

*Electronic Supplementary Information (ESI)*

**Luminescence turn-on detection by an entanglement-protected MOF  
operating via a divided receptor-transducer protocol**

Xin Lian,<sup>‡a</sup> Yu-Jing Zhou,<sup>‡a</sup> Hai-Feng Zhang,<sup>a</sup> Mian Li<sup>\*ab</sup> and Xiao-Chun Huang<sup>\*ab</sup>

*<sup>a</sup>Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structural Materials of Guangdong Province, Shantou University, Guangdong 515063, China  
E-mail: mli@stu.edu.cn (M.L.); xchuang@stu.edu.cn (X.C.H.)*

*<sup>b</sup>Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China*

**Table of Contents**

Experimental Details.....	2
Materials .....	2
Instrumental techniques .....	2
Synthesis .....	2
Computational Details .....	3
Additional Figures and Measurements .....	4
References.....	13

## Experimental Details

### Materials

All analytical grade chemicals such as copper(I) iodide, polyethylene glycol 200/300/400 and concentrated ammonia (28%) were purchased from commercial source and used without further purification.

### Instrumental techniques

<sup>1</sup>H-NMR spectra were measured on Bruker Advance 400 MHz with tetramethylsilane as the internal standard. Powder X-ray diffraction (PXRD) patterns were recorded on Rigaku MiniFlex 600 diffractometer equipped with a Cu-K $\alpha$  source operating at voltage 40 kV and current 40 mA at the Walter Curlook Materials Characterization & Processing Laboratory at the University of Toronto Department of Materials Science. Thermogravimetric analysis was performed using TA Instruments SDT Q600 instrument in nitrogen flow with heating rate of 5 °C/min from room temperature to 800 °C. Photoluminescence spectra were measured using a QunataMaster spectro-fluorimeter (Photon Technology International, Edison, New Jersey) with a Xenon lamp for steady-state measurements. Sample emission was detected after passing through a spectrometer (iHR320, Horiba) and detected on a single photon detector (PPD, Horiba). The optical images are taken under a Zeiss LSM 800 confocal laser scanning microscope (CLSM) with  $\lambda_{\text{ex}} = 400$  nm. The viscosity value was measured by a NDJ-1 rotary viscometer produced by Shanghai Precision Scientific Instrument Co., Ltd.

### Synthesis

The ligand tetra-(4-pyridylphenyl)ethylene (**tppe**) was synthesized and purified according to the reported procedures.<sup>S1</sup> The Cu<sub>2</sub>I<sub>2</sub>Py<sub>4</sub> complex was synthesized according to the reported procedures.<sup>S2</sup> The synthesis of the MOFs were performed using a different method from that in literature.<sup>S3</sup>

The crystals of [Cu<sub>2</sub>I<sub>2</sub>(**tppe**)]- $\alpha$  was obtained by adding **tppe** (0.128 g, 0.2 mmol) and copper(I) iodide (0.190 g, 1 mmol) in a mixture of MeCN (1 mL) and DMF (2 mL) at then heating at 90 °C for 3 days. The crystals were washed by EtOH and H<sub>2</sub>O. Needle-like yellow crystals were harvested by filtration. Yield: 83% (based on **tppe**).

The crystals of [Cu<sub>2</sub>I<sub>2</sub>(**tppe**)]- $\beta$  was obtained with a method similar to that of  $\alpha$ , except that an additive 1,3,5-trimethylbenzene (0.5 mL) was added. The crystals were washed by EtOH and H<sub>2</sub>O. Rod-like yellow crystals were harvested by filtration. Yield: 63% (based on **tppe**).

## Computational Details

GCMC simulations were performed to calculate the NH<sub>3</sub> sorption at a fixed pressure and fixed loading with an original cell of  $\alpha$  and  $\beta$ , set at 298 K and 100 kPa using the Sorption Module of Materials Studio 7.0.<sup>S4</sup> The non-bonded interatomic interaction was modeled as the combination of Lennard-Jones (LJ) potentials between the atoms in  $\alpha$  and  $\beta$  framework with NH<sub>3</sub>, which were taken from the universal force field. The GCMC simulations consisted of  $1 \times 10^6$  equilibration steps and  $1 \times 10^6$  production steps. To eliminate the boundary effect, the periodic boundary conditions were applied in all three dimensions, and the cutoff radius was set as 18.5 Å.

