Electronic Supplementary Information

Two dyes-encapsulated triple-emitting naphthalene-based Zr-MOFs for tunable white-light emission and dual mode detection of inorganic ions

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Chemicals and Instruments.

Zirconium(IV) chloride (ZrCl$_4$, 98%) and 2,6-naphthalenedicarboxylic acid (H$_2$NDC) were purchased from Aladdin and TCI, and rhodamine 6G (Rh6G) and 9,10-bis(phenylethynyl)anthracene (BPEA, 97%) were purchased from Rhawn and Innochem. N,N-dimethylformamide (DMF) and anhydrous ethanol (C$_2$H$_6$O) were purchased from Fuyu. Acetic acid (C$_2$H$_4$O$_2$, 99.5%) was purchased from Innochem. All inorganic metal salts were purchased from Kermel. All commercial chemicals were analytical purity and used without further purification. The UV-vis absorption spectra of liquid samples were obtained by TU-1901 UV-vis spectrophotometer. Powder X-ray diffraction (PXRD) measurements were obtained from the TD-3500 diffractometer with a 2θ range from 3° to 40° at a scan speed of 5° min^{-1}. The fluorescence spectra were acquired at room temperature using the Shimadzu RF-6000 fluorescence spectrophotometer. Fluorescence lifetime were determined by the Quanta Master 8000 fluorescence spectrometer at room temperature. Thermogravimetric analysis (TGA) data were acquired from the PerkinElmer TGA-8000 thermogravimetric analyzer over a temperature range of room temperature to 800 ^{o}C. The morphology of samples was characterized by EM-30Plus benchtop scanning electron microscopy. N$_2$ sorption measurements were measured at the liquid nitrogen temperature, using a Micrometritics ASAP 2020 system.
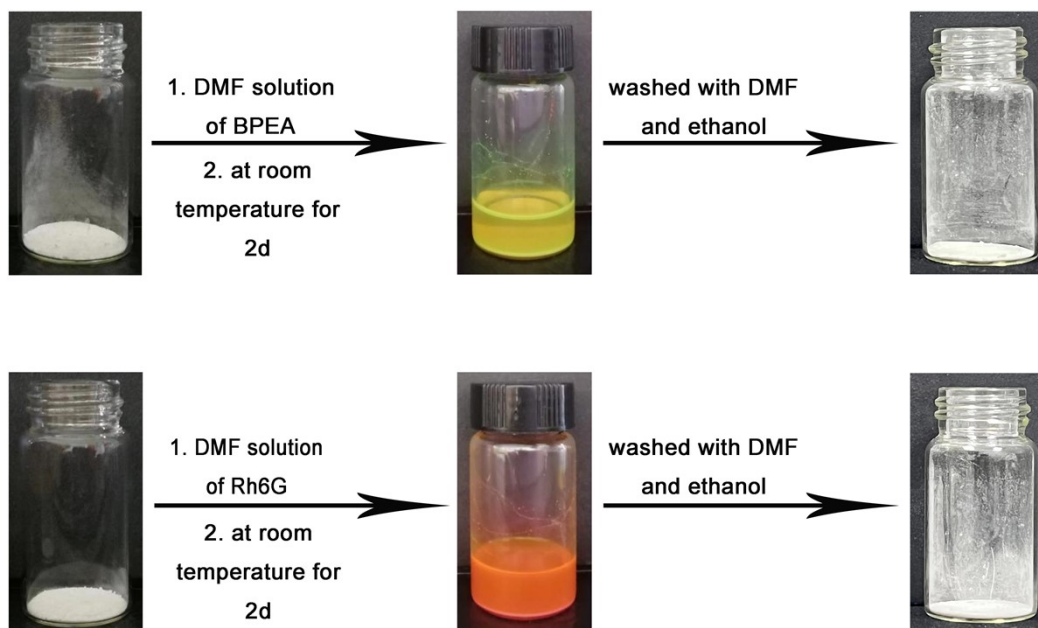
Fig. S1 The pristine DUT-52 before and after soaked in 4 mL BPEA and Rh6G solution (6.275 mg mL^{-1} and 11.9 mg mL^{-1}, DMF solvent) at room temperature, respectively.
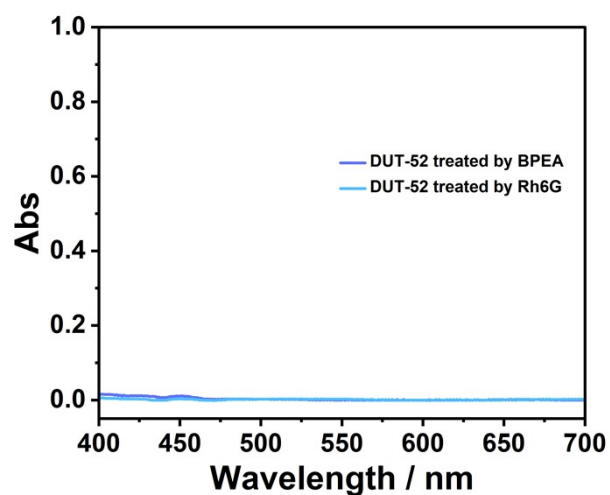

