Electronic Supporting Information

“Turn-on” fluorescence sensing of volatile organic compounds using a 4-amino-1,8-naphthalimide-Tröger’s base functionalized triazine organic polymer

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Experimental section

Materials and methods. All reagents, solvents, and starting materials were purchased from Sigma-Aldrich, Merck, or Fisher Scientific were of reagent grade and were used as received. Solvents used were HPLC grade unless otherwise stated. 4-Nitro-1,8-naphthalic anhydride, trifluoroacetic acid, 4-aminobenzonitrile, *m*-cresol, and isoquinoline were purchased from Sigma-Aldrich and used as received. Deuterated solvent $(CD_3)_2SO$ used for NMR analyses of monomers were purchased from Sigma-Aldrich or Apollo Scientific. The monomers 9,18-methano-1,8-naphthalic anhydride-[*b,f*][1,5]diazocine (**TBNap**) and 1,3,5-tris-(4-aminophenyl)triazine (**TAPT**) were synthesised following the procedure reported in the literature.[1-2]

The elemental analysis for C, H and N were performed on an Exeter analytical CE-450 elemental analyzer at University College Dublin (UCD).

FT-IR spectra were recorded in the range 4000-550 cm^{-1} on a Perkin-Elmer spectrometer equipped with a universal ATR sampling accessory.

The ^{13}C NMR spectra of precursors were acquired in DMSO-d_6 at 100.55 MHz at 25°C. The solid-state CP/MAS ^{13}C-NMR spectrum of **TB-TZ-COP** was acquired at 201.1 MHz using a 3.2 mm double-resonance MAS probe. The spectrum was acquired under magic angle spinning (MAS) at 20 kHz, if not otherwise specified, using ramped-amplitude cross-polarization, and SPINAL64 decoupling with a ^{1}H-decoupling field of about 80 kHz. A 3 ms contact time and a pulse delay of 5 s were used. Chemical shifts were calibrated setting the ^{13}C low field signal of adamantane to 38.48 ppm.

Thermogravimetric analysis (TGA) was performed on an analyzer equipped with an ultra-microbalance with a sensitivity of 0.1 μg. The temperature range was from 25°C to 800°C with a scan rate of 10°C/min under N_2 purge.

X-ray powder diffraction pattern was collected using a Bruker D2 Phaser instrument with Cu Kα radiation ($\lambda = 1.5418$ Å). The sample was ground into a fine powder and mounted on silicon sample holders, and data was collected in the 2θ range 5−55° at room temperature.

Morphology of **TB-TZ-COP** was imaged by field emission scanning electron microscopy (FE-SEM) with an SE2 on the in-lens detector. The sample was prepared by drop-casting the aqueous suspension (1 mg in 100 μL of Millipore water) of as-synthesised **TB-TZ-COP** on silica wafers, then coated with Au and dried under vacuum before the imaging.

UV-visible absorption spectra were recorded in 1 cm quartz cuvettes (Hellma) on a Varian Cary 50 spectrometer. Baseline correction was applied for all spectra.

Emission spectra were recorded on a Varian Cary Eclipse Fluorimeter. The temperature was kept constant throughout the measurements at 298 K by using a thermostatic unit block.

Synthesis of TB-TZ-COP:

A Pyrex tube was charged with **TBNap** (180 mg, 0.39 mmol, 3 equiv.) and **TAPT** (91.9 mg, 0.26 mmol, 2 equiv.) in a solution of *m*-cresol (5 mL)/toluene (5 mL)/isoquinoline (0.5 mL). The mixture was then stirred vigorously under argon flow for 15 minutes. The tube was then sealed and heated in the following schedule at 60°C for 6 h, 100°C for 12 h, 150°C for 22 h, and 180°C for 32 h. A bright yellow precipitate was formed, isolated by filtration, and washed successively with THF, CH_3OH, DCM and diethyl ether until the filtrate ran clear. Afterward, the yellow solid was immersed in fresh THF for 24 hours, during which time the solvent was replaced five times with fresh THF. The solid product was finally dried under high vacuum to isolate the desired polyimide **TB-TZ-COP** (115 mg, 64 % based on the monomer **TBNap**) as a bright yellow powder. Anal. Calcd (%) for $C_{123}H_{66}N_{18}O_{12}$: C, 74.31; H, 3.35; N, 12.68; found: C, 73.20; H, 2.99; N, 11.56. CP-MAS ^{13}C-NMR: δc 171.2, 163.9, 150.4, 136.4, 129.3, 118.6, 114.6, 67.5, 57.3. FTIR$_{\upsilon max}$ (ATR, cm^{-1}) 3363, 1772, 1709, 1667, 1594, 1507, 1459, 1437, 1405, 1365, 1352, 1302, 1239, 1176, 1084, 956, 927, 860, 818, 783, 695, 663, 638, 585.

Gas uptake measurements

All the gas (N_2, H_2, and CO_2) adsorption measurements were carried out using a Quantachrome Autosorb IQ automated gas sorption analyzer. The as-synthesized **TB-TZ-COP** was immersed in diethyl ether for 3 days. During the immersion, the diethyl ether was refreshed 5 times with fresh diethyl ether and the resulting solvent exchanged polymer was transferred to a quartz cell. The sample was evacuated under vacuum at 100°C for 72 hours. BOC gases ultrahigh-purity grade N_2, H_2, and CO_2 were used in all adsorption measurements. The isotherms at 278 K were measured in a water-ice-acetone bath. The surface area of **TB-TZ-COP** was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated using the NL-DFT model.

Preparation of the stock solution of TB-TZ-CP: 10 mg of **TB-TZ-CP**, after drying under high vacuum for 6 hours, was placed in a 100-mL standard measuring flask and 100 mL of respective solvents were added to it. Then, the mixture was sonicated for 30 minutes and aged for 48 h to get a uniform suspension for the spectroscopic studies.

Solvent-dependent emission studies: 100 μL of the suspension of **TB-TZ-COP** in different solvents was taken in a quartz cuvette and 1800 μL of respective solvent was added to it and then the emission intensity was monitored. For all the emission measurements, the excitation wavelength was kept at λ_{ex} = 360 nm and the emission spectra were recorded in the range of λ_{em} = 370-700 nm.

Reversible test: After each measurement, **TB-TZ-COP** was isolated by centrifugation (4000 rpm for 10 minutes) and the precipitate was washed several times with ethanol and diethyl ether. Then, the solid was dried under high vacuum for 6 hours and reused for the next emission study cycle.

Thin film preparation and vapor phase sensing study: 200 μL of aqueous suspension (1 mg in 1 mL, sonicated for 30 minutes to get a uniform suspension) of **TB-TZ-COP** was added over a clean surface of quartz plate and then the plate was dried at natural evaporation in the air to get the thin film. The vapor phase sensing study was performed by inserting the freshly made thin film of **TB-TZ-COP** into a 3-mL quartz cuvette containing 200 μL of 1,4-dioxane. After a constant interval (after every 2 minutes), the emission intensity of the film was measured. For all the fluorescence measurements, the excitation wavelength was kept at λ_{ex} = 360 nm and the emission spectra were recorded in the range of λ_{em} = 370-750 nm. The percentage of emission enhancement efficiency was calculated from the following equation:

$$\text{Enhancement efficiency (\%)} = (I-I_0)/I \times 100$$

Where I_0 is the initial emission intensity of the thin film and I is the intensity after a period of exposure time.

References:

1. S. Shanmugaraju, D. McAdams, F. Pancotti, C. S. Hawes, E. B. Veale, J. A. Kitchen, and T. Gunnlaugsson, *Org. Biomol. Chem.* , 2017, **15**, 7321-7329.
2. R. Gomes and A. Bhaumik, *RSC Adv*., 2016, **6**, 28047-28054.