Periodic DFT calculations were performed to optimize the host-guest system of  $\alpha$ ·NH<sub>3</sub> and  $\beta$ ·NH<sub>3</sub> (primitive cell), and to calculate binding energy of  $\alpha$  and  $\beta$  with NH<sub>3</sub> using Perdew-Burke-Ernzerhof (PBE) method<sup>S5</sup> with Grimme's DFT-D correction<sup>S6</sup> in Forcite and Dmol3 module of Materials Studio 7.0.<sup>S4</sup> The overall binding energy ( $\Delta E$ ) is defined as follow:

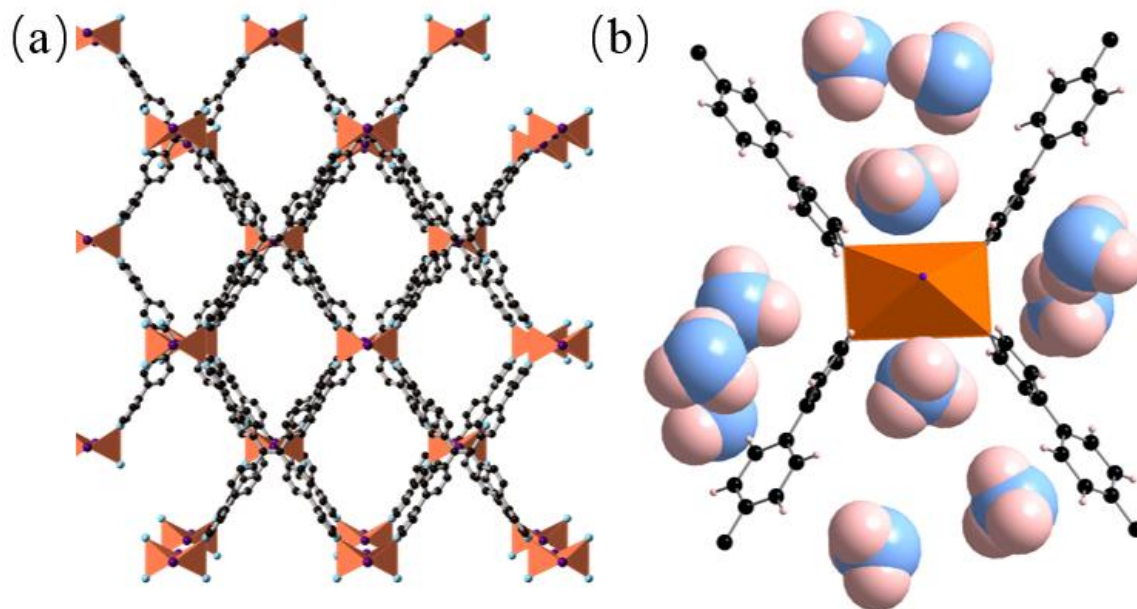
$$\Delta E_{TOTAL} = \Delta E_{GUEST-GUEST} + \Delta E_{HOST-GUEST} = (E_{MOF\_nNH3} - E_{MOF} - nE_{NH3})/n$$

$$\Delta E_{GUEST-GUEST} = (E_{nNH3} - nE_{NH3})/n$$

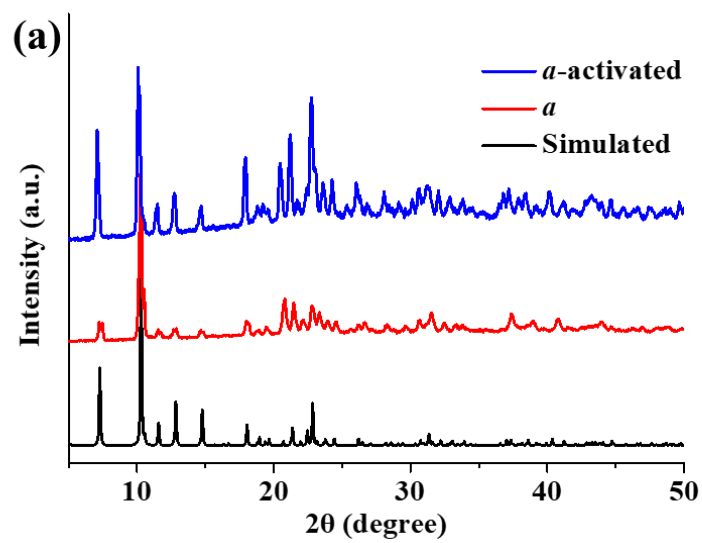
$$\Delta E_{HOST-GUEST} = (E_{MOF\_nNH3} - E_{MOF} - E_{nNH3})/n$$

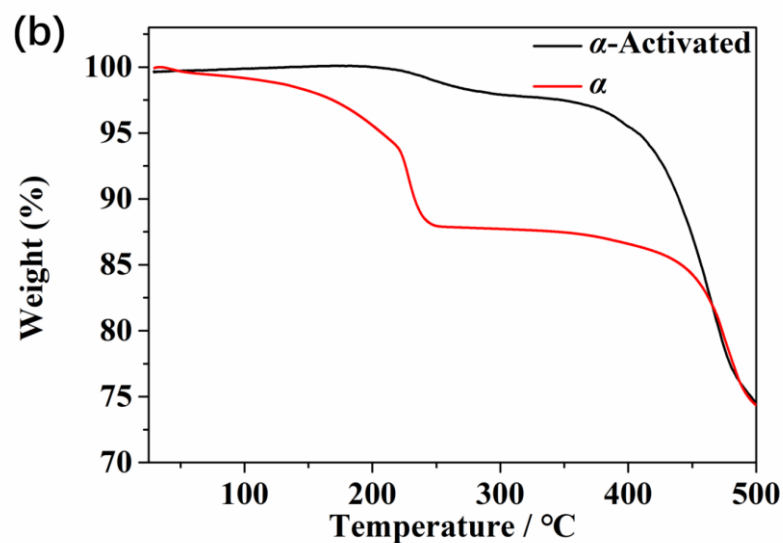
Here,  $\Delta E_{TOTAL}$  is the total interaction between per NH<sub>3</sub> and MOF,  $E_{MOF\_nNH3}$  is the energy of optimized MOF containing nNH<sub>3</sub>,  $E_{MOF}$  is the energy of optimized MOF,  $E_{NH3}$  is the energy of optimized NH<sub>3</sub>,  $E_{nNH3}$  is the energy of nNH<sub>3</sub> with the structure in MOF\_nNH<sub>3</sub>.

