Electronic Supplementary Information

Dual-emissive Dye@MOF composite for ratiometric detection and discrimination of two isomers of tetrachlorobenzenediol

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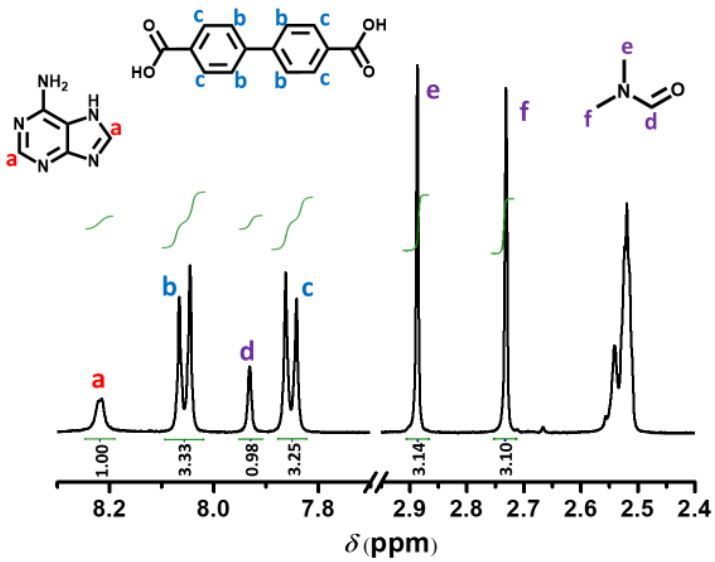

Fig. S1 ^{1}H NMR spectrum of the digested solution of bio-MOF-1. Based on the integrated areas of the peaks at 8.22, 7.85, 7.95, 8.07, 2.89 and 2.73 ppm, the molar ration among ad, $bpdc^{2-}$ and DMF is determined to be 2 : 3 : 4.

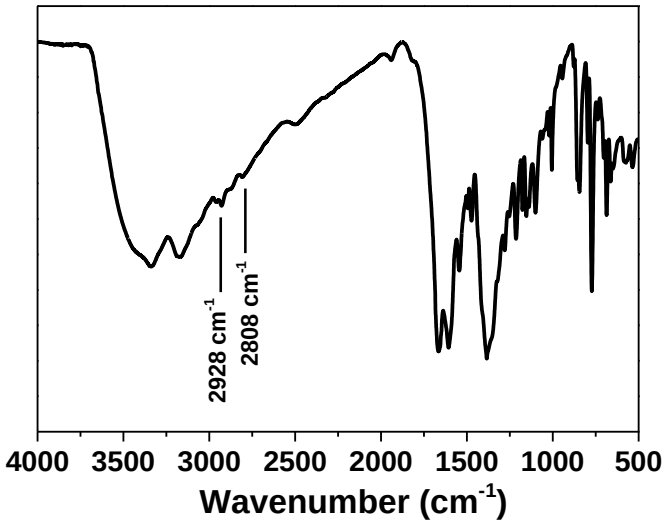

Fig. S2 FT-IR spectra of as-synthesized bio-MOF-1 sample. The absorption peaks at 2928 and 2808 cm^{-1} prove the presence of $Me_2NH_2^+$ ion.

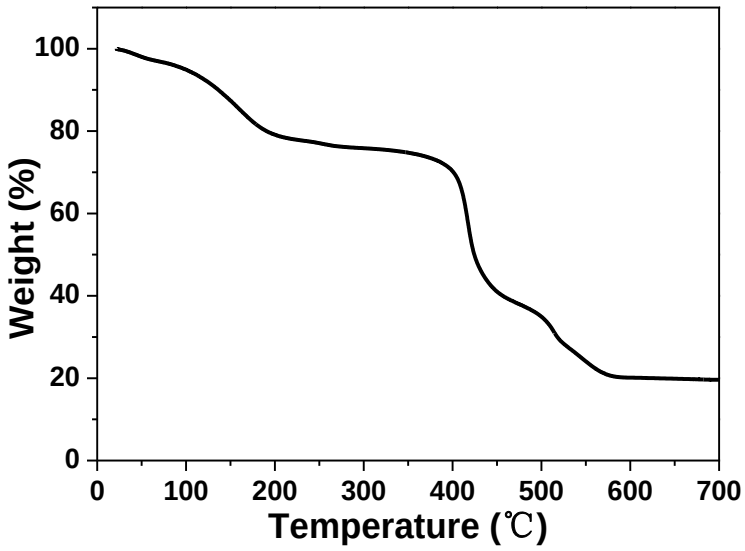

Fig. S3 Thermogravimetric curve of as-synthesized bio-MOF-1 sample. The overall weight loss from room temperature to 700 ℃ is 80.42 %, which is consistent with the loss of all H_2O molecules and organic components with ZnO as residue (calcd. 80.81 %) based on the formula of $[Zn_8(ad)_4(bpdc)_6O]\cdot2(Me_2NH_2)\cdot8DMF\cdot11H_2O$.