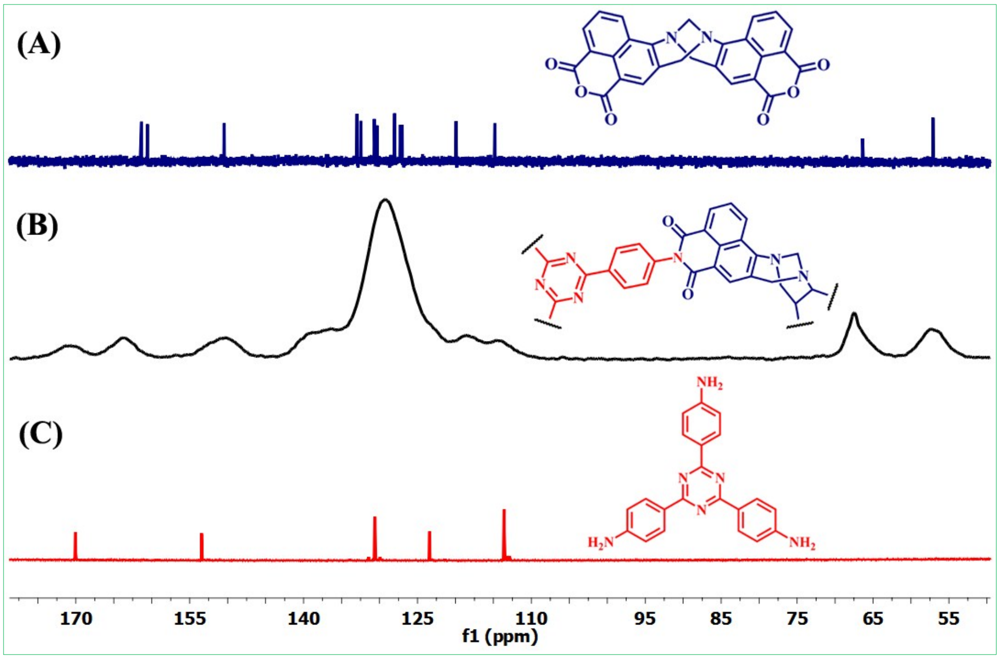

Fig. S1. ^{13}C-NMR spectra (in DMSO-d$_6$, 400 MHz) of monomers (A) **TBNap**, (C) **TAPT**. (B) Solid-state CP-MAS ^{13}C-NMR (800 MHz) spectrum of polymer **TB-TZ-COP**.

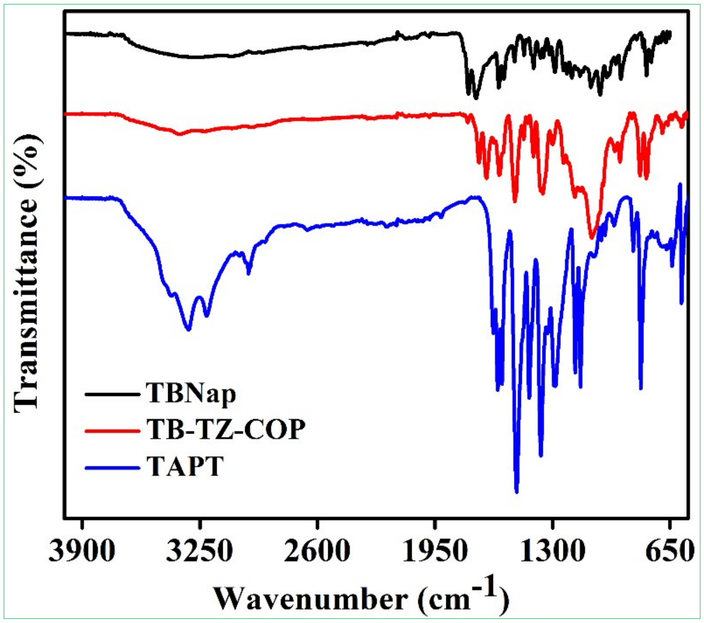

Fig. S2. FTIR spectra of **TBNap** (black), **TAPT** (blue) and polymer **TB-TZ-COP** (red).

