Supplementary Information

Trace-doped metal-organic gels with remarkably enhanced luminescence

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Experimental section

Materials and methods. All regents were analytical grade and used as received without further purification. Scanning electron microscopy (SEM) images were collected on a Hitachi SU8010 Ultra-high Resolution FE-SEM. Before measurement, the gel sample was dispersed in ethanol with the aid of sonication, put on silicon plate, and sputter coated with gold. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) investigation were carried out on a FEI Tecnai G2 Spirit 120 kV transmission electron microscope with an energy dispersive X-ray spectrometer. The gel sample was dispersed in ethanol with the aid of sonication, and mounted on a carbon coated copper grid. X-ray diffraction investigations were carried out on a Rigaku Smart Lab diffractometer equipped with Cu Kα radiation (λ =

1.54056 Å). Thermogravimetric (TG) analyses were measured on a NETZSCHSTA 449 F3 Jupiter instrument in a flowing nitrogen atmosphere with a 10 K min^{-1}. N_2 adsorption measurements were performed using a Quantachrome Autosorb-IQ_2 analyzer. Before sorption measurements, the sample was degassed at 80°C for 16 h under high vacuum. Absorption measurements were carried out on a UV-2450 spectrophotometer. Photoluminescence measurements and time-resolved emission decay behaviours were recorded on an Edinburgh Instruments FLS980 combined lifetime and steady state fluorometer. Absolute photoluminescence quantum yields were determined on a Hamamatsu C9920-03G absolute PL quantum yield measurement system.

ZrBDC gels. Synthetic procedure represented by **ZrBDC-1:1-0.15** system. H_2BDC (99.6 mg, 0.6 mmol) was dissolved in DMF (2.0 mL) and $ZrCl_4$ (140.0 mg, 0.6 mmol) was dissolved in EtOH (2.0 mL), and the two solutions were rapidly mixed together. The resulting homogeneous solution was then allowed to stand at 353 K for gelation in a closed container. A gel was obtained after 1.5 h. After gelation, the wet gel was aged for 1 d at 353 K.

Subsequently, the wet gel was subjected to solvent exchange with DMF for 12 h for 3 times, then the wet gel was subjected to solvent exchange with EtOH for 12 h for 3 times. The as-prepared gel was placed into a high-pressure Soxhlet extractor (0.75 L). The solvent in the wet gel was extracted with liquid CO_2 (265–270 g) for 24 h, and

the extraction temperature was maintained at 308 K. After depressurizing the stainless-steel autoclave slowly at room temperature for 2 h a white solid was obtained (175 mg).

ZrBDC-TCPE*x* gels. Synthetic procedure represented by **ZrBDC-TCPE0.01%** system. H_2BDC (99.6 mg, 0.6 mmol) was dissolved in a solution of H_2TCPE in DMF (2.0 mL, 3.0×10^{-5} mol L^{-1}), $ZrCl_4$ (140.0 mg, 0.6 mmol) was dissolved in EtOH (2.0 mL), and the two solutions were rapidly mixed together. The resulting homogeneous solution was then allowed to stand at 353 K for gelation in a closed container. A gel was obtained after 4 h. After gelation, the wet gel was aged for 1 d at 353 K. After drying, a white solid was obtained (176 mg).

ZrTCPE gel. A solution of H_4TCPE (38.1 mg, 0.075 mmol) in DMF (0.5 mL), and a solution of $ZrCl_4$ (35.0 mg, 0.15 mmol) in EtOH (0.5 mL) was mixed and the resulting homogeneous solution was allowed to stand at 353 K for gelation in a closed container. A camel gel was obtained after 5 h.

Fluorescence experiments. ZrBDC-TCPE0.01% wet gel was dispersed in 100 mL of H_2O by ultrasonic to obtain a dispersion (10 g L^{-1}, mass was determined after the gel was dried under vacuum). The fluorescence response was monitored upon excitation after incremental addition of analyte solutions (0.1 mM). ***Caution!*** *PA are highly explosive and should be handled carefully and in small amounts.* Analyte (0-400 μL, 0.1 mM stock solution) was added to the dispersion of **ZrBDC-TCPE0.01%**

and fluorescent intensity was recorded. By plotting fluorescence intensity with increasing concentration of analyte, slope of graph (m) was calculated. The standard deviation (σ) was calculated from eleven blank measurements of **ZrBDC-TCPE0.01%** gel dispersion. The detection limit was calculated based on the fluorescence titration and calculated with the equation LOD = $3\sigma/m$.

Table S1 Gelation test of $ZrCl_4$ and H_2BDC (T = 80 °C, solvent EtOH:DMF =1:1).

sample	L	Zr:L	c(L)/mol L^{-1}	Result	Time/h
ZrBDC-1:1-0.15	H_2BDC	1:1	0.15	white opaque gel	1.5
ZrBDC-3:2-0.15	H_2BDC	3:2	0.15	white opaque gel	1.5
ZrBDC-2:1-0.15	H_2BDC	2:1	0.15	white opaque gel	1
ZrBDC-1:2-0.15	H_2BDC	1:2	0.15	white precipitate	
ZrBDC-2:3-0.15	H_2BDC	2:3	0.15	white precipitate	
ZrBDC-1:1-0.2	H_2BDC	1:1	0.2	white opaque gel	1.5

Table S2 Porosity properties of **ZrBDC-1:1-0.15** and **ZrBDC-TCPE***x* (x = 0.01, 0.1, 1, 10%).

Sample	S_{BET} [a)]/m^2 g^{-1}	V_t [b)]/cm^3 g^{-1}	V_{micro} [c)]/cm^3 g^{-1}	V_{meso} [d)]/cm^3 g^{-1}
ZrBDC-1:1-0.15	1236	0.929	0.439	0.471
ZrBDC-1:1-0.15[e)]	1140	1.107	0.669	0.471
ZrBDC-TCPE0.01%	1145	0.832	0.409	0.403
ZrBDC-TCPE0.01%[e)]	1280	0.598	0.437	0.571
ZrBDC-TCPE0.1%	1213	0.612	0.435	0.141
ZrBDC-TCPE0.1%[e)]	1219	0.806	0.431	0.335
ZrBDC-TCPE1%	1044	0.613	0.374	0.212
ZrBDC-TCPE10%	901	0.682	0.315	0.340

[a)] S_{BET} is BET specific surface area; [b)] V_t is the total specific pore volume; [c)] V_{micro} was calculated by SF method; [d)] V_{meso} was calculated by BJH method; [e)] Parallel samples.

Table S3 Fluorescence lifetime data of **ZrBDC-TCPE***x* (x = 0.01, 0.1, 1, 10%), **ZrBDC-1:1-0.15**, and **ZrTCPE** gels dispersed in water (10 g L^{-1}).