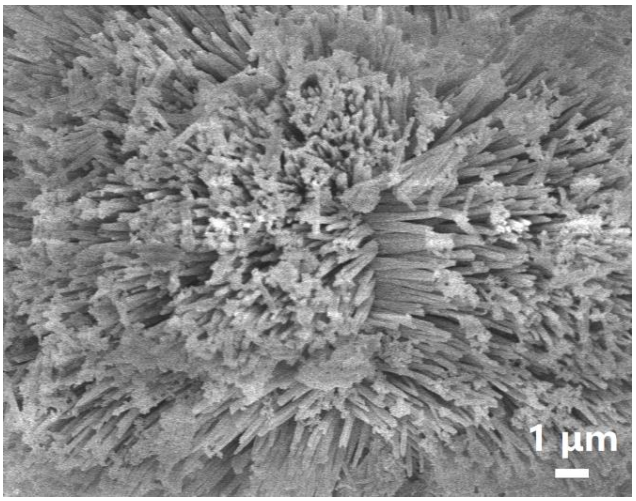

Fig. S4 Low resolution SEM image of bio-MOF-1.

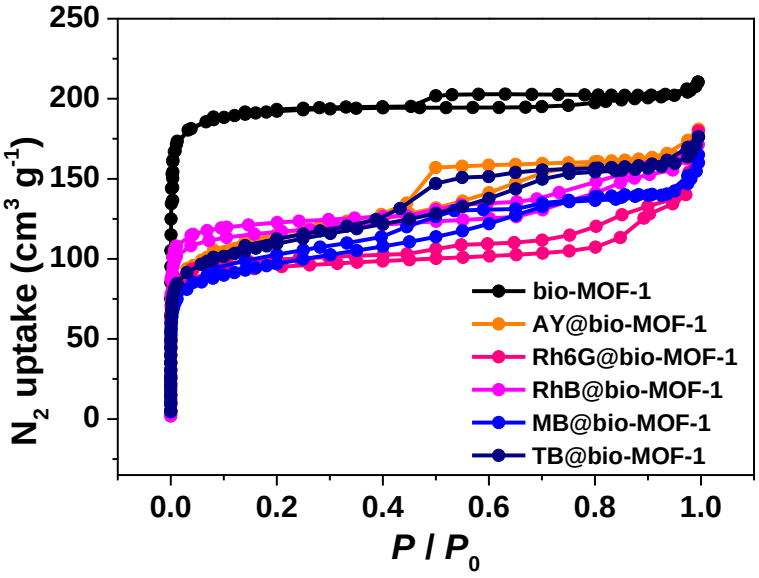

Fig. S5 N_2 adsorption isotherms (at 77 K) of bio-MOF-1 precursor and its products after dye encapsulation. The adsorption hysteresis shown in the isotherm could be attributed to the mesopores formed by the randomly stacking of the nanorods of MOF, as the cases of inorganic materials (for example, Ref. 1 and 2).

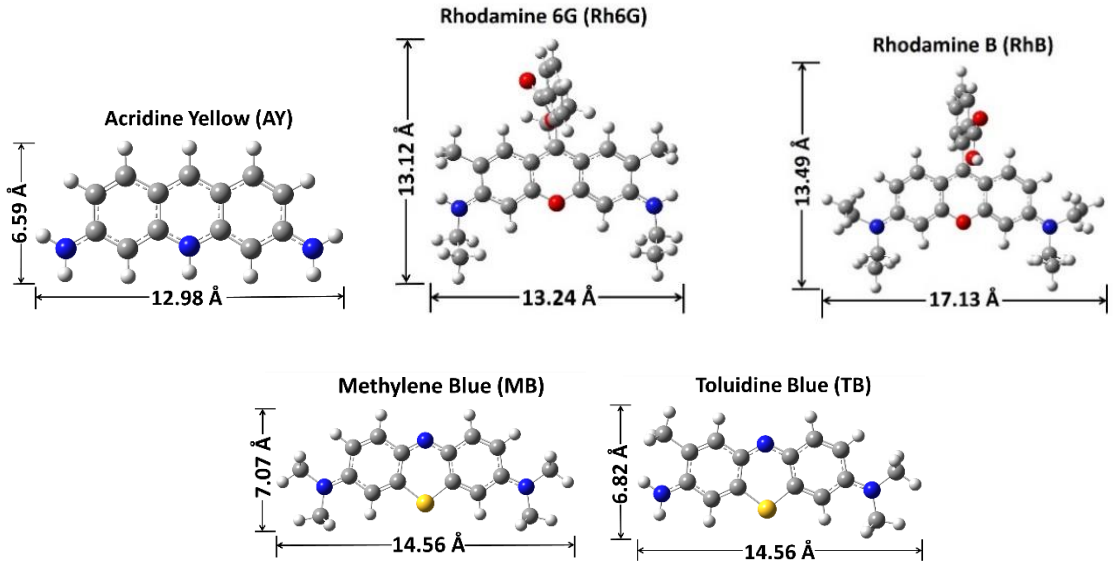

Fig. S6 Molecular sizes of five dyes, optimized at B3LYP/6-31+G(d) level.