## Additional Figures and Measurements

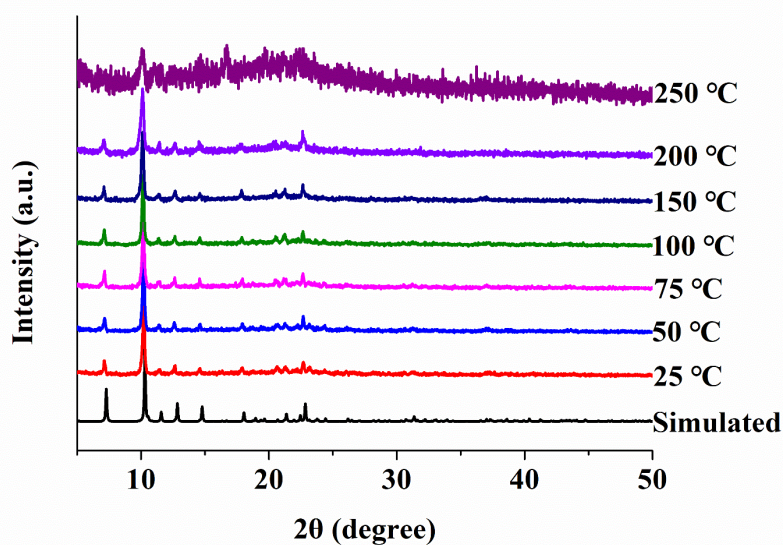


**Fig. S1** (a) The framework of  $\beta$  viewed down *a* direction. (b) GCMC simulated configuration of NH<sub>3</sub> in  $\beta$ , showing the host-guest interaction sites involving exposed copper sites (polyhedra in orange).





**Fig. S2** (a) The PXRD patterns of simulated, as-synthesized and activated  $\alpha$ . (b) Thermal gravity analysis of  $\alpha$  after soaked MeOH for 12 h and activated at 90 °C under vacuum for 3 hours. In red TGA curves, the weight loss (*ca.* 15%) before 200 °C indicates loss of guests of acetonitrile and N,N-dimethylformamide and the weight loss from 400 °C relates to decomposition of the framework.



**Fig. S3** Temperature-dependent PXRD patterns of  $\alpha$ .

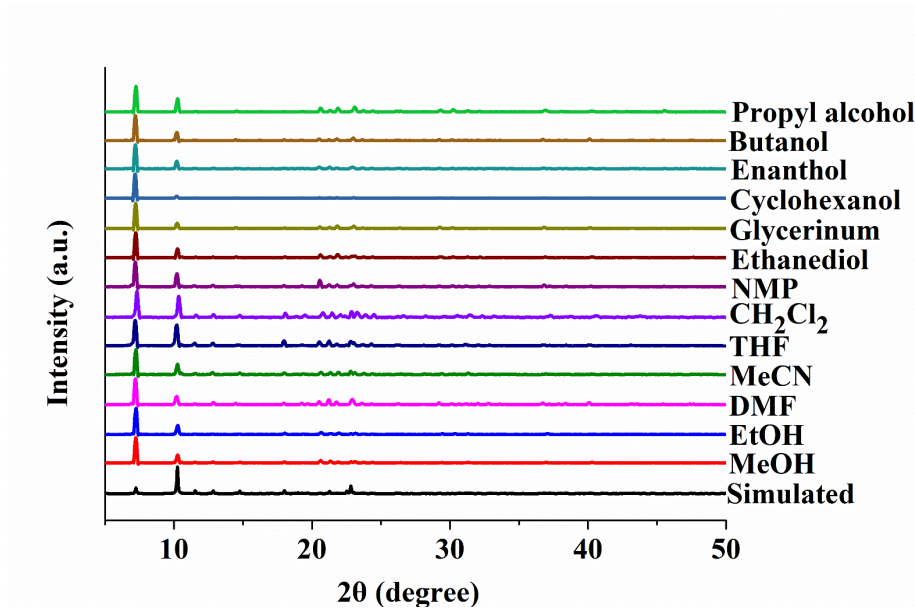


Fig. S4 The PXRD patterns of  $\alpha$  after immersing in different organic solvents for 48 h.