Sample [a)]	τ_1 [b)]/ns	A_1[c)]	τ_2 [b)]/ns	A_2[c)]	$<\tau>$ [d)]/ns	Φ[e)]
ZrBDC-TCPE0.01%	2.13	0.44	4.25	0.56	3.32	59%
ZrBDC-TCPE0.1%	3.87	0.96	11.45	0.04	4.17	57%
ZrBDC-TCPE1%	2.35	0.30	4.54	0.70	3.87	76%
ZrBDC-TCPE10%	0.03	0.11	4.48	0.89	3.98	80%
ZrBDC-1:1-0.15	0.52	0.70	5.83	0.30	2.11	14%
ZrTCPE	1.90	0.36	5.34	0.64	4.12	86%

[a)] The resulting signals were fitted with a double exponential decay function, which obtained the best fit with respect to both the recorded phase and intensity information; [b)] Fluorescence lifetime; [c)] Fractional contribution; [d)] Weighted mean lifetime was calculated using the equation $<\tau> = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$; [e)] Absolute fluorescence quantum yield was obtained for the wet gel with solvent exchanged with ethanol.

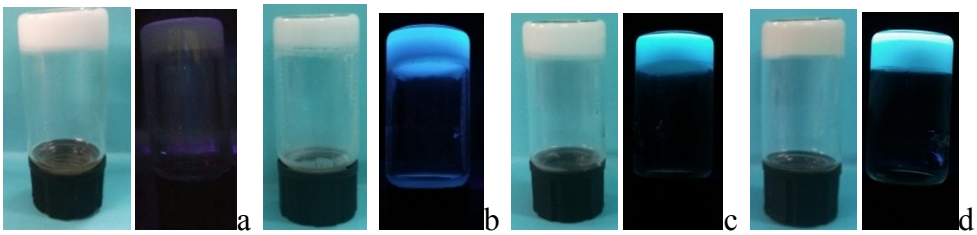


Fig. S1 Photographs of (from left to right) **ZrBDC-1:1-0.15**, **ZrBDC-TCPE0.01%**, **ZrBDC-TCPE0.1%**, **ZrBDC-TCPE1%** and **ZrBDC-TCPE10%** wet gels taken under day light and under irradiation with 365 nm UV light.

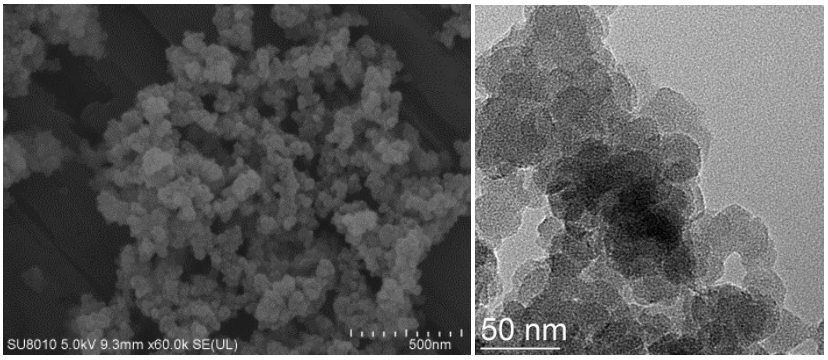


Fig. S2 SEM (left) and TEM (right) images of **ZrBDC-TCPE0.1%**.

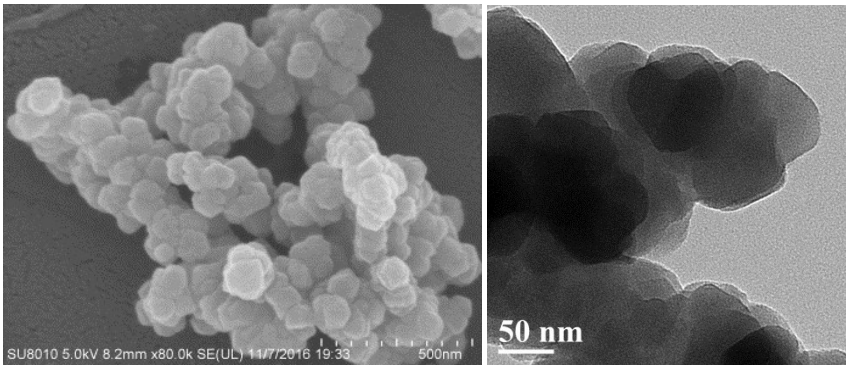


Fig. S3 SEM (left) and TEM (right) images of **ZrBDC-TCPE1%**.

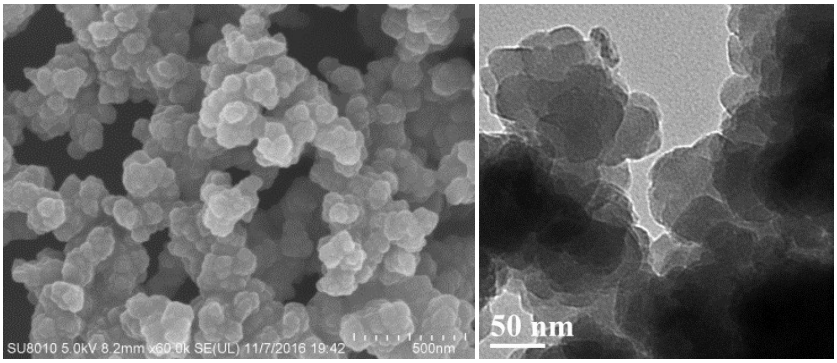


Fig. S4 SEM (left) and TEM (right) images of **ZrBDC-TCPE10%**.

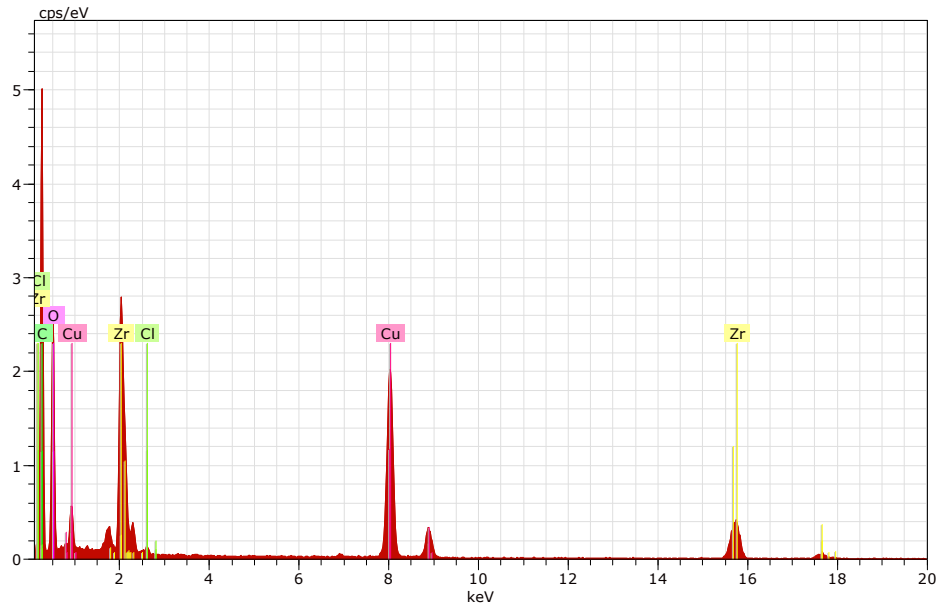


Fig. S5 EDX spectrum of **ZrBDC-1:1-0.15** (mounted on a carbon coated copper grid) showing atomic composition of Zr 6.42 and Cl 0.22%.

