Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

A dual-emissive MOF for the simultaneous detection of tetrachlorobenzoquinone isomers in their mixtures

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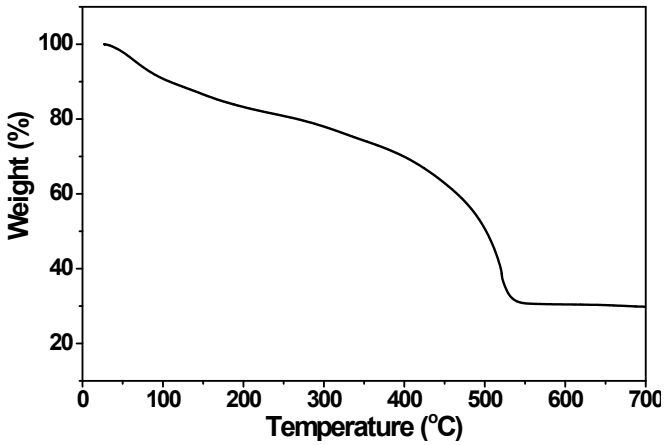

Fig. S1 Thermogravimetric curve of as-synthesized UiO-66-$(COOH)_2$ sample in air atmosphere. The overall weight loss from room temperature to 700 °C is 70.18%, which is in good consistence with the calculated value of 70.25% for the loss of all H_2O molecules, OH^- ions and organic components based on the formula of $[Zr_6(O)_4(OH)_4(H_2btec)_6(H_2O)_{16}]$.

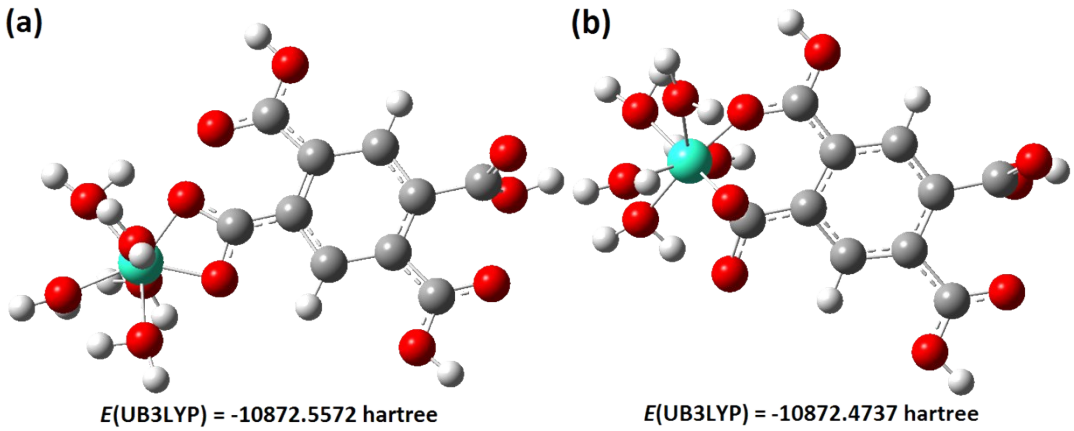

Fig. S2 Optimized structures of the coordination compounds formed between H_2btec^{2-} and Tb^{3+} ion with (a) one and (b) two carboxyl groups take part in coordination. Both the geometry optimization and single point energy calculation were performed using B3LYP functional and a mixed basis set of SDD for Tb and 6-31G(d) for other atoms. The solvent effect was modulated with SMD model (aqueous solvent). The sub-structure of terephthalate in the H_2btec^{2-} ligand was picked up from the crystalline structure of UiO-66, and protons were added to carboxylate groups for charge balance. Two carboxyl groups were added to the central benzene ring, and Tb atom was placed near one of them. five H_2O molecules were placed around Tb atom to keep the coordination saturation. During the optimization process, the atoms of the initial two carboxylate groups were fixed to replicate the bulk behavior, while the other atoms were relaxed.

