

Star-shaped triazatruxene derivatives for rapid fluorescence fiber-optic detection of nitroaromatic explosive vapors

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Supporting Information

Measurements. ¹H NMR spectra were recorded on a Bruker Advance III 400 spectrometer. Mass spectra (MS) of compounds were recorded on a Bruker Daltonics-autoflex III smartbeam MALDI TOF/TOF mass spectrometer. UV–visible absorption spectra were recorded on a PerkinElmer Lambda 35 UV-vis spectrometer with a scan rate of 480 nm/min. Fluorescence emission spectra were recorded on a PerkinElmer LS 50B luminescence spectrometer with a xenon discharge lamp excitation. The electrochemical properties of three triazatruxene derivatives were investigated by cyclic voltammetry in dry DCM with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The measurement was performed at room temperature with a scan rate of 80 mV/s using a standard three-electrode cell with a platinum plate as the counter electrode, Ag/AgCl electrode as the reference electrode, a platinum disk electrode as the working electrode, and Fc/Fc⁺ as an internal standard. The film thickness was measured by a Veeco Dektak 150 profilometer. Fiber-optic spectra were recorded on an ideaoptics PG2000-Pro spectrometer equipped with a 375 nm LED light source.

Materials. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures.

Synthesis. 2-bromo-9,9'-dihexylfluorene (**1**)^{S1}, *N*-heptadecanyl-2,7-dibromocarbazole (**3**)^{S2}, 2,7,12-Tribromo-5,10,15-trihexyltriazatruxene (**5**)^{S3} and 5,10,15-Trihexyltriazatruxene-2,7,12-triboronic ester (**6**)^{S3} were synthesized according to procedures modified from literatures. The synthesis of three triazatruxene derivatives were shown in **Scheme S1**.

9,9-Dihexylfluorene-2-trimethylene boronate (2). To a solution of compound **1** (4.1 g, 10.0 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (2.5 M in *n*-hexane, 4.0 mL, 10.0 mmol) dropwisely at -78 °C. The reaction mixture was stirred at -78 °C for 2 h before trimethyl borate (1.7 mL, 15.0 mmol) was added slowly by syringe. The mixture was allowed to warm to room temperature, stirred overnight and then was poured into icy 2 M hydrochloric acid. Then the mixture was extracted with diethyl ether and the combined extracts were dried with anhydrous sodium sulfate and then evaporated to give white solid. After the mixture of the intermediate, 1,3-propanediol (1.5 mL, 20.0 mmol) and 50 mL DCM was stirred at 25 °C for 6 h, the mixture was dried with anhydrous sodium sulfate and evaporated to give a white solid. The product was further purified by recrystallization from acetonitrile to afford white solid **2** (3.1 g, 74.2%). ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.66 (m, 4H, Ar-H), 7.34-7.30 (m, 3H, Ar-H), 4.20 (t, *J*=5.4 Hz, 4H, CH₂), 2.05 (m, 2H, CH₂), 1.97(m, 4H, CH₂), 1.11-0.95 (m, 12H, CH₂), 0.75 (t, *J*=7.1 Hz, 6H, CH₃), 0.59(m, 4H, CH₂).

***N*-Heptadecan-*N*-yl-2-bromocarbazole (4).** To a solution of compound **3** (2.3 g, 4.0 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (2.5 M in *n*-hexane, 1.6 mL, 4.0 mmol) dropwisely at -78 °C. The reaction mixture was stirred at -78 °C for 2 h before 1 mL degassed deionized water was added

slowly by syringe. The mixture was allowed to warm to room temperature, stirred overnight and then poured into deionized water. Then the mixture was extracted with DCM and the combined extracts were dried with anhydrous sodium sulfate and then evaporated. The residue was purified by silica gel column chromatography using petrol ether as the eluent to give **4** as white solid (1.2 g, 63.0%). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1H, Ar-H), 7.94 (s, 1H, Ar-H), 7.70-7.40 (m, 3H, Ar-H), 7.30 (d, *J*=7.6 Hz, 1H, Ar-H), 7.22 (t, *J*=7.4 Hz, 1H, Ar-H), 4.55 (m, 1H, CH), 2.23 (m, 2H, CH₂), 1.90 (m, 2H, CH₂), 1.20-1.05 (m, 22H, CH₂), 0.99 (m, 2H, CH₂), 0.82 (t, *J*=7.0 Hz, 6H, CH₃).