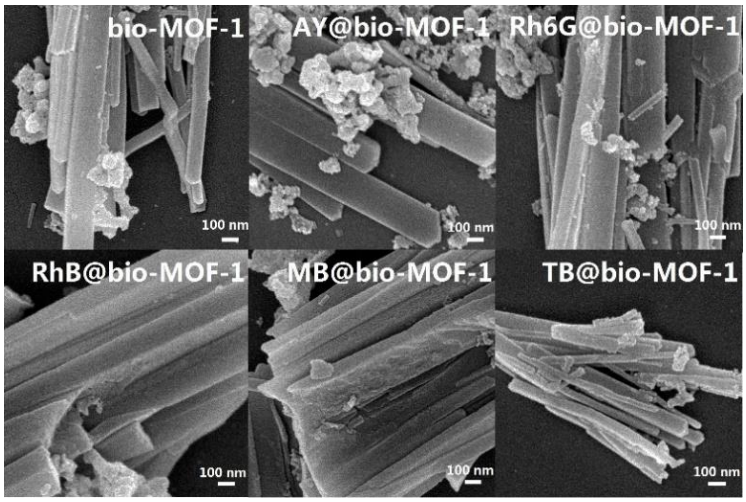

Fig. S7 SEM images of bio-MOF-1 and dye@bio-MOF-1s after 1.5 h of sonication.

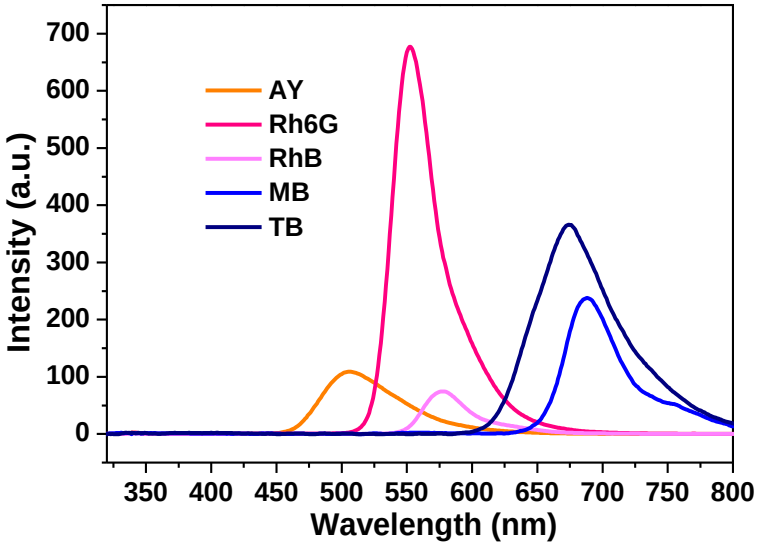

Fig. S8 Fluorescent spectra of dye guests (0.3 mM).

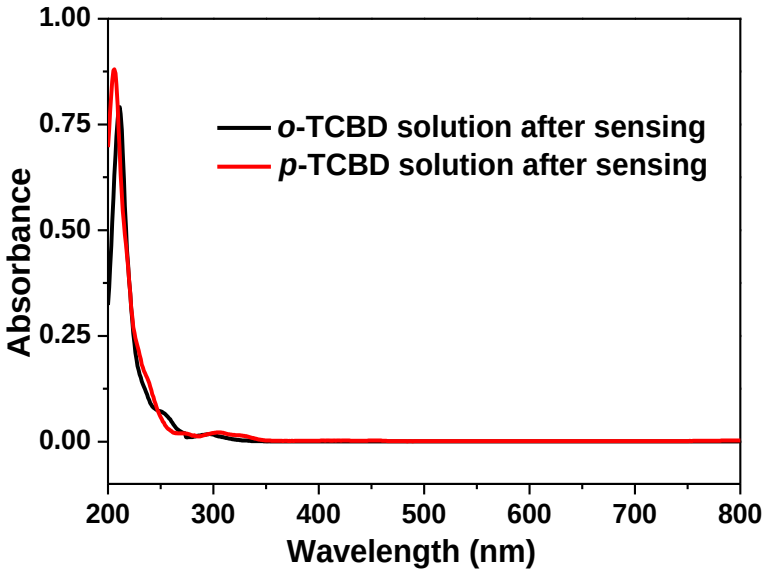

Fig. S9 UV-vis spectra of the solutions of *o*- and *p*-TCBD after the sensing by TB@bio-MOF-1.