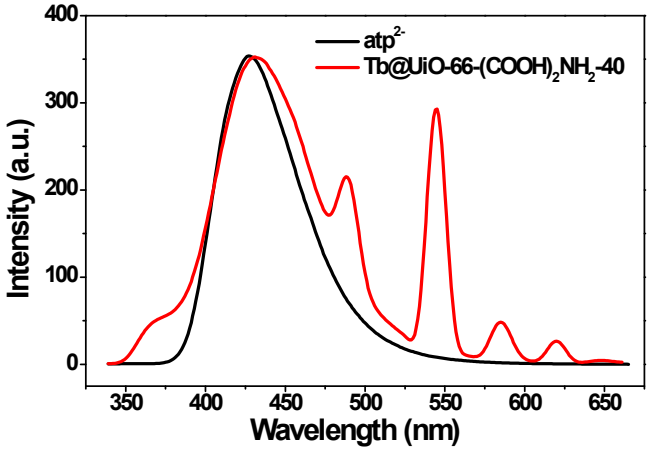

Fig. S3 Comparison between the photoluminescent spectra of Tb@UiO-66-$(COOH)_2NH_2$ (50 mg L^{-1}) and free atp^{2-} ligand (4 μM, dissolving H_2atp by 2 equiv of NaOH) in H_2O-ethanol mixed solvent (v/v = 3/1), λ_{ex} = 290 nm.

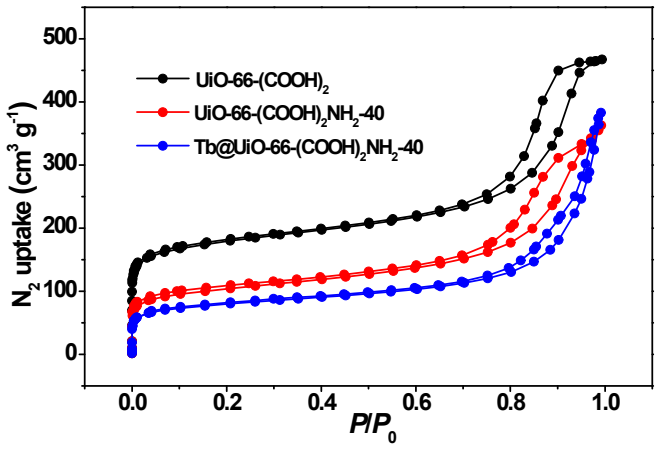

Fig. S4 N_2 adsorption isotherms (at 77 K) of UiO-66-$(COOH)_2$ precursor and its product after post-synthetic modification.

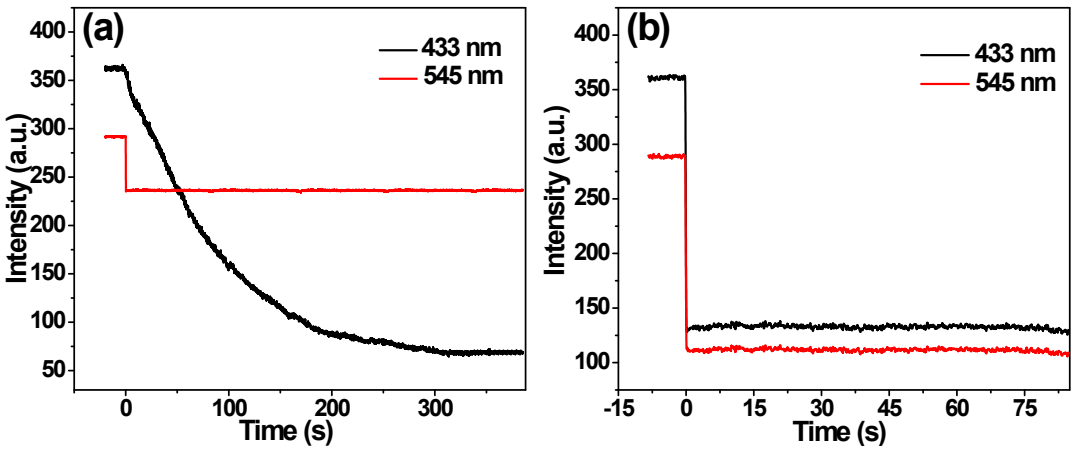

Fig. S5 Temporal fluorescent change of Tb@UiO-66-$(COOH)_2NH_2$-40 emission intensity upon the addition of (a) *o*-TCBQ (100 μM) and (b) *p*-TCBQ (100 μM). 50 mg L^{-1} MOF, in H_2O-ethanol mixed solvent (v/v = 3/1), λ_{ex}=290 nm.