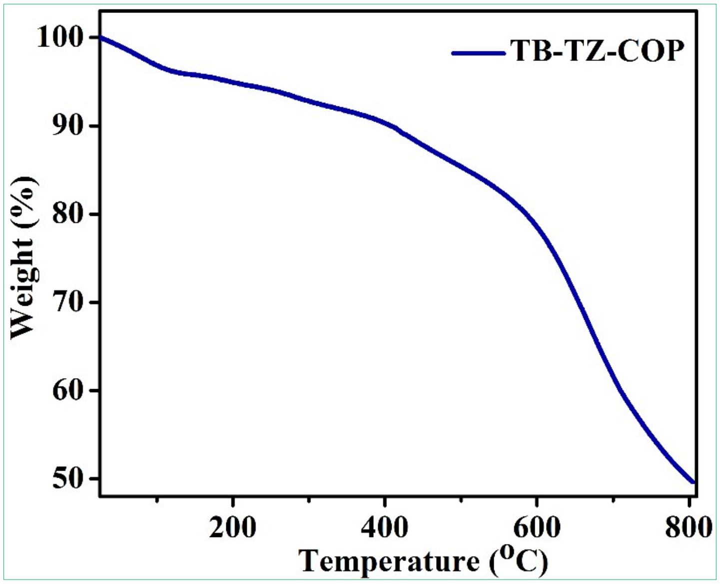

Fig. S3. Thermogravimetric analysis (TGA) of as-synthesized **TB-TZ-COP** measured under N_2.

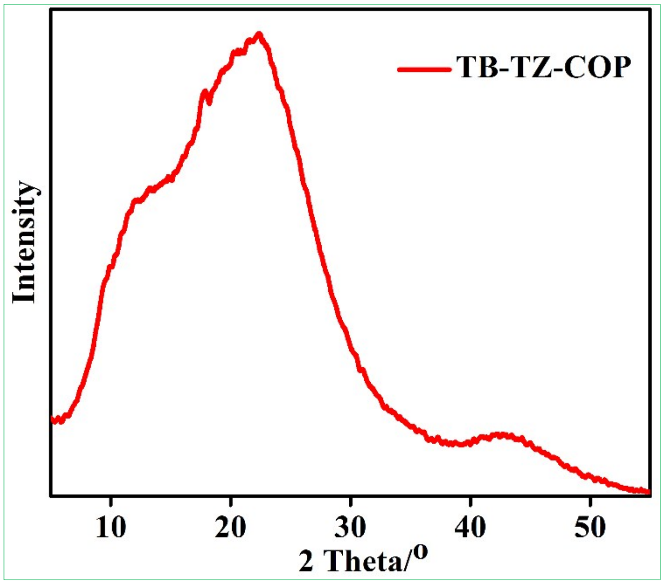

Fig. S4. X-ray powder diffraction pattern of as-synthesized **TB-TZ-COP**.

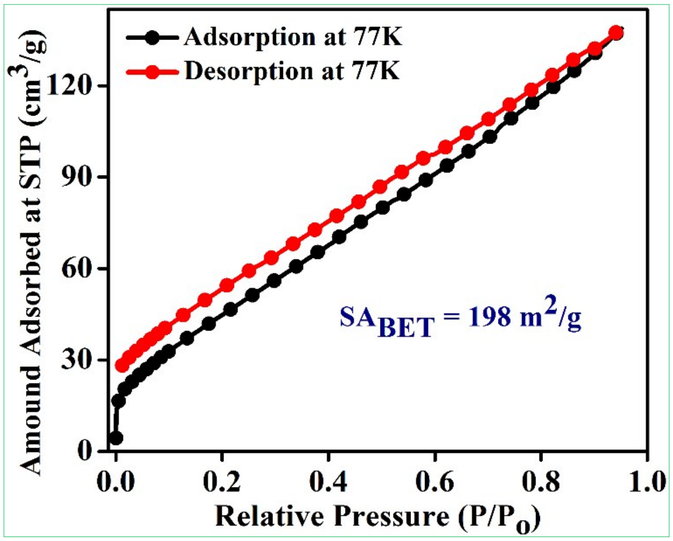

Fig. S5. The N_2 adsorption-desorption isotherm of **TB-TZ-COP** measured at 77 K.