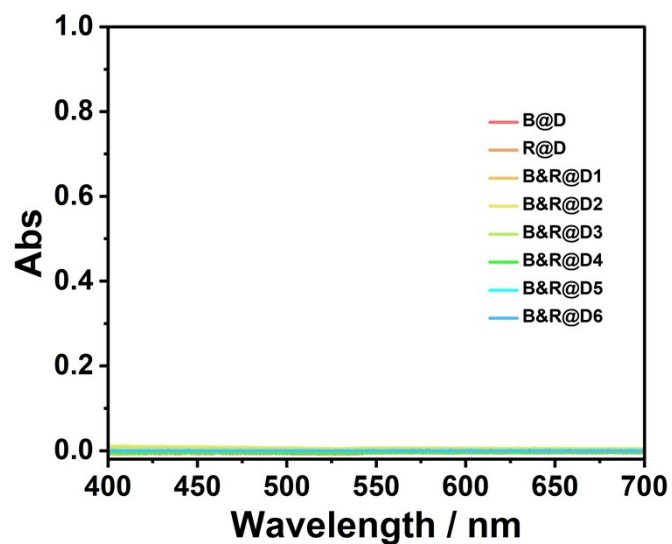**Fig. S2** The UV-vis absorption spectra of decomposition solution of dut-52 treated by BPEA/Rh6G.

Fig. S3 The UV-vis absorption spectra of the supernatant of soaked DUT-52, B@D, R@D, and six B&R@D composites DMF solution (8 mL, 48 h).
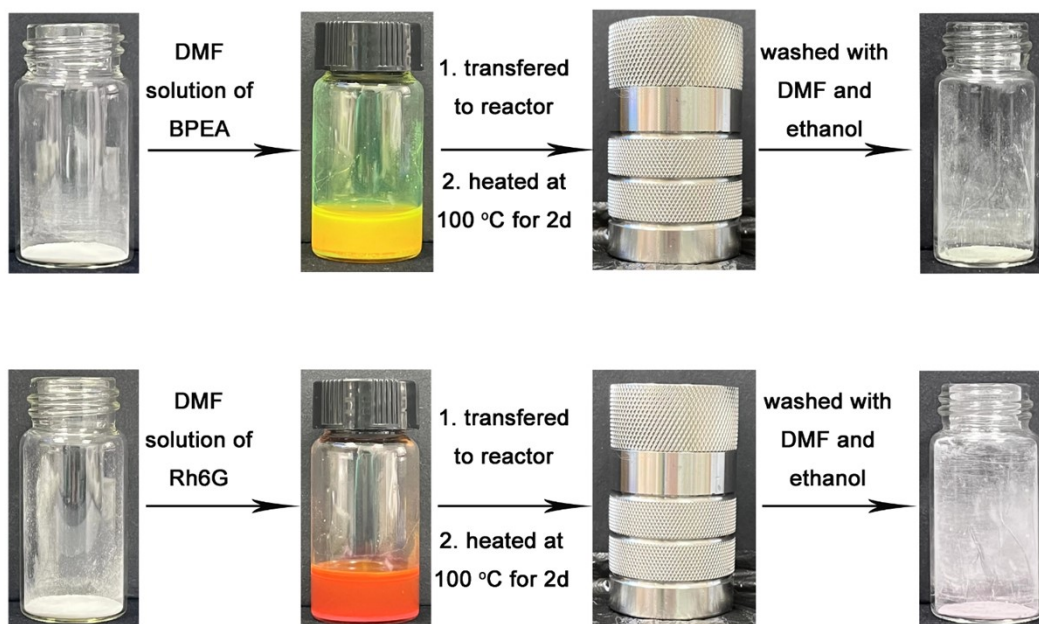

