

## Electronic Supplementary Information (ESI)

### Fluorescence Analysis for Characterizing Alkali Stability of Metal-Organic Frameworks: an Informative Complement to X-Ray Diffraction

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## Experimental section

**Physical measurements.** The Fourier transform infrared spectra (FTIR) were recorded on a Nicolet NEXUS 670 spectrophotometer in the 4000 – 500  $\text{cm}^{-1}$  regions, using KBr pellets. The phase purity and chemistry stability of sample were confirmed by powder X-ray diffraction patterns (PXRD), which were carried out on a Rigaku D/Max-2500 diffractometer equipped with a Cu-target tube and a graphite monochromator at 40 kV, 30 mA. Thermogravimetric (TG) analyses were measured using a Mettler Toledo TGA/SDTA851 instrument at the heating rate of 10  $^{\circ}\text{C min}^{-1}$  in the temperature range of 25 – 800  $^{\circ}\text{C}$  under flowing air. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope. Fluorescence spectra were carried out on a Hitachi F-4500 spectrofluorometer. pH of aqueous solution was measured using a PHS-3C acidity meter.

**Materials.** All the reagents were analytical grade and used as purchased.

**CAUTION!** Although not encountered in our experiments, perchloric acid and perchlorate salts are potentially explosive. These substances should be used in small amounts with caution.

**Synthesis of MOFs.** The synthesis of powdered Zr-TCPBP was reported in our previous work.<sup>1</sup>

The nanoscale UiO-66-NH<sub>2</sub> was synthesized according to reported literature<sup>2</sup> with some modification. ZrCl<sub>4</sub> (40.4 mg, 0.173 mmol) was dissolved in DMF (10 mL) with ultrasonic for 10 min. Then, 2-aminoterephthalic acid (31.4 mg, 0.173 mmol) and acetic acid (0.3 mL) were added and the mixture was sonicated again for 10 min

before heating in a blast oven at 120 °C for 24 h. After slowly cooling to room temperature, the obtained mixture was centrifuged (10000 r/min, 5 min) and the yellow powder was washed many times with DMF until the supernatant was colorless making sure to get rid of the excess ligands, and then the obtained precipitate was washed three times with EtOH. Finally, the light yellow powder was dried in vacuum oven at 80 °C for 12 h before further measurements.

**Luminescent Experiments.** Zr-TCPBP (3 mg) was dispersed in different pH aqueous solution (10 mL, pH  $\geq$  4.4) to form a uniform dispersion by the ultrasound method before fluorescence test. pH of aqueous solution was adjusted by adding HClO<sub>4</sub> (0.1 M) or NaOH solution and measured using a pH meter.

UiO-66-NH<sub>2</sub> (1 mg) was suspended in different pH aqueous solution (10 mL, pH  $\geq$  6.9) to form a uniform dispersion by the ultrasound method before fluorescence test. pH-dependent fluorescence response of the saturated solution of 2-aminoterephthalic acid was studied. pH of the saturated solution was adjusted by NaOH solution.

**Stability tests.** A given amount (specified in the main text) of UiO-66-NH<sub>2</sub> or Zr-TCPBP was stirred in aqueous solutions (10 or 100 mL) at different pH (adjusted with NaOH) for 60 min, and then the residue was collected by filtering, washed with water and acetone, and naturally dried for further measurements (PXRD, SEM and TG).

**Calculations of TCPBP/Zr ratios from TG plots.** Assuming that the plateau of the TG curve for an Zr-TCPBP sample before ligand decomposition corresponds to Zr<sub>y</sub>(TCPBP)<sub>x</sub>O<sub>2(y-x)</sub> and that the residue corresponds to ZrO<sub>2</sub>, we have

$$\frac{m_1}{m_2} = \frac{y * M(\text{Zr}) + x * M(\text{TCPBP}) + 2(y - x) * M(\text{O})}{y * M(\text{ZrO}_2)}$$

where  $m_1$  and  $m_2$  are the observed plateau and residue weights, respectively, and  $M$ 's are the formula weight of the compounds or elements in the parentheses. The equation can be easily transformed as follows.