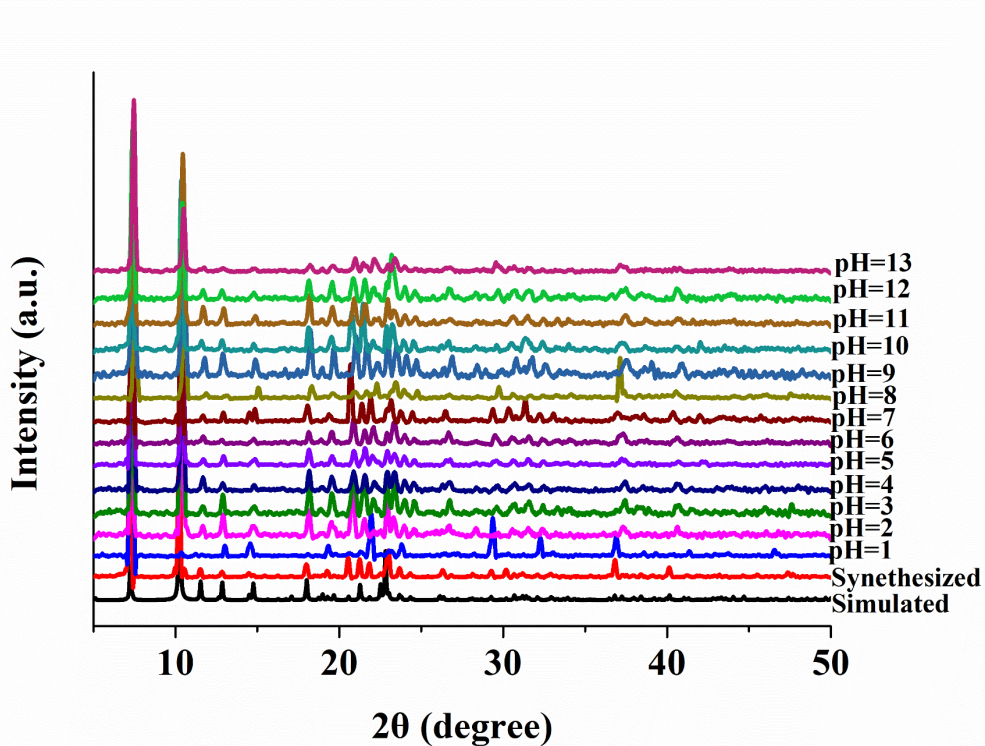
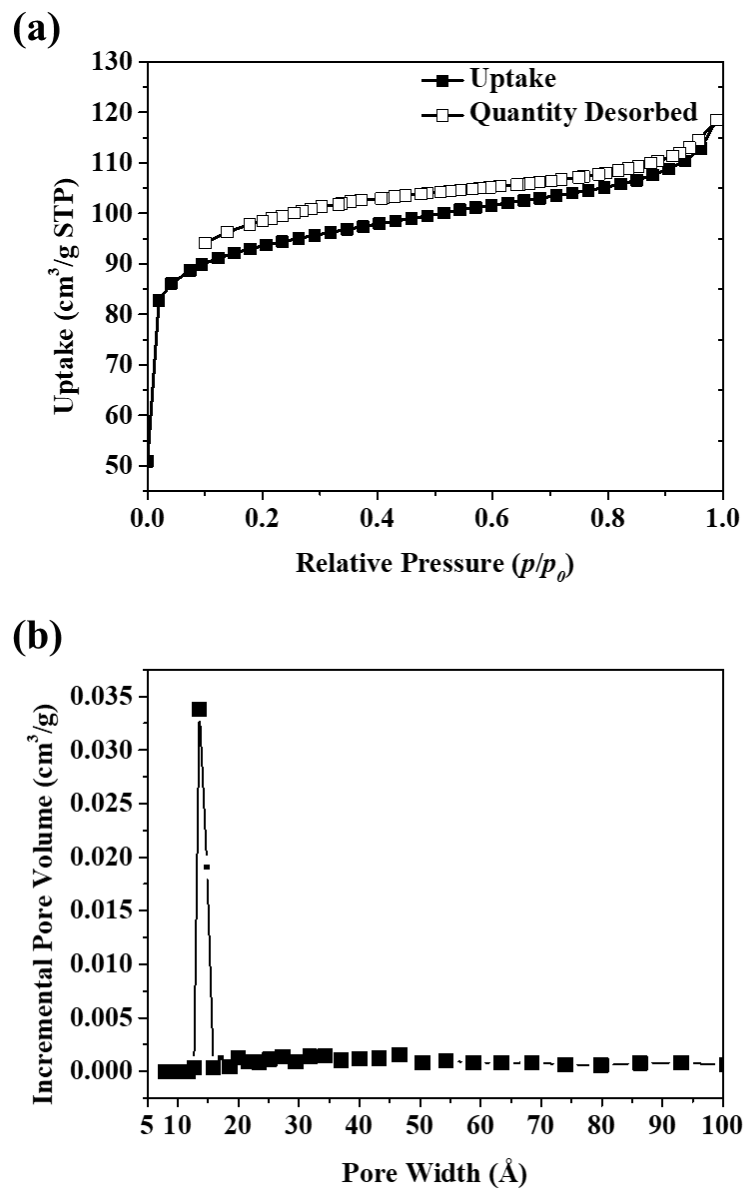
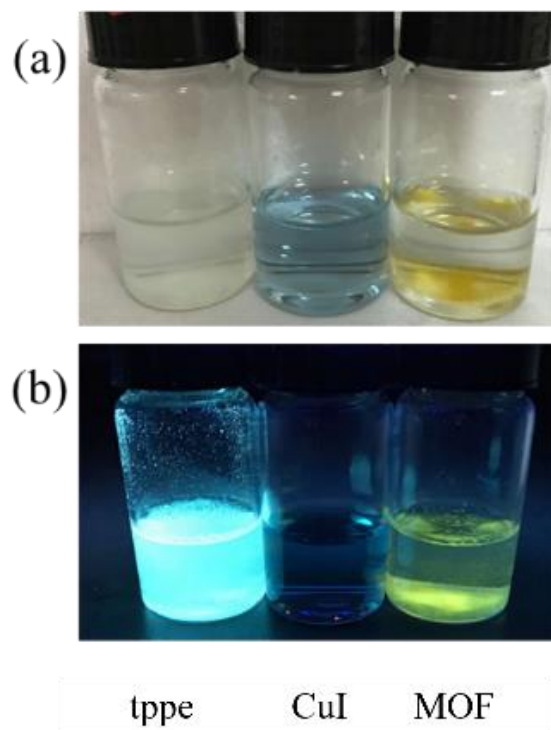