Fig. S4 The pristine DUT-52 before and after reacted with BPEA and Rh6G solution (6.275 mg mL^{-1} and 11.9 mg mL^{-1}, DMF solvent) at 100 °C, respectively.
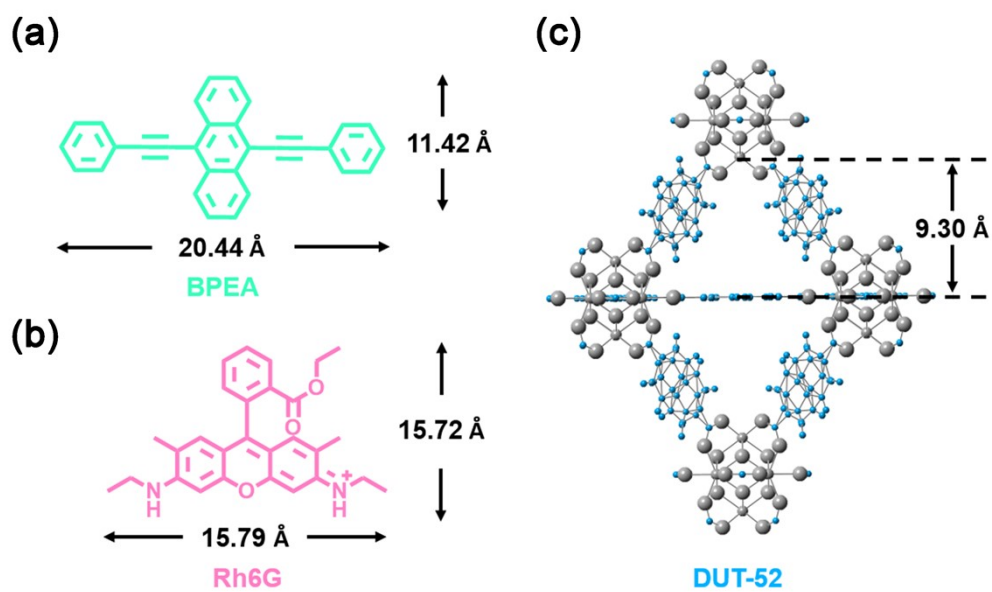
Fig. S5 (a, b) Chemical structures and molecular sizes of 9,10-bis(phenylethynyl)anthracene (BPEA) and rhodamine 6G (Rh6G). (c) Window size of DUT-52 with *fcu* topology.
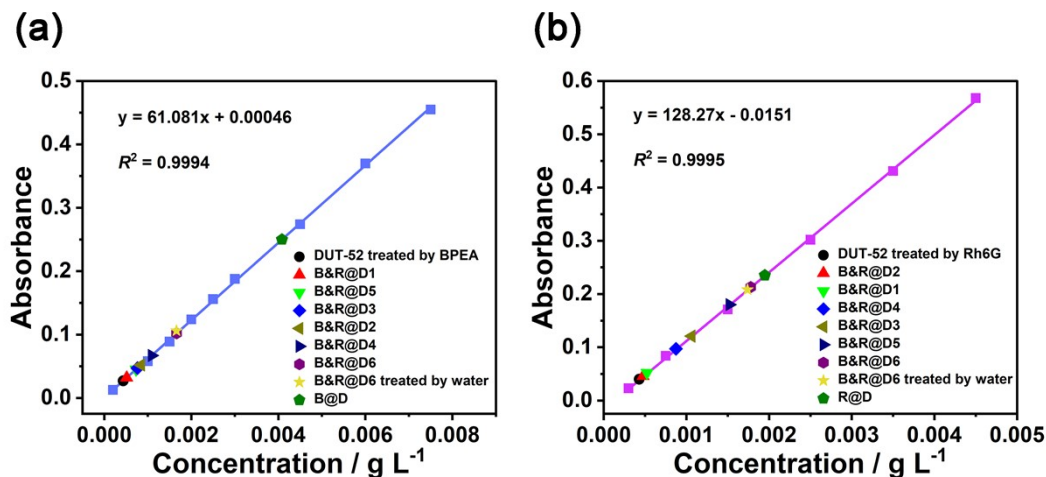
Fig. S6 (a) The standard absorbance curve of BPEA acidic solution (square) and the absorbance of acidic hydrolysis solution for BPEA&Rh6G@DUT-52 composites and DUT-52 in control experiments (solvothermal treatment by BPEA solution) (other shaped points). (b) The standard absorbance curve of Rh6G acidic solution (square) and the absorbance of acidic hydrolysis solution for BPEA&Rh6G@DUT-52 composites and DUT-52 in control experiments (solvothermal treatment by Rh6G solution) (other shaped points).
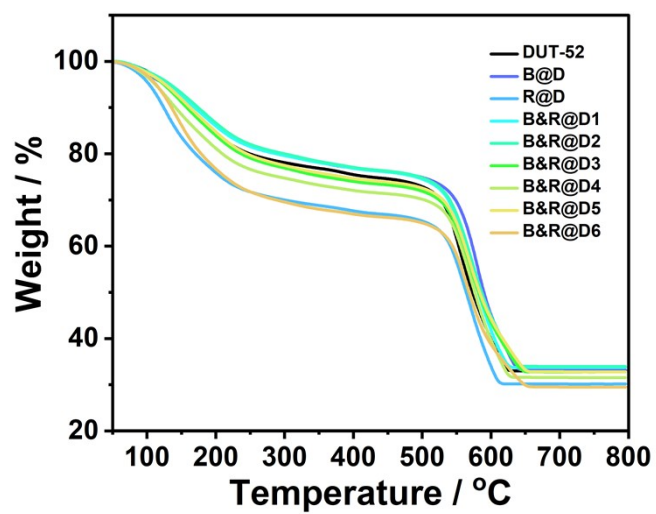
Fig. S7 The TG curves of as-synthesized DUT-52, BPEA@DUT-52, Rh6G@DUT-52 and six BPEA&Rh6G@DUT-52 composites.

The acidic hydrolysis procedure of BPEA&Rh6G@DUT-52 composites or DUT-52 in control experiments.

15 mg BPEA&Rh6G@DUT-52 composites or DUT-52 in control experiments were dispersed in 5 mL acidic solution of DMF ($V_{DMF} : V_{HCl} = 4 : 1$) and heated at 60 °C for 2 hours to completely hydrolyse MOF composites and release BPEA and Rh6G molecules. The concentrations of BPEA and Rh6G solutions of acidic hydrolysis solutions were calculated by the standard curves of BPEA and Rh6G ($y = 61.081x - 0.00046$, $y = 128.27x - 0.0151$), respectively. The loaded mole fractions of BPEA and Rh6G in samples are represented as X_{BPEA} and X_{Rh6G}.

Table S1 The loaded mole fractions of BPEA and Rh6G in different samples

Samples	B&R@D1	B&R@D2	B&R@D3	B&R@D4	B&R@D5	B&R@D6	B@D	R@D	D&B	D&R
ρ_{BPEA} / g mL^{-1}	0.516±0.002	0.844±0.003	0.762±0.002	1.090±0.006	0.729±0.004	1.662±0.005	4.085±0.006		0.434±0.002	
ρ_{Rh6G} / g mL^{-1}	0.523±0.001	0.476±0.002	1.063±0.004	0.874±0.005	1.521±0.005	1.778±0.003		1.949±0.004		0.429±0.002
$m_{samples}$ / g	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015		
M_{BPEA} / g mol^{-1}	378	378	378	378	378	378	378		378	
M_{Rh6G} / g mol^{-1}	479	479	479	479	479	479		479		479
$M_{samples}$ / g mol^{-1}	2187	2175	2254	2340	2254	2497	2234	2448	2240	2240
X_{BPEA} / %	0.10%	0.16%	0.15%	0.22%	0.14%	0.37%	0.8%		0.09%	
X_{Rh6G} / %	0.08%	0.07%	0.17%	0.14%	0.24%	0.31%		0.33%		0.07%

The calculations of ρ_{Rh6G} and ρ_{BPEA} are based on standard absorbance curves for Rh6G and BPEA acidic solutions, respectively (Fig. S6).