5, 10, 15-trihexyltriazaatruxene (TATC6). To a solution of compound **5** (1.7 g, 2.0 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (2.5 M in *n*-hexane, 2.6 mL, 6.6 mmol) dropwisely at -78 °C. The reaction mixture was stirred at -78 °C for 2 h before 1 mL degassed deionized water was added slowly by syringe. The mixture was allowed to warm to room temperature, stirred overnight and then poured into deionized water. Then the mixture was extracted with DCM and the combined extracts were dried with anhydrous sodium sulfate and then evaporated. The residue was purified by silica gel column chromatography using petrol ether/DCM (4:1 v/v) as the eluent to give **TATC6** as white solid (1.1 g, 94.5%). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 7.7 Hz, 3H, Ar-H), 7.63 (d, *J* = 8.1 Hz, 3H, Ar-H), 7.44 (t, *J* = 7.4 Hz, 3H, Ar-H), 7.33 (t, *J* = 7.6 Hz, 3H, Ar-H), 4.92 (t, *J*=8.0 Hz, 6H, CH₂), 2.05-1.90 (m, 6H, CH₂), 1.38-1.10 (m, 18H, CH₂), 0.80 (t, *J* = 7.0 Hz, 9H, CH₃). MALDI-TOF MS(*m/z*): Calcd. for C₄₂H₅₁N₃, Exact Mass: 597.41, Mol. Wt.: 597.89; Found: 597.3(M⁺).

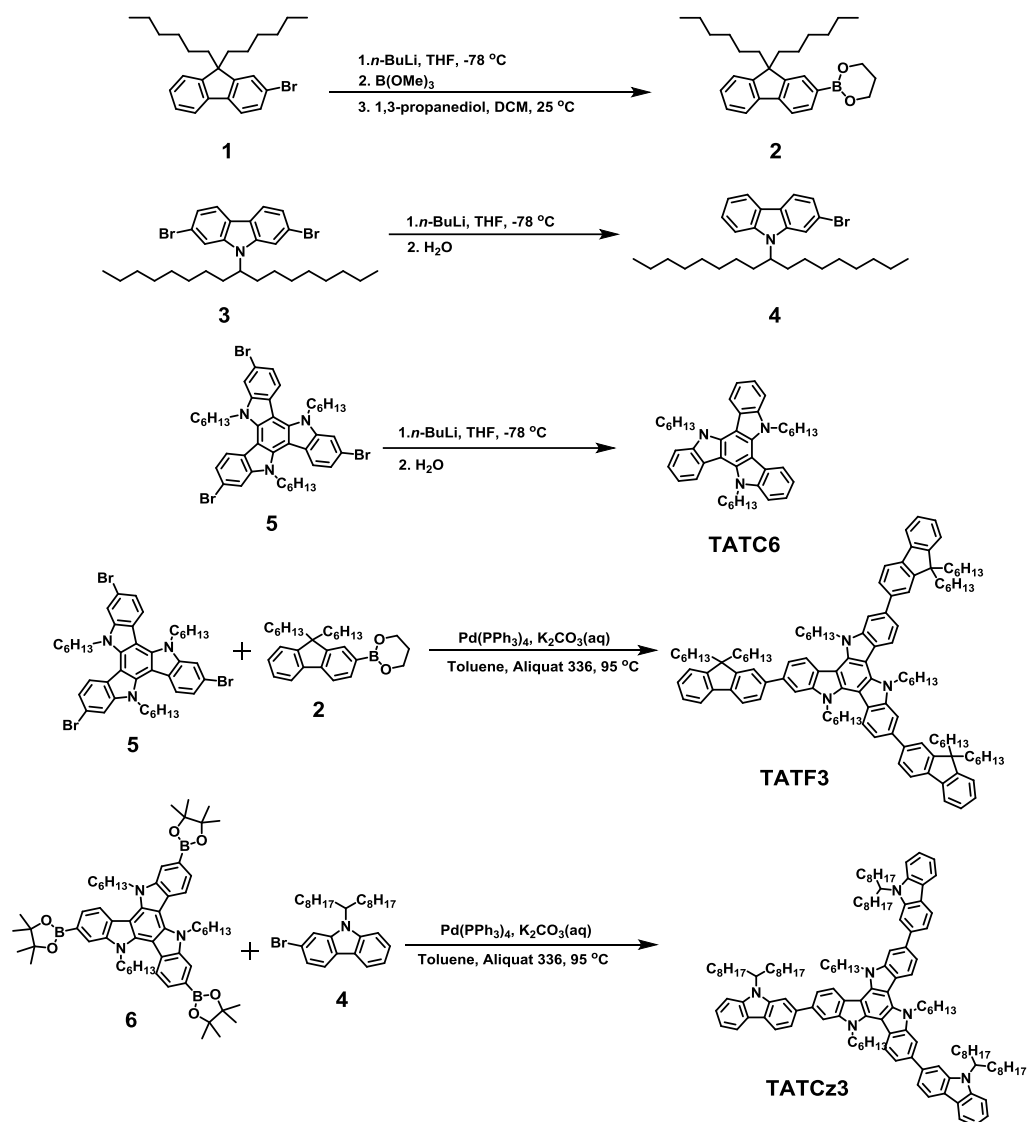
2,7,12-Tris(9,9-dihexylfluoren-2-yl)-5,10,15-trihexyltriazaatruxene (TATF3). To a mixture of compound **5** (417.3 mg, 0.5 mmol), compound **2** (627.6 mg, 1.5 mmol), and Pd(PPh₃)₄ (34.6 mg, 0.03 mmol) was added three drops of Aliquat 336, degassed toluene (20 mL), and aqueous 2 M potassium carbonate (3.0 mL, 6.0 mmol) under a dry argon atmosphere. The mixture was heated to 95 °C and stirred in the dark for 36 h. The reaction mixture was allowed to cool to room temperature and then poured into water. Then the mixture was extracted with DCM and the combined extracts were dried with anhydrous sodium sulfate and then evaporated. The residue was purified by silica gel column chromatography using petrol ether/DCM (5:1 v/v) as the eluent to give **TATF3** as light yellow solid (620.1 mg, 77.8%). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, 3H), 7.91 (s, 3H), 7.88-7.82 (m, 3H), 7.82-7.74 (m, 9H), 7.73-7.65 (m, 3H), 7.43-7.29 (m, 9H), 5.07 (t, 6H), 2.23-1.95 (m, 18H), 1.47-1.22 (m, 18H), 1.20-1.00 (m, 36H), 0.81 (m, 39H). MALDI-TOF MS(*m/z*): Calcd. for C₁₁₇H₁₄₇N₃, Exact Mass: 1594.16, Mol. Wt.: 1595.48; Found: 1594.2(M⁺).