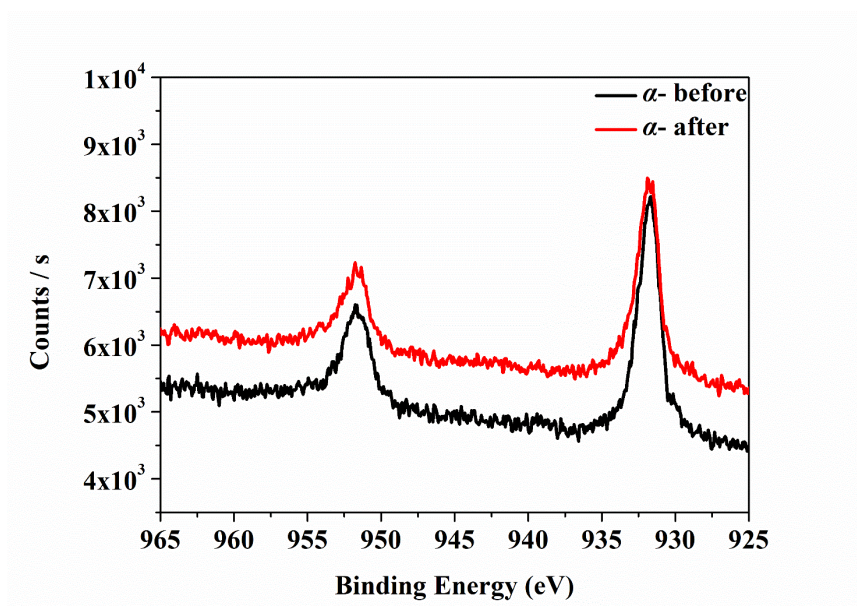
Fig. S5 The PXRD patterns of  $\alpha$  after immersing in aqueous solution with pH 1 to 13 for 48 h.



**Fig. S6** (a)  $\text{N}_2$  adsorption and desorption isotherms for  $\alpha$  at 77 K. (b) Pore size distribution diagram.

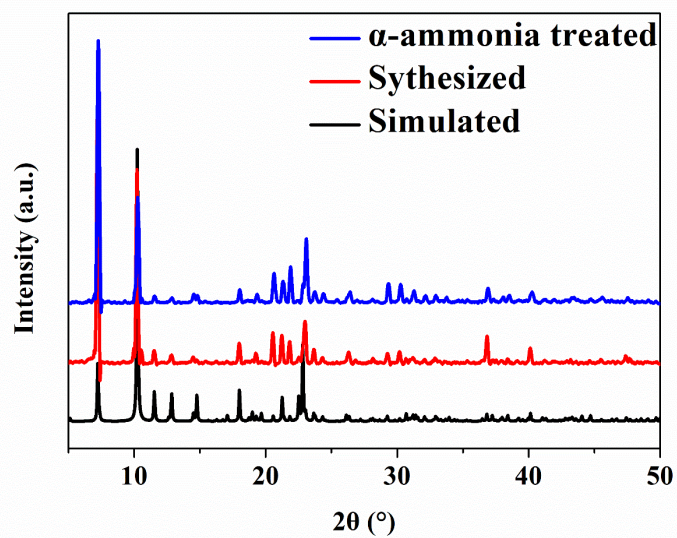


**Fig. S7** Photographs of tpe, CuI and  $\alpha$  immersed in ammonia aqueous solution under (a) naked eyes and (b) 365 nm UV light.