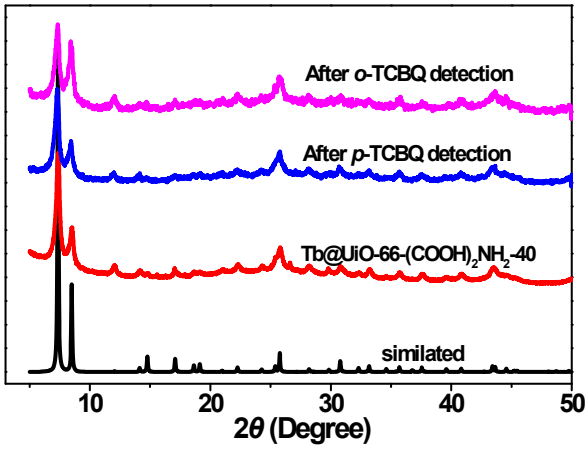

Fig. S6 Comparison among the PXRD patterns of Tb@UiO-66-$(COOH)_2NH_2$-40 before and after the detection of *o*- and *p*-TCBQs.

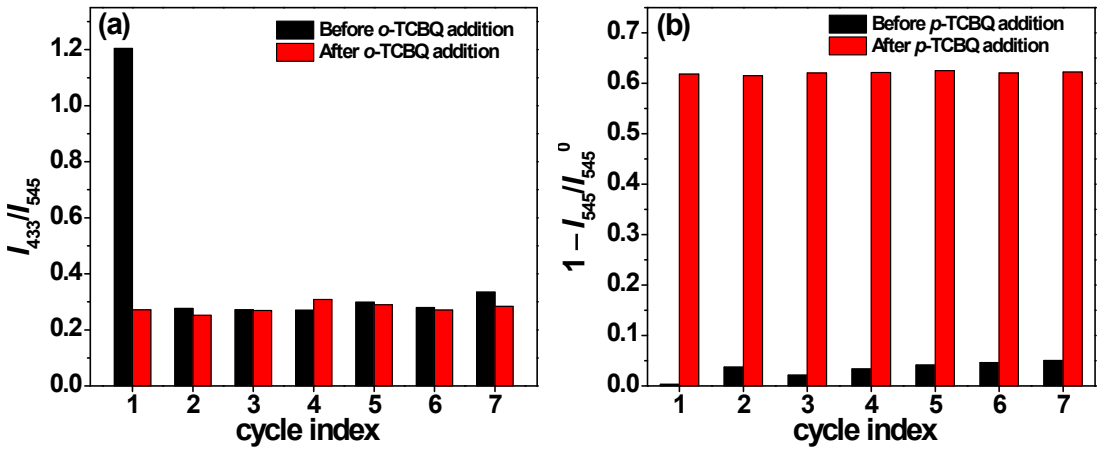

Fig. S7 Fluorescent signals of Tb@UiO-66-$(COOH)_2NH_2$-40 during 7 consecutive detection and generating cycles with the analyte of (a) *o*-TCBQ (100 μM) and (b) *p*-TCBQ (100 μM). 50 mg L^{-1} MOF, in H_2O-ethanol mixed solvent (v/v = 3/1), λ_{ex}=290 nm.