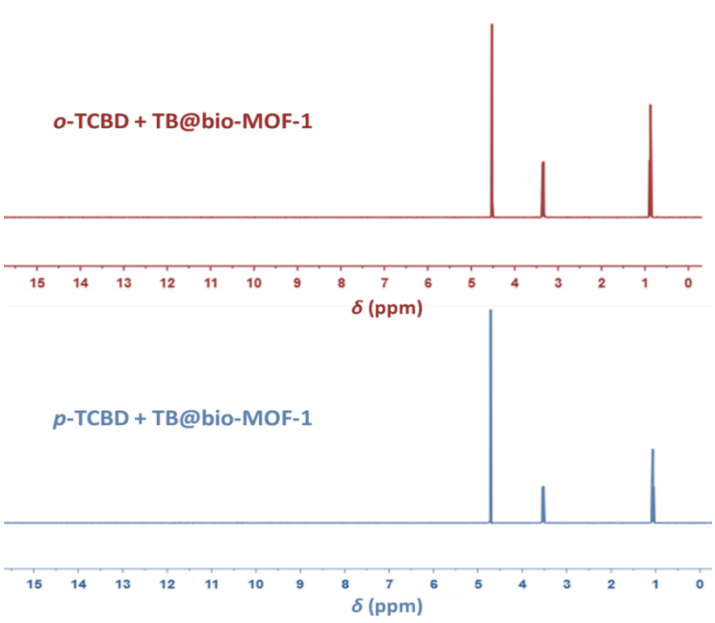

Fig. S10 ^{1}H NMR spectra of the D_2O suspensions containing TB@bio-MOF-1 (33.3 mg mL^{-1}) and TCBDs (20 mM). No signal from TB was shown in the spectra.

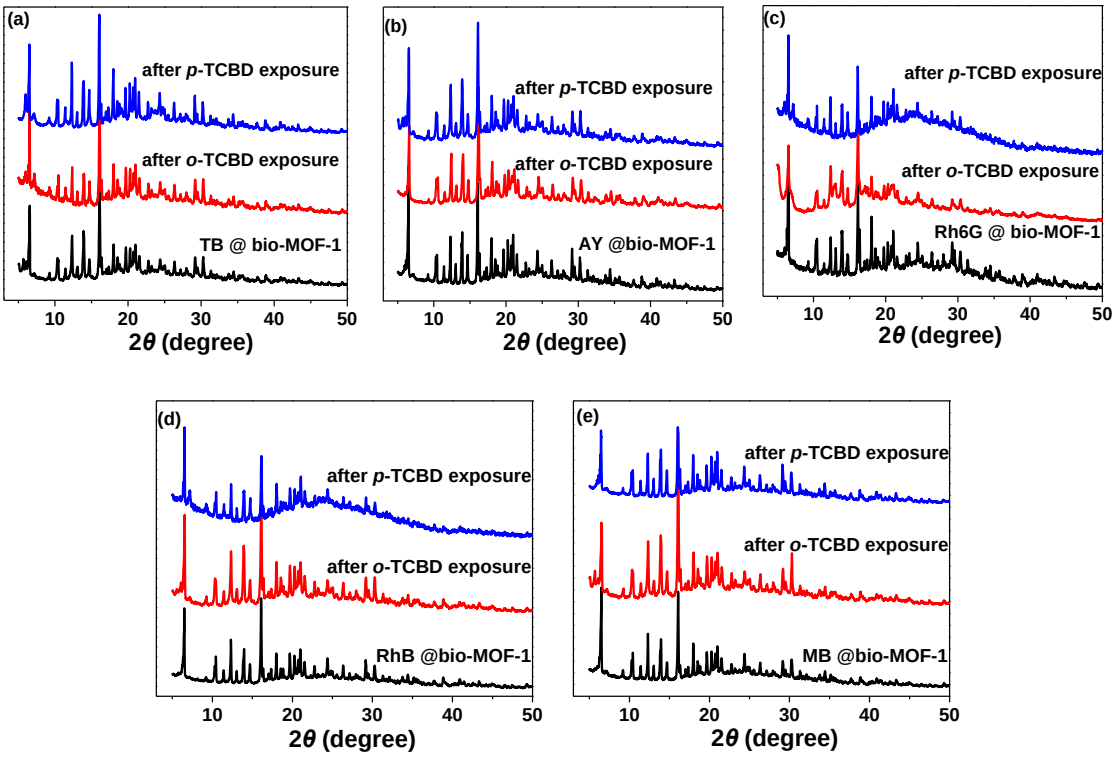

Fig. S11 PXRD patterns of (a) TB, (b) AY, (c) Rh6G, (d) RhB and (e) MB@bio-MOF-1s before and after the exposure to *o*- and *p*-TCBDs (200 μM).

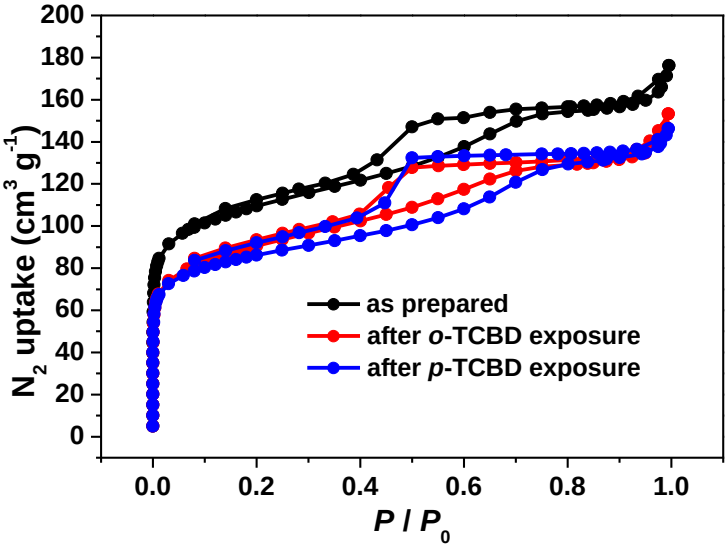

Fig. S12 N_2 adsorption isotherms (at 77 K) of TB@bio-MOF-1 before and after the exposure to *o*- and *p*-TCBD.