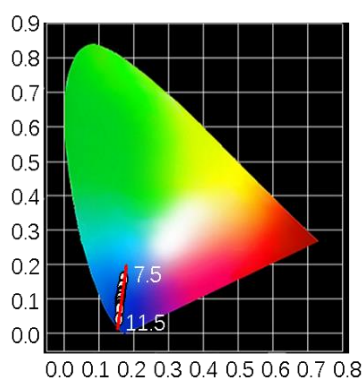
$$\frac{x}{y} = \frac{m_1 - m_2}{4.87m_2}$$

Then the TCPBP-to-Zr atomic ratio ( $x/y$ ) can be obtained from TG plots (Fig. S3).

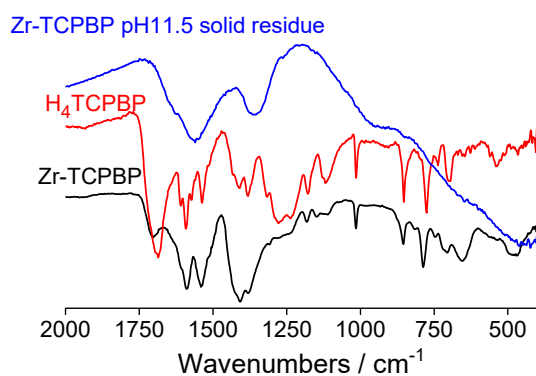
The relevant data are collected in Table S1.

Table S1. Calculations of TCPBP/Zr atomic ratios

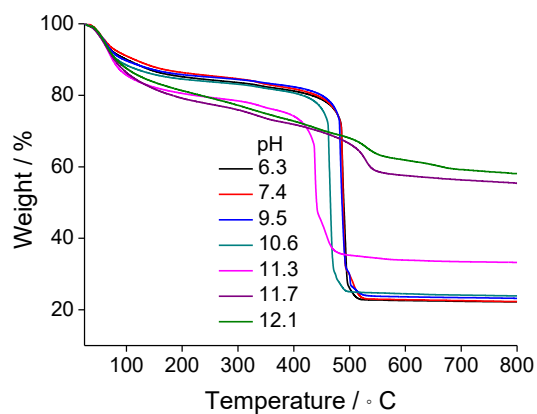
|         | $m_1$  | $m_2$  | TCPBP/Zr |
|---------|--------|--------|----------|
| pH 6.3  | 79.08% | 22.66% | 0.51     |
| pH 7.4  | 79.26% | 22.88% | 0.51     |
| pH 9.5  | 80.41% | 23.75% | 0.49     |
| pH 10.6 | 78.60% | 24.63% | 0.45     |
| pH 11.3 | 73.26% | 33.97% | 0.24     |
| pH 11.7 | 67.93% | 57.02% | 0.04     |
| pH 12.1 | 64.68% | 61.68% | 0.01     |



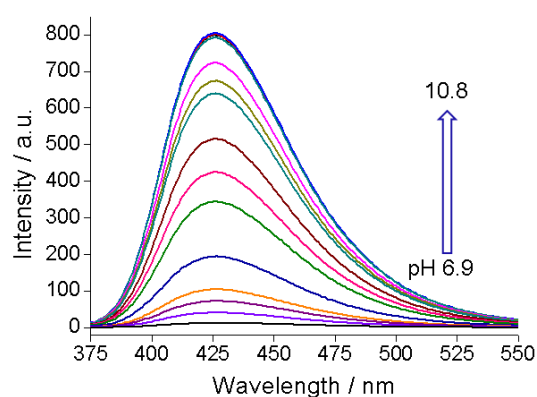
**Fig. S1** The Commission Internationale de l'Éclairage (CIE) chromaticity diagram showing the emission color of Zr-TCPBP aqueous dispersion variation with pH.



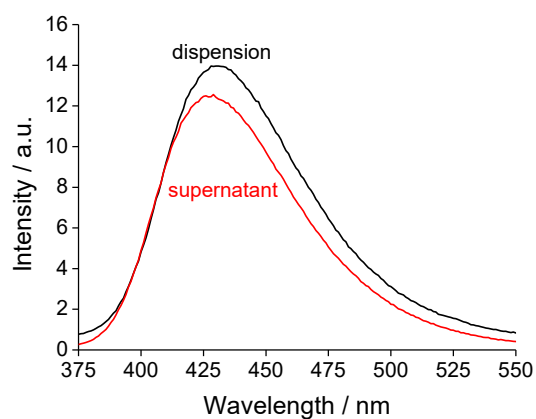
**Fig. S2** FTIR of Zr-TCPBP, H<sub>4</sub>tcpbp and the residue of pH 11.5 suspension.