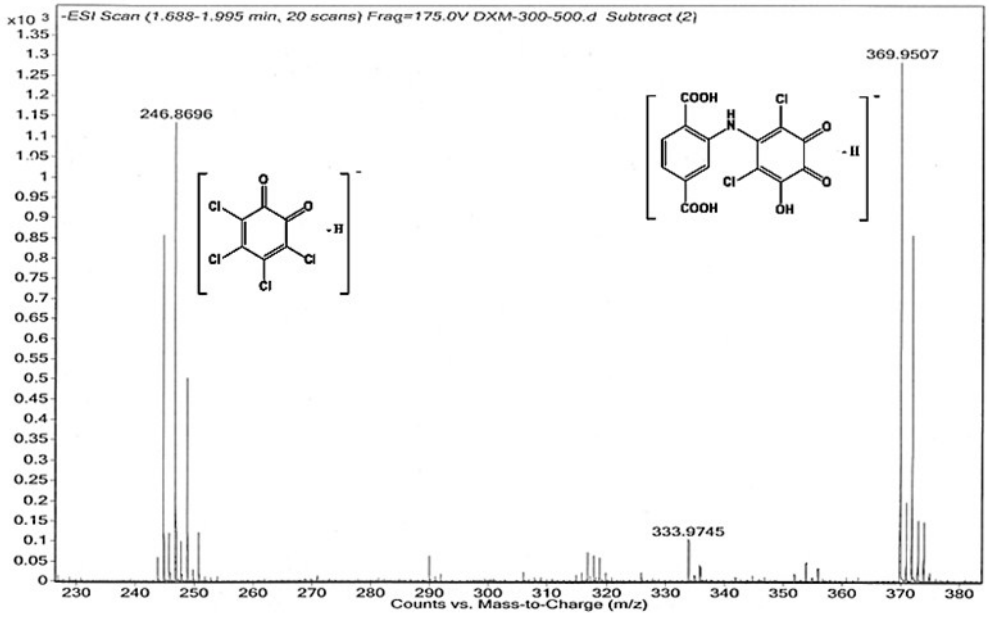

Fig. S8 ESI-MS (negative mode) of the digested solution of UiO-66-NH_2 after the treatment by *o*-TCBQ.

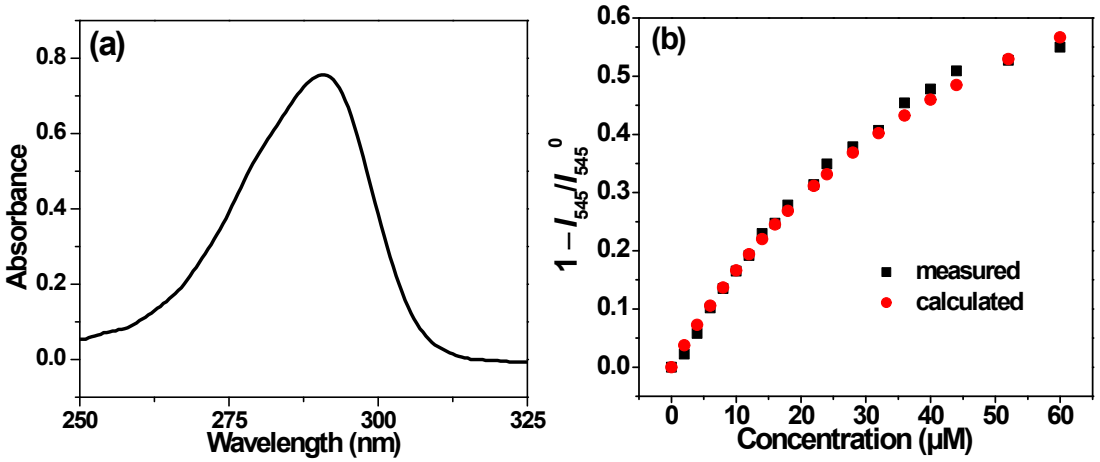

Fig. S9 (a) Absorption spectrum of *p*-TCBQ (50 μM). (b) Comparison between the calculated and measured quenching efficiency of Tb@UiO-66-$(COOH)_2NH_2$-40 (50 mg L^{-1}) upon the exposure to different concentrations of *p*-TCBQ, λ_{ex}=290 nm.