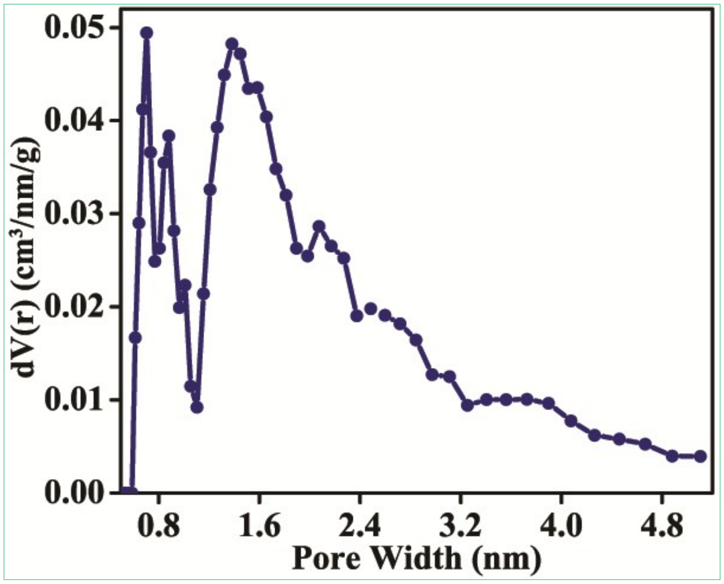

Fig. S6. The DFT pore size distribution of **TB-TZ-COP**.

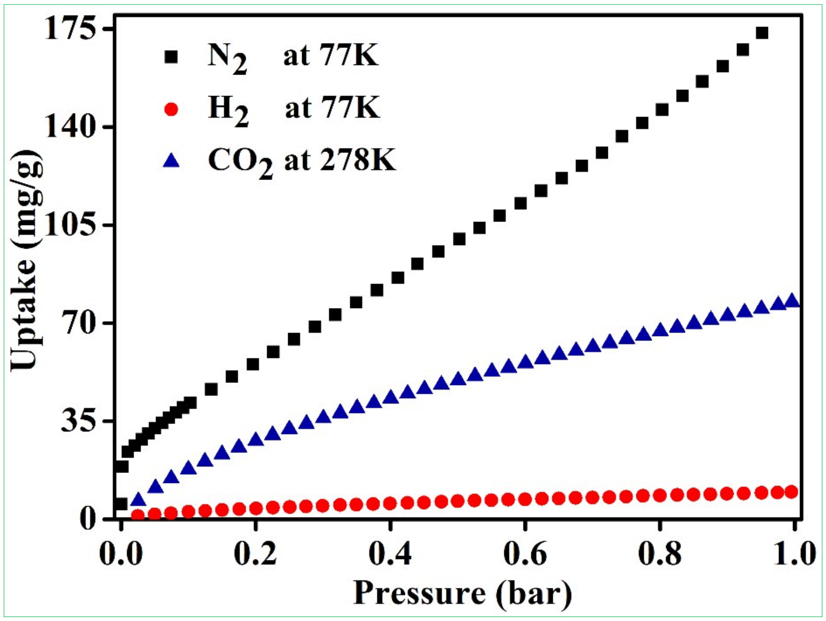

Fig. S7. The gas uptake capacitates of **TB-TZ-COP** for CO_2, $N_{2,}$ and H_2.