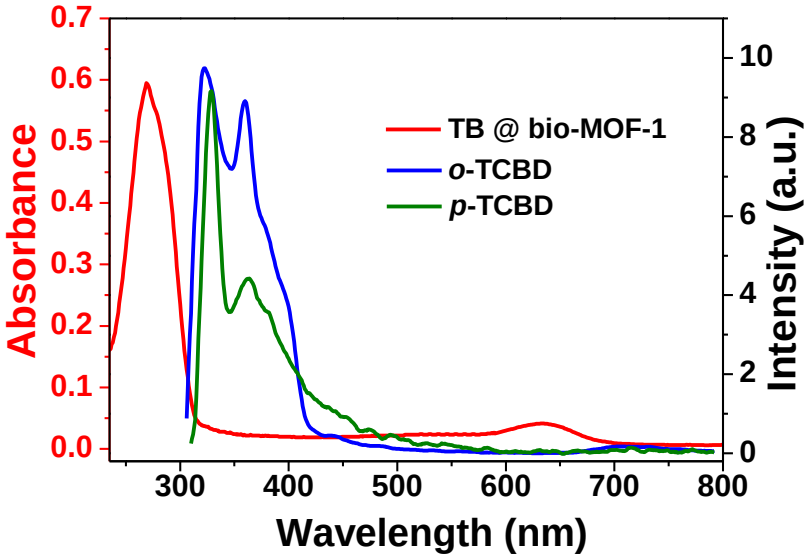

Fig. S13 Comparison of the absorption spectrum of TB@bio-MOF-1 with the emission spectra of two TCBD isomers.

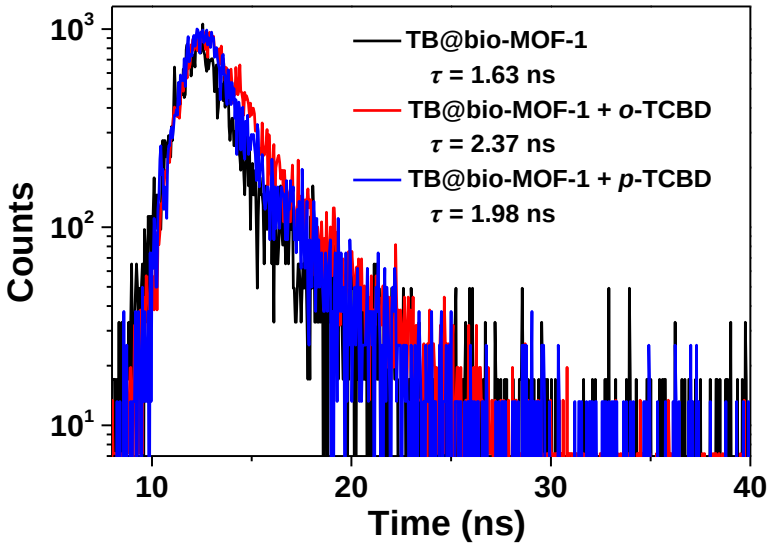

Fig. S14 Time-resolved fluorescent decays of TB@bio-MOF-1 in the presence of *o*- and *p*-TCBDs. 33.3 mg L^{-1} TB@bio-MOF-1, 200 μM *o*- or *p*-TCBD, λ_{ex} = 305 nm, λ_{em} = 371 nm.

