Supporting Information

Charged ligand-driven photoluminescent sensing enhancements in terbium-modified two-dimensional metal–organic frameworks

Ya-Mei Weng[a], Tzu-Chi Lin[a], Chi-Lun Chuang[a], Yin-Chu Tai[a] and Chung-Wei Kung*[a,b]

[a] Department of Chemical Engineering, National Cheng Kung University, Tainan City, 70101, Taiwan.

[b] Program on Key Materials, Academy of Innovative Semiconductor and Sustainable Manufacturing, National Cheng Kung University, Tainan City, 70101, Taiwan.

* Email: cwkung@mail.ncku.edu.tw

Table of contents

Section	Page number
Section 1. Experimental Section	S-2
Section 2. Supporting Figures and Tables	S-7
Section 3. References	S-20

Section 1. Experimental Section

1. Chemicals

Benzoic acid (99.5%), iron(III) sulfate hydrate ($Fe_2(SO_4)_3$, 97%), betaine hydrochloride (≥99%), 4-sulfobenzoic acid potassium salt (95%), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.9 atom% D) and sulfuric acid-d_2 solution (D_2SO_4, 96-98 wt.% in D_2O, 99.5 atom% D) were purchased from Sigma-Aldrich. Zirconium(IV) chloride anhydrous ($ZrCl_4$, 98%) was purchased from Acros Organics. Sodium nitrite ($NaNO_2$, 98%), 1,3,5-tri(4-carboxyphenyl)benzene (H_3BTB, 97%) and terbium (III) acetate hydrate (99.9%) were received from Alfa Aesar. N,N-dimethylformamide (DMF, ≥99.8%) and dimethyl sulfoxide (DMSO, 99%) were obtained from Duksan Pure Chemicals. Hydrochloric acid (HCl, 36.5%-38.0%) was purchased from J. T. Baker. Hydrogen peroxide solution (H_2O_2, 30–31%), sulfuric acid (H_2SO_4, 95.0–98.0%), and nitric acid (HNO_3, ≥65%) were obtained from Honeywell Fluka. Acetone (98%) and ethanol (99.5%) were obtained from ECHO Chemical Co, Ltd., Taiwan. Information regarding other salts used for interferent tests can be found in our previous studies.[1, 2] Deionized water was used as the water source through the whole work.

2. Synthesis of ZrBTB

ZrBTB was synthesised by the procedure reported in our previous studies.[1, 3] First, 100 mg of $ZrCl_4$ (0.429 mmol), 100 mg of H_3BTB (0.228 mmol), 6 g of benzoic acid (49.1 mmol), 5 mL of water and 30 mL of DMF were added into a DURAN® glass laboratory bottle (100 mL). The mixture was sonicated for 10 min and subsequently heated at 120 °C for 48 h in an oven. After cooling the mixture to room temperature, the white precipitate was washed with 35 mL of fresh DMF three times by centrifugation to remove the excessive reagents. The MOF powder was then obtained after the solvent exchange with acetone three times, with immersing periods of 2 h, overnight, and 2 h in between, respectively. The obtained powder was activated in a vacuum oven at 60 °C overnight, and the sample was named as “BA-ZrBTB”.

To remove the coordinated benzoate from the hexa-zirconium nodes of BA-ZrBTB, 100 mg of BA-ZrBTB was dispersed in a solution containing 30 mL of DMSO, 0.8 mL of 12 M HCl (aq) and 0.4 mL of water, and the mixture was maintained at room temperature for 18 h. Thereafter, the solid product was washed with 35 mL of fresh DMSO four times by centrifugation over the course of 8 h, followed by acetone solvent exchange three times as described above. Finally, the product was activated under vacuum at 60 °C overnight to give the activated material, "ZrBTB".

3. Synthesis of SO_3-ZrBTB and TMA-ZrBTB

Solvent-assisted ligand incorporation (SALI) was employed to coordinate the positively charged ligand with sulfonate group or the negatively charged ligand with trimethylammonium group on the six-connected heza-zirconium node of ZrBTB.[4] It should be noticed that both the same ligands, betaine hydrochloride and 4-sulfobenzoic acid potassium salt, have been installed onto the nodes of another 3D Zr-MOF with six-connected nodes, MOF-808, in our previous studies.[5, 6] In brief, 50 mg of ZrBTB was ultrasonically dispersed in a solution containing 117.4 mg of 4-sulfobenzoic acid potassium salt (0.488 mmol; 18 equivalents of 50 mg of ZrBTB)[1] and 18 mL of DMF in a scintillation vial. After sealing the vial, the mixture was placed in an oven at 60 °C for 24 h. The obtained solid was separated from the solution and washed with 35 mL of DMF three times through centrifugation. The solvent-exchange process with 35 mL of acetone was then performed three times overnight, similar to that used during the synthesis of ZrBTB. After drying the resulting solid in a vacuum oven at 60 °C overnight, the "SO_3-ZrBTB" powder was obtained. For the preparation of trimethylammonium-functionalised ZrBTB, the same procedure was followed except that 4-sulfobenzoic acid potassium salt was replaced by 75 mg of betaine hydrochloride (0.488 mmol; 18 equivalents of the MOF), and DMF was replaced by 18 mL of ethanol in order to solubilise the ligand. After washing the solid product with 35 mL of ethanol three times, solvent exchange with 35 mL of acetone three times, and the vacuum activation as described above, "TMA-ZrBTB" was obtained.

4. Synthesis of Tb-Zr-BTB, Tb-SO_3-ZrBTB and Tb-TMA-ZrBTB

To further install terbium ions in ZrBTB, SO_3-ZrBTB and TMA-ZrBTB, solvothermal deposition in MOFs (SIM) was employed.[7] The similar SIM process with terbium ions and ZrBTB has been utilised in our previous studies.[1, 2] In brief, 131 mg of terbium(III) acetate hydrate ($Tb(OAc)_3$; 0.390 mmol) was dissolved in 12 mL of DMF by ultrasonication to obtain a colourless solution. Thereafter, 40 mg of each 2D MOF powder (ZrBTB, SO_3-ZrBTB or TMA-ZrBTB) was fully dispersed in the obtained solution by ultrasonication, and the mixture was heated at 120 °C for 18 h. The resulting solid was washed with 12 mL of fresh DMF three times by centrifugation to remove the uncoordinated terbium precursor from the MOF solid. The solid was thereafter subjected to the solvent-exchange process with 12 mL of acetone three times over the course of overnight. After activating the solid in a vacuum oven at 60 °C overnight, the resulting materials were named as "Tb-ZrBTB", "Tb-SO_3-ZrBTB" and "Tb-TMA-ZrBTB", respectively.

5. PL experiments

A FluoroMax® spectrometer (HORIBA Scientific) was used for all PL measurements. For all PL measurements of suspensions, 4.0 mg of the activated MOF solid was accurately weighed and ultrasonically dispersed in 10 mL of ethanol. Thereafter, 1.5 mL of the obtained suspension of MOF was mixed with 1.5 mL of water in a cuvette for the following PL measurements. The concentration of MOF in all suspensions subjected to PL measurements is 0.2 mg mL^{-1}, and the slit size of 1 nm was used for all measurements with suspensions.

For measuring the PL quantum yield (PLQY), the same FluoroMax® spectrometer equipped with a PLQY integrating sphere (QuantaPhi-2) was used, and the solid MOF powder was packed into a sample tray of QuantaPhi-2.

For sensing experiments toward nitrite ions and Fe^{3+} ions, the 1.5 mL of water in the above procedure was replaced by 1.5 mL of the aqueous solution containing a certain concentration of the targeted analyte ($NaNO_2$ or $Fe_2(SO_4)_3$). After mixing the sample, the PL spectrum was collected at the excitation wavelength of 310 nm. Calibration lines for both nitrite ions and Fe^{3+} ions were obtained by recording the emission intensity of terbium at 543 nm in the presence of various concentrations of analyte in the tested samples. Stern–Volmer equation was then used to obtain the linear relationship,[8]

$$\frac{I_0}{I} = 1 + K_{sv}[C] \tag{1}$$

where I_0 is the emission intensity of sample without adding the analyte, I represents the emission intensity of sample at a given concentration of targeted analyte, and K_{sv} is the Stern-Volmer constant. It should be noted that the concentration of analyte here is defined as the final concentration in the 3-mL mixture.