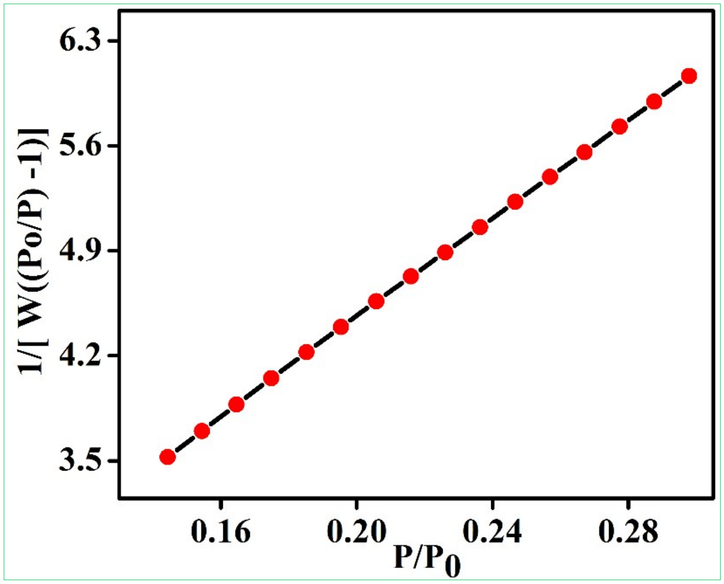

Fig. S8. BET linear plot of **TB-TZ-COP** calculated from N_2 adsorption isotherm at 77 K.

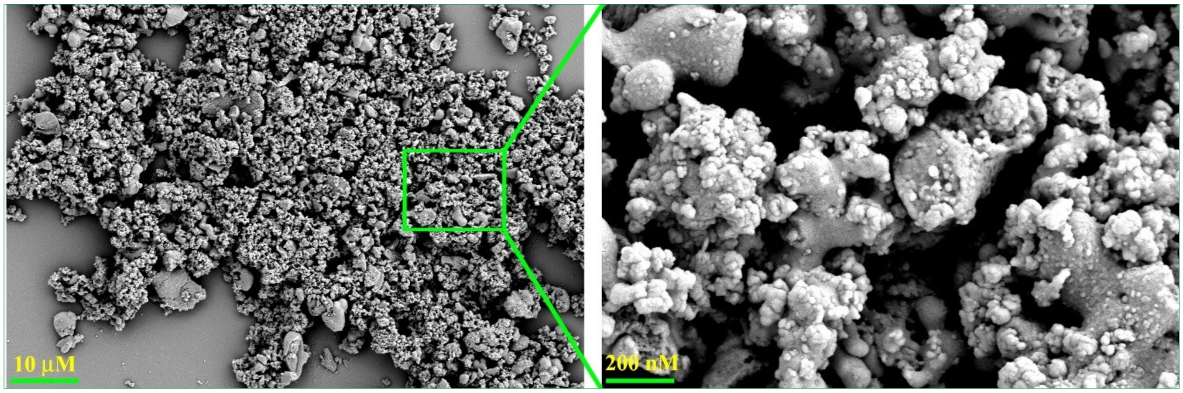

Fig. S9. FESEM images of **TB-TZ-COP** at different magnification.