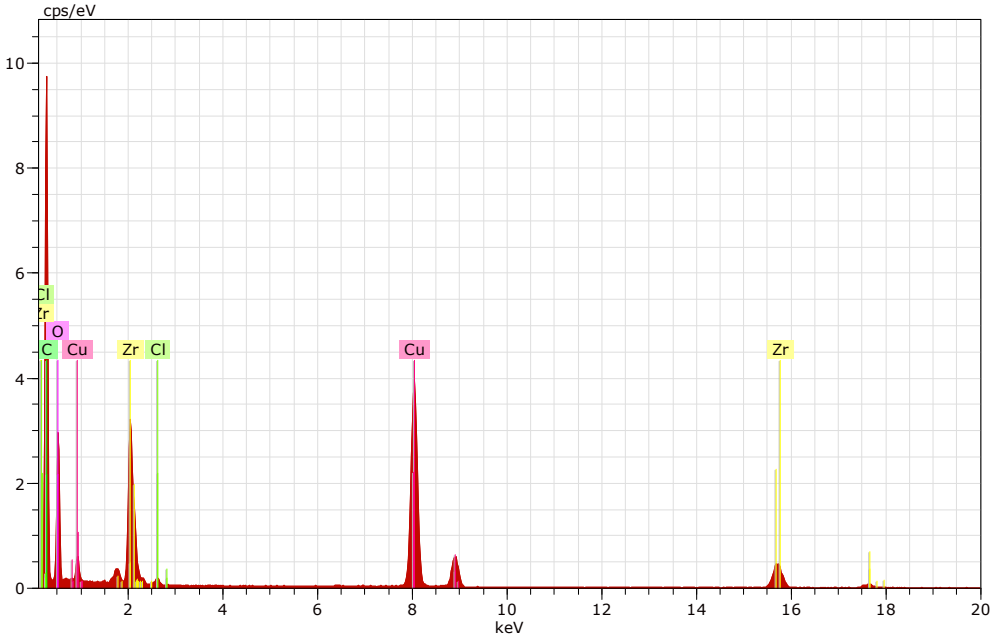


Fig. S6 EDX of **ZrBDC-TCPE0.01%** wet gel (mounted on a carbon coated copper grid) showing atomic composition of Zr 3.97 and Cl 0.20%.

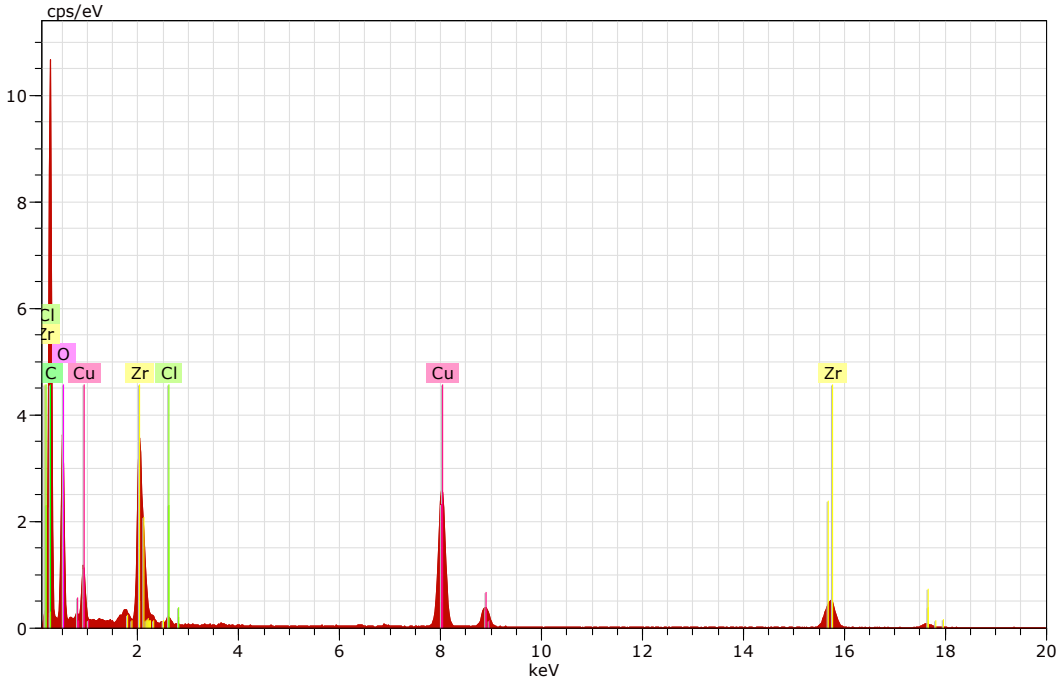


Fig. S7 EDX of **ZrBDC-TCPE0.1%** wet gel (mounted on a carbon coated copper grid) showing atomic composition of Zr 4.28 and Cl 0.18%.

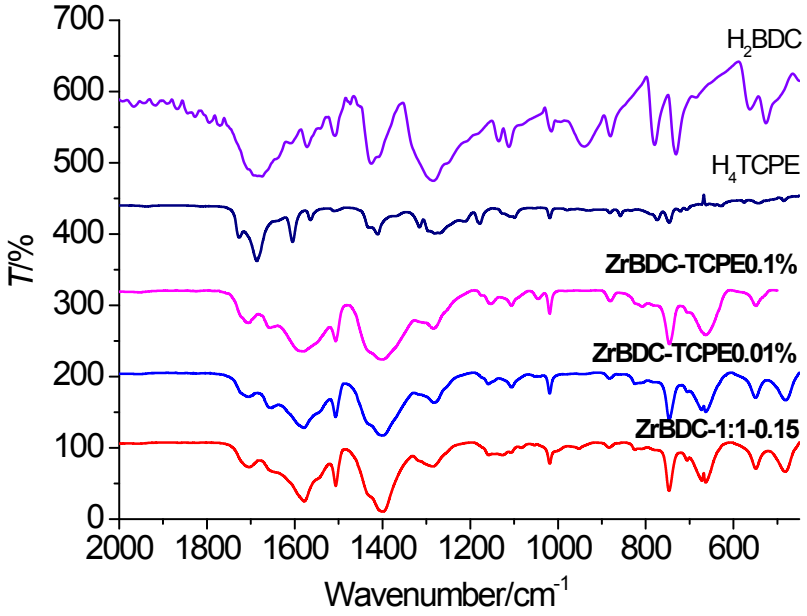


Fig. S8 FT-IR spectra of **ZrBDC-1:1-0.15**, **ZrBDC-TCPE0.01%**, **ZrBDC-TCPE0.1%**, 1,4-benzenedicarboxylic acid and tetrakis(4-carboxyphenyl)ethylene.