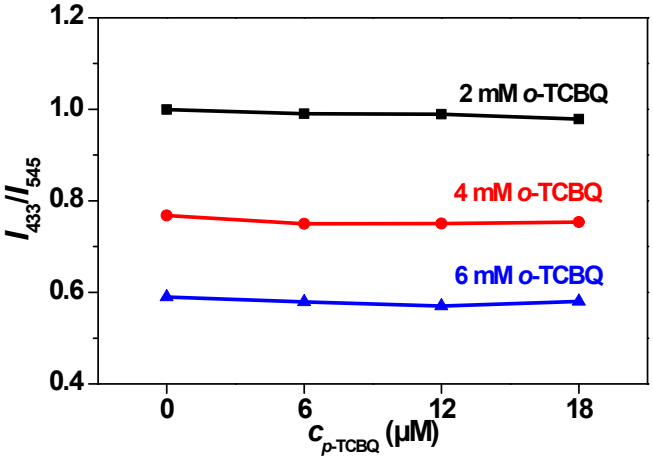

Fig. S10 Effect of *p*-TCBQ on the ratiometric fluorescent signal induced by *o*-TCBQ, λ_{ex} = 290 nm.

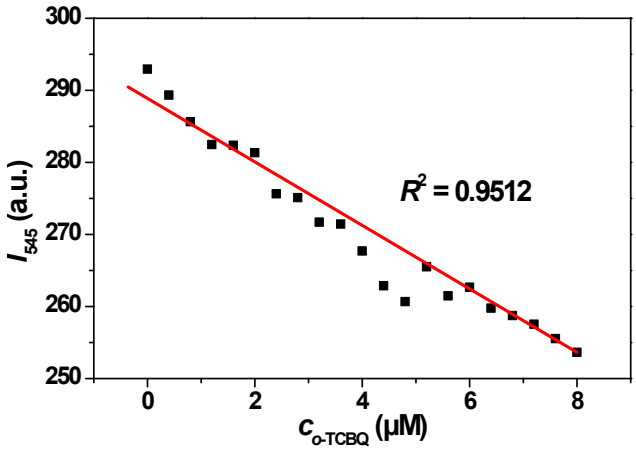

Fig. S11 Linear fitting of the intensity change of Tb@UiO-66-$(COOH)_2NH_2$-40 at 545 nm with the addition of different concentrations of *o*-TCBQ.