Calculation of $M_{samples}$ is based on TGA curves by using Zr_6O_{12} {six ZrO_2 vs. $[Zr_6O_4(OH)_4L_6]_n$} as residue (Fig. S7).

$X_{BPEA} = n_{BPEA} / n_{samples} = (m_{BPEA} / M_{BPEA}) / (m_{samples} / M_{samples})$.

$X_{Rh6G} = n_{Rh6G} / n_{samples} = (m_{Rh6G} / M_{Rh6G}) / (m_{samples} / M_{samples})$.

Interpretation: The formula is to calculate the molar percentage of dyes in the composites (B&R@D, B@D, R@D). X = the molar percentage of dyes in the composites (B&R@D, B@D, R@D); n = amount of substance; m = mass; M = molar mass; BPEA = 9,10-bis (phenylethynyl)anthracene; Rh6G = rhodamine 6G; samples = MOF composites.
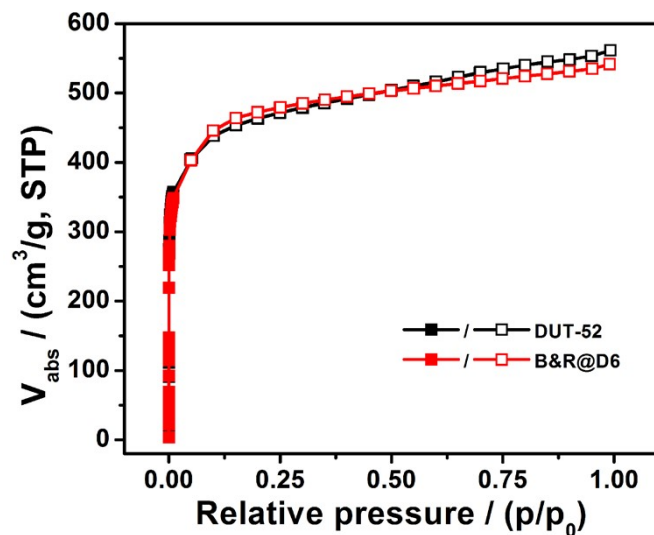
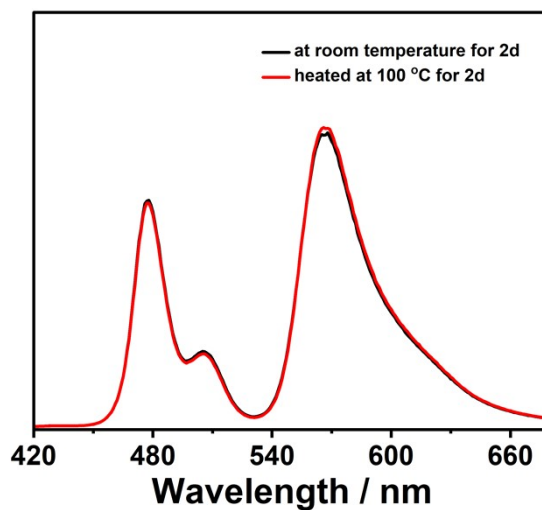**Fig. S8** N_2 adsorption-desorption isotherms of DUT-52 and B&R@D6 at 77 K.