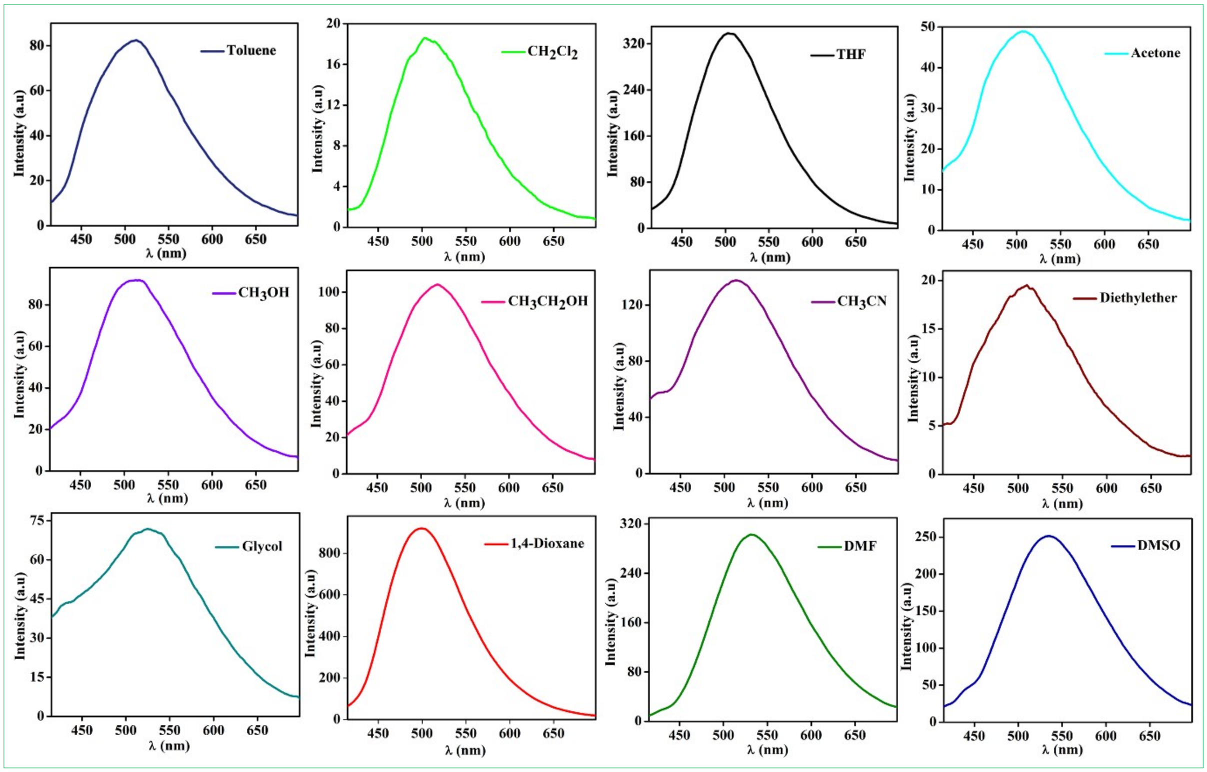

Fig. S10. Emission spectra of **TB-TZ-COP** dispersed in different organic solvents.

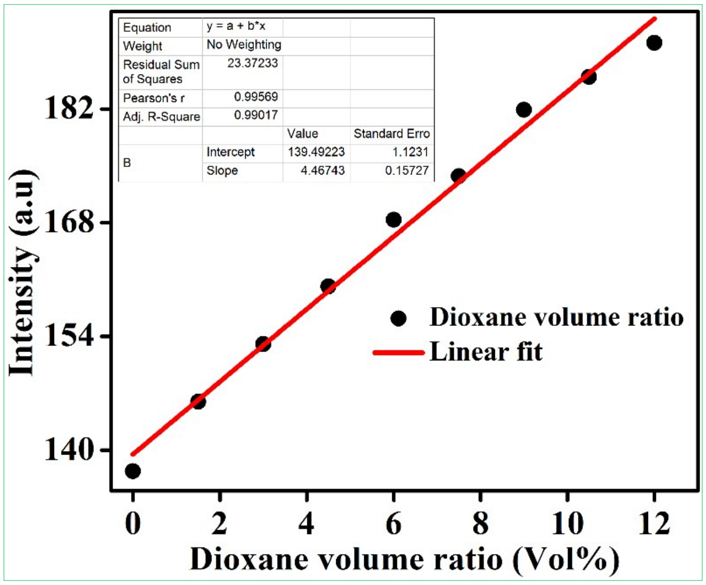

Fig. S11. Plot maximum emission intensity (monitored at λ = 517 nm) of **TB-TZ-COP** recorded in a different percentage volume ratio of 1,4-dioxane in glycol (λ_{ex} = 360 nm).