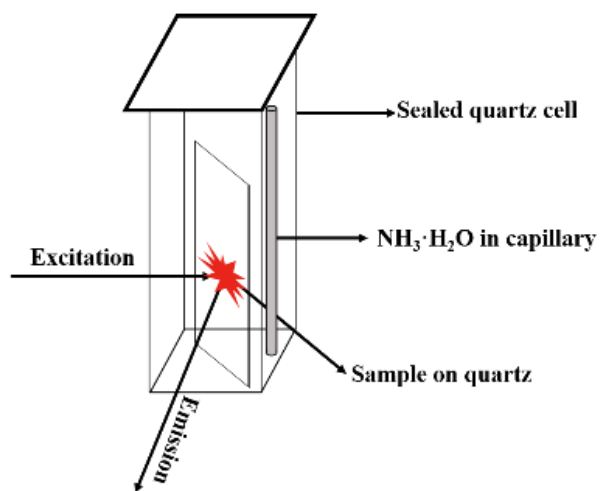


**Fig. S8** XPS of  $\alpha$  soaked in ammonia aqueous solution for 2 hours.





**Fig. S9** The PXRD pattern of  $\alpha$  exposed to ammonia aqueous solution after 2 days.



**Fig. S10** Experimental setup for the solid-gas detection of  $\text{NH}_3$ .<sup>S7</sup>

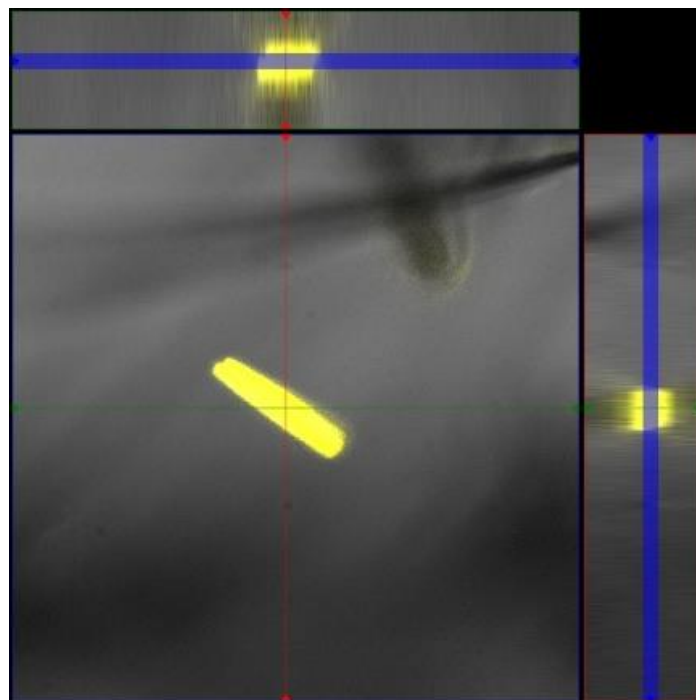


Fig. S11 The images of face, side and top views of  $\alpha$  crystal under CLSM.