For interferent tests, a series of aqueous solutions containing common anionic and cationic interferents were employed to evaluate the selectivity of the MOF-based PL sensors.[1, 2] In brief, 4.0 mg of Tb-TMA-ZrBTB or Tb-SO_3-ZrBTB was dispersed in 10 mL of ethanol by sonication, and 1.5 mL of the obtained suspension was mixed with 1.5 mL of the aqueous interferent solution. The final concentration of each interferent in the 3-mL mixture is 10 μM for Tb-TMA-ZrBTB-based nitrite sensing and 100 μM for Tb-SO_3-ZrBTB-based Fe^{3+} sensing, respectively.

6. Stability tests

To test the chemical stability of the 2D MOF, 16 mg of Tb-ZrBTB, Tb-SO_3-ZrBTB or Tb-TMA-ZrBTB was immersed and dispersed in the testing solution containing 40 mL of ethanol and 40 mL of water, with the final concentration of 10 μM of nitrite ions or 100 μM of Fe(III) ions. The mixture was kept at room temperature for 1 h. After the exposure, the MOF solid was collected by centrifugation, washed with the water-ethanol cosolvent three times, and subjected to the solvent exchange with acetone three times over the course of overnight. The thermally activated samples were named as Tb-TMA-ZrBTB(Fe^{3+}), Tb-SO_3-ZrBTB(Fe^{3+}), Tb-ZrBTB(Fe^{3+}), Tb-TMA-ZrBTB(NO_2^-), Tb-SO_3-ZrBTB(NO_2^-) and Tb-ZrBTB(NO_2^-), respectively.

7. Instrumentations

Powder X-ray diffraction (PXRD) patterns of samples were measured using a SmartLab (Rigaku) with CuKα radiation (λ = 0.15406 nm). Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements were conducted by using a JY 2000–2 spectrometer (Horiba Scientific). For preparing the ICP-OES sample, approximately 2.5 mg of the terbium-functionalised MOF powder was placed in a microwave vial (2–5 mL, Biotage). Then, 0.75 mL of concentrated H_2SO_4 and 0.25 mL of 30% H_2O_2 solution were added to the vial. The vial was crimped, and the mixture was sonicated for 10 min and subsequently digested using a Biotage® Initiator+ microwave reactor at 150 °C for 20 min. After the completion of the digestion, the resulting solution was diluted to 40 mL with 3% nitric acid prior to ICP–OES measurements. ^{1}H nuclear magnetic resonance (NMR) spectra were collected by a Bruker AVANCE 600NMR spectrometer. For NMR sample preparation, around 0.5 mg of SO_3-ZrBTB, TMA-ZrBTB, Tb-SO_3-ZrBTB or Tb-TMA-ZrBTB was digested in 100 μL of concentrated D_2SO_4 by sonication, and 0.7 mL of DMSO-d_6 was further added into the solution. The resulting mixture was thereafter transferred into an NMR tube to collect ^{1}H NMR spectra. Nitrogen adsorption-desorption isotherms were collected at 77 K using a 3FLEX (Micromeritics) after degassing the powder samples overnight at 110 °C with a VacPrep (Micromeritics). Fourier transform infrared (FTIR) measurements were performed on a Nicolet 6700 (Thermo Fisher Scientific). A JEM-1400 Flash (JEOL) was used to collect transmission electron microscopic (TEM) images and corresponding energy-dispersive X-ray spectroscopic (EDS) data under an operative voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) spectra were collected using a Theta Probe angle-resolved XPS spectrometer (Thermo Fisher Scientific). All spectra were corrected by referencing the C 1s peak to 284.8 eV. Zeta-potential measurements of MOF suspensions in water were performed using an ELSZ-2000ZS (Otsuka).

Section 2. Supporting Figures and Tables

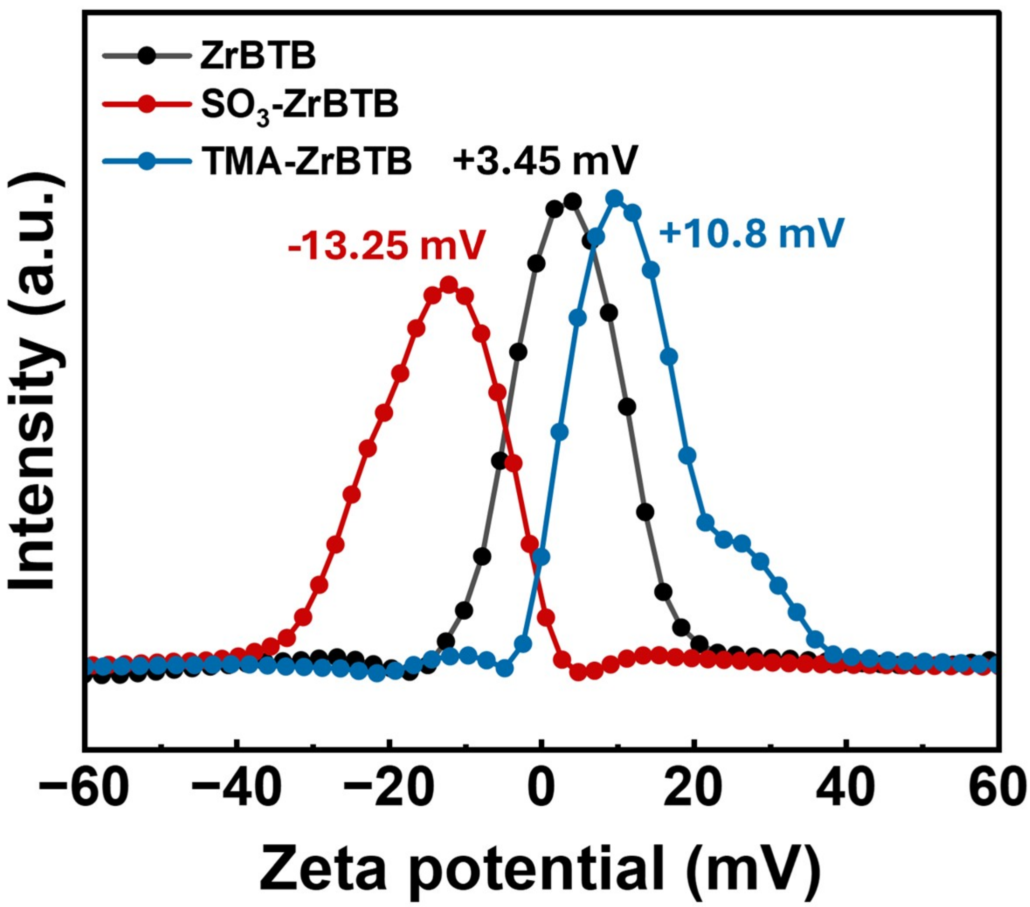

Figure S1. Zeta-potential data of MOFs with and without charged ligands, dispersed in water with a concentration of 0.1 wt%.

Digested MOF samples were subjected to NMR experiments to quantify their loadings of coordinated ligands. Results are plotted in Figure S2 and Figure S3. The intense peak at around 7.9 ppm originates from fifteen protons in the H_3BTB linker.[1, 9, 10] A small peak from residual formate ligands, which should come from DMF during the MOF growth and coordinate on the hexa-zirconium clusters of the Zr-MOF,[11] can be found in all spectra as well. For the SO_3 ligand, 4-sulfobenzoic acid, two sets of characteristic doublet peaks come from four protons on its phenyl ring.[5] Therefore, from Figure S2(a), it suggests that SO_3-ZrBTB has an average loading of 1.39 SO_3 ligands per BTB linker. It thus leads to a loading of 2.78 ligands per node in SO_3-ZrBTB, as the linker-to-node ratio in ZrBTB is two. On the other hand, for the coordinated TMA ligand, betaine, a characteristic peak at around 4.2 ppm comes from two protons of the single methylene group of betaine.[6] From Figure S2(b), the average loading of TMA ligands in TMA-Zr-BTB was estimated as 2.74 per linker, namely, 5.47 ligands per node. It should be noticed that for ZrBTB possessing six-connected hexa-zirconium nodes, ideally, the maximum loading of monocarboxylic ligands through coordination should be six per node. After the second step of PSM to coordinate terbium ions in both 2D MOFs, as shown in Figure S3(a) and Figure S3(b), the average loadings of ligands significantly decrease to 0.87 ligands per node and 0.75 ligands per node for Tb-SO_3-ZrBTB and Tb-TMA-Zr-BTB, respectively.

