

Electronic Supplementary Information (ESI)

A photoluminescent covalent triazine framework: CO₂ adsorption, light-driven hydrogen evolution and sensing of nitroaromatics

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Supporting information
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1. Powder X-ray diffraction pattern

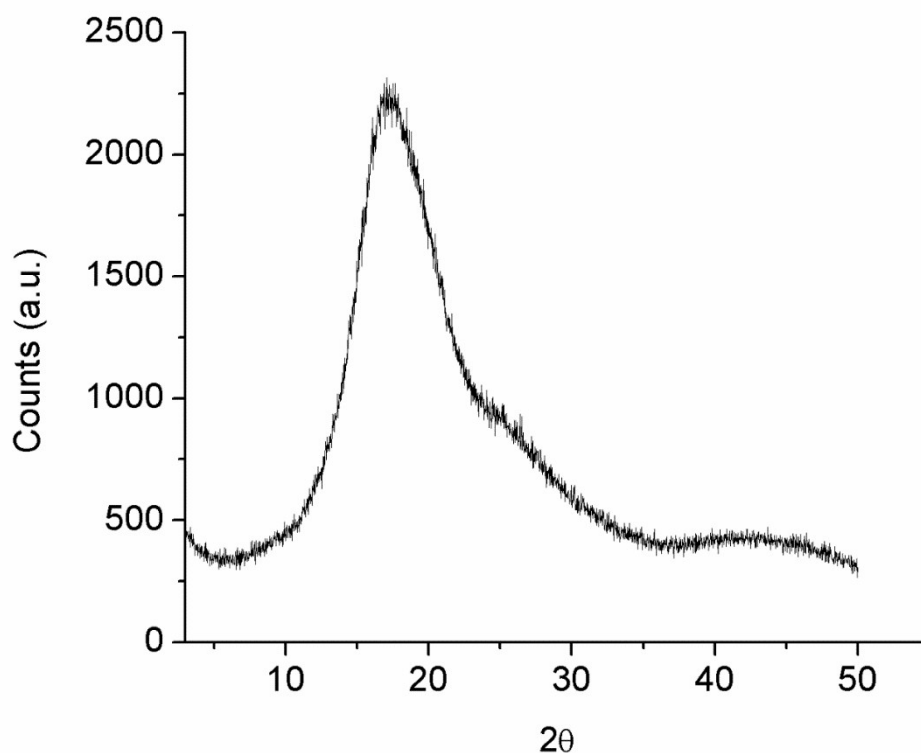


Fig. S1: Powder X-ray pattern of PCTF-8.

2. Elemental analysis of PCTF-8

Elemental analysis suggested that the formula unit ($C_{30}H_{16}N_4$) contain additional three water molecules which is in good agreement with results found by Karl-Fischer titration (KFT). The calculated and found values are in the Table S1.

Table S1: Elemental analysis of PCTFs

Compound	Calculated (% and molar ratio)					Found (% and molar ratio)				
	C	H	N	C/H	C/N	C	H	N	C/H	C/N
^a PCTF-8	83.32	3.73	12.95	2	8	74.96	4.55	11.16	1	8
^b PCTF-8	74.06	4.56	11.52	1	8	74.96	4.55	11.16	1	8

^aFormula unit without water molecule. ^bFormula unit contain three water molecules.

3. Thermogravimetric analysis (TGA)

PCTF-8 is thermally stable up to 420 °C. The weight loss step that occurs below the decomposition temperature of the PCTF-8 can be ascribed to the removal of the solvent molecules as well as guest molecules from the pore.

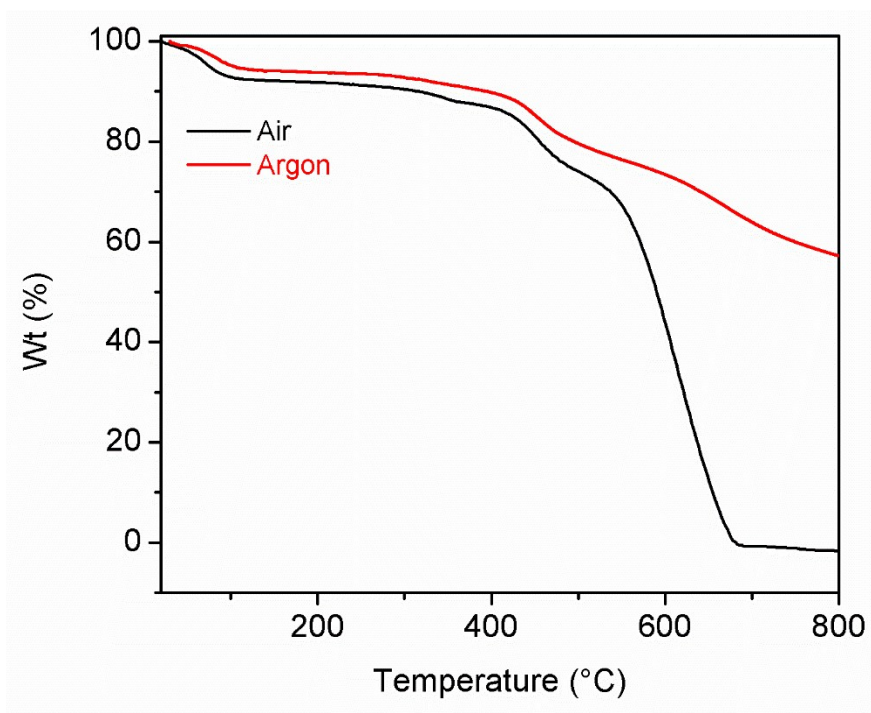


Fig. S2: TGA plot for PCTF-8 under air (black colour) and argon (red colour).

4. Analyses for water content

Karl-Fischer titration (KFT):

Water content of a PCTF-8 sample was determined by KFT. We found about 10 wt% water in the material which is in good agreement with the oxygen content found by CHN analysis. The PCTF-8 material had been stored under ambient air after vacuum drying at 120°C for 24 h.

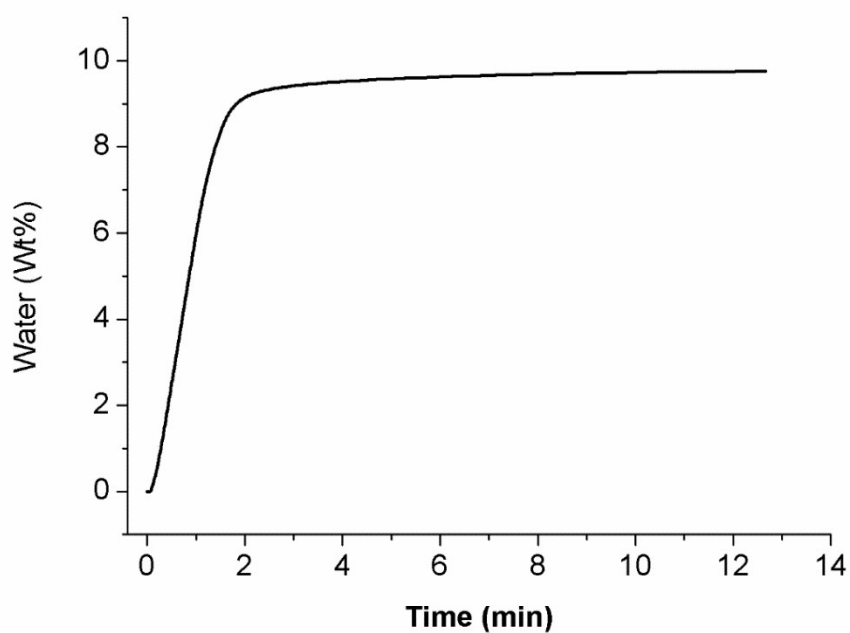


Fig. S3: Karl-Fischer titration plot for PCTF-8.