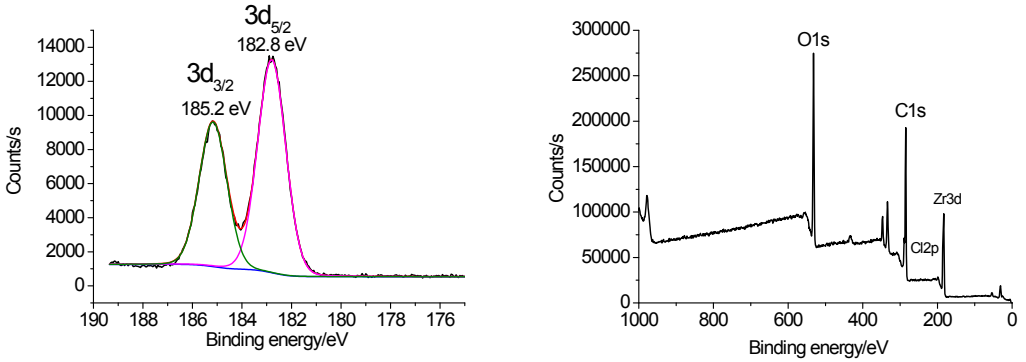


Fig. S9 Zr 3d core level spectrum (left) and XPS survey (right) of **ZrBDC-1:1-0.15**.

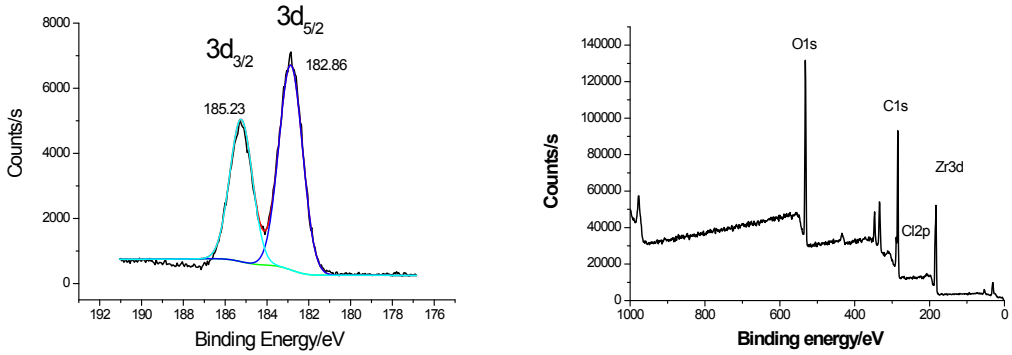


Fig. S10 Zr 3d core level spectrum (left) and XPS survey (right) of **ZrBDC-TCPE0.01%**.

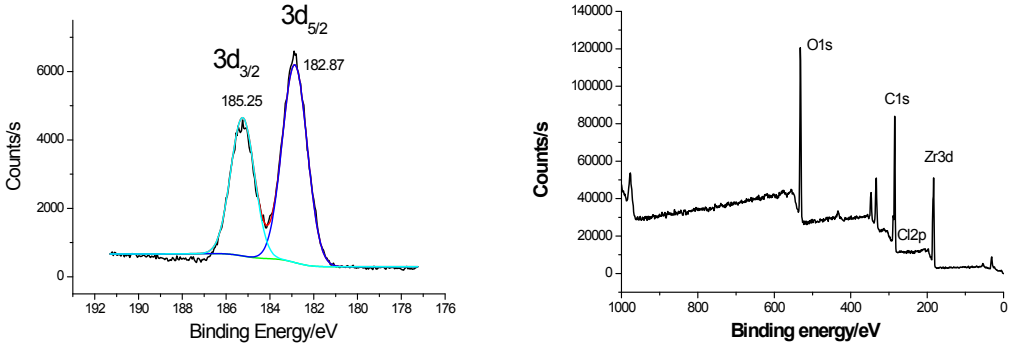


Fig. S11 Zr 3d core level spectrum (left) and XPS survey (right) of **ZrBDC-TCPE0.1%**.

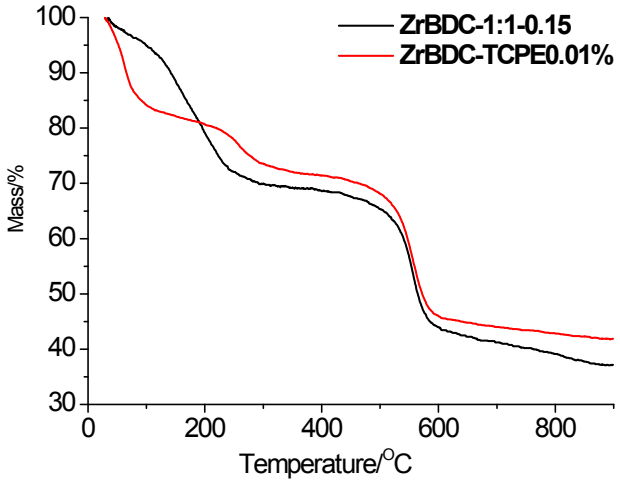


Fig. S12 TG curve of **ZrBDC-1:1-0.15** and **ZrBDC-TCPE0.01%**.