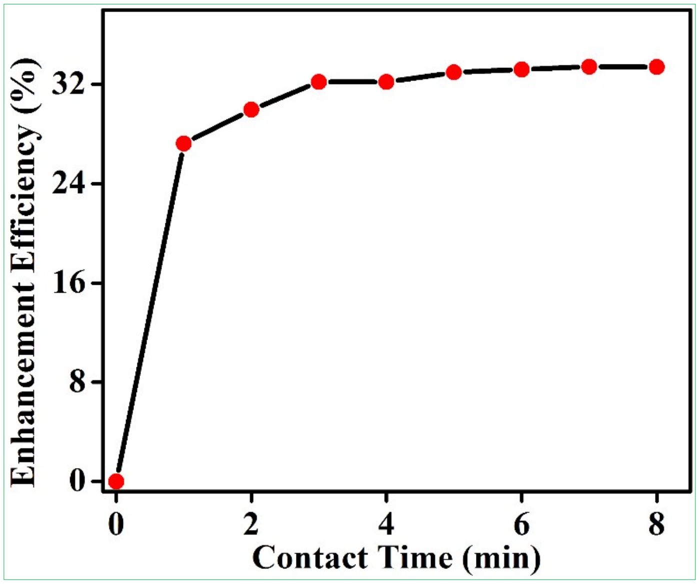

Fig. S12. A plot of enhancement efficiency as a function of contact time (0→8 minutes).

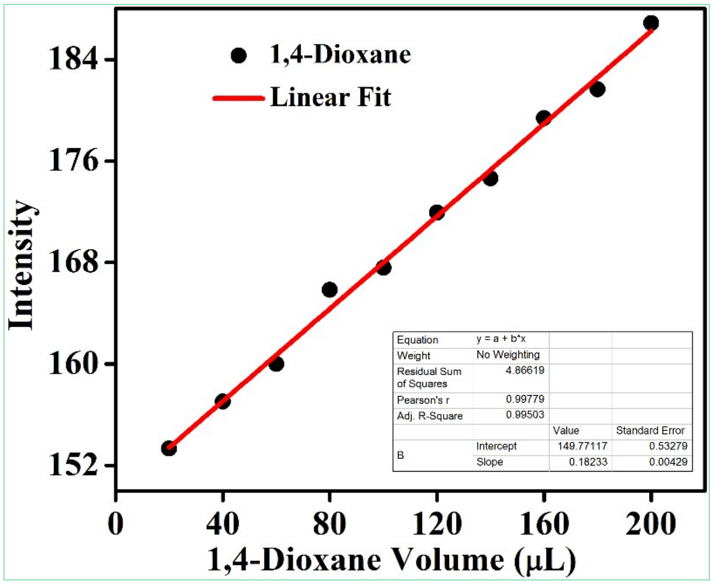

Fig. S13. Change in emission intensity of **TB-TZ-COP** at a different volume fraction of 1,4-dioxane in glycol.

The limit of detection for dioxane in glycol was calculated using the following equation:

$$\textbf{Limit of detection} = 3\sigma/K = 22.2 \times 10^{-6}\ \text{L} = 22.2\ \text{ppm}$$

Where σ (1.35) is the standard deviation of the initial emission intensity of **TB-TZ-COP** in glycol before the addition of dioxane and *K* is the slope of the linear curve.

Table 1: The HOMO and LUMO energy of **TB-TZ-COP** and various **VOCs** in comparison to number fold emission enhancement.

	HOMO (eV)	LUMO (eV)	Emission Enhancement (Number fold)
1,4-Dioxane	-8.34	2.31	43.7
Ether	-8.83	2.21	0.9
MeOH	-9.41	2.03	4.4
EtOH	-9.32	2.00	4.9
Glycol	-9.40	1.85	3.4
DMF	-8.26	1.82	14.4
THF	-8.44	1.80	16.0
CH_3CN	-10.82	1.75	6.5
DMSO	-7.91	1.72	11.9
Acetone	-8.73	0.92	2.3
Toluene	-8.00	0.78	3.9
DCM	-10.24	0.74	0.9
TB-TZ-COP	-7.63	-1.84	-