2,7,12-Tris(*N*-(heptadecan-*N*-yl)-carbazol-2-yl)-5,10,15-trihexyltriazaatruxene (TATCz3). To a mixture of compound **6** (487.8 mg, 0.5 mmol), compound **4** (726.9 mg, 1.5 mmol), and Pd(PPh₃)₄ (34.6 mg, 0.03 mmol) was added three drops of Aliquat 336, degassed toluene (20 mL), and aqueous 2 M potassium carbonate (3.0 mL, 6.0 mmol) under a dry argon atmosphere. The mixture was heated to 95 °C and stirred in the dark for 36 h. The reaction mixture was allowed to cool to room temperature and then poured into water. Then the mixture was extracted with DCM and the combined extracts were dried with anhydrous sodium sulfate and then evaporated. The residue was purified by silica gel column chromatography using petrol ether/DCM (4:1 v/v) as the eluent to give **TATCz3** as light yellow solid (790.2 mg, 87.4%). ¹H NMR (400 MHz, CDCl₃) δ 8.53 – 8.31 (m, 3H, Ar-H), 8.21 (m, 6H, Ar-H), 7.96 (s, 6H, Ar-H), 7.87-7.59 (m, 9H, Ar-H), 7.56-7.36 (m, 6H, Ar-H), 5.23-4.95 (m, 6H, CH₂), 4.80-4.59 (m, 3H, CH), 2.58-2.26 (m, 6H, CH₂), 2.07 (d, 12H, CH₂), 1.49-1.03 (m, 90H, CH₂), 0.91-0.72 (m, 27H, CH₃). MALDI-TOF MS(*m/z*): Calcd. for C₁₂₉H₁₇₄N₆, Exact Mass: 1807.38, Mol. Wt.: 1808.85; Found: 1807.4(M⁺).

Film Preparation. The polystyrene (PS) doping films were fabricated by spin-coating the fluorophores THF solution (3 mg/mL) with PS ($M_w \sim 350$ K, PDI ~ 2.0 , 10 mg/mL) onto glass substrates at a spin rate of 2000 rpm at room temperature. The thicknesses of films doped with PS were measured by a profilometer giving **TATC6** films with thickness of 88 ± 6 nm, **TATCz3** films with thickness of 90 ± 4 nm, **TATF3** films with thickness of 92 ± 3 nm, and pyrene films with thickness of 89 ± 5 nm. The **TATCz3** and **TATF3** neat films were fabricated by spin-coating their THF solution (10 mg/mL) onto glass substrates at a spin rate of 2000 rpm at room temperature, respectively. The thicknesses of **TATCz3** and **TATF3** neat films were 92 ± 4 nm and 90 ± 3 nm, respectively. Five individual measurements on three separate films were performed to determine the thickness of these films. The films on optic-fiber tips were fabricated by dip-coating the **TATCz3** THF solution (10 mg/mL) at room temperature and drying in air.