5. Surface area and pore volume data for PCTF-8

Table S2: Porosity data for PCTF-8 from N₂ isotherms at 77 K

Compound	S _{BET} ^a	S _{Lang} ^a	V _{0.1} ^b	V _{tot} ^c	V _{0.1} /V _{tot}
	(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	
PCTF-8	625	758	0.25	0.32	0.78

^aCalculated BET surface area over the pressure range 0.01–0.05 P/P₀; ^bPore volume at P/P₀ = 0.1; ^cTotal pore volume at P/P₀ = 0.95.

6. Isothermic heat of adsorption of CO₂ for PCTF-8

From two adsorption isotherms acquired at different temperatures T_1 and T_2 , the differential heat of adsorption $\Delta H_{ads,diff}$, that is isosteric heat of adsorption Q_{st} can be calculated for any amount of adsorbed substance after determining the required relative pressures p_1 and p_2 . A modified form of the Clausius-Clapeyron equation is used (eq (1)).¹ $\Delta H_{ads,diff}$ was calculated over the whole adsorption range from the 273 K and 293 K isotherms for CO₂.

$$\Delta H_{ads,diff} = Q_{st} = -R \ln \left(\frac{p_2}{p_1} \right) \frac{T_1 T_2}{T_2 - T_1} \quad (1)$$

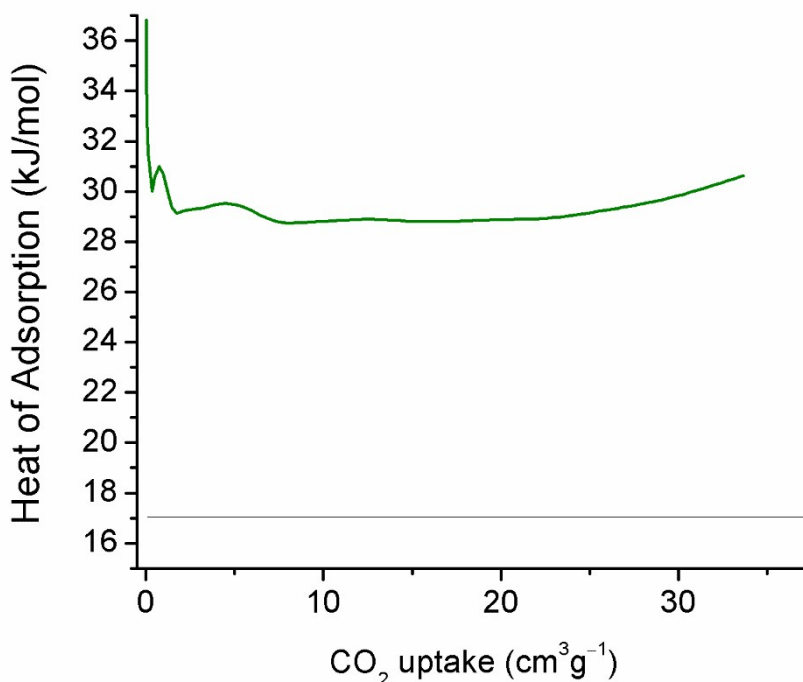


Fig. S4: Isothermic differential heat of adsorption (adsorption enthalpy, $Q_{ads,diff}$) as a function of CO₂ uptake for PCTF-8.

7. Pore size distribution from a CO₂ adsorption isotherm

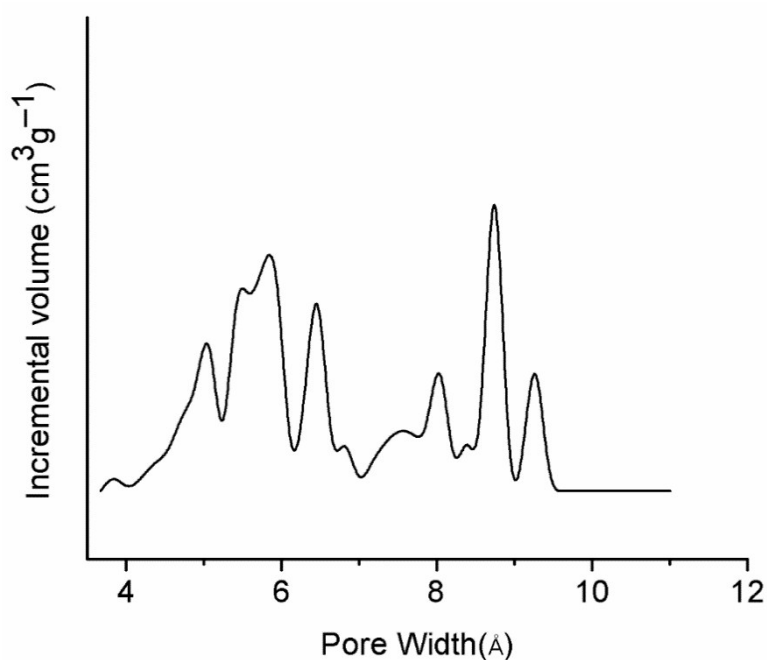


Fig. S5: The pore size distribution from a CO₂ adsorption isotherm at 273 K, calculated by the NL-DFT with a “CO₂ on carbon based slit-pore” model at 273 K.

8. Selectivity studies

TableS3: Langmuir fitting parameters of CO₂, CH₄, and N₂ adsorption isotherms of PCTF-8 at 273 K and 1 bar.

PCTF-8@273K	$q_{\text{sat,A}}$ (mmol/g)	b_A (bar ⁻¹)	$q_{\text{sat,B}}$ (mmol/g)	b_B (bar ⁻¹)	Adj. R ²
CO ₂	0.76614	8.44818	3.87379	0.8761	1
CH ₄	2.14138	0.52433			0.99997
N ₂	1.29082	0.21243			0.99997

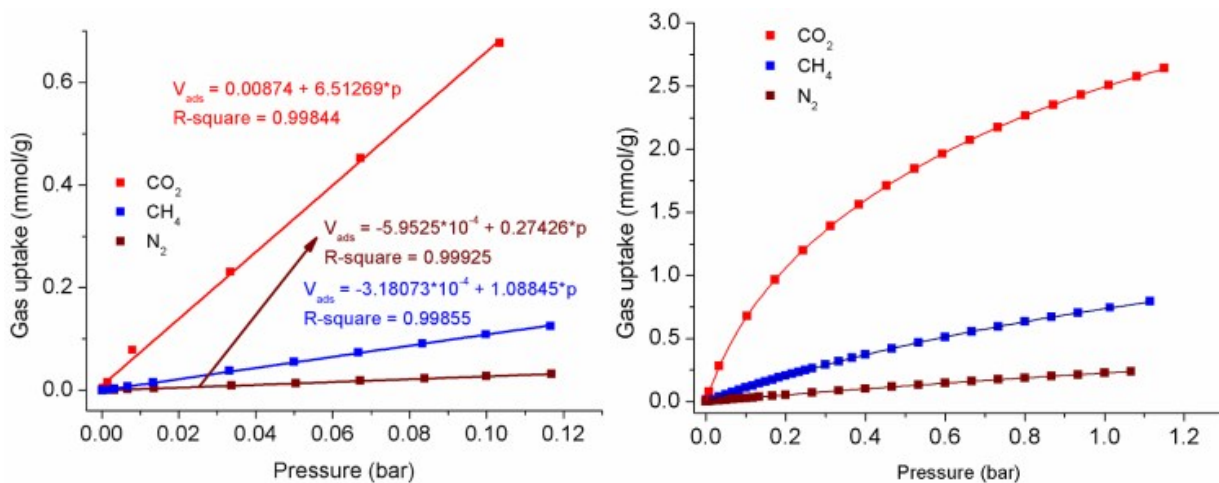


Fig. S6: Adsorption selectivity for PCTF-8 using Henry equation (left) and IAST (right).