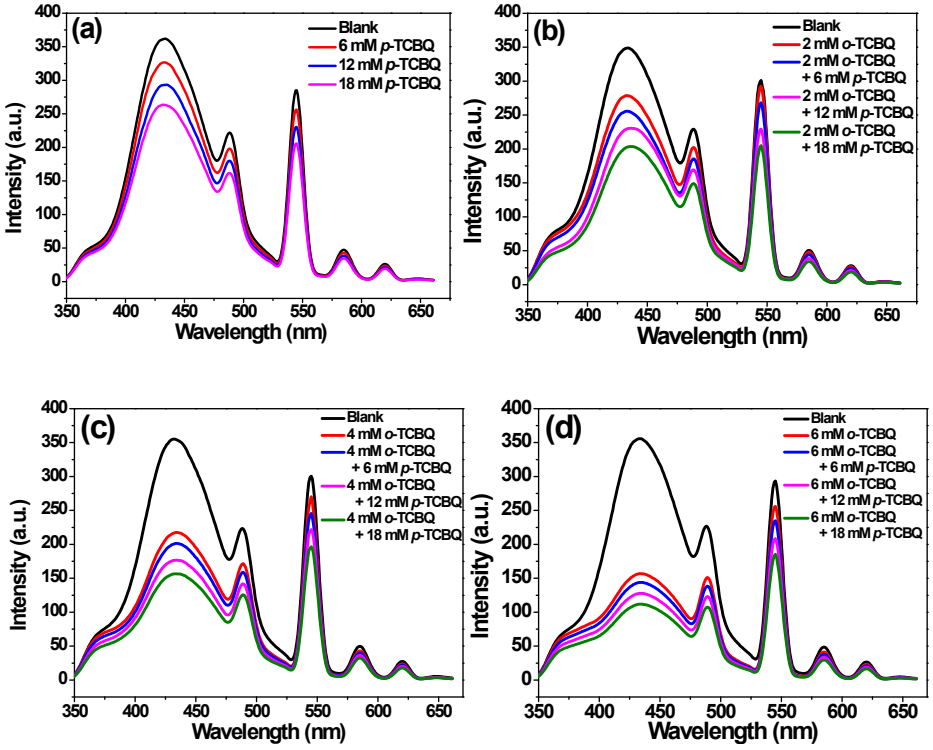

Fig. S12 The photoluminescent spectra of Tb@UiO-66-$COOH_2NH_2$-40 (50 mg L^{-1}) in the mixed solutions of *o*- and *p*-TCBQs, λ_{ex} = 290 nm.

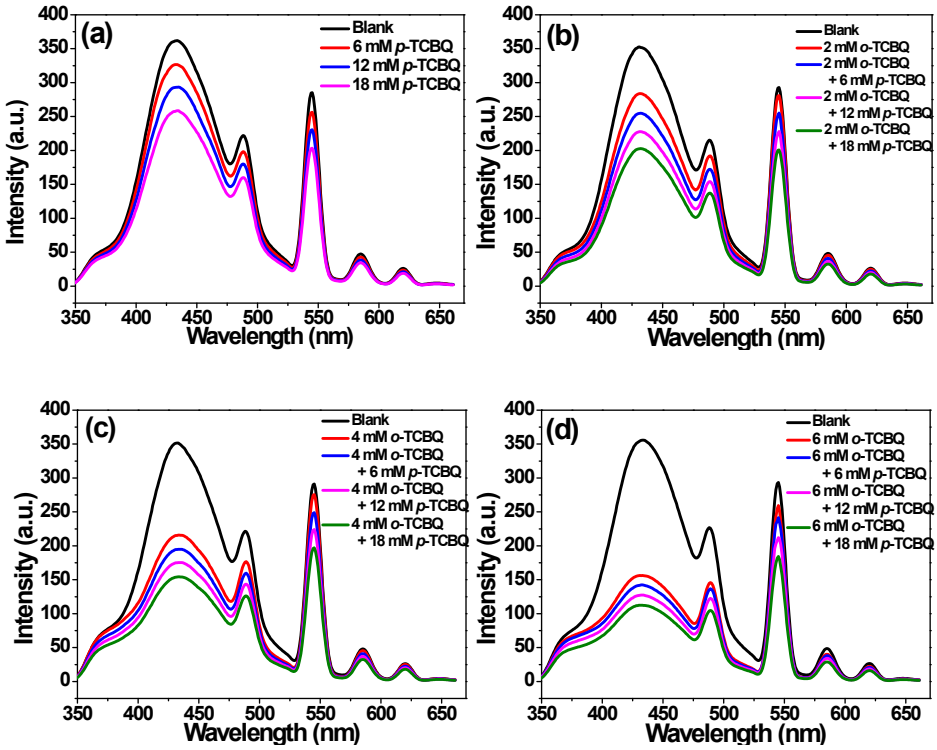

Fig. S13 The photoluminescent spectra of Tb@UiO-66-$COOH_2NH_2$-40 (50 mg L^{-1}) in artificial urine under the addition of different concentrations of *o*- and *p*-TCBQs, λ_{ex} = 290 nm.

Table S1 The ICP-OES results of Tb@UiO-66-$(COOH)_2NH_2$-40 before and after detection experiment

Material	Zr (Wt%)	Tb (Wt%)	Molecular ratio Zr:Tb
As-prepared	13.7	4.82	2.84:1
After *o*-TCBQ detection	11.36	4.04	2.81:1
After *p*-TCBQ detection	12.90	4.62	2.79:1