Stern–Volmer Measurement. The nitroaromatics used in this study were TNT, DNT, *p*-nitrotoluene (*p*NT), and nitrobenzene (NB), all of which bear similar chemical structure and have high electron affinities. Benzophenone (BP) and duroquinone (DQ) were used as electron-deficient interferents, as they are high-electron-affinity aromatic compounds without nitro groups. Solutions of the triazatruxene derivatives with a concentration of 10^{-6} M were prepared in spectrophotometric grade tetrahydrofuran. Analyte solutions were prepared by dissolving measured quantities of each analyte into known volumes of the triazatruxene derivative solution to maintain the concentration of the triazatruxene derivative as a constant throughout the experiment. Both the absorption and emission spectra (excited at the peak absorbance wavelength) of 2.5 mL of the triazatruxene derivative solution in a 10×10 mm quartz cuvette were recorded before and after gradual additions of small aliquots of analyte solution. The concentration of analyte was chosen so that the maximum absorbance of the solution at the excitation wavelength did not exceed ~ 0.6 . The fluorescence intensity were corrected for both inner filter effect and absorption of the UV excitation by the analyte according to the methods developed by Meredith and coworkers.⁵⁴ All measurements were repeated for three times with separate analyte solutions.

Vapors Detection. The fluorescence responses of films to the vapors of various analytes were studied by inserting the prepared films into a quartz cuvette containing analytes at room temperature. A small quantity of the analytes was placed beneath some cotton wool in a sealed quartz cuvette and left overnight to allow the analytes vapors to reach equilibrium (fully saturated). Films were placed in the quartz cuvette and fluorescence spectra were recorded after exposing the film to analytes for specific time intervals. A single time-dependent fluorescence quenching curve was obtained by the combination of the data from three separate measurements.



Scheme S1. Synthesis of three triazatruxene derivatives.

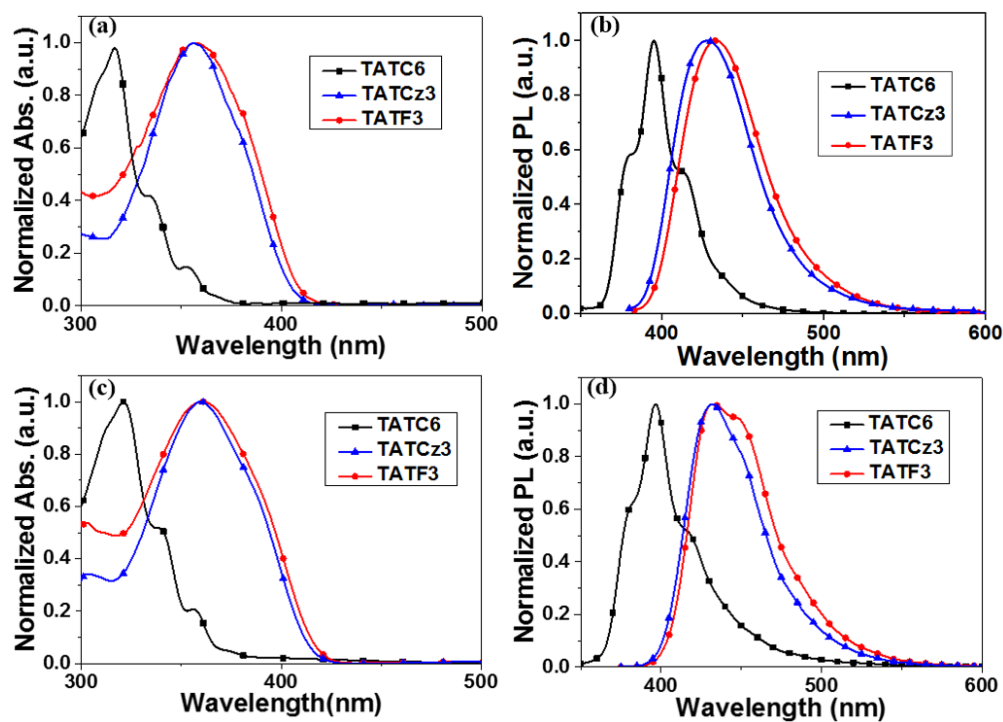


Figure S1. UV-vis absorption and fluorescence spectra of three triazatruxene derivatives in dilute THF solution ((a) absorption and (b) fluorescence) and in thin films ((c) absorption and (d) fluorescence).