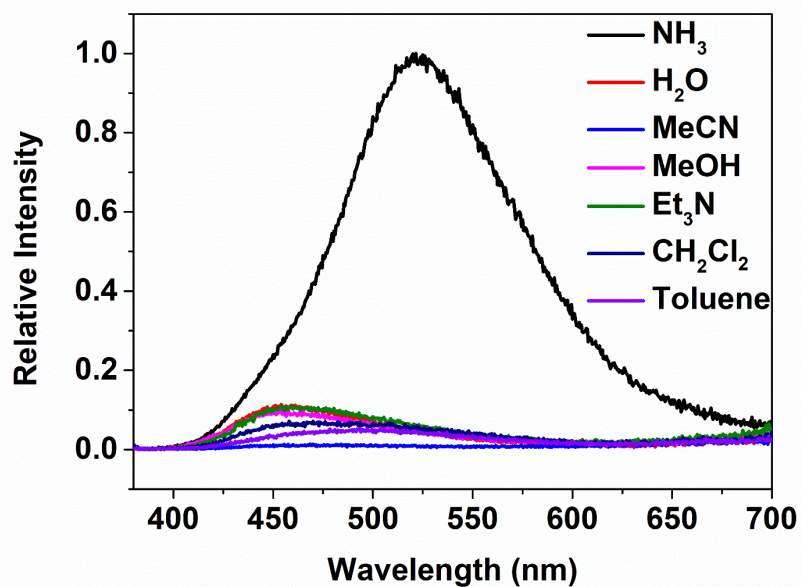
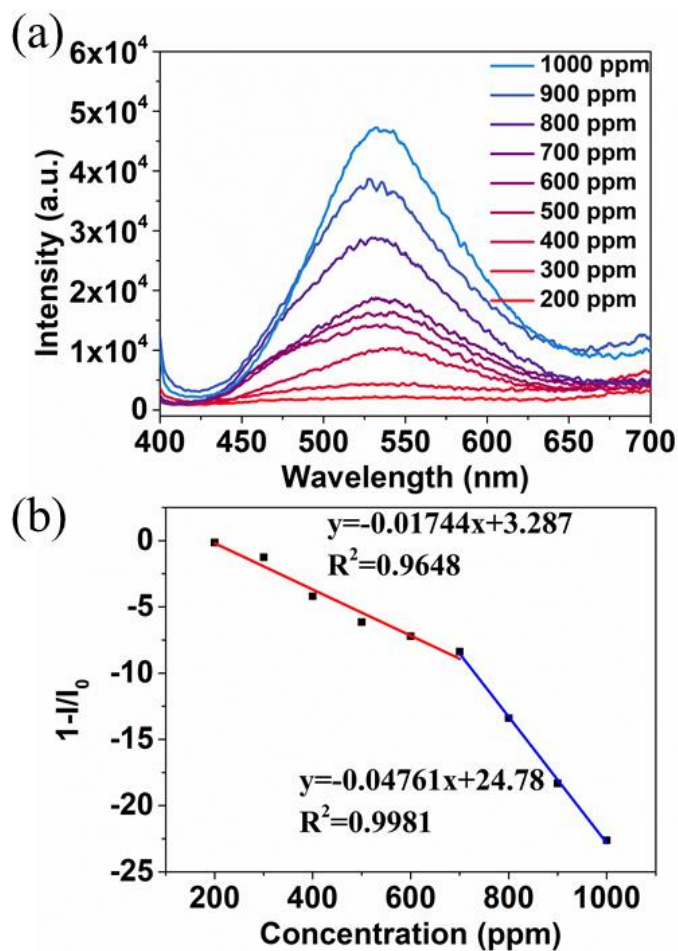
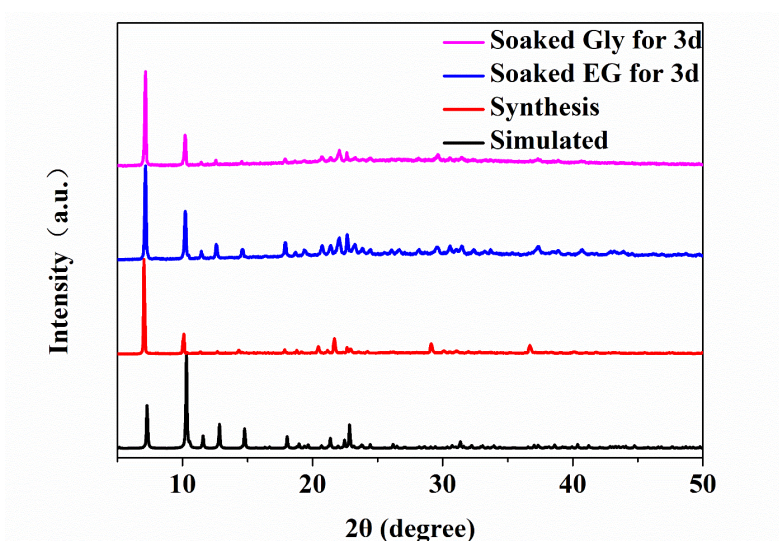


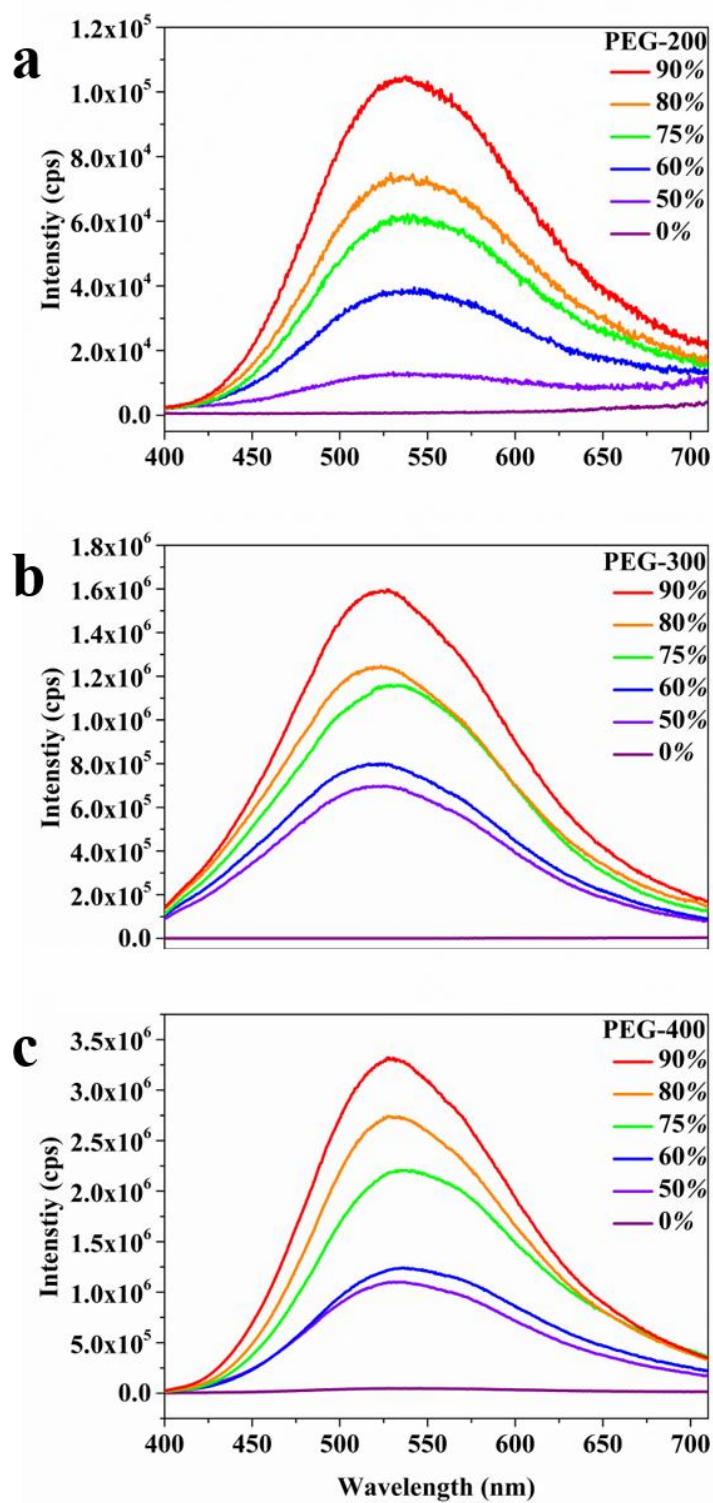
Fig. S12 Selectivity tests by immersing samples of  $\alpha$  in various volatile organic compounds (VOCs) monitored by emission spectra.