9. Emission spectrum of PCTF-1

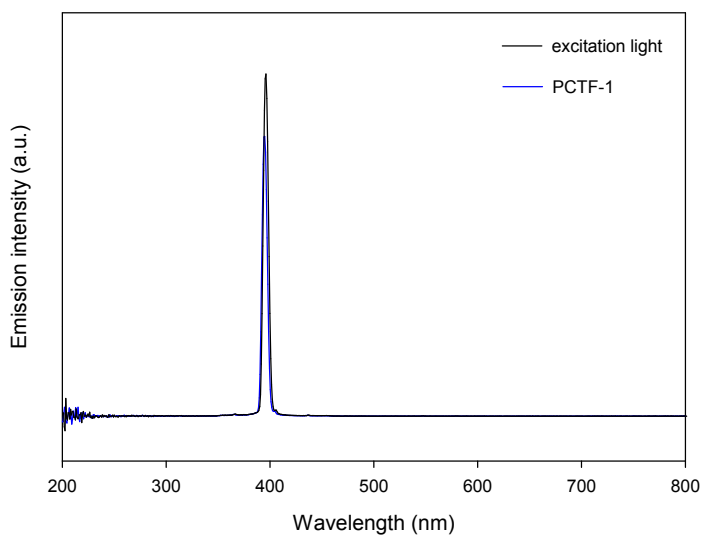


Fig. S7: Emission spectrum of PCTF-1 and the excitation light.

10. H₂ Evolution Experiments

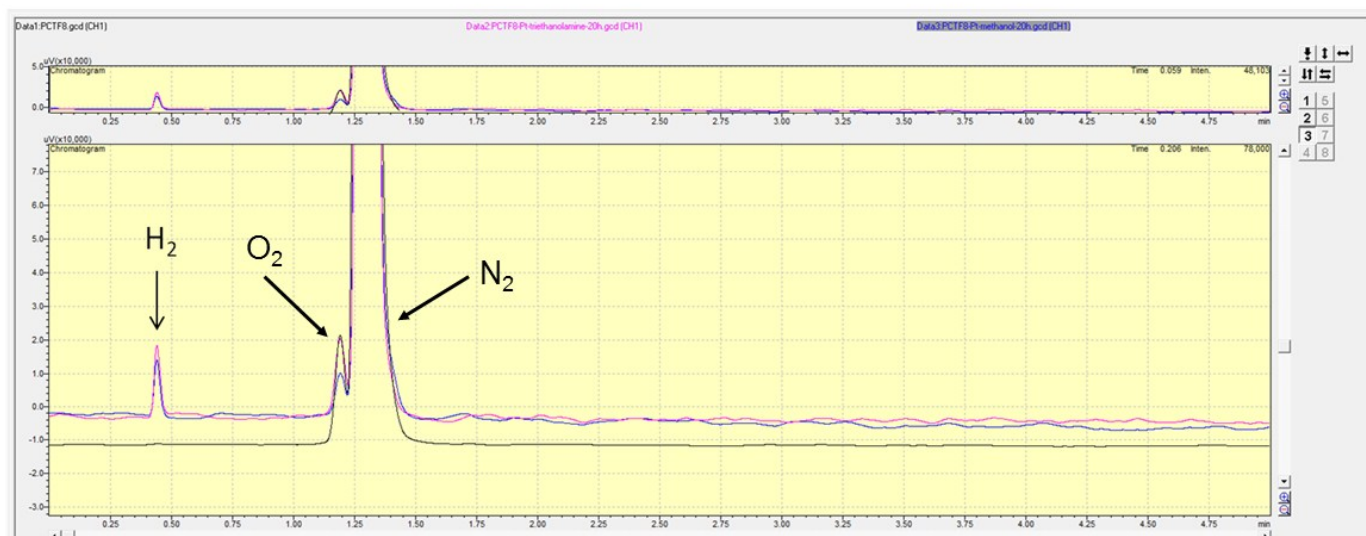


Fig. S8: Gas chromatograms: The peak of hydrogen evolution for Pt-loaded PCTF-8 in the presence of methanol (blue colour line) and triethanolamine (magenta colour line) sacrificial electron donor (10%) under simulated light for 24 h. Black colour line represent the hydrogen evolution experiment of PCTF-8 without using cocatalyst (Dihydrogen hexachloroplatinate).

11. Nitroaromatic Explosives Detections

The fluorescence quenching of dispersed PCTF-8 were investigated at room temperature. The dispersions were prepared using 1 mg PCTF-8 in 3 mL acetonitrile. The resulting suspensions were ultrasonicated for 10 min before adding different analytes (TNP, 2,4-DNP, 2,6-DNT, 2,4-DNT, NT and NB). The analytes (0 to 1×10^{-6} mol/L) were added into the dispersion of PCTF-8 via micro pipette. After 2-3 minutes, the fluorescence emission spectra were recorded ($\lambda_{exc} = 395$ nm for all spectra).

The K_{SV} values we report are not corrected for the inner filter effect for two main reasons. Out of the six studied nitroaromatic analytes, four (2,4-DNP, 2,4-DNT, NB and NT) have negligible absorption at either 395 nm or 405 nm, as shown in Fig. S9. In spite of the fact that the NIST database page does not report the solvent used for the measurements, we do not expect any significant shift in the absorption which can involve an increase in the extinction coefficients above 390 nm. In the same way, the absorption bands of these compounds are far from the onset of the emission of PCTF-8, and therefore no primary nor secondary inner filter effect contributions are expected to arise from these analytes, making any correction of the reported K_{SV} unnecessary. In the case of TNP and 2,6-DNT, in spite of the fact that the absorption spectra of these compounds (Fig.

S10) overlap with the absorption spectrum of PCTF-8, given that the concentrations we used for the quenching experiments were extremely low ($30 \mu\text{M}$ at most), we do not expect any significant impact of the possible corrections for the inner filter effect, which we estimate to be less than the experimental error in the determination of the fluorescence intensities. At the same time, even for Anthracene (example given in J. R. Lakowicz, Principles of fluorescence spectroscopy, Springer, New York, 3rd ed., 2006 page 56, Figure 2.47), the linear range of the fluorescence emission intensity vs. concentration goes up to the Mm scale, while in our work we are using μM concentrations of the analytes.