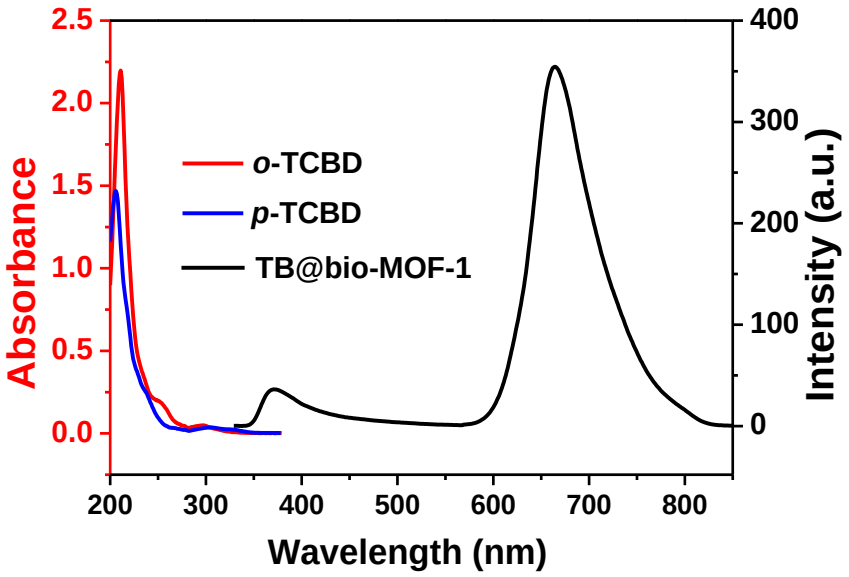

Fig.S15 Comparison among the absorption spectra of *o*- and *p*-TCBDs (100 μM) and the photoluminescence spectra of TB@bio-MOF-1 (33.3 mg L^{-1}), λ_{ex} = 305 nm.

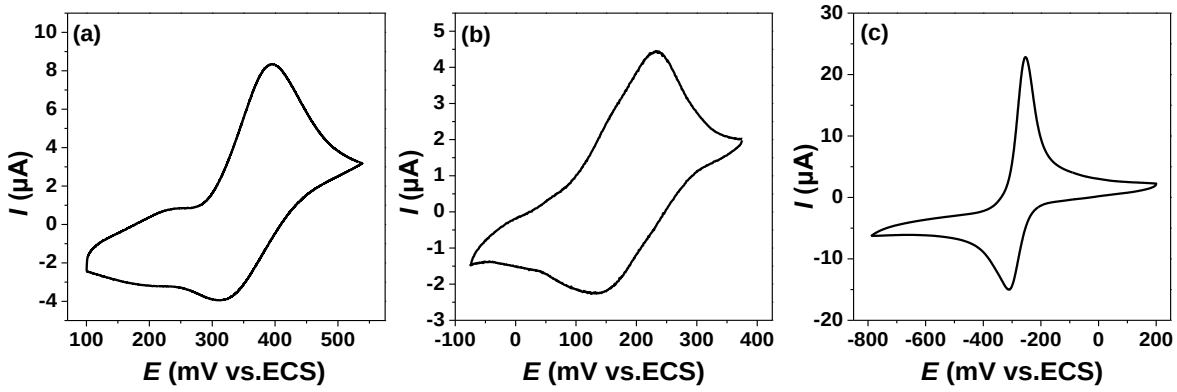

Fig.S16 Cyclic voltammetry curves of (a) *o*-TCBD, (b) *p*-TCBD and (c) TB.