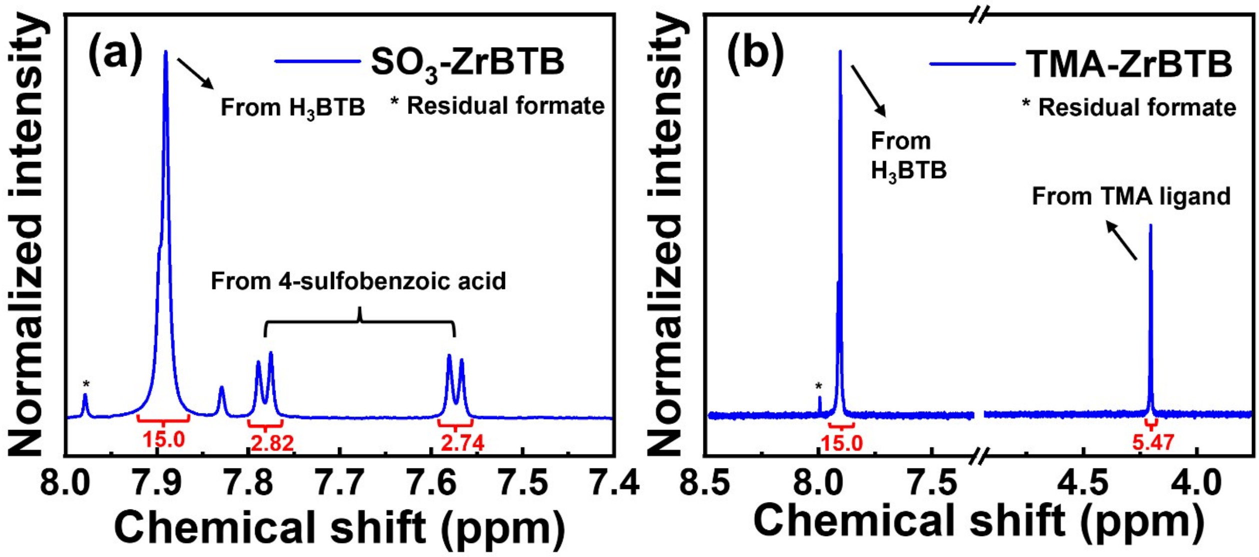

Figure S2. NMR spectra of digested (a) SO_3-ZrBTB and (b) TMA-ZrBTB.

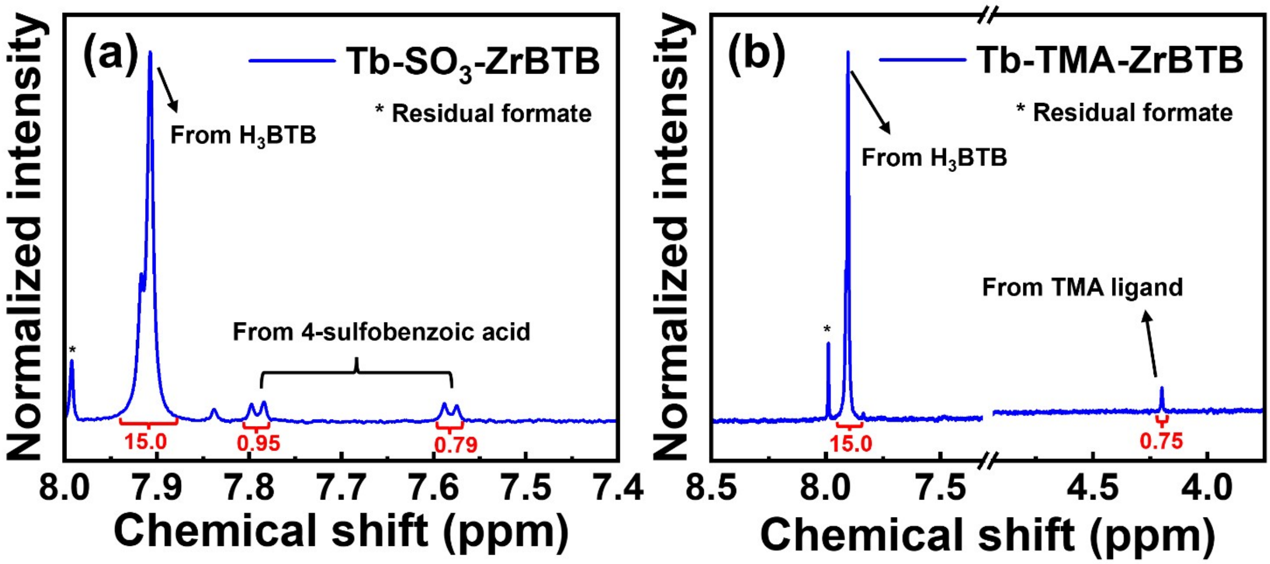

Figure S3. NMR spectra of digested (a) Tb-SO_3-ZrBTB and (b) Tb-TMA-ZrBTB.