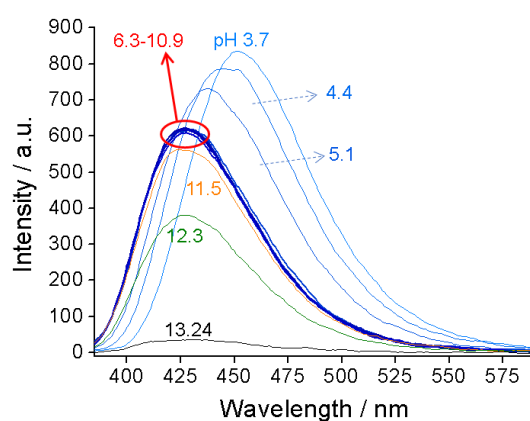
**Fig. S3** Thermogravimetric plot of Zr-TCPBP (30 mg) soaked in 100 mL aqueous solution of different pH and isolated solids.



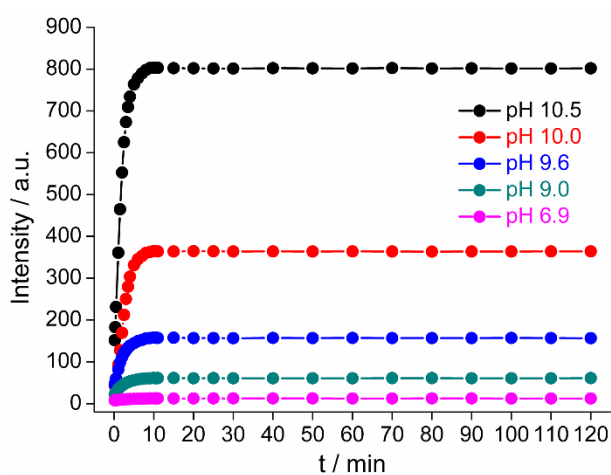
**Fig. S4** Emission spectra of the supernatants obtained by filtering the dispersion of UiO-66-NH<sub>2</sub> at different pH conditions.



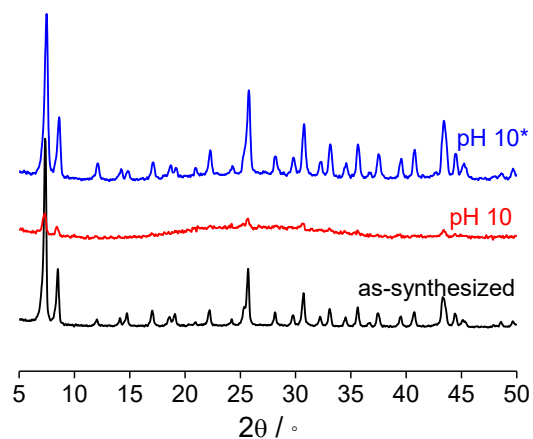
**Fig. S5** Emission spectra of dispersion and corresponding supernatant of UiO-66-NH<sub>2</sub> at pH 6.9.



**Fig. S6** Variation of emission spectra of 2-aminoterephthalic acid solution with pH.



**Fig. S7** Time dependence of the fluorescent intensity (425 nm) of UiO-66-NH<sub>2</sub> dispersed at different pH.



**Fig. S8** PXRD patterns of UiO-66-NH<sub>2</sub> before and after treated with basic solutions at pH 10. 10 mg MOF in 100 mL solution for pH 10, and 20 mg MOF in 100 mL solution for pH 10\*.

## References

1. S.-L. Yang, G. Li, M.-Y. Guo, W.-S. Liu, R. Bu and E.-Q. Gao, Positive Cooperative Protonation of a Metal-Organic Framework: pH-Responsive Fluorescence and Proton Conduction. *J. Am. Chem. Soc.*, 2021, **143**, 8838-8848.
2. J. Aguilera-Sigalat and D. Bradshaw, A colloidal water-stable MOF as a broad-range fluorescent pH sensor via post-synthetic modification. *Chem. Commun.*, 2014, **50**, 4711-4713.