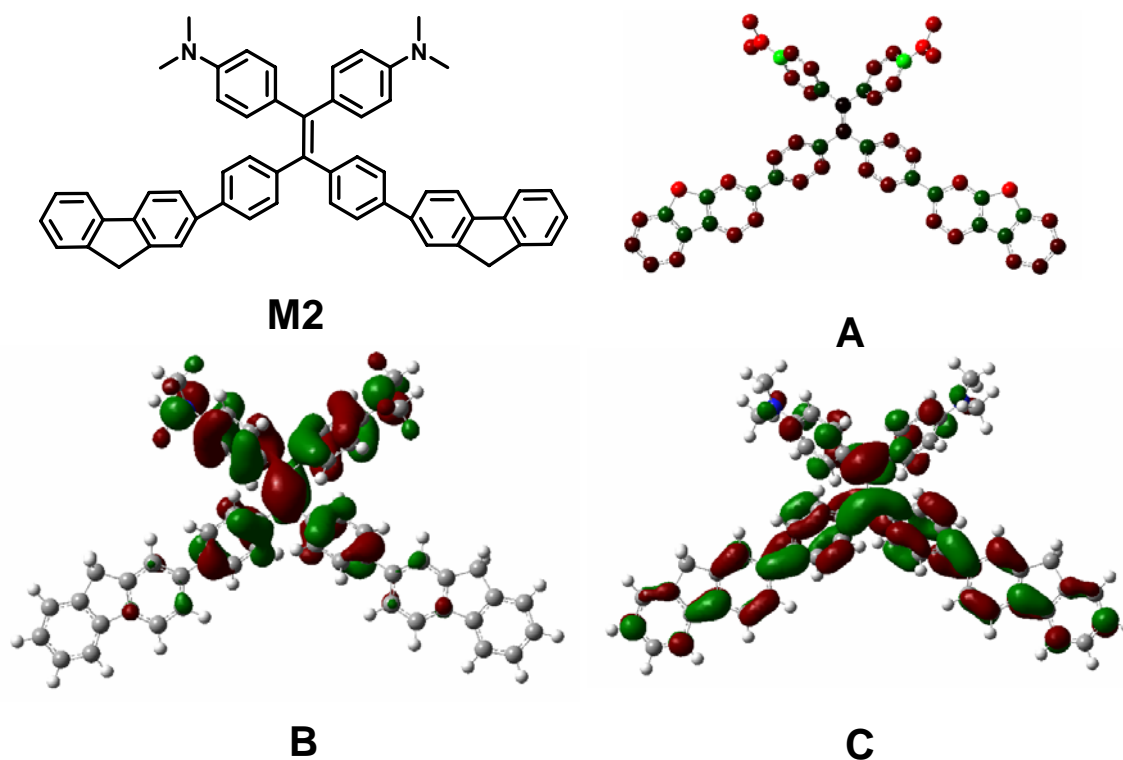


Figure S11. Ab initio DFT calculations on **M2** at the B3LYP/6–31G(d) level. (A) Electrostatic potentials for **M1**. Colors range from -0.473 to 0.370 , with green denoting the electron-deficient regions and red denoting the electron-rich regions. (B) HOMO of **M2**. (C) LUMO of **M2**.