Table S1. Physical properties of three triazatruxene derivatives.

TAT derivatives	$\lambda_{\text{abs}}/\text{nm}$		$\lambda_{\text{em}}/\text{nm}$		QY ^a	$E_g^{\text{opt}}/\text{eV}^b$	$E_{\text{HOMO}}/\text{eV}^c$	$E_{\text{LUMO}}/\text{eV}^d$
	Solution	Film	Solution	Film				
TATC6	318	321	393	397	7.0%	3.38	-5.11	-1.73
TATCz3	356	360	428	432	71.4%	3.07	-5.07	-1.99
TATF3	357	360	434	433, 450 (sh)	49.8%	3.04	-5.07	-2.03

^aMeasured in dilute THF, 9,10-Diphenylanthracene in cyclohexene was used as standard. ^bEstimated from the onset of absorption spectra. ^cMeasured by the method of cyclic voltammetry. ^dCalculated from $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$.

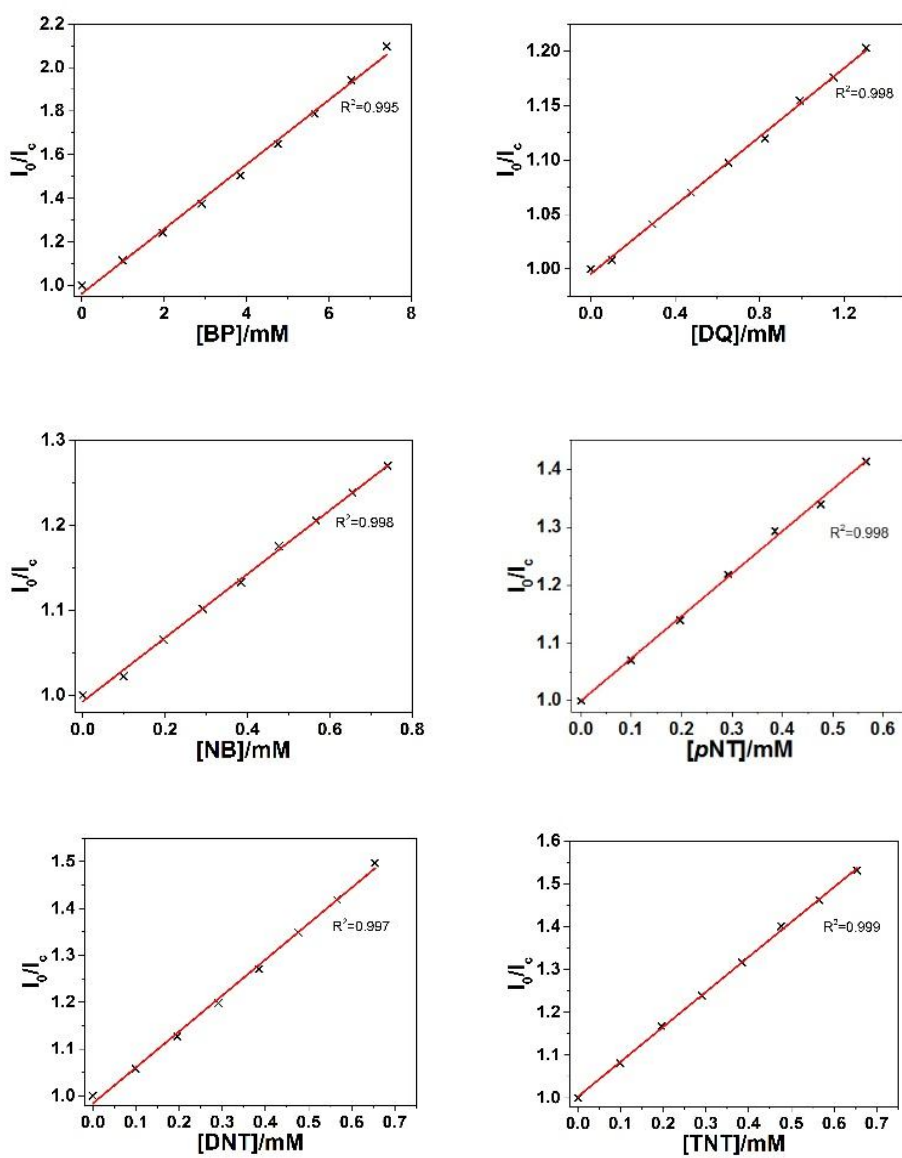


Figure S2. Stern-Volmer plots and fits for TATC6 with different analytes.