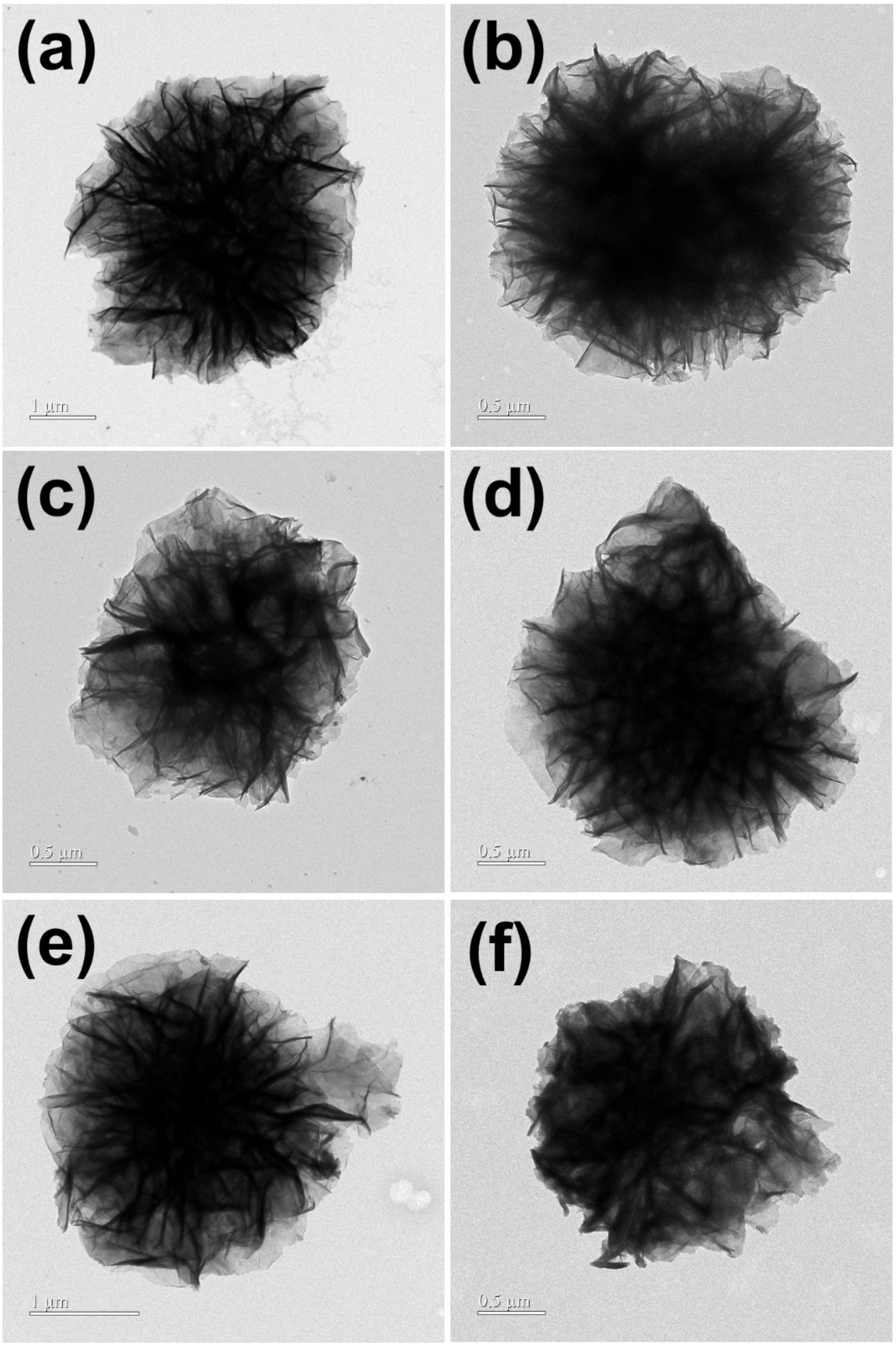

Figure S4. TEM images of (a) ZrBTB, (b) SO_3-ZrBTB, (c) TMA-ZrBTB, (d) Tb-ZrBTB, (e) Tb-SO_3-ZrBTB and (f) Tb-TMA-ZrBTB.

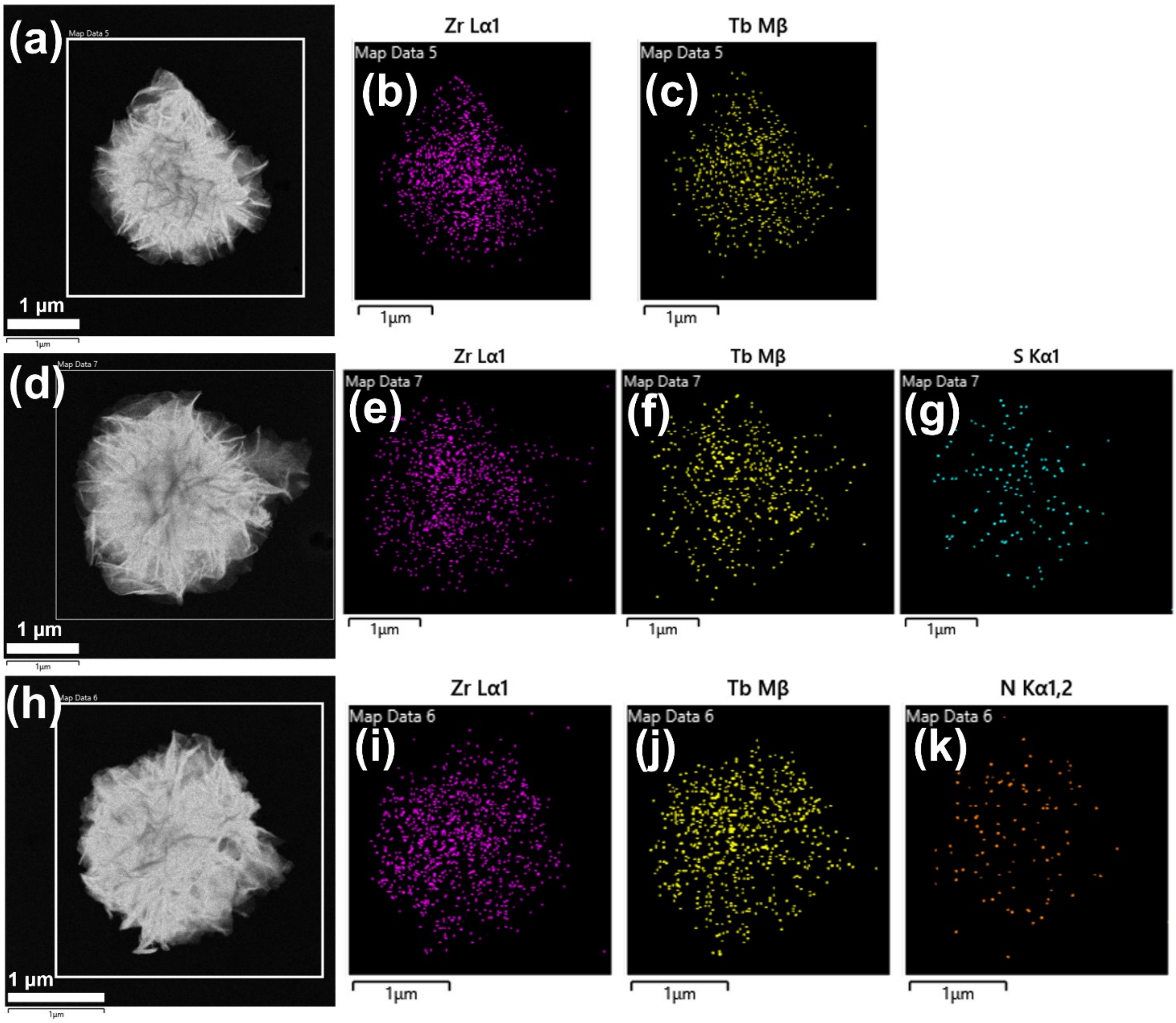

Figure S5. Dark-field scanning TEM images of (a) Tb-ZrBTB, (d) Tb-SO_3-ZrBTB and (h) Tb-TMA-ZrBTB. Elemental distributions from EDS mapping data collected in indicated rectangular regions are shown for (b-c) Tb-ZrBTB, (e-g) Tb-SO_3-ZrBTB and (i-k) Tb-TMA-ZrBTB.

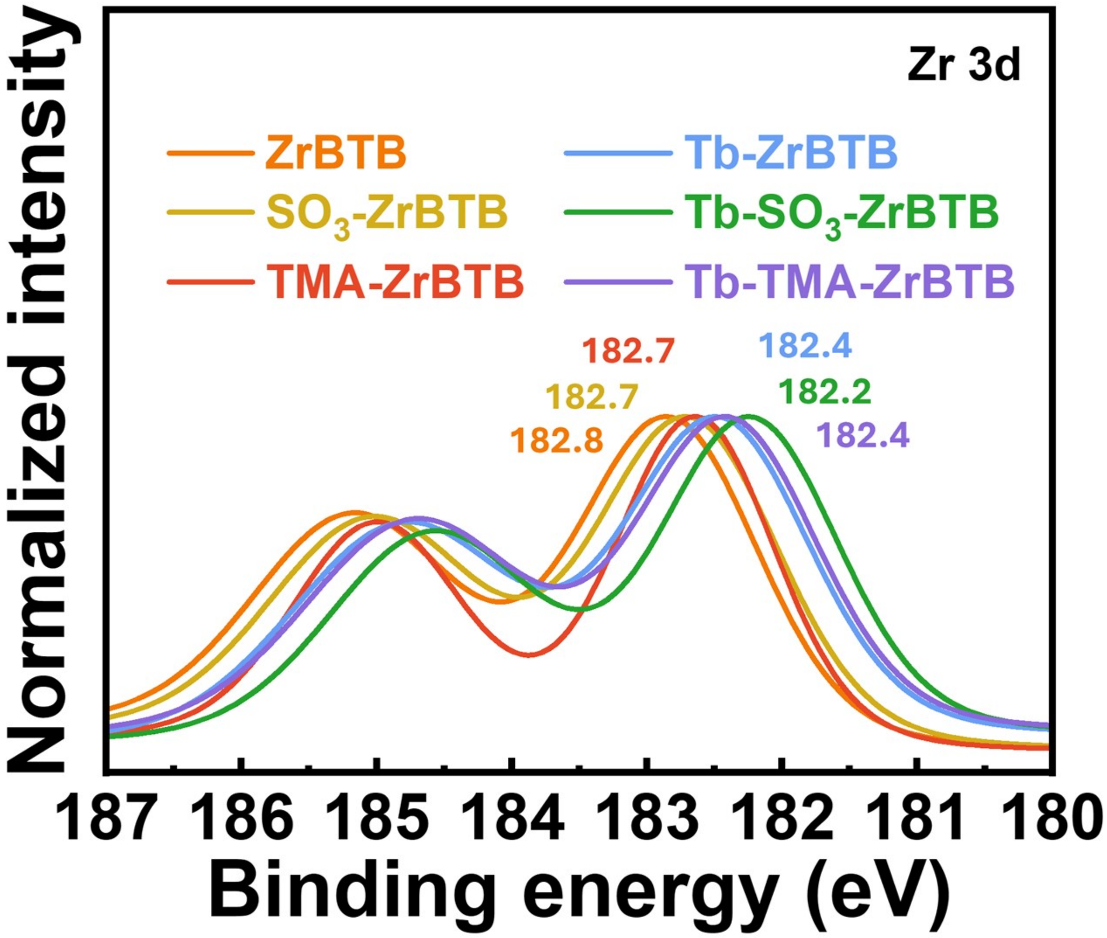

Figure S6. XPS spectra of various MOF materials, collected in the region of Zr 3d. Locations of Zr $3d_{5/2}$ peaks are marked.