Fig. S9 Fluorescence spectra of a mixed solution of BPEA and Rh6G (6.275 mg mL^{-1} and 11.9 mg mL^{-1}, DMF solvent) before and after a solvothermal reaction.
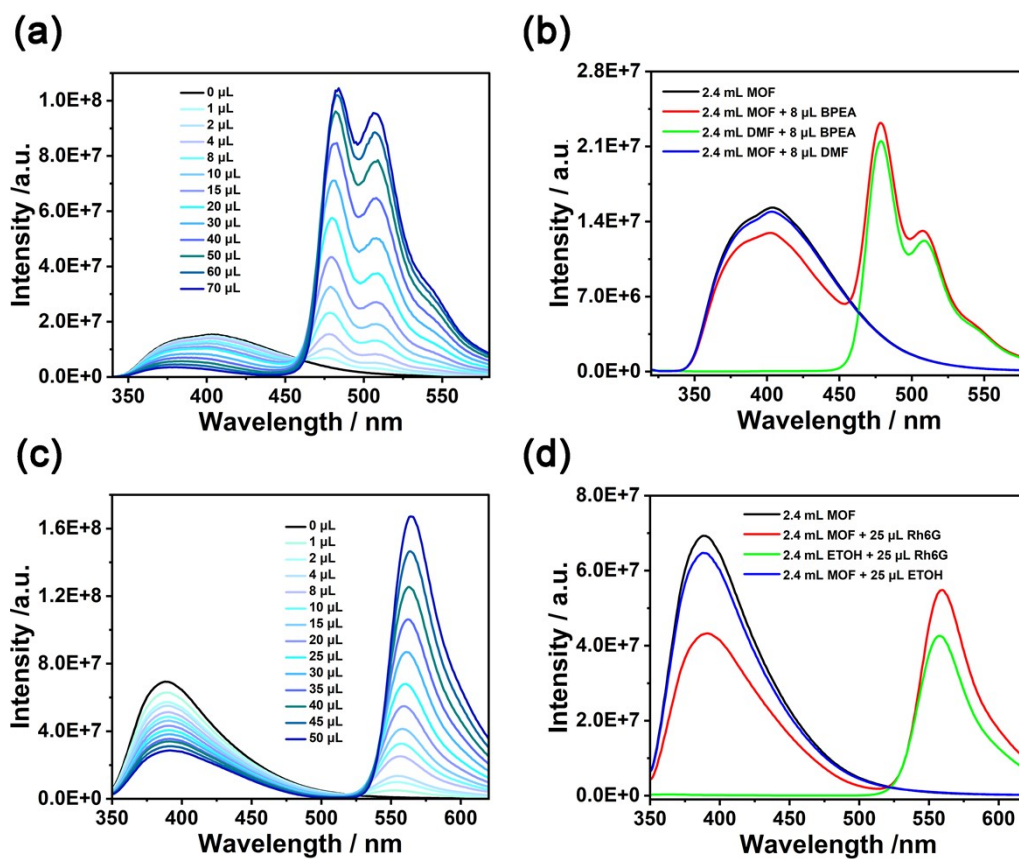
Fig. S10 (a) Fluorescence response of DUT-52 DMF suspension (2.4 mL) by gradually adding BPEA DMF solution (0.1 g L^{-1}). (b) Fluorescence spectra of the controlled experiments. (c) Fluorescence response of DUT-52 ethanol suspension (2.4 mL) by gradually adding Rh6G ethanol solution of (0.1 g L^{-1}). (d) Fluorescence spectra of the controlled experiments.
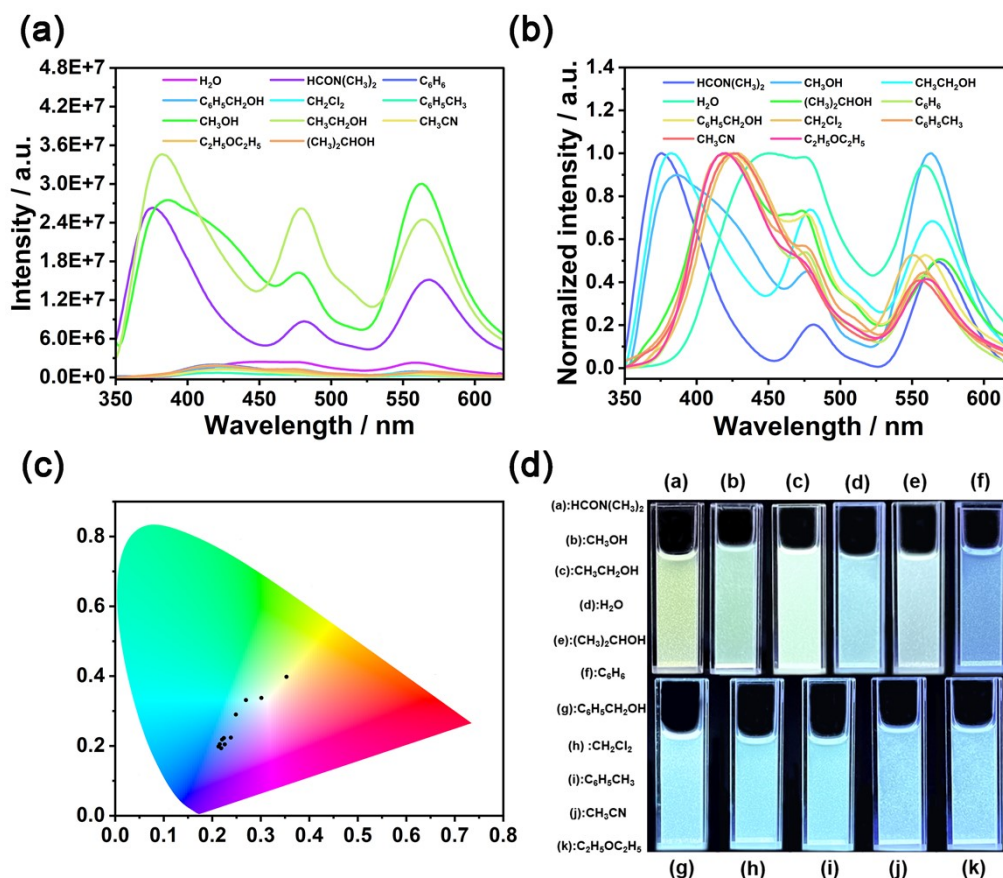
Fig. S11 (a) Fluorescent spectra of B&R@D6 composites at different solvent (λ_{ex} = 320 nm). (b) Normalized fluorescent spectra of B&R@D6 composites at different solvent (λ_{ex} = 320 nm). (c) The corresponding CIE coordinates. (d) Optical photographs of B&R@D6 composites at different solvent (λ_{ex} = 365 nm).