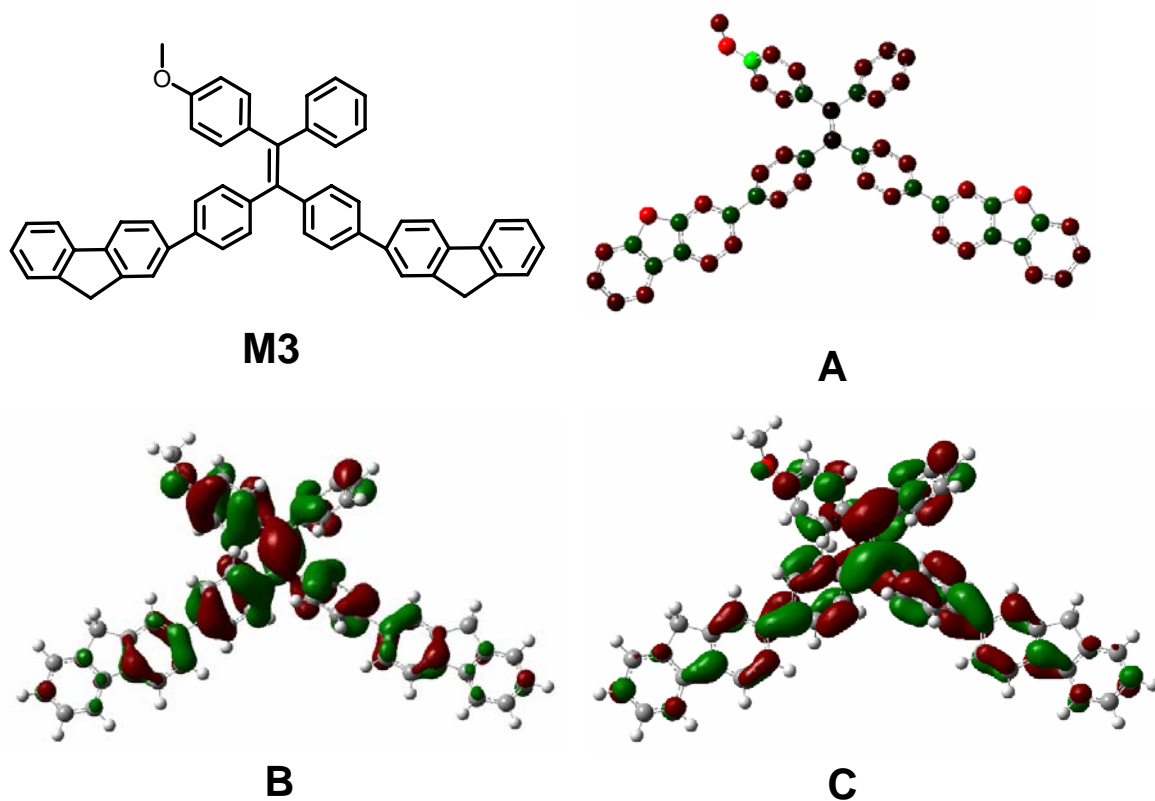


Figure S12. Ab initio DFT calculations on **M3** at the B3LYP/6-31G(d) level. (A) Electrostatic potentials for **M1**. Colors range from -0.506 to 0.376, with green denoting the electron-deficient regions and red denoting the electron-rich regions. (B) HOMO of **M3**. (C) LUMO of **M3**.

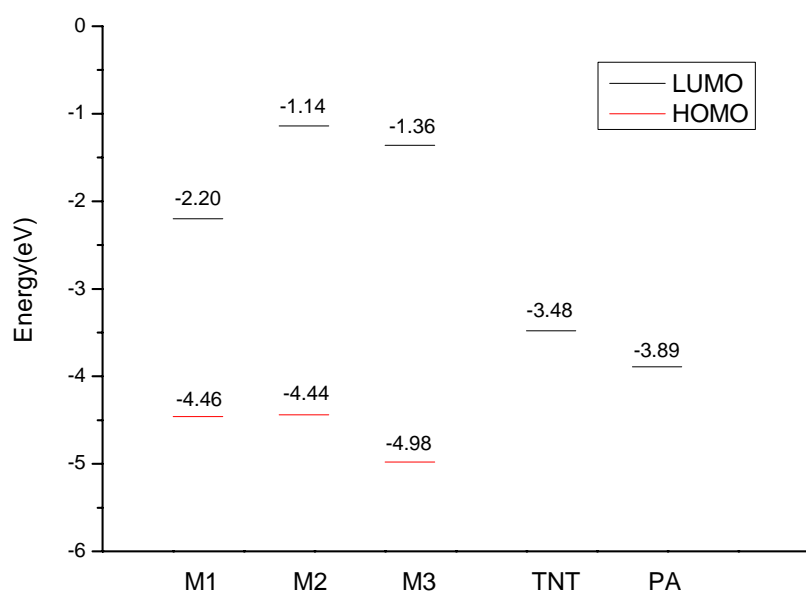


Figure S13. HOMO and LUMO energy levels calculated for the model compounds **M1–M3**, TNT and PA at the B3LYP/6–31G(d) level of theory.

References

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- [2] J. S. Yang, T. M. Swager, *J. Am. Chem. Soc.*, **1998**, 120, 5321.
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