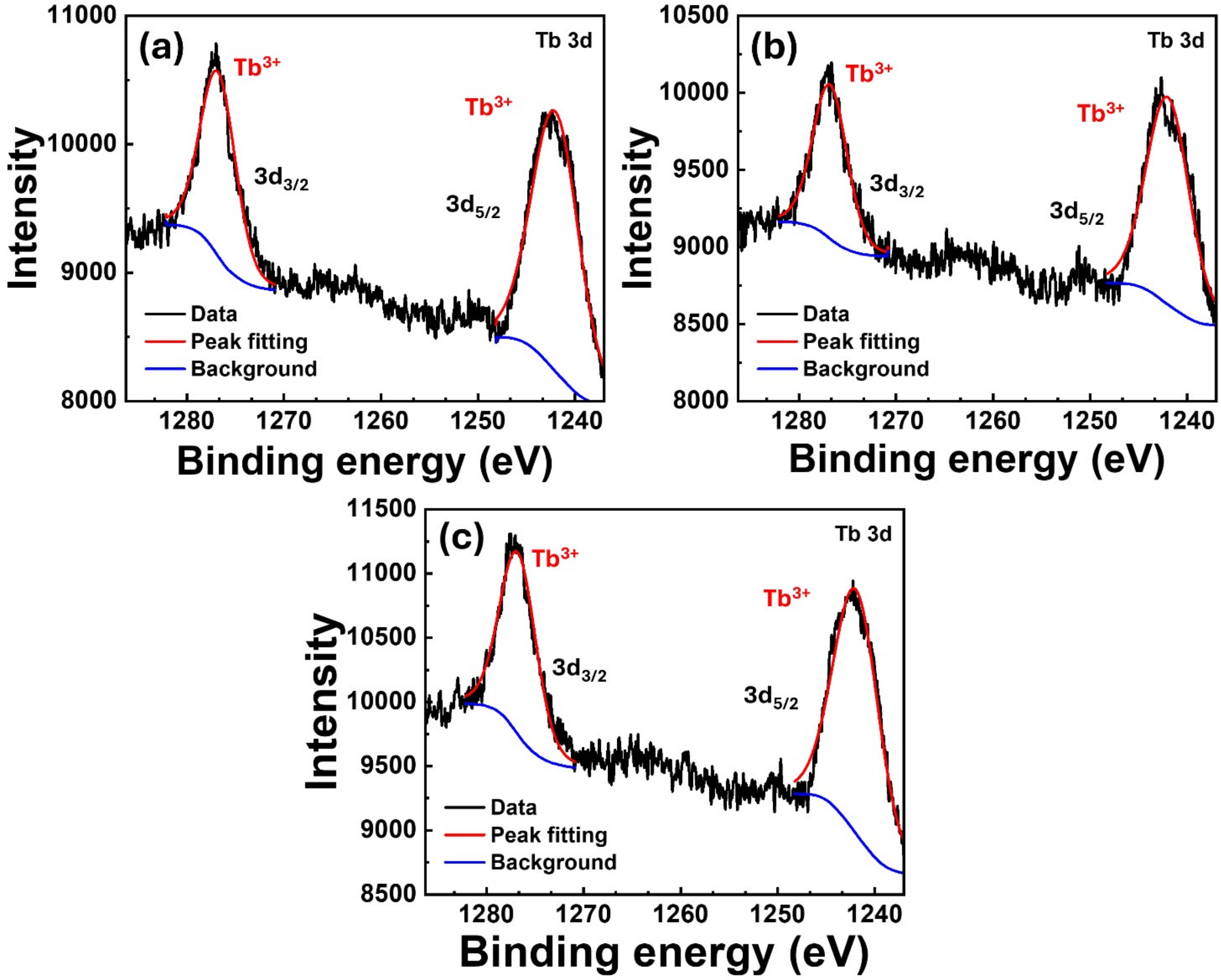

Figure S7. XPS spectra of (a) Tb-ZrBTB, (b) Tb-SO_3-ZrBTB and (c) Tb-TMA-ZrBTB, collected in the region of Tb 3d.

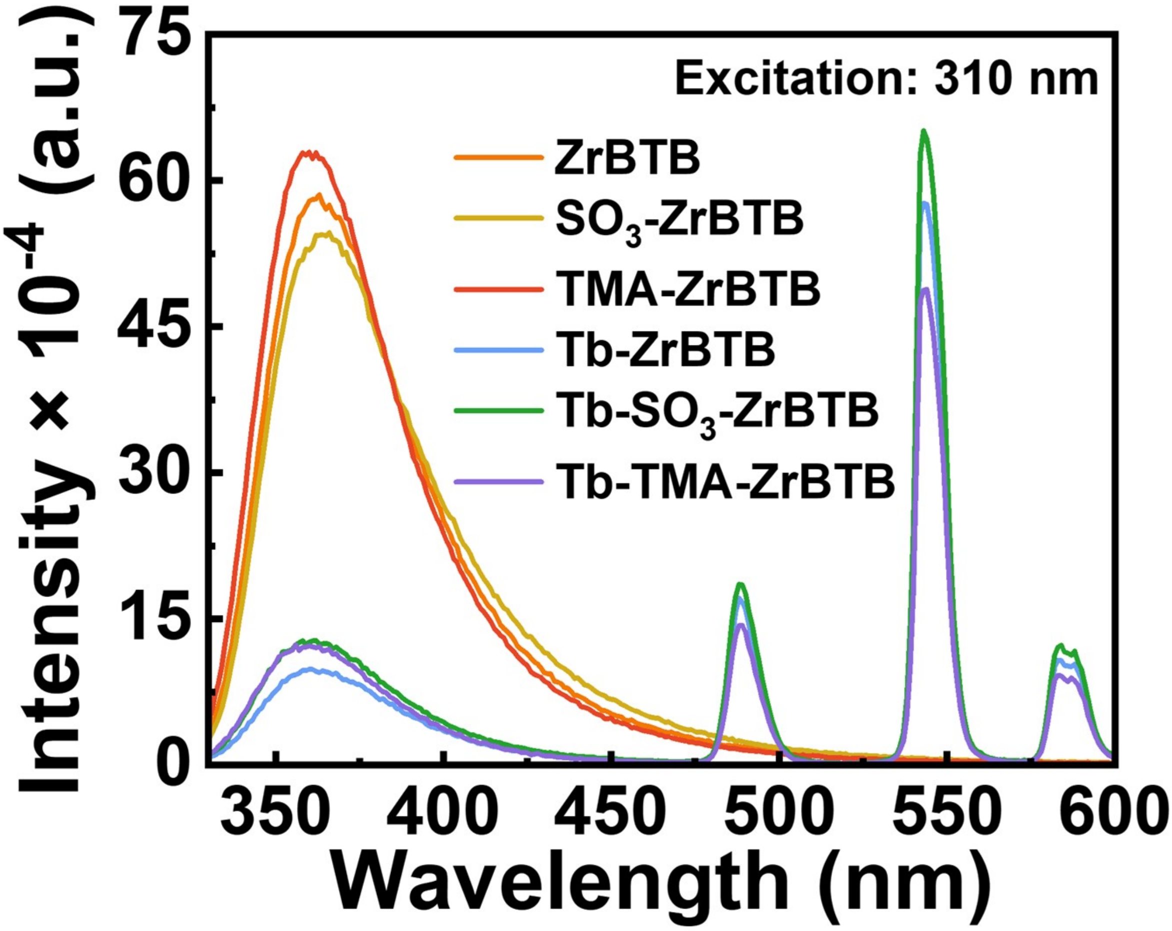

Figure S8. Emission spectra of ZrBTB, SO_3-ZrBTB, TMA-ZrBTB, Tb-ZrBTB, Tb-SO_3-ZrBTB and Tb-TMA-ZrBTB. Excitation at 310 nm was used to collect all spectra, and each sample was dispersed in water and ethanol (v:v = 1:1). The concentration of the MOF-based solid is 0.2 mg mL^{-1}.