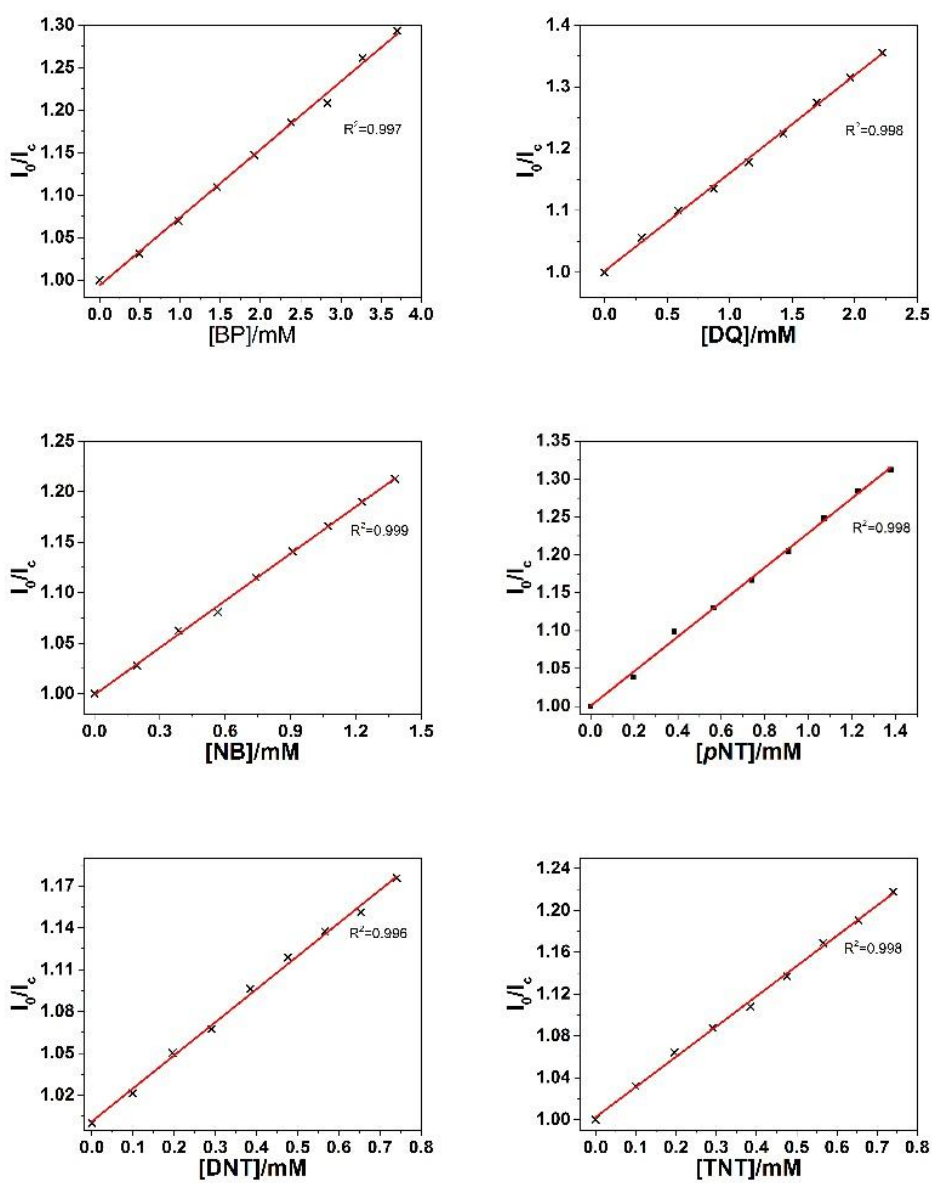


Figure S3. Stern-Volmer plots and fits for **TATCz3** with different analytes.