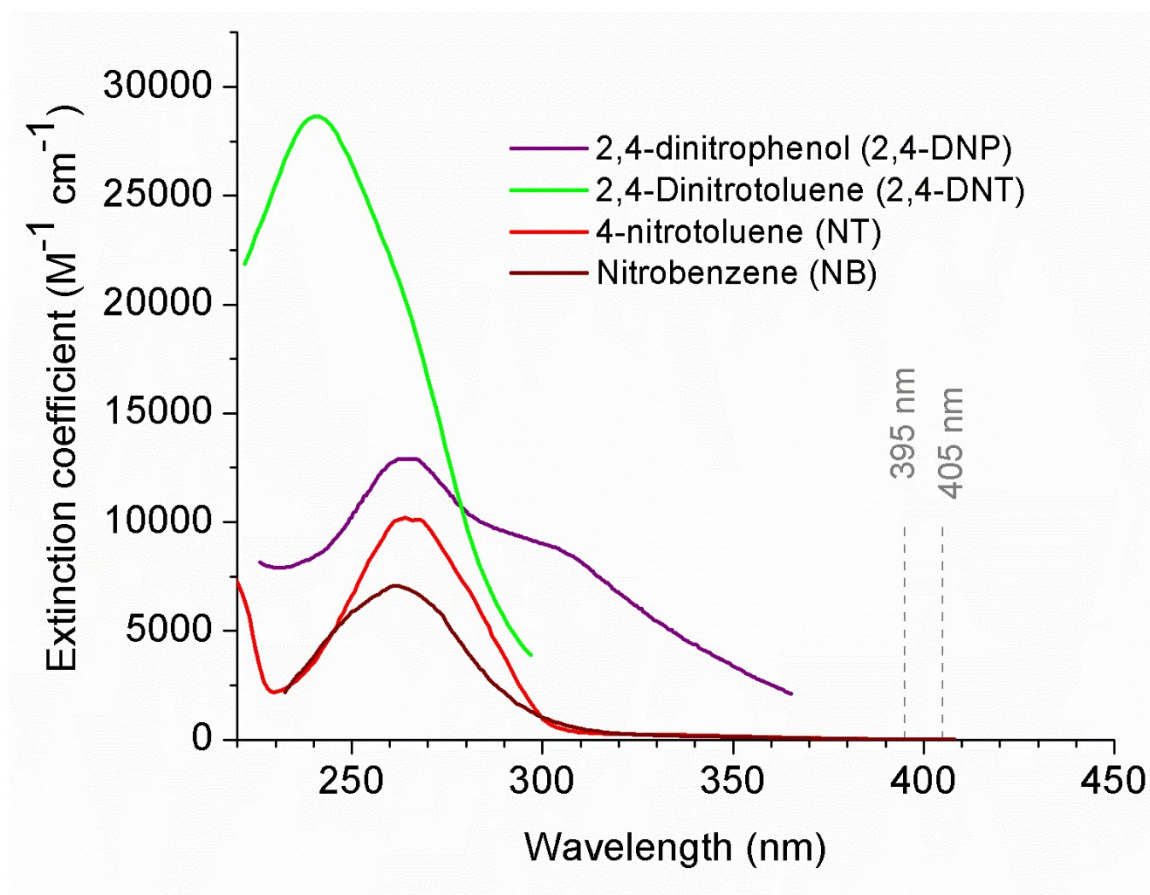


Fig. S9: Extinction coefficients of four nitroaromatic analytes. Data from NIST Standard Reference Database. 2,4-dinitrophenol has negligible absorption beyond 360 nm.

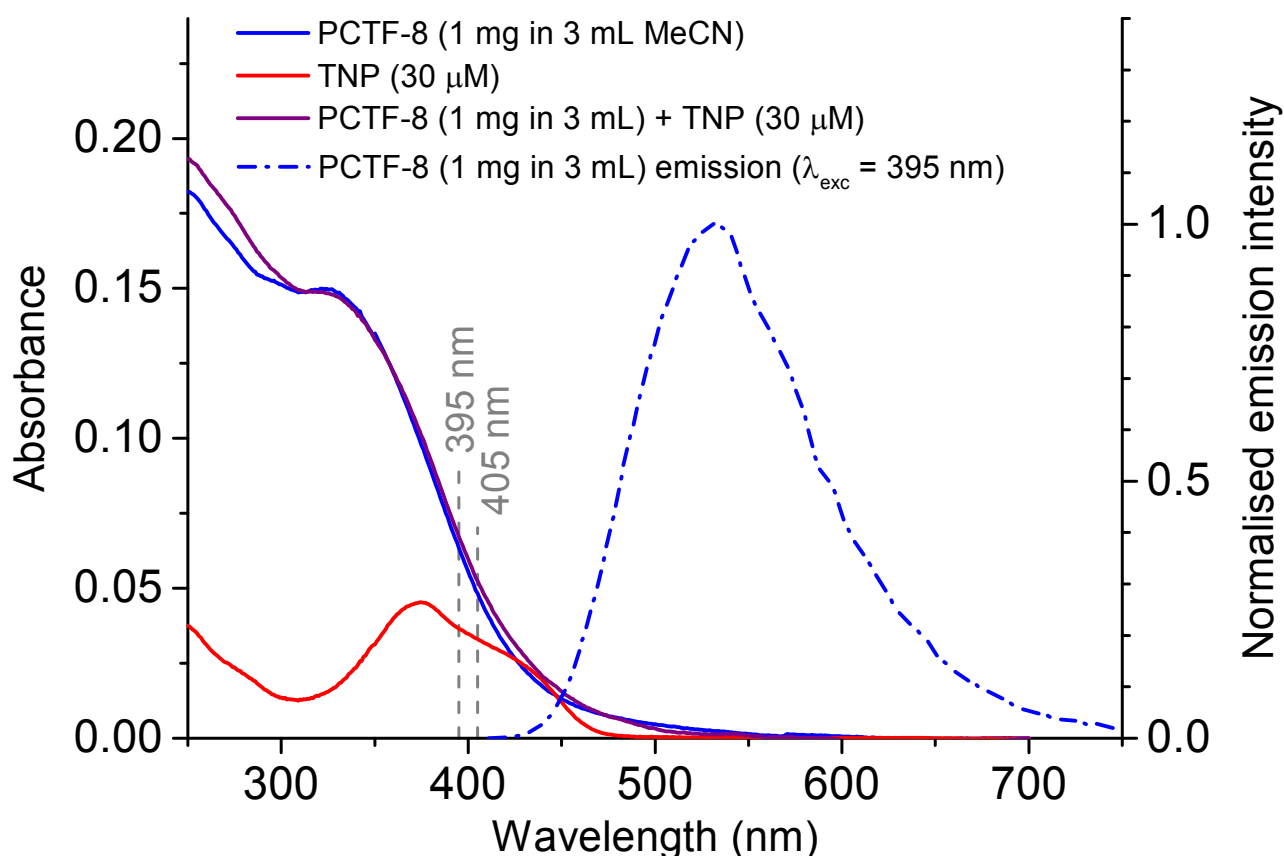


Fig. S10: Absorption and emission spectra of PCTF-8 (1 mg in 3 mL MeCN, $\lambda_{exc} = 395 \text{ nm}$), together with absorption spectra of TNP ($30 \mu\text{M}$) and a mixture of TNP and PCTF-8 (1 mg in 3 mL)

In the range of concentrations that we used, and as evidenced in Fig. S10, the absorption of picric acid (TNP, $30 \mu\text{M}$ solution in MeCN) and of PCTF-8 (1 mg in 3 mL MeCN), as well as a solution containing both the TNP analyte and PCTF-8 (identical concentrations) at either 395 nm (wavelength used for steady-state quenching experiments) or at 405 nm (wavelength used for TCSPC studies) is below 0.1 (approx. 0.06, as shown in Fig. S10), and therefore we conclude that corrections to our reported K_{SV} values are not necessary, as no significant contributions from the inner filter effect are expected with this very low absorbance. As an additional comment, the linearity of our Stern-Volmer plots also reflects the absence of inner filter effects and other possible deviations from the standard behavior in the concentration range of the analytes that we employed. 2,6-dinitrophenol has a lower extinction coefficient than TNP at either 395 or 405 nm, and therefore no corrections are expected to be needed for this analyte in the studied concentration range, either.