Table S2 Comparison of BPEA&Rh6G@DUT-52 sensor with other MOF fluorescent sensors for the detection of Fe^{3+} ions

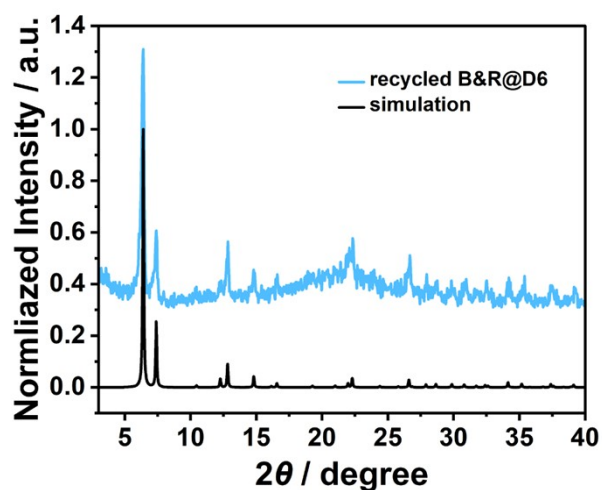|	MOF	Analyte	K_{SV} (M^{-1})	LOD (M)	Sensing method	Ref.
1	$\{[ZnL_{0.5}(4,4'-bbib)]\cdot 3DMF\cdot 3H_2O\}_n$	Fe^{3+}	2.43×10^2	-	quenching	[1]
2	$\{[Zn(ATA)(L)]\cdot H_2O\}_n$	Fe^{3+}	0.557×10^3	3.76×10^{-6}	quenching and colorimetry	[2]
3	$[Zr_6O_4(OH)_8(H_2O)_4(L^1)_2]\cdot S$	Fe^{3+}	2.17×10^3	3.8×10^{-6}	quenching	[3]
4	$[Cd(2-bpeb)(sdba)]$	Fe^{3+}	2.86×10^3	-	quenching	[4]
5	$Eu(btc)$	Fe^{3+}	2.9×10^3	3.13×10^{-6}	quenching	[5]
6	$\{[Eu(dpc)(2H_2O)]\cdot(Hbibp)_{0.5}\}_n$	Fe^{3+}	3.34×10^3	2.89×10^{-5}	quenching	[6]
7	BPEA&Rh6G@DUT-52	Fe^{3+}	3.09×10^3	2.8×10^{-6}	quenching and colorimetry	This work

Fig. S12 PXRD patterns of the recycled B&R@D6 composite.

Table S3 Comparison of BPEA&Rh6G@DUT-52 sensor with other MOF fluorescent sensors for the detection of $Cr_2O_7^{2-}$ ions

|	MOF	Analyte	K_{SV} (M^{-1})	LOD (M)	Sensing method	Ref.
1	Eu^{3+}@UiO-66-CA	$Cr_2O_7^{2-}$	4.698×10^5	8.5×10^{-6}	quenching	[7]
2	SQDs@UiO-66-NH$_2$	$Cr_2O_7^{2-}$	3.12×10^4	0.16×10^{-6}	quenching and colorimetry	[8]
3	[Cd$_3$(cpota)$_2$(phen)$_3$]$_n$·5nH$_2$O	$Cr_2O_7^{2-}$	1.21×10^4	0.37×10^{-6}	quenching	[9]
4	[Zn(dptz)(BDC) (H$_2$O)] $_n$	$Cr_2O_7^{2-}$	1.26×10^4	0.36×10^{-6}	quenching	[10]
5	[Zn$_2$(tpeb)(bpdc)$_2$]·0.5DMA·4H$_2$O	$Cr_2O_7^{2-}$	1.122×10^4	1.04×10^{-6}	quenching	[11]
6	Cd(II)-MOF	$Cr_2O_7^{2-}$	2.45×10^4	4.88 ppb	quenching	[12]
7	BPEA&Rh6G@DUT-52	$Cr_2O_7^{2-}$	4.68×10^5	18.5×10^{-9}	quenching and colorimetry	This work
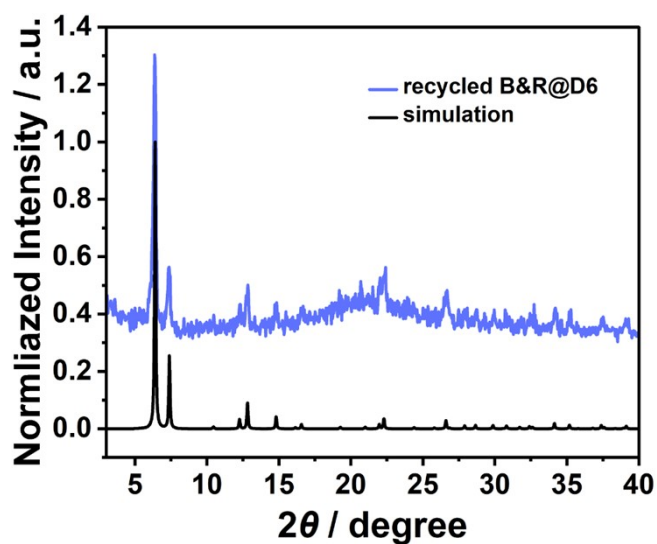
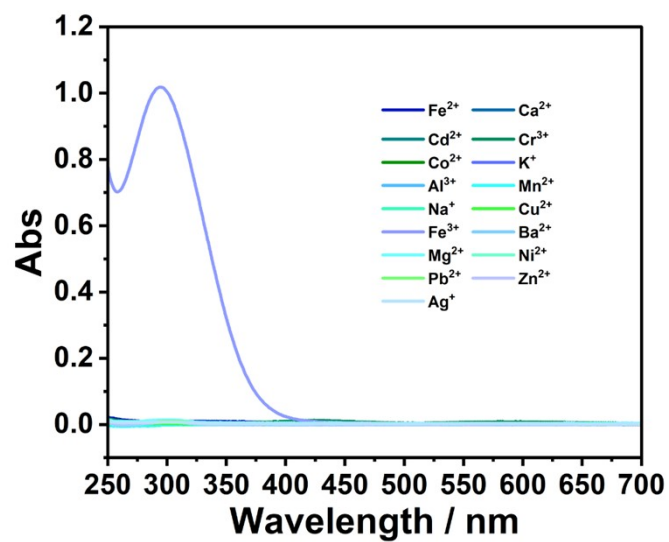**Fig. S13** PXRD patterns of the recycled B&R@D6 composite.