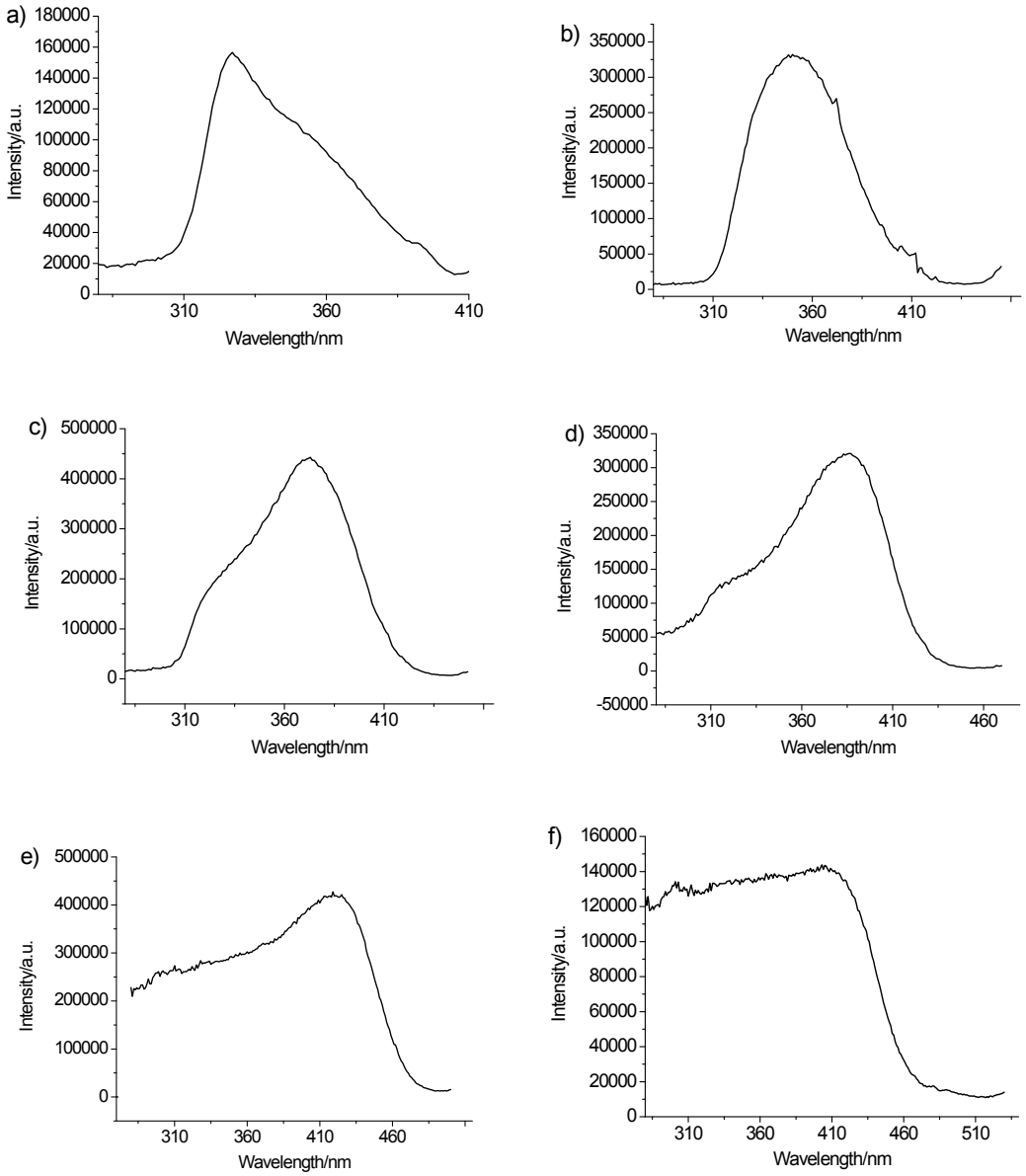
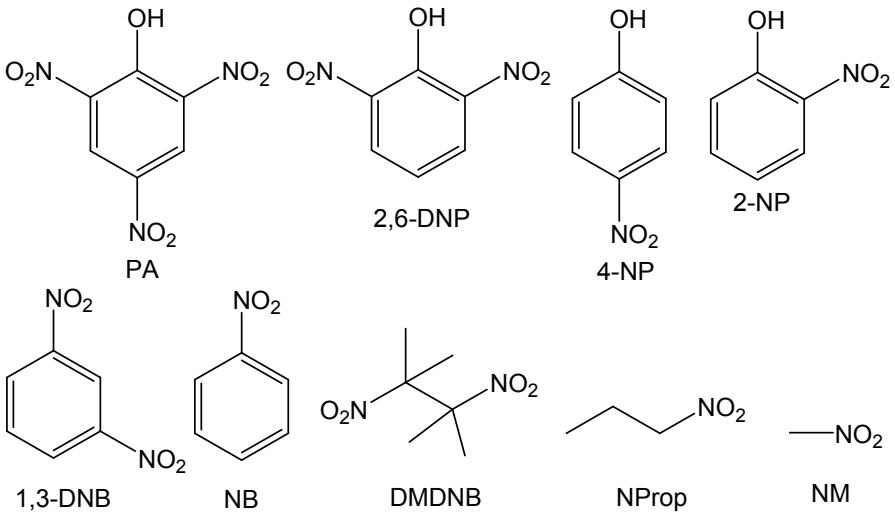


Fig. S13 Excitation spectra of a) **ZrBDC-1:1-0.15** (λ_{em} = 398 nm), b) **ZrBDC-TCPE0.01%** (λ_{em} = 461 nm), c) **ZrBDC-TCPE0.1%** (λ_{em} = 468 nm), d) **ZrBDC-TCPE1%** (λ_{em} = 477 nm), e) **ZrBDC-TCPE10%** (λ_{em} = 521 nm) and f) **ZrTCPE** (λ_{em} = 540 nm) gels dispersed in water (10 g L^{-1}).



Scheme S1. Nitroaromatic compounds tested for fluorescence quenching titrations.