Table S1. PLQY values of terbium-functionalised 2D Zr-MOFs from excited BTB linkers to terbium ions, measured under the excitation of the BTB linker at 310 nm.

Material	PLQY of terbium ions between 475 and 630 nm (%)
Tb-ZrBTB	5.3
Tb-SO_3-ZrBTB	5.1
Tb-TMA-ZrBTB	6.0

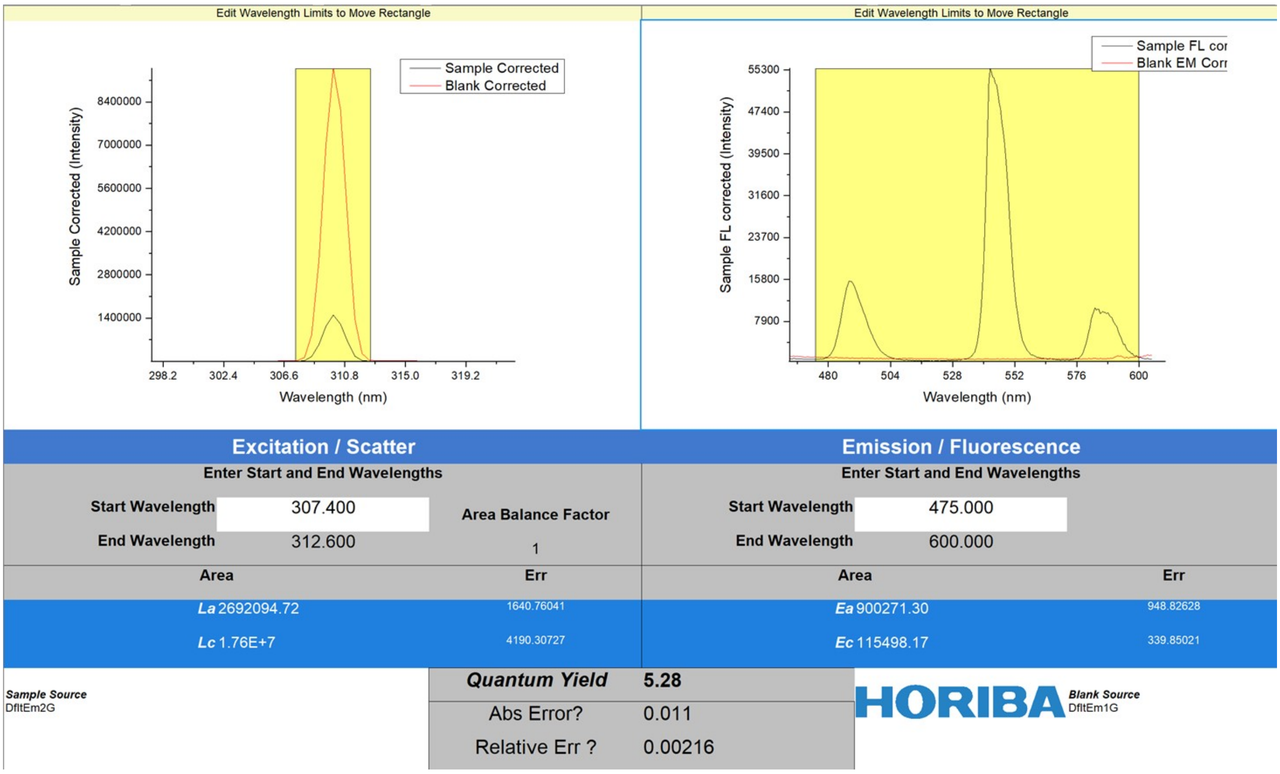

Figure S9. Raw data of the PLQY measurement for the Tb-ZrBTB solid powder, under the excitation at 310 nm. Emissions of lanthanide ions between 475 nm and 630 nm are all considered.

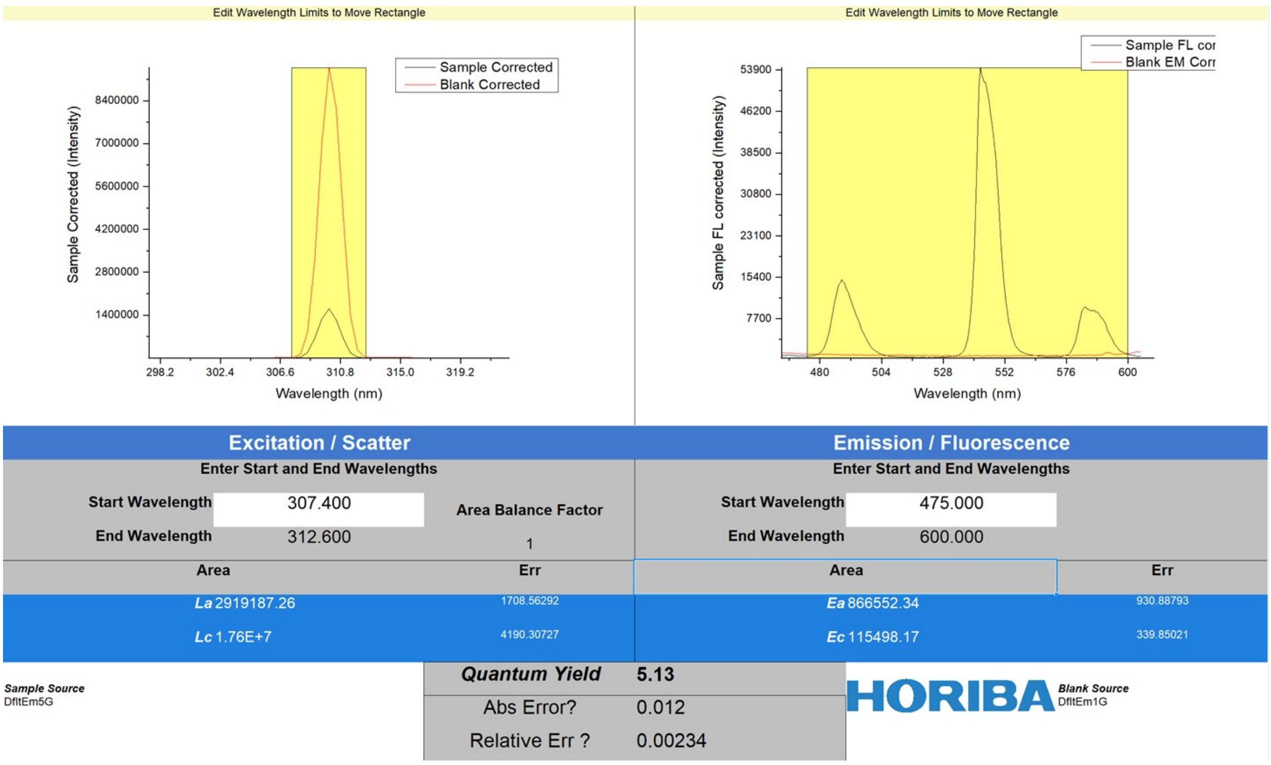

Figure S10. Raw data of the PLQY measurement for the Tb-SO_3-ZrBTB solid powder, under the excitation at 310 nm. Emissions of lanthanide ions between 475 nm and 630 nm are all considered.