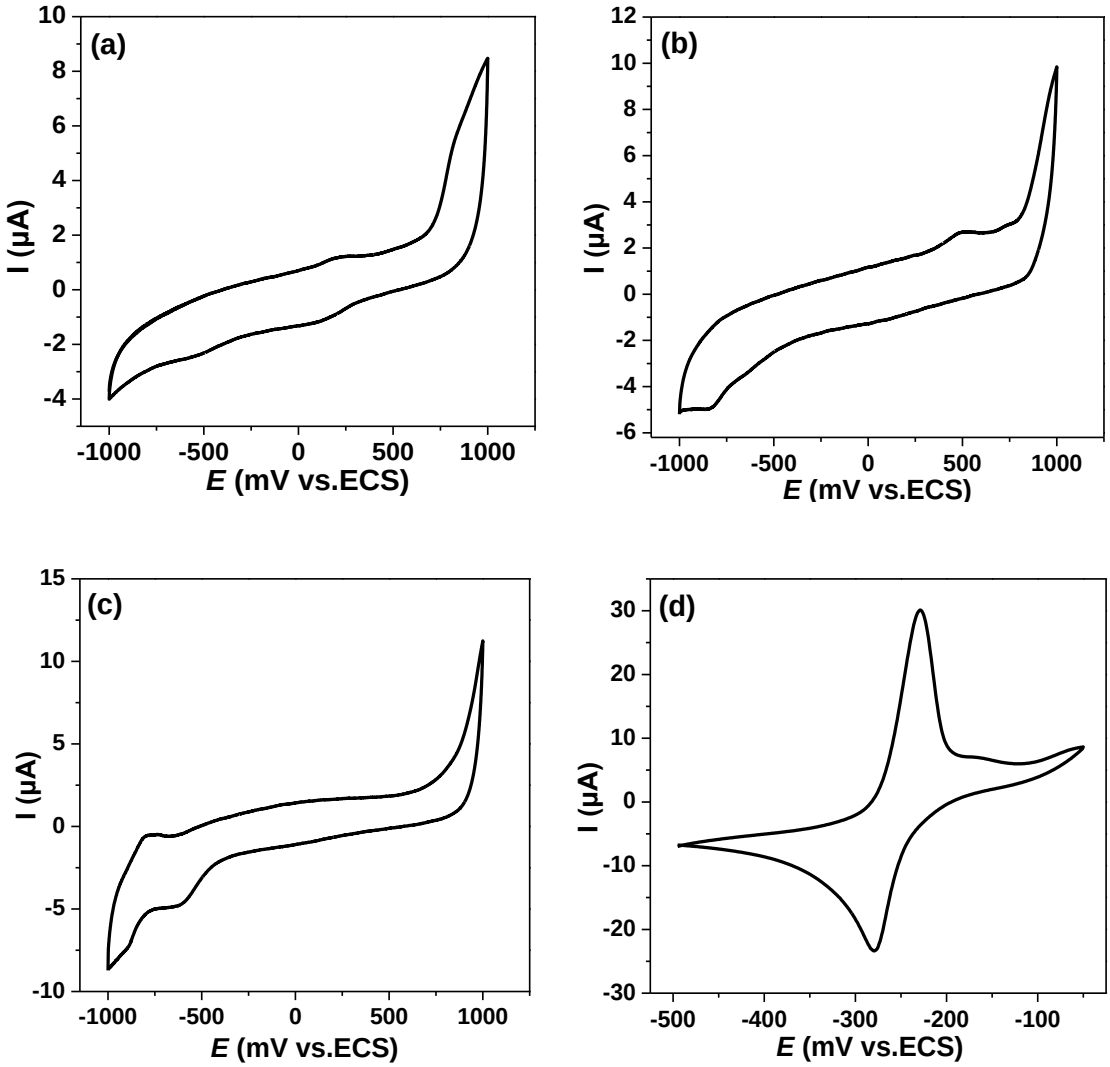

Fig.S17 Cyclic voltammetry curves of (a) AY, (b) Rh6G, (c) RhB and (d) MB. Only MB showed remarkable reduction peak in the measurement range. The measured reduction potential of MB was −0.279 V, and based on this value, the Δ*G*s for the PET processes from *o*- and *p*-TCBDs to MB were calculated to be −1.134 and −1.297 eV, respectively, with the Rehm-Weller equation.

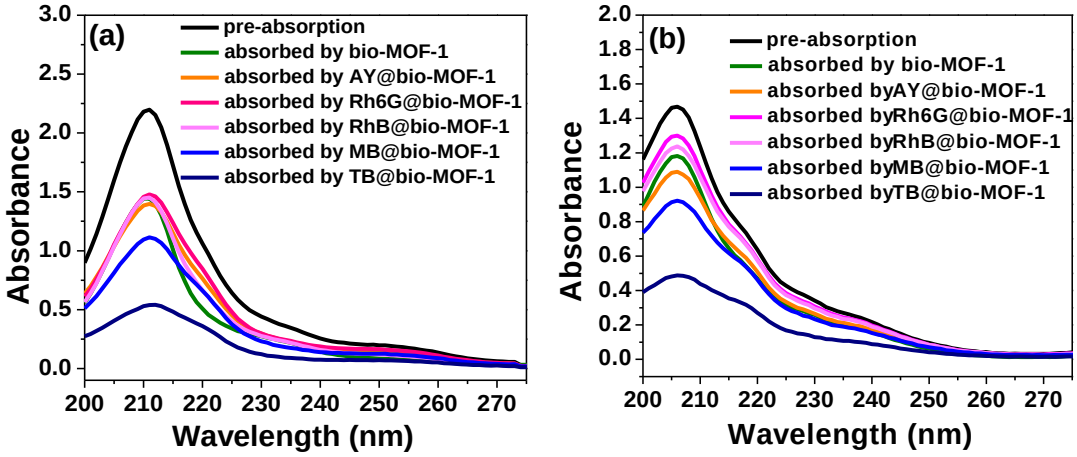

Fig. S18 Absorption spectra of the solutions of (a) *o*- and (b) *p*-TCBDs (c_{TCBD}^{0} = 3 mM) before and after the adsorption by pristine bio-MOF-1 and dye@bio-MOF-1 composites (0.5 mg L^{-1}). The adsorption percentage of *o*-/*p*-TCBD is calculated from the weakening percentage of its absorption band upon adsorption.