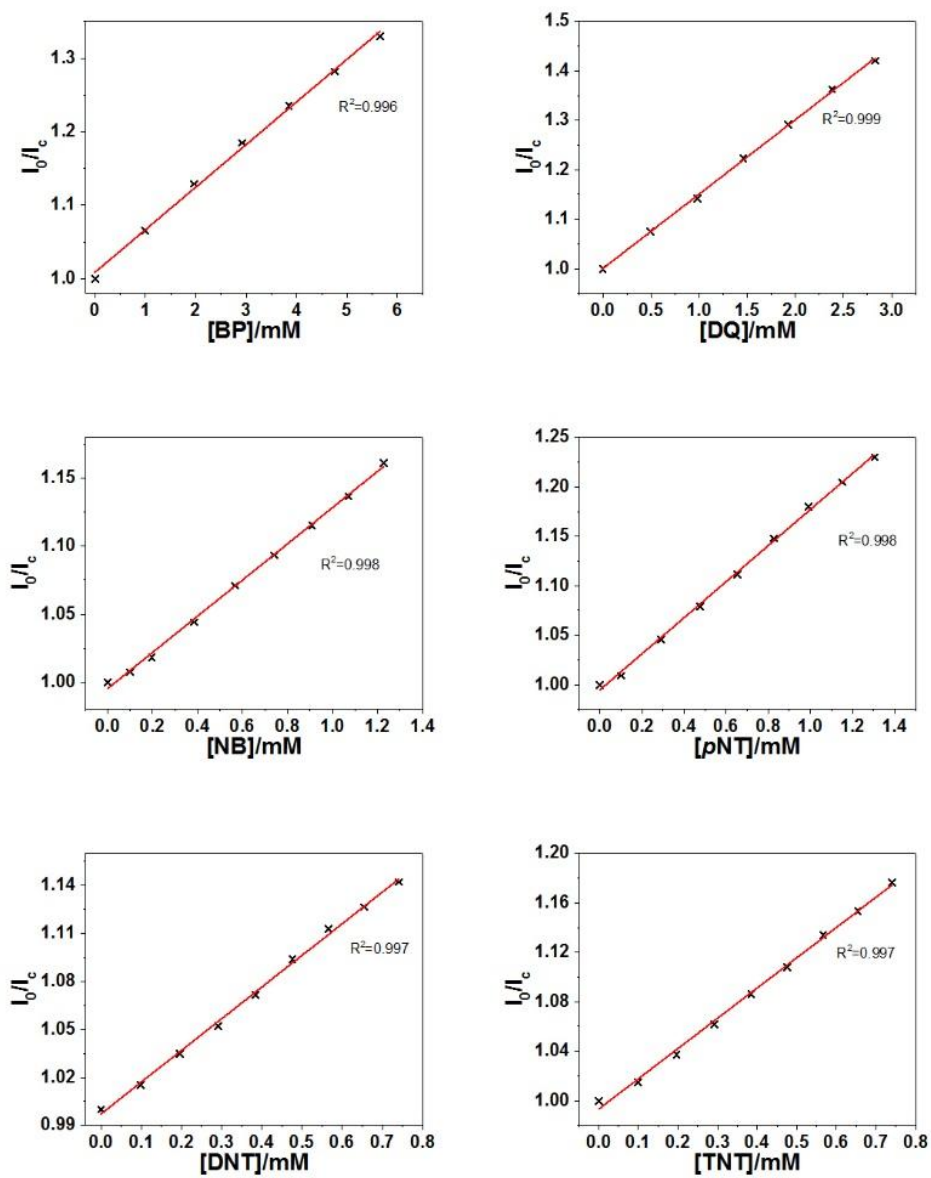


Figure S4. Stern-Volmer plots and fits for TATF3 with different analytes.

Table S2. Summary of the Stern-Volmer Constants (K_{SV}) for Each TAT Derivative with Analytes.

TAT derivative	TNT/ M^{-1}	DNT/ M^{-1}	<i>p</i> NT/ M^{-1}	NB/ M^{-1}	DQ/ M^{-1}	BP/ M^{-1}
TATC6	815 \pm 9	767 \pm 16	732 \pm 15	375 \pm 6	157 \pm 3	148 \pm 4
TATCz3	289 \pm 5	237 \pm 5	228 \pm 4	155 \pm 2	158 \pm 2	80 \pm 2
TATF3	245 \pm 5	198 \pm 4	182 \pm 3	133 \pm 2	150 \pm 2	58 \pm 1

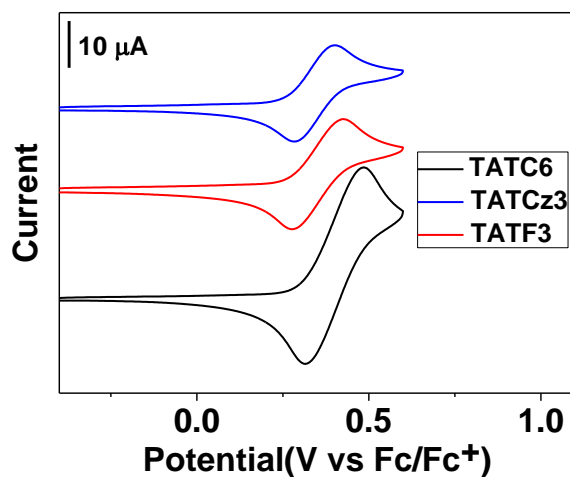


Figure S5. Cyclic voltammograms of the triazatruxene derivatives in dichloromethane and TBAPF₆ was used as supporting electrolyte.