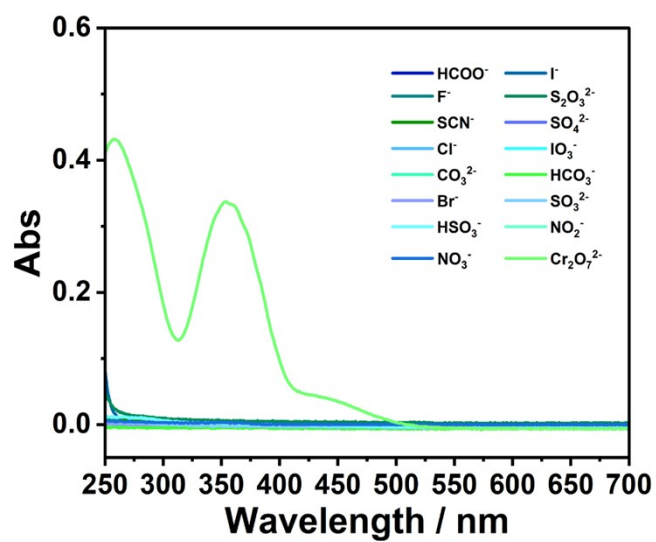**Fig. S14** The UV-vis absorption spectra of 17 cations in aqueous solution (0.5 mM).

Fig. S15 The UV-vis absorption spectra of 16 anions in aqueous solution (0.1 mM).
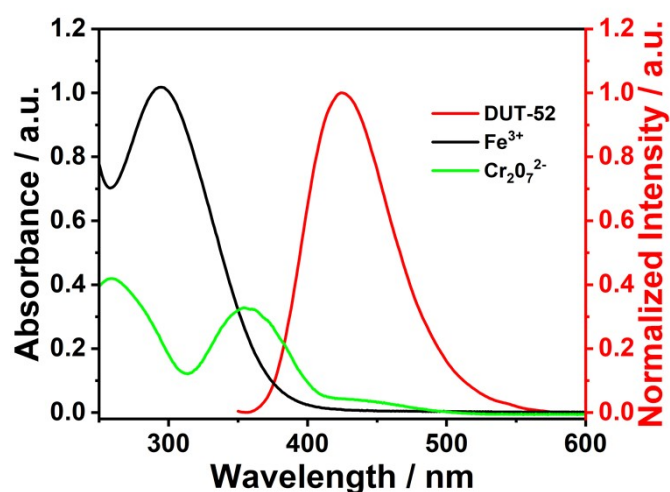
Fig. S16 Absorption spectra of Fe^{3+} (0.5 mM), $Cr_2O_7^{2-}$ (0.1 mM) and normalized emission spectra of DUT-52 in the solid state.
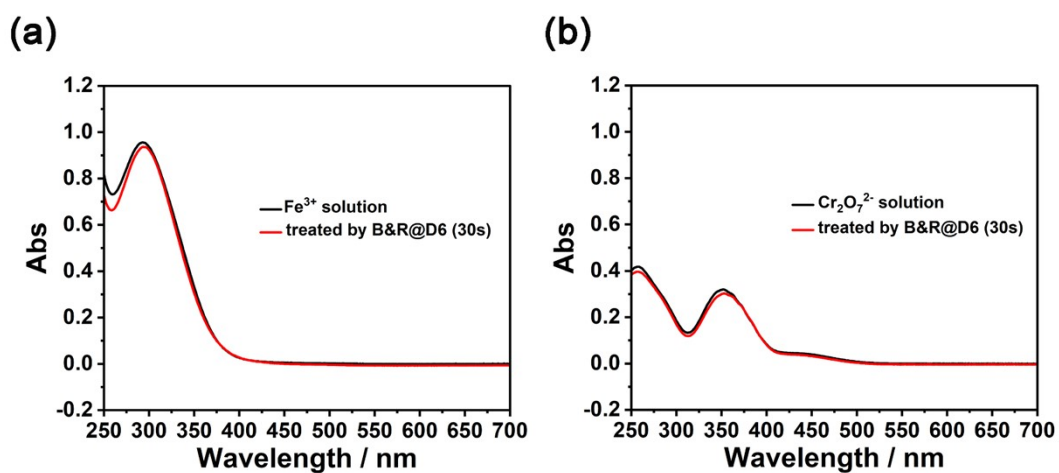