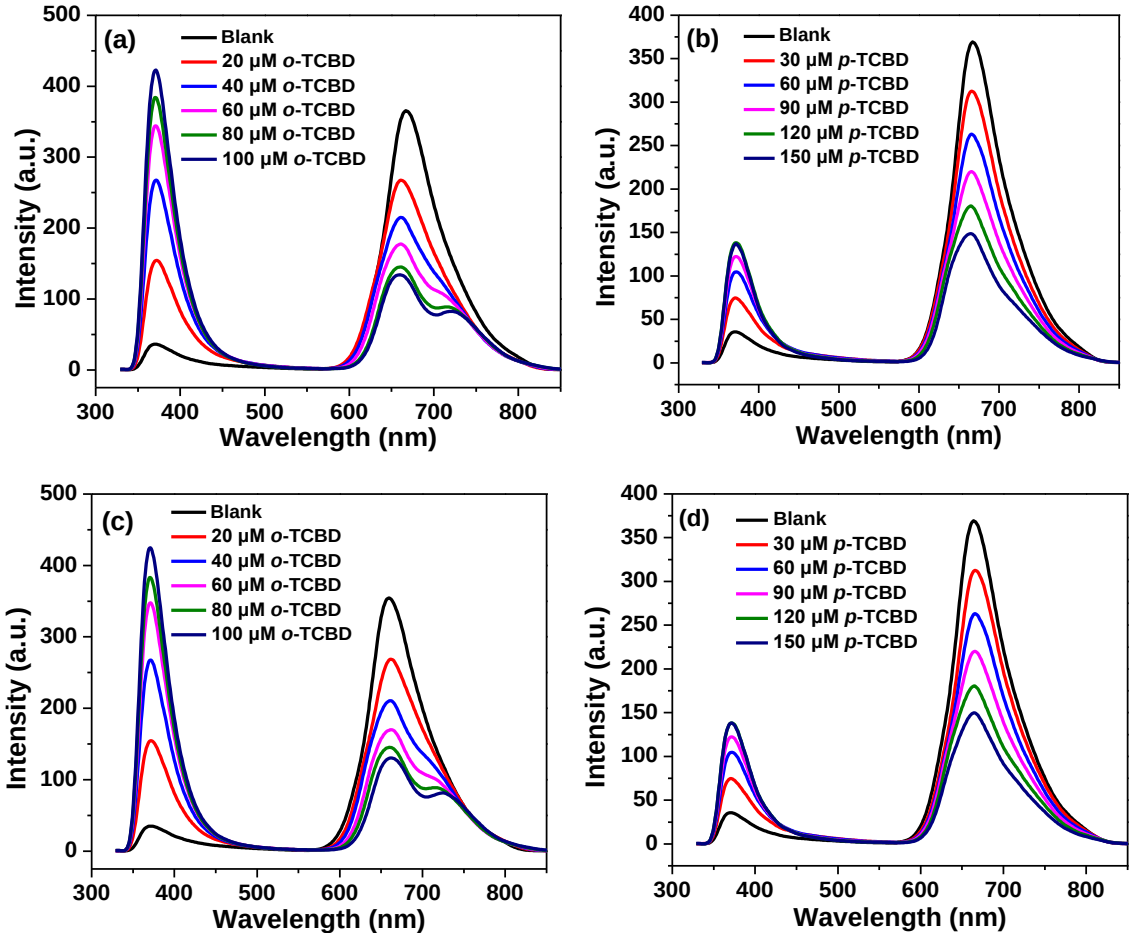

Fig. S19 Photoluminescent spectra of TB@bio-MOF-1 in artificial urine (a, b) and human serum (c, d) samples after the addition of different concentrations of *o*- and *p*-TCBDs. 33.3 mg L^{-1} TB@bio-MOF-1, λ_{ex} = 305 nm.

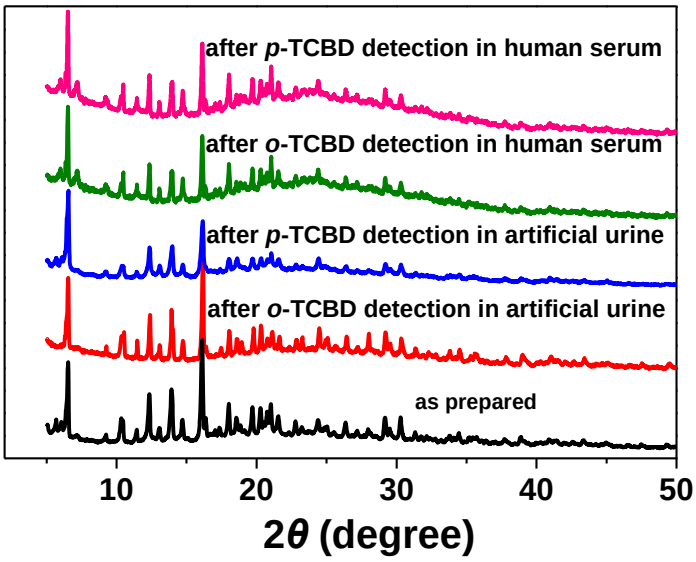

Fig. S20 PXRD patterns of TB@bio-MOF-1 after the detection of TCBDs in artificial urine and human serum samples.

Table S1 Dye loading amounts in dye@bio-MOF-1s[a]

Dye	Adsorption percentage (%)	Loading amount (mmol/g)	Loading amount (molecule per unit of MOF)
AY	91.72	0.367	1.244
Rh6G	64.35	0.257	0.873
RhB	59.12	0.236	0.803
MB	78.16	0.312	1.063
TB	80.33	0.322	1.089

[a] Measured by the LiCl exchanging method reported by Qian et al.[3]

References

1 Y. Z. Li, Q. Sun, M. Kong, W. Q. Shi, J. C. Huang, J. W. Tang and X. J. Zhao, *J. Phys. Chem. C*, 2011, **115**, 14050–14057.

2 Y. W. Wang, L. Z. Zhang, K. J. Deng, X. Y. Chen and Z. G. Zou, *J. Phys. Chem. C*, 2007, **111**, 2709–2714.

3 J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen and G.D. Qian, *Nat. Commun.*, 2013, **4**, 2719–2719.