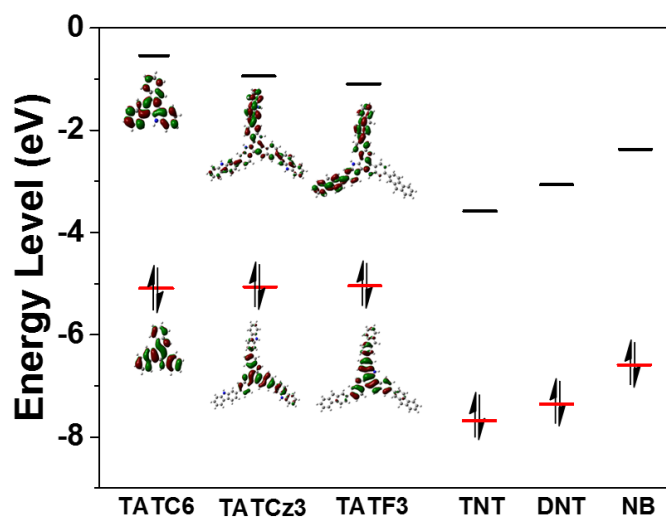


Figure S6. Theoretical calculations of the triazatruxene derivatives and three nitroaromatic compounds by density functional theory at the B3LYP/6-31g* level.

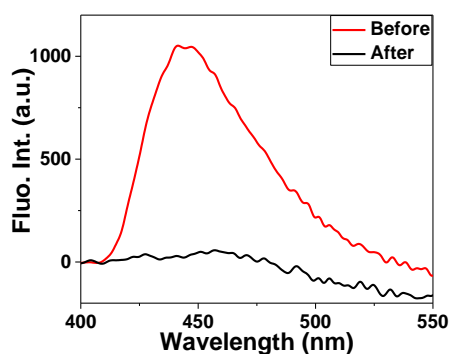


Figure S7. Fluorescence spectra of **TATCz3** film coated on fiber-optic tip before and after exposure to saturated DNT vapor.

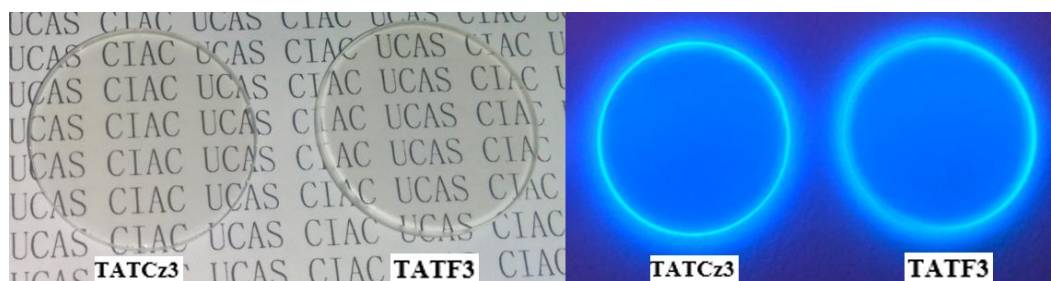


Figure S8. Images of **TATCz3** and **TATF3** neat films coated on quartz plates under sunlight (left) and UV lamp (right).

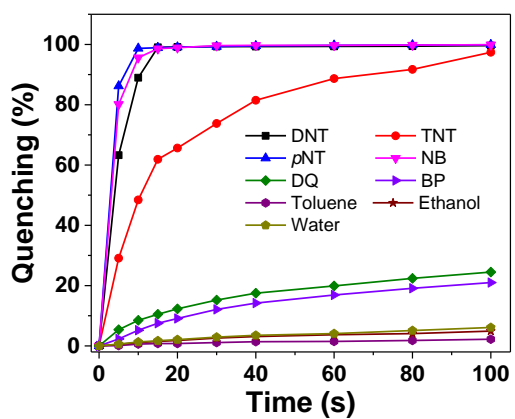


Figure S9. Time-dependent fluorescence quenching of **TATCz3** coated on fiber-optic tips upon exposure to saturated DNT, TNT, *p*NT, NB, DQ, BP, toluene, ethanol and water vapors.

Because the vapor pressures of NB (0.46 mmHg) and *p*NT (4.13×10^{-2} mmHg) are much higher than those of TNT (5.50×10^{-6} mmHg) and DNT (2.63×10^{-4} mmHg), their quenching speeds are even faster than TNT and DNT vapors.

Reference:

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- S4. H. Cavaye, H. Barcena, P. E. Shaw, P. L. Burn, S.-C. Lo, P. Meredith, *Proc. SPIE*, 2009, **7418**, 741803.