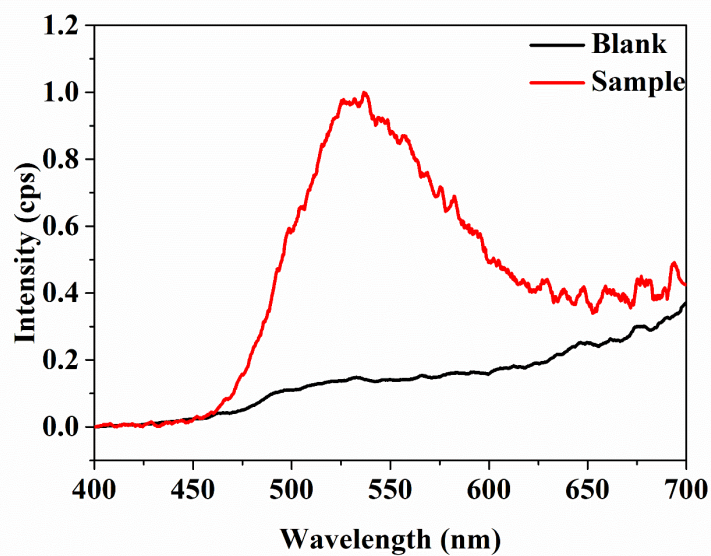
**Fig. S13** (a) Sensitivity test by immersing samples of  $\alpha$  in aqueous ammonia with various concentrations ( $\lambda_{\text{ex}} = 360 \text{ nm}$ ). (b) Linear range study by plotting  $1 - I/I_0$  versus  $\text{NH}_3$  concentrations.



**Fig. S14** The PXRD pattern of  $\alpha$  soaked in EG and Gly for 3 days.



**Fig. S15** Emission spectra ( $\lambda_{\text{ex}} = 360 \text{ nm}$ ) of **a** in PEG/DMF mixture with varied PEG-200/300/400 percentage. Solvent viscosity: PEG-200, 22 to 30; PEG-300, *ca.* 30; PEG-400, 37 to 45.



**Fig. S16** Monitoring of EG in qualified toothpaste products (3.5 g) on sale.<sup>S8</sup> The sample of  $\alpha$  (1 mg) was added in toothpaste suspension (200 mL) mixed with EG (5 mL) for luminescence detection.

## References

- S1 Z. Hu, W. P. Lustig, J. Zhang, C. Zheng, H. Wang, S. J. Teat, Q. Gong, N. D. Rudd and J. Li, *J. Am. Chem. Soc.*, 2015, **137**, 16209–16215.
- S2 A. W. Kelly, J. V. Handy, A. D. Nicholas, F. H. Barnes, H. H. Patterson, L. Wojtas, R. D. Pike, *J. Inorg. Organomet. Polym.*, 2017, **27** (Suppl 1), S90–S100.
- S3 S.-S. Zhao, L. Chen, X. Zheng, L. Wang and Z. Xie, *Chem. Asian J.*, 2017, **12**, 615–620.
- S4 Materials Studio v 7.0. Accelrys Software Inc., San Diego, CA 92121, USA.
- S5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- S6 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- S7 J.-H. Wang, M. Li and D. Li, *Chem. Sci.*, 2013, **4**, 1793–1801.
- S8 General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China. GB 22114-2008 Humectants for toothpastes-glycerin and macrocol [S]. Beijing: China Standard Press, 2008.