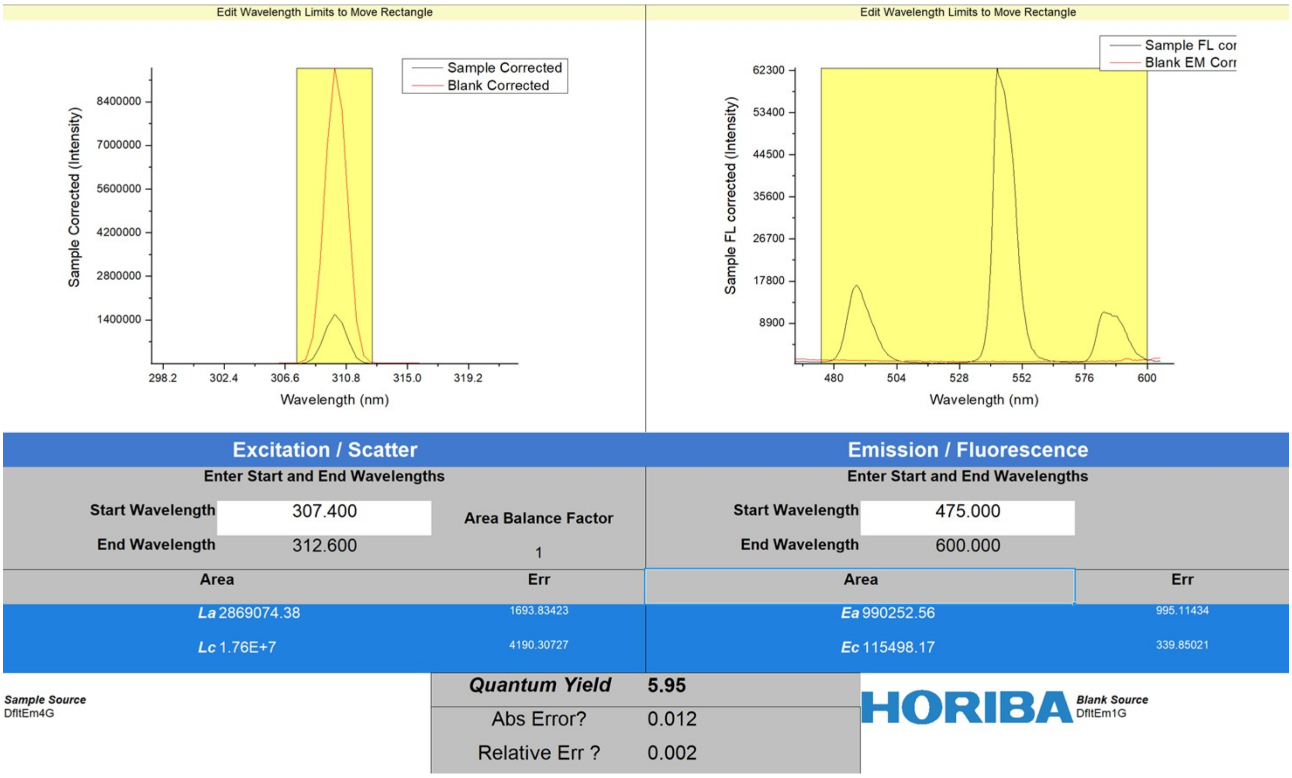

Figure S11. Raw data of the PLQY measurement for the Tb-TMA-ZrBTB solid powder, under the excitation at 310 nm. Emissions of lanthanide ions between 475 nm and 630 nm are all considered.

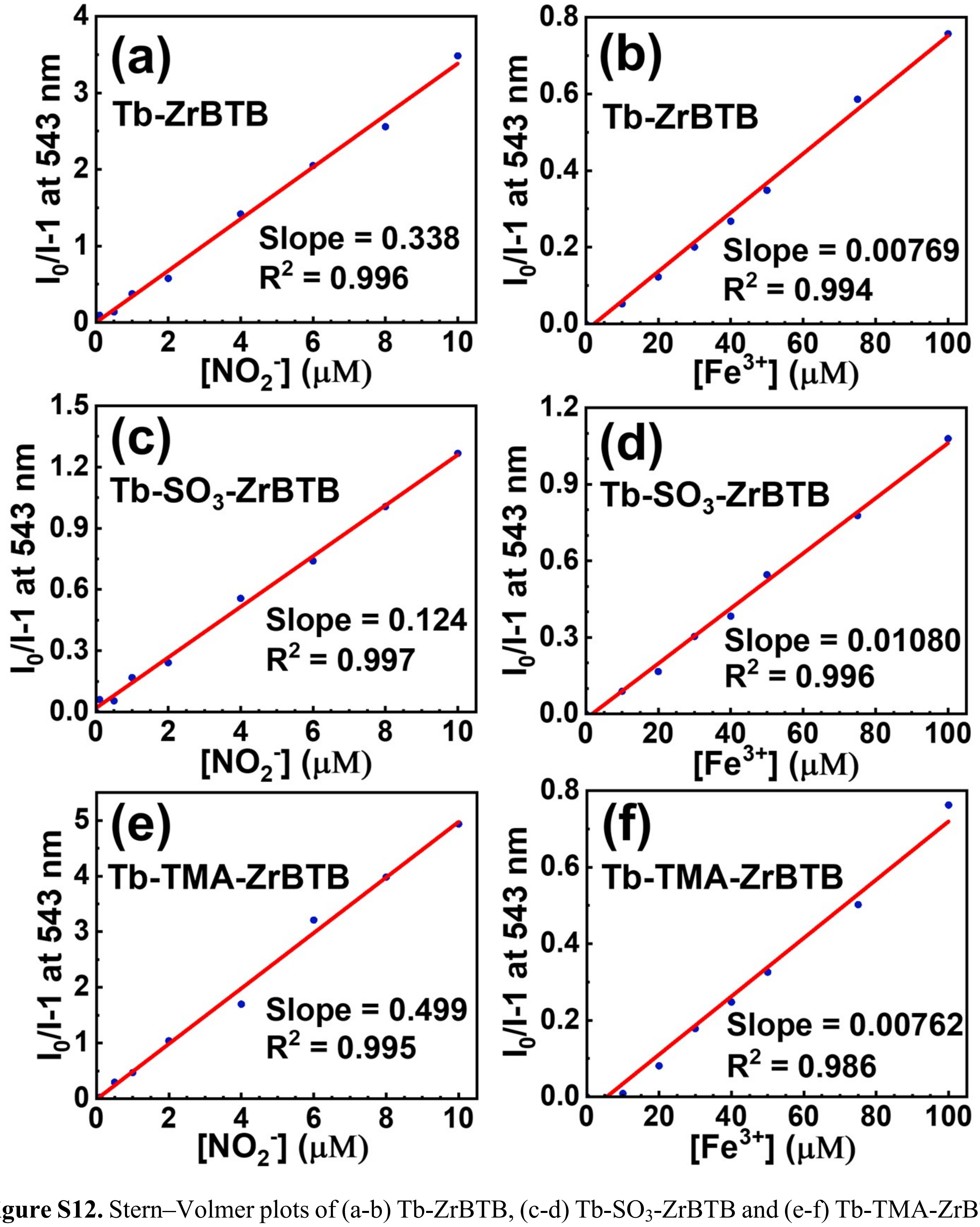

Figure S12. Stern–Volmer plots of (a-b) Tb-ZrBTB, (c-d) Tb-SO_3-ZrBTB and (e-f) Tb-TMA-ZrBTB suspensions for various concentrations of (a,c,e) NO_2^- and (b,d,f) Fe^{3+}. Data points were extracted from the spectroscopic data shown in Figure 3 of the main text.