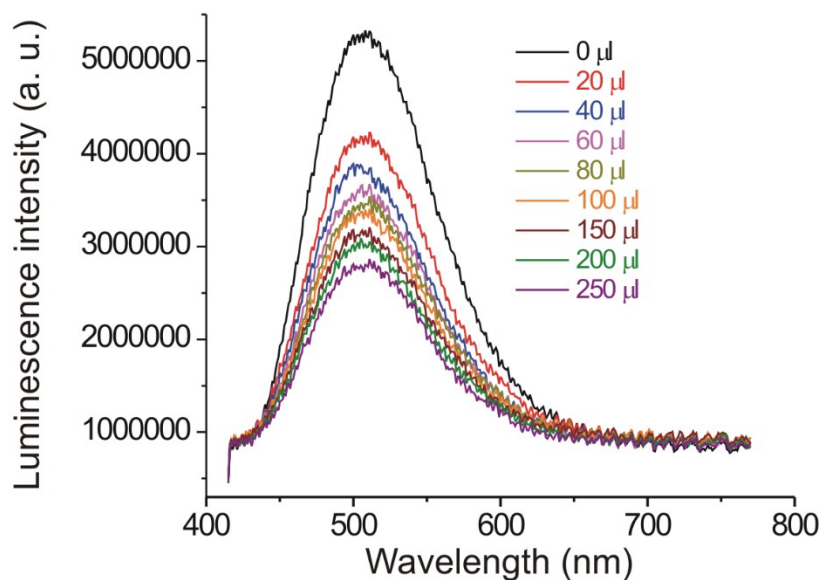


Fig. S11: Fluorescence quenching ($\lambda_{exc} = 395 \text{ nm}$) of PCTF-8 by 2,4-DNP ($0 - 1 \times 10^{-6} \text{ mol/L}$) at room temperature (1 mg PCTF-8 in 3 mL acetonitrile).

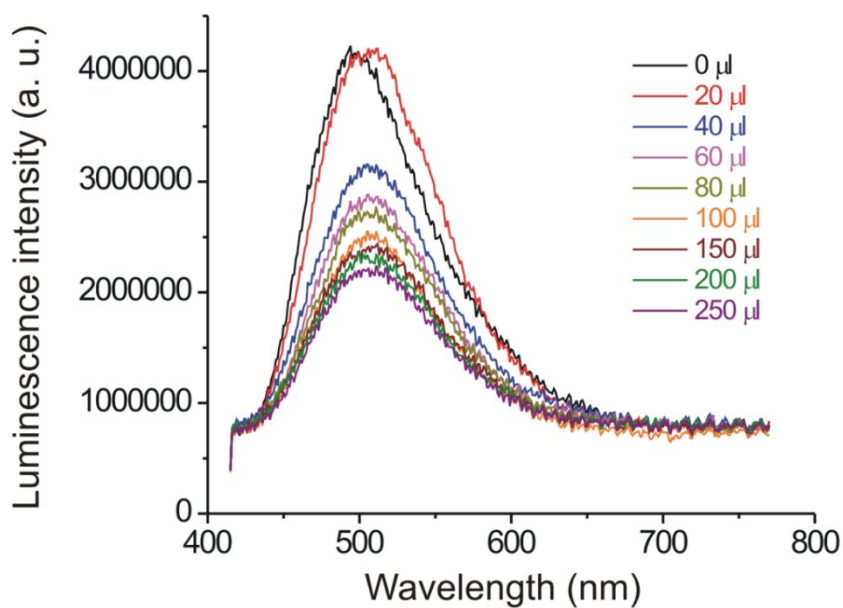


Fig. S12: Fluorescence quenching ($\lambda_{exc} = 395 \text{ nm}$) of PCTF-8 by 2,6-DNT ($0-1 \times 10^{-6} \text{ mol/L}$) at room temperature (1 mg PCTF-8 in 3 mL acetonitrile).

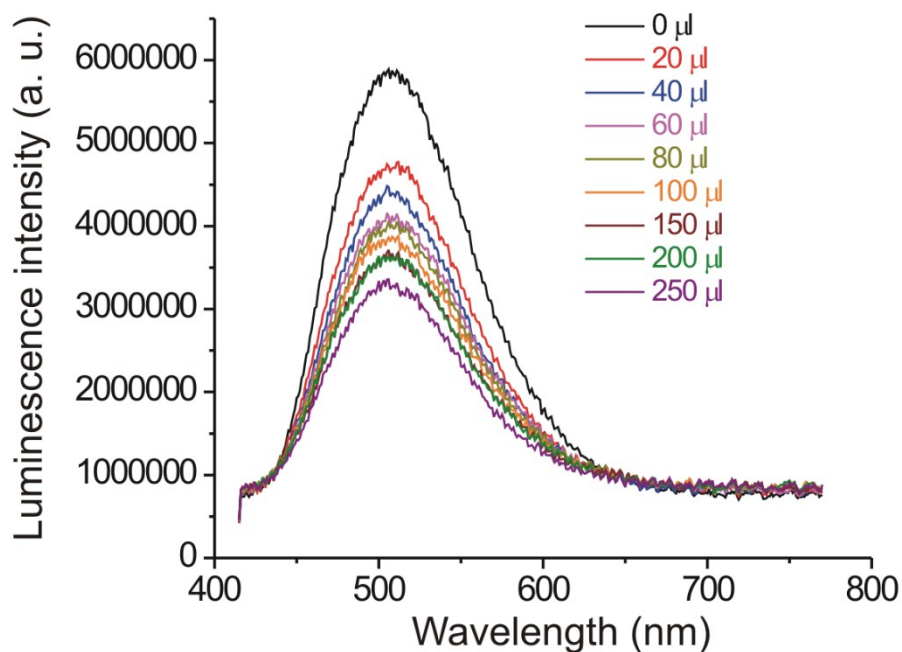


Fig. S13: Fluorescence quenching ($\lambda_{exc} = 395 \text{ nm}$) of PCTF-8 by 2,4-DNT ($0 - 1 \times 10^{-6} \text{ mol/L}$) at room temperature (1 mg PCTF-8 in 3 mL acetonitrile).

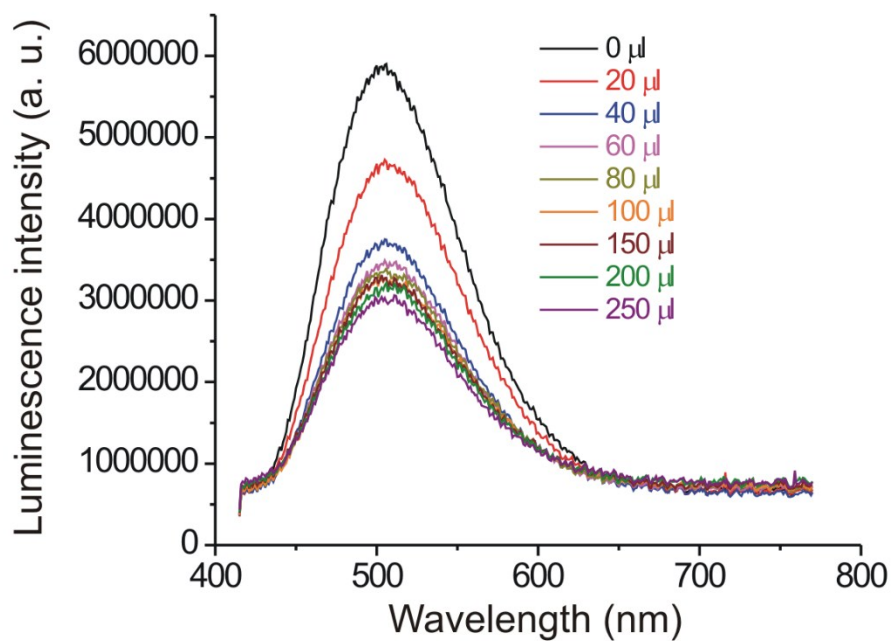


Fig. S14: Fluorescence quenching ($\lambda_{exc} = 395 \text{ nm}$) of PCTF-8 by NT ($0 - 1 \times 10^{-6} \text{ mol/L}$) at room temperature (1 mg PCTF-8 in 3 mL acetonitrile).