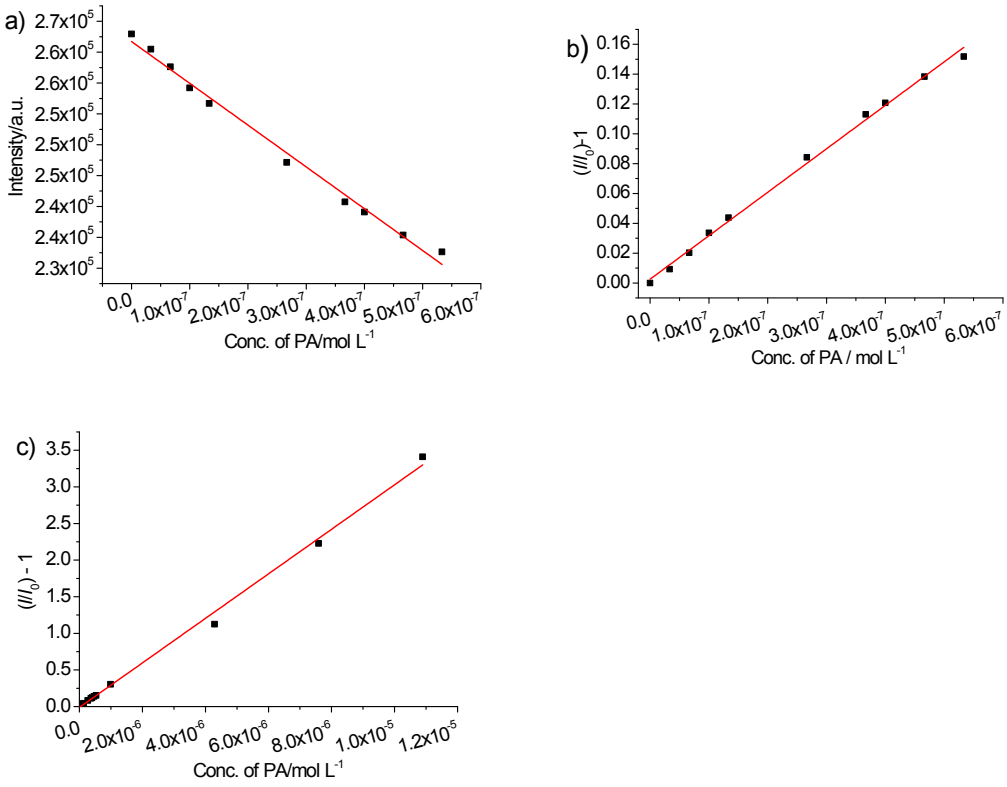


Fig. S14 Linear region of fluorescence intensity of **ZrBDC-TCPE0.01%** gel (10 g L^{-1}) dispersed in water upon addition of PA aqueous solution (λ_{ex} = 363 nm) (R^2 = 0.9912). b) Stern-Volmer traces of PA (0.1 mmol L^{-1}) in water dispersion of **ZrBDC-TCPE0.01%** (10 g L^{-1}) (R^2 = 0.9962) (0 – 0.53 µmol L^{-1}) with $K_{SV} = 2.91 \times 10^5$ L mol^{-1}. c) Stern-Volmer traces of PA (0.1 mmol L^{-1}) in water dispersion of **ZrBDC-TCPE0.01%** gel (10 g L^{-1}) (R^2 = 0.9963) (0 – 10.09 µmol L^{-1}) with $K_{SV} = 3.04 \times 10^5$ L mol^{-1}.

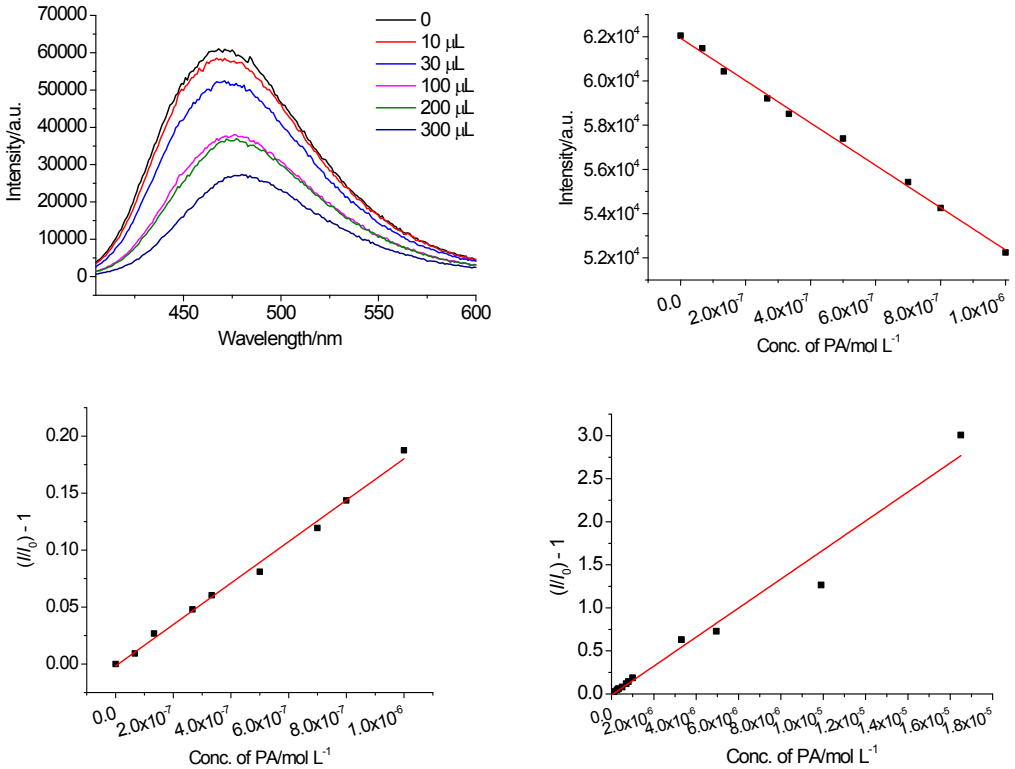


Fig. S15 a) Fluorescence spectra of **ZrBDC-TCPE0.1%** gel dispersed in water (10 g L^{-1}) upon incremental addition of an aqueous solution of PA (0.1 mmol L^{-1}) (λ_{ex} = 383 nm). b) Linear region of fluorescence intensity of **ZrBDC-TCPE0.1%** gel dispersed in water (10 g L^{-1}) upon addition of PA solution (R^2 = 0.9963). c) Stern-Volmer traces of PA (0.1 mmol L^{-1}) in water dispersion of **ZrBDC-TCPE0.1%** gel (10 g L^{-1}) (R^2 = 0.9935) (0 – 1 μmol L^{-1}) with $K_{SV} = 1.82 \times 10^5$ L mol^{-1}. d) Stern-Volmer traces of PA (0.1 mmol L^{-1}) in water suspension of **ZrBDC-TCPE0.1%** gel (10 g L^{-1}) (R^2 = 0.9710) (0 – 16.5 μmol L^{-1}) with $K_{SV} = 1.69 \times 10^5$ L mol^{-1}.