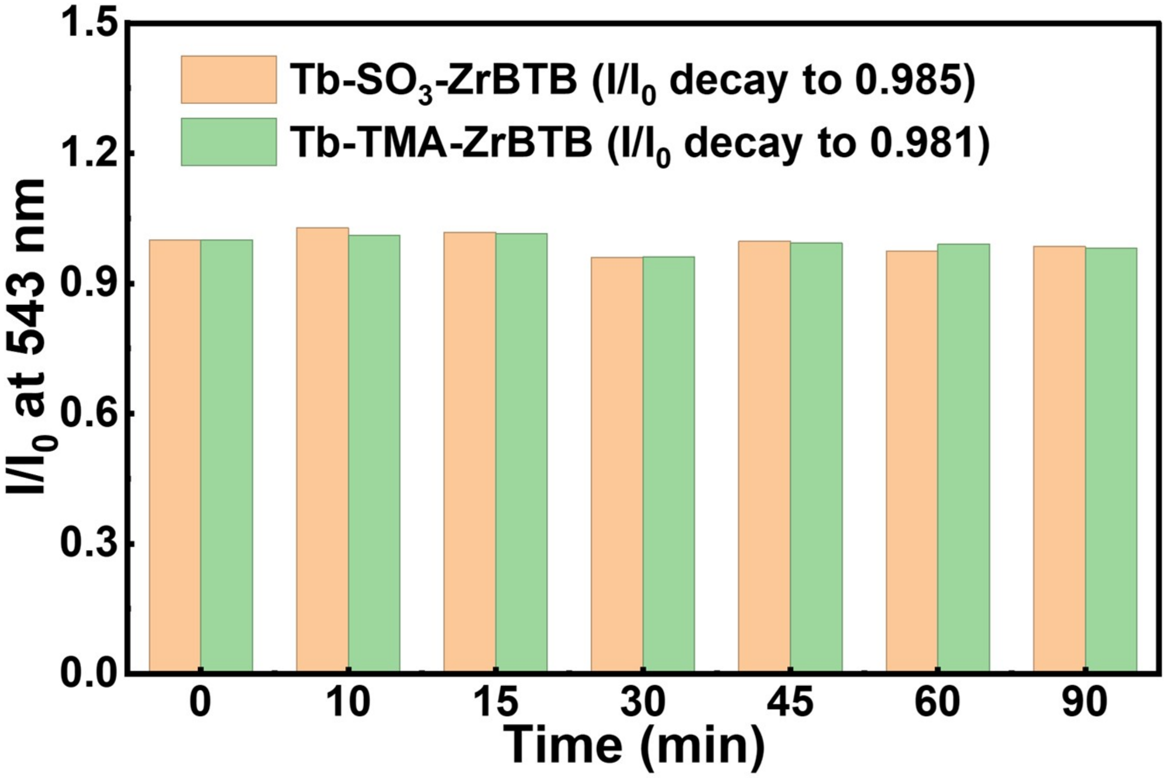

Figure S13. Photoluminescent decay measured from the suspensions of Tb-SO_3-ZrBTB and Tb-TMA-ZrBTB, with a concentration of 0.2 mg mL^{-1} in water/ethanol mixture (v:v = 1:1). Both suspensions were placed at room temperature under static conditions. The emission intensity was extracted at the wavelength of 543 nm. I and I_0 stand for intensity and initial intensity, respectively.

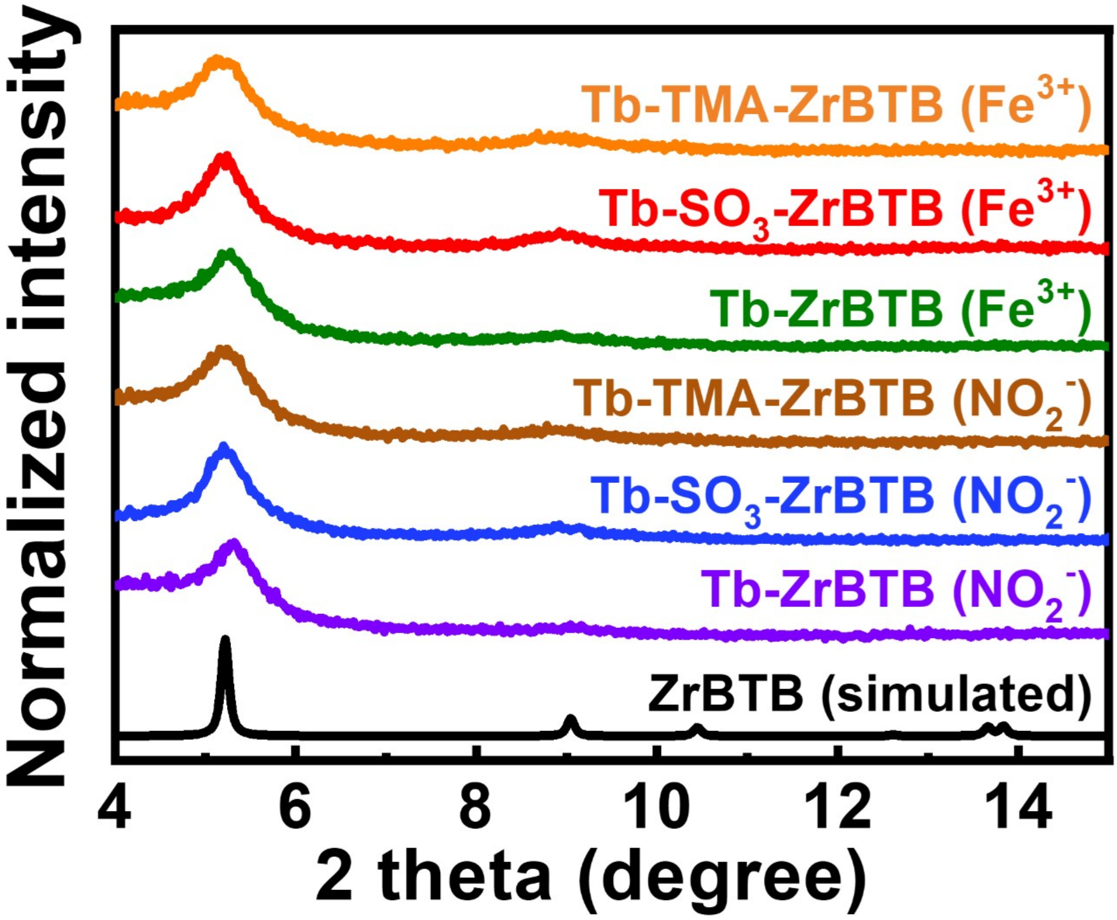

Figure S14. PXRD patterns of materials after the one-hour exposure to Fe^{3+} or NO_2^-. See experimental details for the preparation of these materials in the experimental section.

Section 3. References

1. Y.-L. Chen, C.-H. Shen, C.-W. Huang and C.-W. Kung, *Mol. Syst. Des. Eng.*, 2023, **8**, 330-340.
2. J.-W. Chang, T.-C. Lin, Y.-L. Chen, P.-C. Han, S.-C. Yang, M.-D. Tsai, K. C. W. Wu and C.-W. Kung, *CrystEngComm*, 2024, **26**, 2852-2861.
3. M.-D. Tsai, Y.-L. Chen, J.-W. Chang, S.-C. Yang and C.-W. Kung, *ACS Appl. Energy Mater.*, 2023, **6**, 11268-11277.
4. P. Deria, J. E. Mondloch, E. Tylianakis, P. Ghosh, W. Bury, R. Q. Snurr, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2013, **135**, 16801-16804.
5. Y.-J. Gu, Y.-A. Lo, A.-C. Li, Y.-C. Chen, J.-H. Li, Y.-S. Wang, H.-K. Tian, W. Kaveevivitchai and C.-W. Kung, *ACS Appl. Energy Mater.*, 2022, **5**, 8573-8580.
6. Y.-S. Tsai, S.-C. Yang, T.-H. Yang, C.-H. Wu, T.-C. Lin and C.-W. Kung, *ACS Appl. Mater. Interfaces*, 2024, **16**, 62185-62194.
7. H. Noh, Y. Cui, A. W. Peters, D. R. Pahls, M. A. Ortuño, N. A. Vermeulen, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2016, **138**, 14720-14726.
8. H. Min, Z. Han, M. Wang, Y. Li, T. Zhou, W. Shi and P. Cheng, *Inorg. Chem. Front.*, 2020, **7**, 3379-3385.
9. M. Padmanaban, P. Müller, C. Lieder, K. Gedrich, R. Grünker, V. Bon, I. Senkovska, S. Baumgärtner, S. Opelt and S. Paasch, *Chem. Commun.*, 2011, **47**, 12089-12091.
10. Y.-B. Zhang, H. Furukawa, N. Ko, W. Nie, H. J. Park, S. Okajima, K. E. Cordova, H. Deng, J. Kim and O. M. Yaghi, *J. Am. Chem. Soc.*, 2015, **137**, 2641-2650.
11. Z. Lu, J. Liu, X. Zhang, Y. Liao, R. Wang, K. Zhang, J. Lyu, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2020, **142**, 21110-21121.