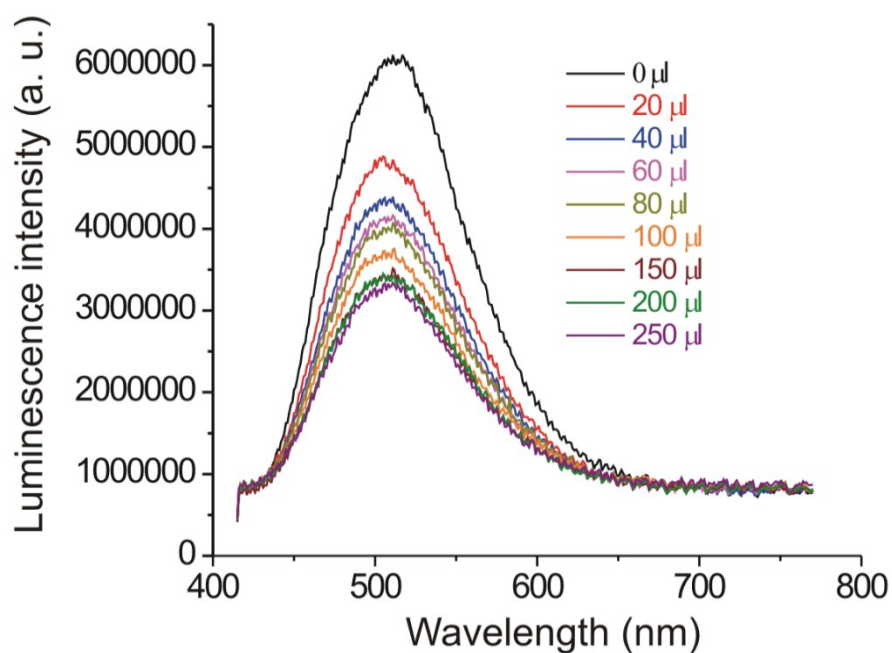


Fig. S15: Fluorescence quenching ($\lambda_{exc} = 395 \text{ nm}$) of PCTF-8 by NB ($0 - 1 \times 10^{-6} \text{ mol/L}$) at room temperature (1 mg PCTF-8 in 3 mL acetonitrile).

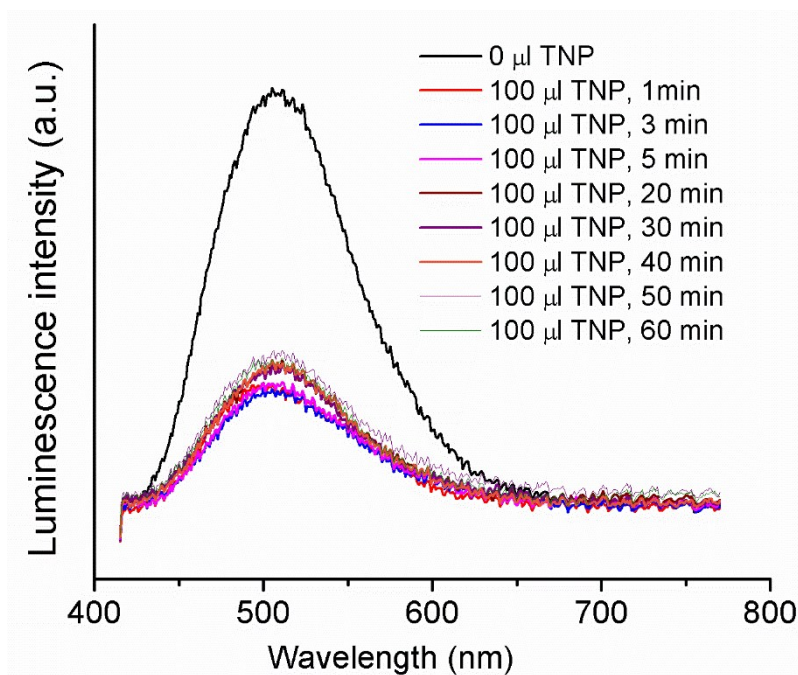


Fig. S16: Fluorescence quenching ($\lambda_{exc} = 395 \text{ nm}$) of PCTF-8 with time by TNP ($5 \times 10^{-4} \text{ mol/L}$) at room temperature.

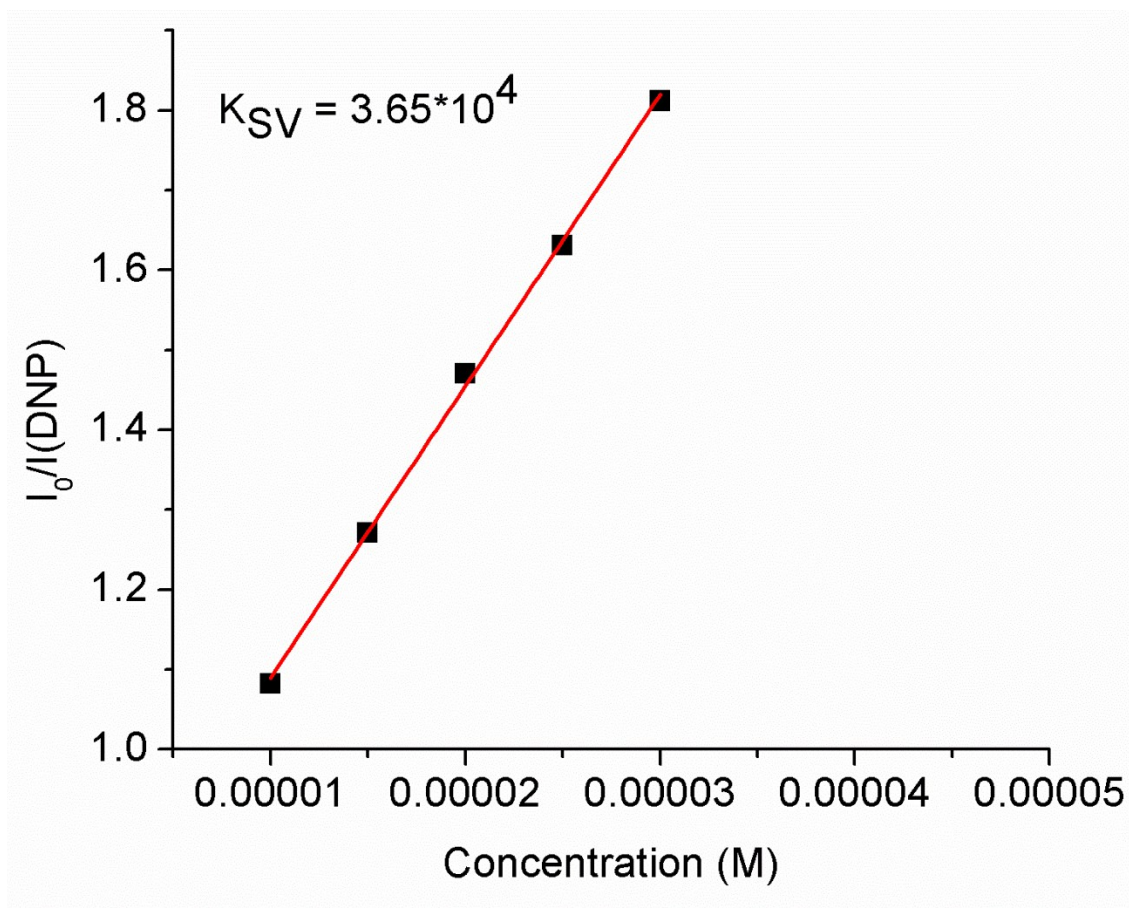


Fig. S17: Linear Stern–Volmer plots for the quenching of PCTF-8 by DNP.