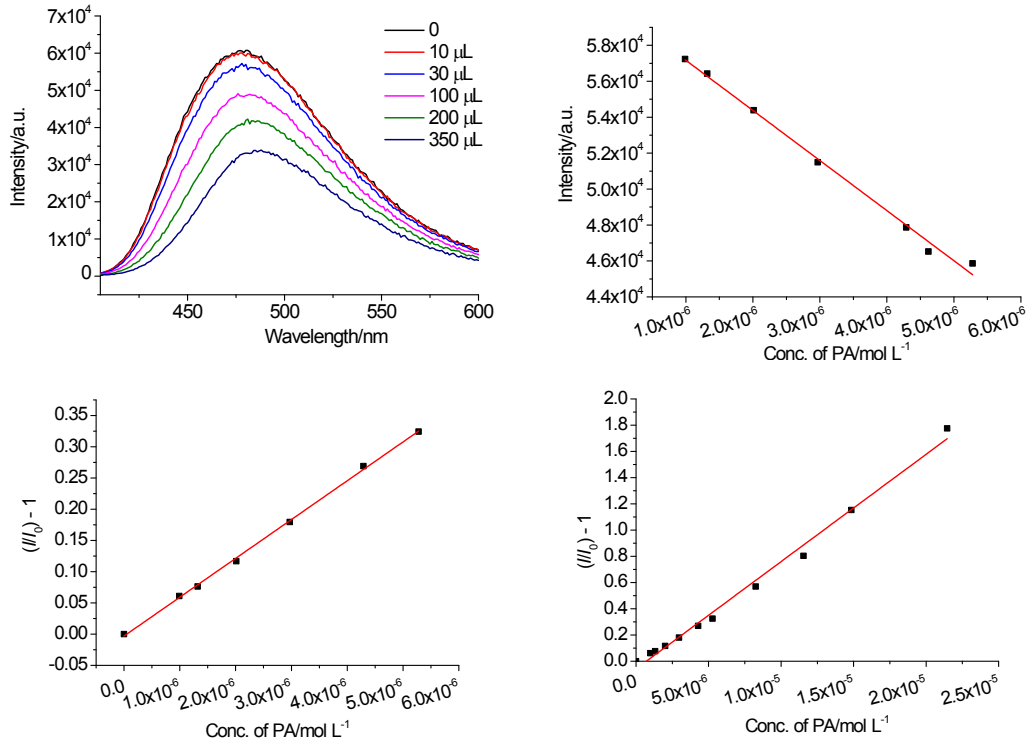


Fig. S16 a) Fluorescence spectra of **ZrBDC-TCPE1%** gel dispersed in water (10 g L^{-1}) upon incremental addition of an aqueous solution of PA (0.1 mmol L^{-1}) (λ_{ex} = 393 nm). b) Linear region of fluorescence intensity of **ZrBDC-TCPE1%** gel (10 g L^{-1}) dispersed in water upon addition of PA solution (R^2 = 0.9931). c) Stern-Volmer traces of PA (0.1 mmol L^{-1}) in water dispersion of **Zr-BDC-TCPE1%** gel (10 g L^{-1}) (R^2 = 0.9988) (0 - 5.28 μmol L^{-1}) with $K_{SV} = 6.22 \times 10^4$ L mol^{-1}. d) Stern-Volmer traces of PA (0.1 mmol L^{-1}) in water dispersion of **Zr-BDC-TCPE1%** gel (10 g L^{-1}) (R^2 = 0.9914) (0 – 21.45 μmol L^{-1}) with $K_{SV} = 8.18 \times 10^4$ L mol^{-1}.

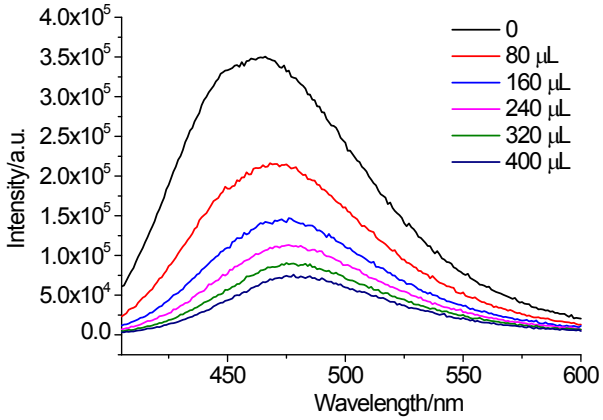


Fig. S17 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of PA aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

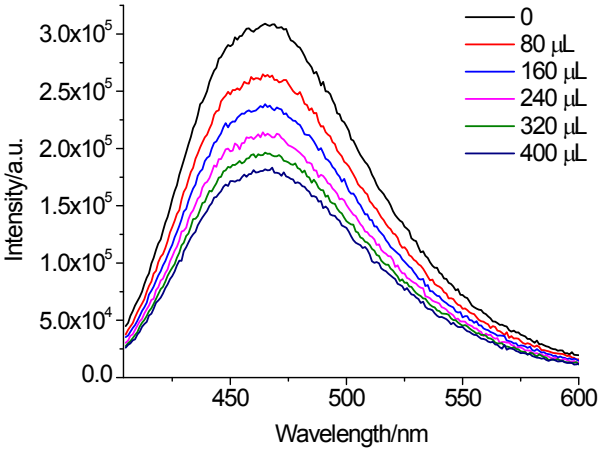


Fig. S18 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of 2,6-DNT aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

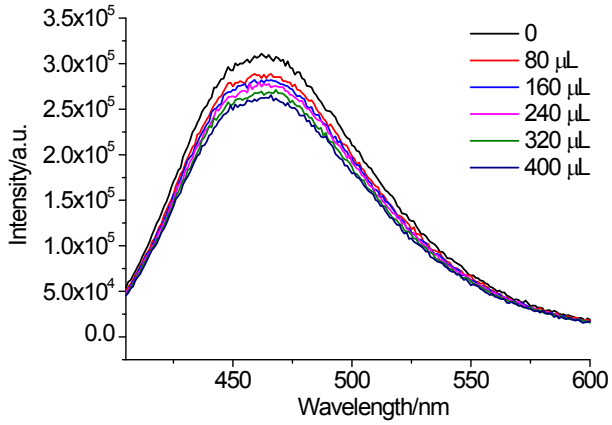


Fig. S19 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of 1,3-DNB aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

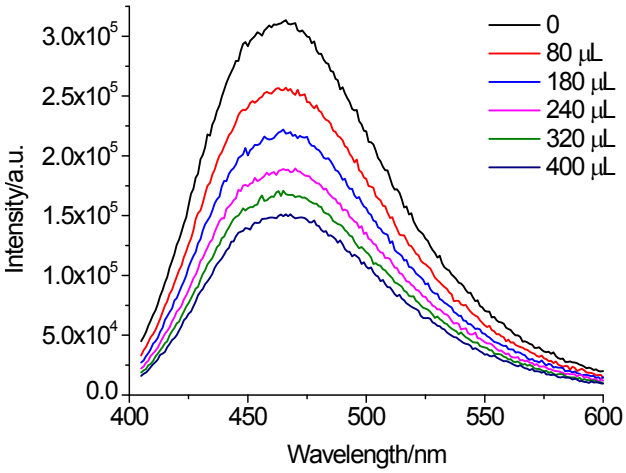


Fig. S20 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of 4-NP aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

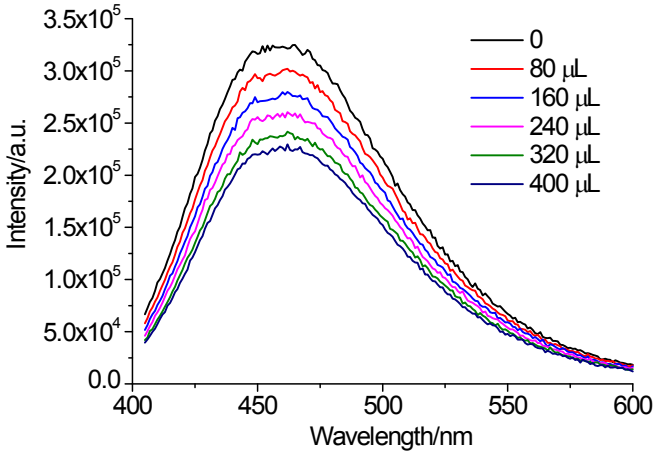


Fig. S21 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of 2-NP aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

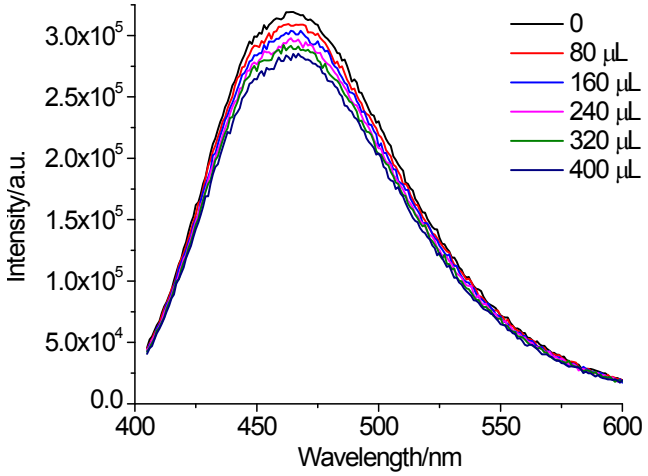


Fig. S22 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of DMDNB aqueous solution (0.1 mM) (λ_{ex} = 363 nm).