Fig. S17 Adsorption tests of B&R@D6 composites toward (a) Fe^{3+} (0.5 mM) and (b) $Cr_2O_7^{2-}$ (0.1 mM) in sensing process.
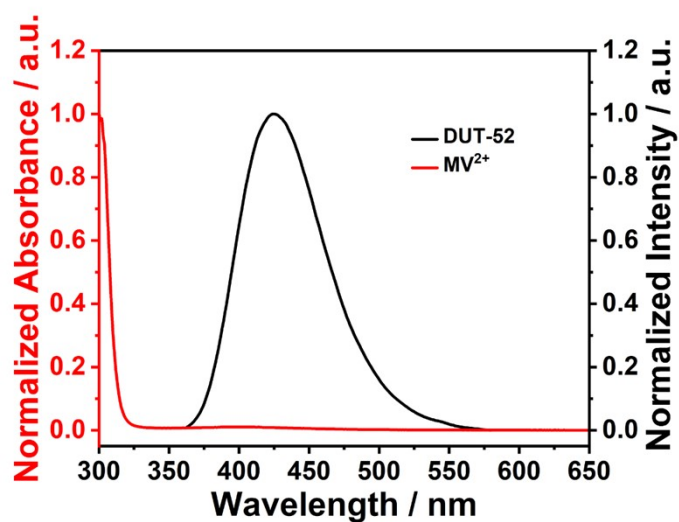
Fig. S18 Normalized of emission spectra of DUT-52 in solid state (black) and absorption spectra of MV^{2+} aqueous solution (red, 0.01 M).
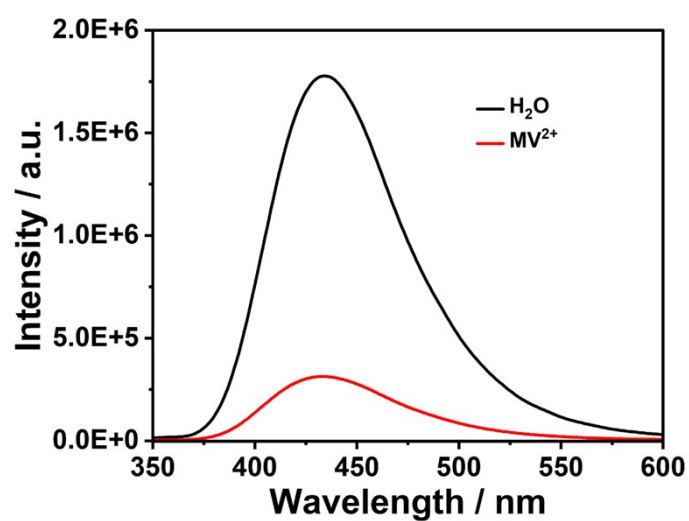

Fig. S19 Fluorescence response of DUT-52 aqueous suspension by adding MV^{2+} aqueous solution (0.01 M).
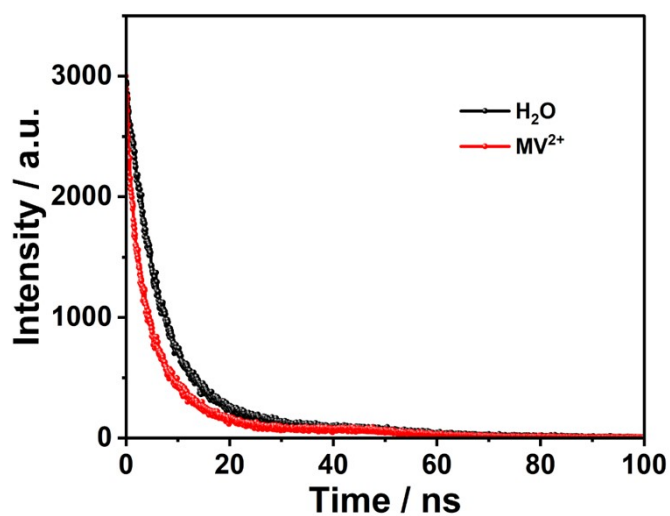
Fig. S20 Luminescence decay curves of DUT-52 aqueous suspension and MV^{2+} aqueous solution (0.01M).

Table S4 Detection of Fe^{3+} concentration in actual water samples

Sample	Spiked (μM)	Found (μM)	Recovery (%)	RSD (%) (n = 3)
Songhua River (China. Harbin)	25.00	25.38±0.09	101.5	0.34
	50.00	52.30±0.15	104.6	0.29
	75.00	78.53±0.08	104.7	0.36
Majiagou Lake (China. Harbin)	25.00	26.98±0.05	107.9	0.19
	50.00	56.25±0.15	112.5	0.27
	75.00	85.58±0.06	114.1	0.07
Tap water for Northeast Forestry	25.00	25.43±0.05	101.7	0.18
University campus (China. Harbin)	50.00	52.40±0.09	104.8	0.17
	75.00	79.20±0.04	105.6	0.36

Table S5 Detection of $Cr_2O_7^{2-}$ concentration in actual water samples

Sample	Spiked (μM)	Found (μM)	Recovery (%)	RSD (%) (n = 3)
Songhua River (China. Harbin)	5.00	5.02±0.02	100.3	0.39
	10.00	9.71±0.02	97.1	0.21
	15.00	14.13±0.02	94.2	0.11
Majiagou Lake (China. Harbin)	5.00	5.01±0.01	100.1	0.12
	10.00	8.86±0.02	88.6	0.29
	15.00	13.02±0.01	86.8	0.06
Tap water for Northeast Forestry	5.00	4.70±0.01	94.0	0.21
University campus (China. Harbin)	10.00	9.26±0.03	92.6	0.37
	15.00	13.98±0.05	93.2	0.33

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