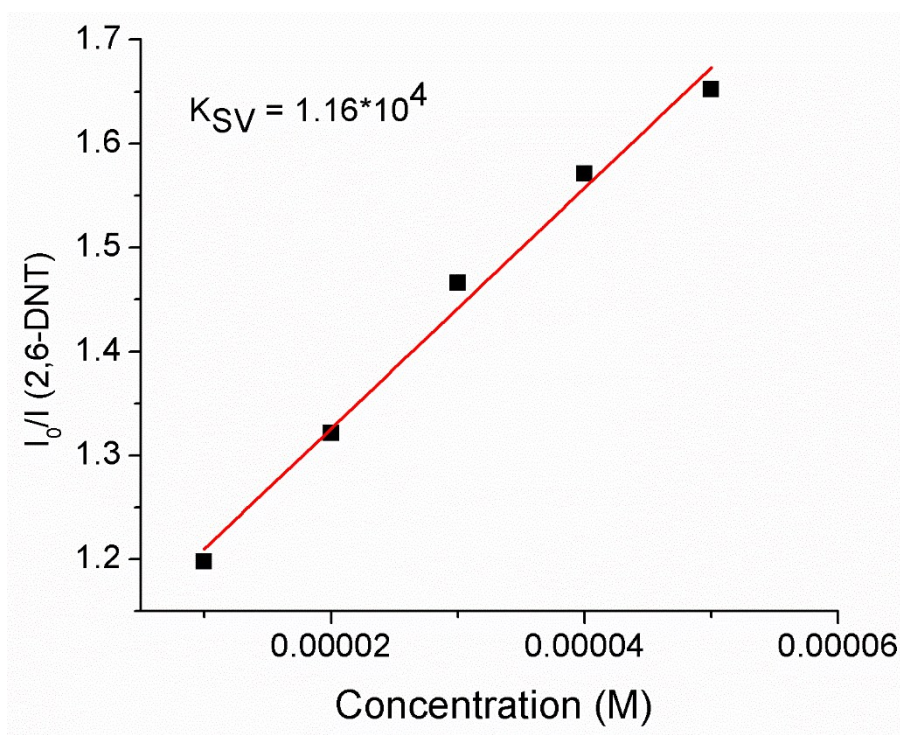


Fig. S18: Linear Stern–Volmer plots for the quenching of PCTF-8 by 2,6-DNT.

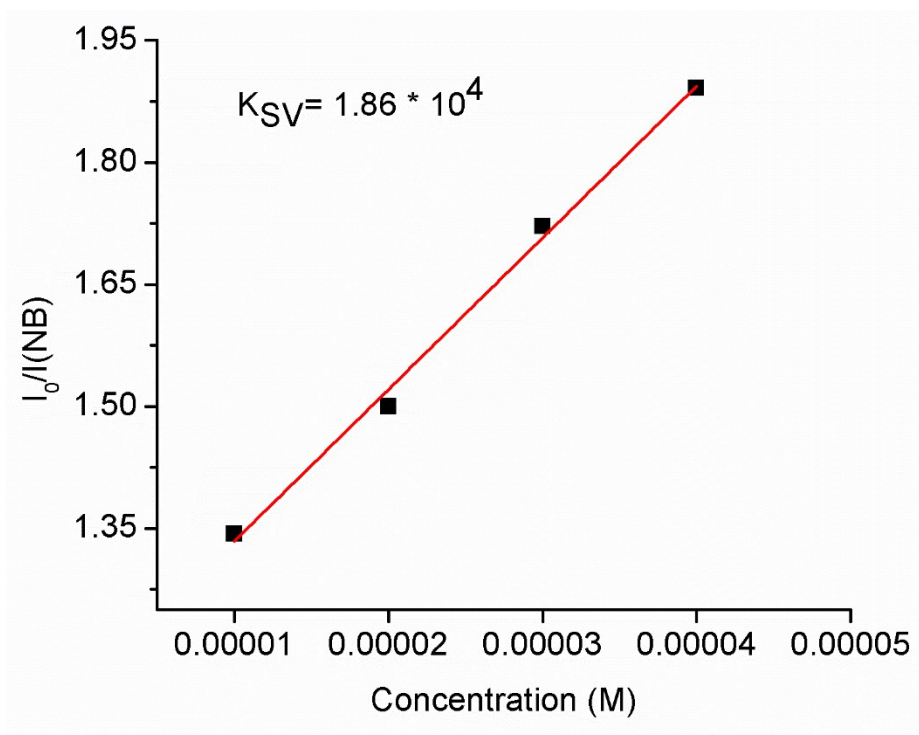


Fig. S19: Linear Stern–Volmer plots for the quenching of PCTF-8 by NB.

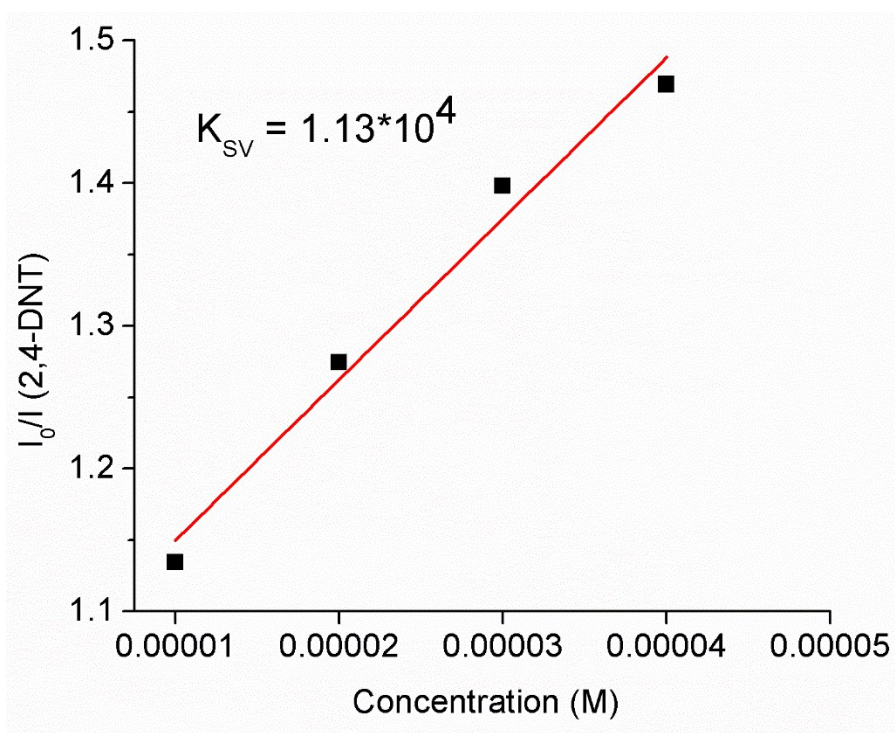


Fig. S20: Linear Stern–Volmer plots for the quenching of PCTF-8 by 2,4-DNT.