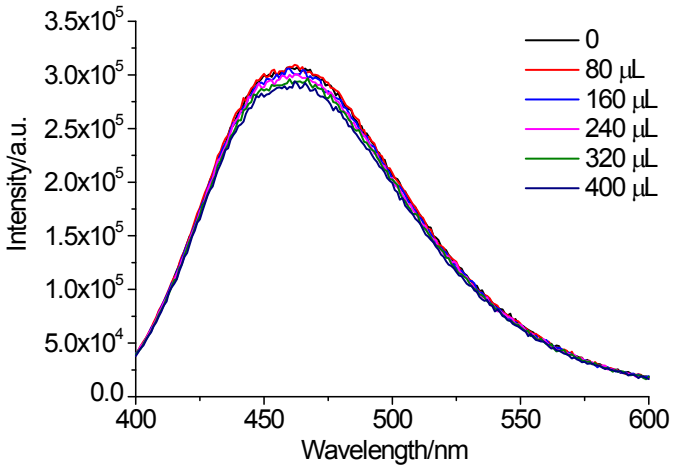


Fig. S23 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of NProp aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

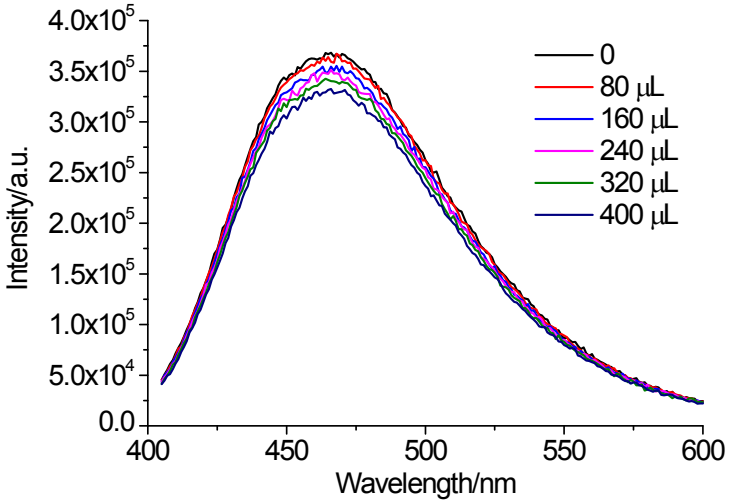


Fig. S24 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of NB aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

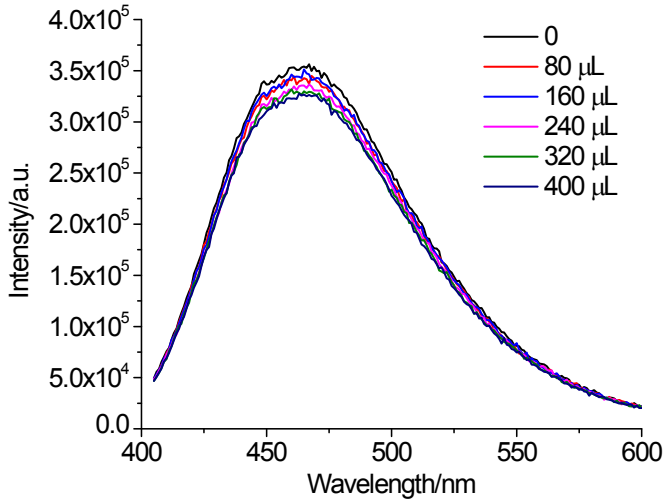


Fig. 25 Emission spectra of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}) upon incremental addition of NM aqueous solution (0.1 mmol L^{-1}) (λ_{ex} = 363 nm).

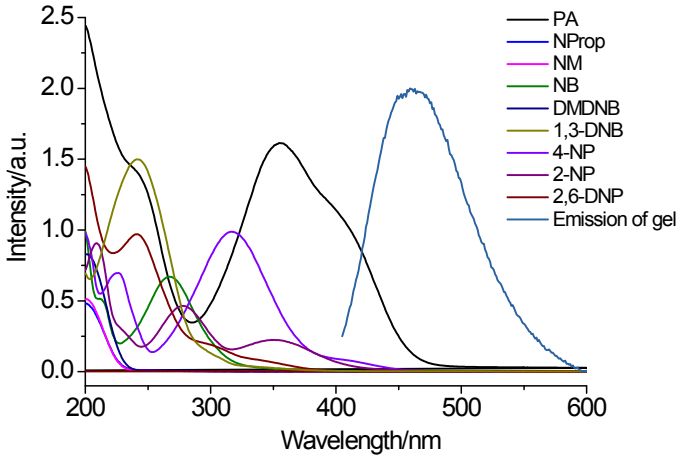


Fig. S26 Spectral overlap between the UV-vis adsorption spectra of analytes (0.1 mmol L^{-1}) in aqueous solutions and the emission spectrum of **ZrBDC-TCPE0.01%** gel dispersed in water (10 g L^{-1}).

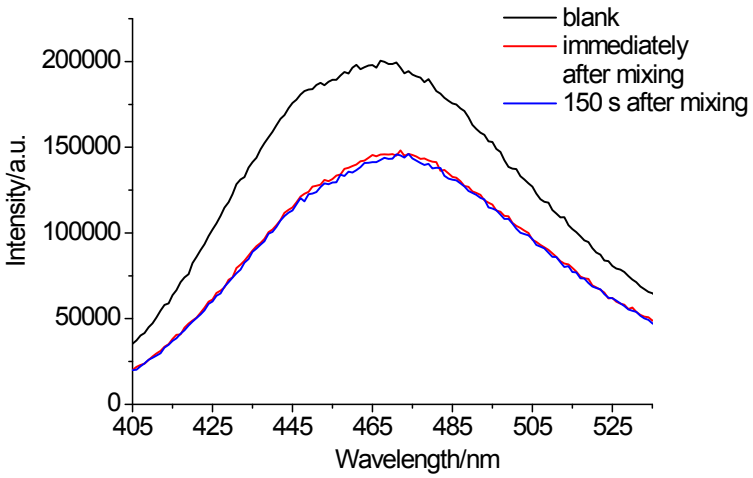


Fig. S27 The fluorescent spectra of quenching efficiency vs. exposure time, blank dispersion of **ZrBDC-TCPE0.01%**, collected immediately after mixing with 80 μL of PA aqueous solution (0.1 mmol L^{-1}), collected 150 s after mixing.