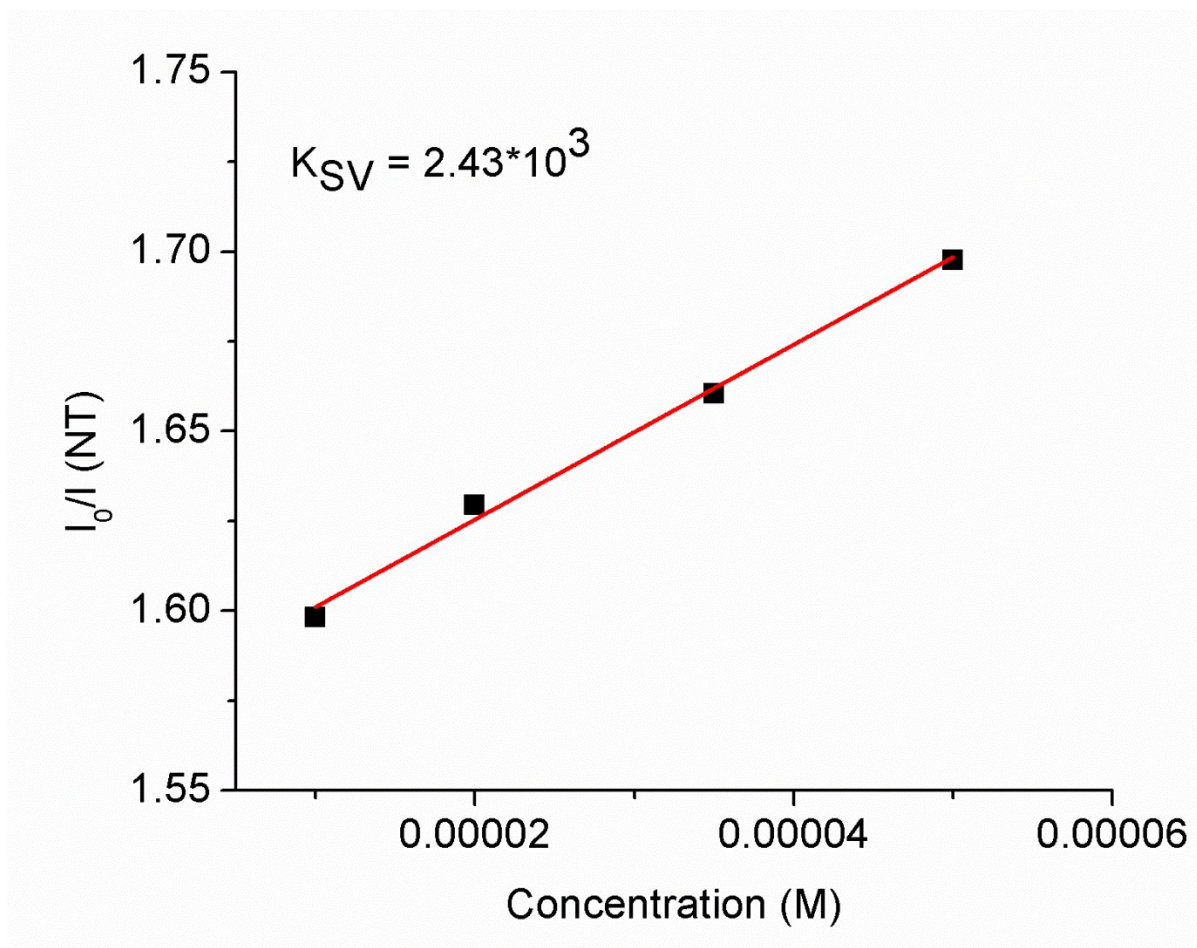


Fig. S21: Linear Stern–Volmer plots for the quenching of PCTF-8 by NT.

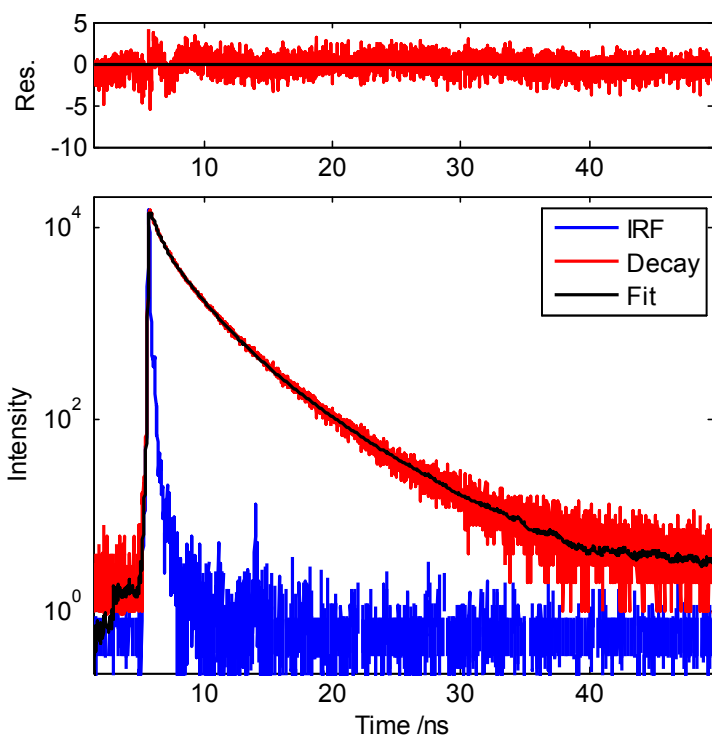


Fig. S22: TCSPC fit of pure PCTF-8 in acetonitrile.

The static quenching behaviour of PCTF-8:

In a recent paper (*J. Mater. Chem. A*, 2015, 3, 4604), the selective detection of TNP by microspheres from poly(cyclotriphosphazene-co-curcumin) is reported. The authors of this paper propose a mechanism to explain the selective detection of TNP, based on the combination of excited-state energy transfer and the formation of a ground-state non-fluorescent complex via proton transfer from the acidic phenol to the basic nitrogen sites in the cyclotriphosphazene ring (Fig. S23, reproduced from *J. Mater. Chem. A*, 2015, 3, 4604 with permission).

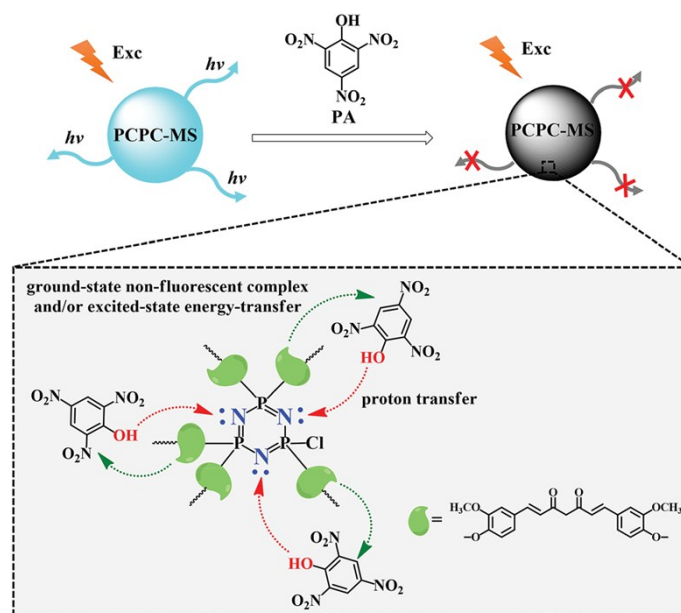


Fig. S23: Proposed mechanism to explain selective detection of TNP by cyclotriphosphazene-based framework (Fig. S23 reproduced from *J. Mater. Chem. A*, 2015, 3, 4604 with permission).

As seen in Fig. S10 it can be evidenced that none of the analytes have overlapping absorption bands with the emission of the fluorophore, thus ruling out any possible excited-state energy transfer to the phenols. At the same time, a similar chemical feature of the building unit of PCTF-8 presented in our work are the triazine rings. In this sense, the basic nitrogen atoms in triazine can be involved in a ground-state proton transfer reaction as the proton acceptors, especially considering the relative acidity of 2,4,6-trinitrophenol vs. other nitroaromatic compounds, which could be a possible explanation for the increased quenching observed by this analyte. Further studies are needed to ascertain the nature of the quenching mechanism.

12. References

- 1 F. Rouquerol, J. Rouquerol and K. Sing, Adsorption by powders and porous solids, F. Rouquerol, J. Rouquerol and K. Sing, ed. Academic Press, San Diego, 1999, vol. 11.