

## Electronic Supplementary Information (ESI)

### Postsynthetic *N*-methylation making a metal-organic framework responsive to alkylamines

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## Experimental Section

**Materials and Synthesis.** Starting materials and solvents were purchased and used without further purification from commercial suppliers. H<sub>2</sub>bpydc<sup>1</sup> and UiO-67-bpy<sup>2</sup> were synthesized according to literature procedures.

**Synthesis of UiO-67-dmbpy.** TfOMe (10 mL) was added to a 50mL vial containing 500 mg UiO-67-bpy (~0.23 mmol). The mixture was stirred for 5 h at room temperature. The solid was isolated by filtration, washed with ethanol for several times, and dried at 80 °C for 2 h under vacuum. The PSM procedure is different from those for the synthesis of similar MOFs,<sup>3</sup> where the reactions were performed in CHCl<sub>3</sub> or THF for 48 h at room temperature or for 72 h at 100°C (solvothermal conditions). Our method is superior for obvious advantages such as no use of solvents, room temperature, and much shorter time.

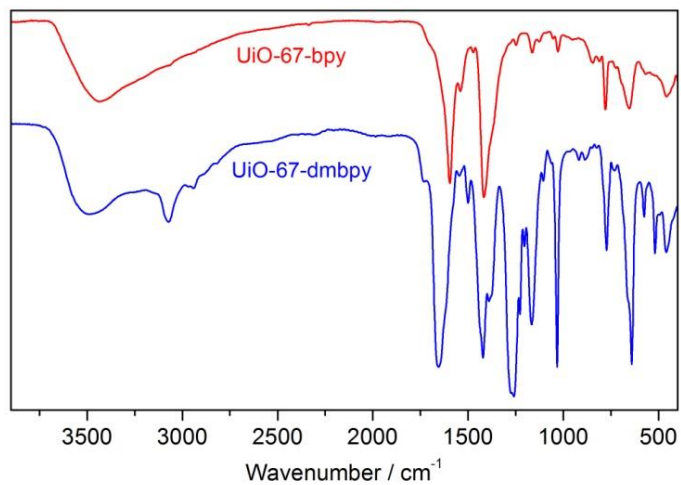
**Vapochromic test.** A suspension of UiO-67-dmbpy (50 mg) in 4 ml EtOH was dropped onto a filter paper and dried in air. 0.5 ml of amines or other VOCs was placed at the bottoms of 25 ml bottles. The bottles was sealed and allowed to stand at room temperature for 0.5 h. Then the above-mentioned filter paper with UiO-67-dmbpy was put into the bottle and allowed to stand for a given time, without contact with the liquid.

**Fluorescence sensor experiments.** Dispersing the MOF (3 mg) in ethanol (4 mL) by ultrasonic gave a stable milk-white suspension. An amine solution (40 µL, with a given concentration) in EtOH was added into the above suspension and stirred for 10 min, and then fluorescence was measured (excitation wavelength: 235 nm). According to a dynamic study (Fig. S12), the fluorescence quenching occurs quickly upon addition of amine and the emission intensity does not show appreciable change after 5 min.

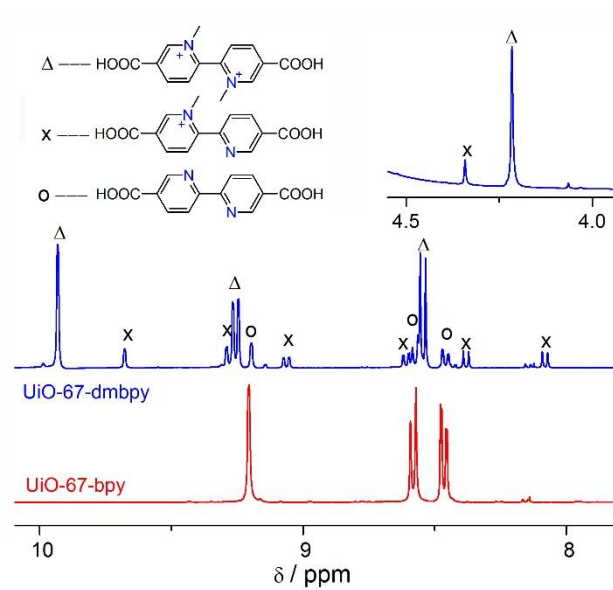
**Physical measurements.** <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer. The FT-IR spectra were recorded in the range 500-4000 cm<sup>-1</sup> using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Powder X-ray diffraction (PXRD) at ambient pressure was recorded on a Rigaku D/Max-2500 diffractometer at 35kV, 25mA for a Cu-target tube and a graphite monochromator. UV-vis diffuse reflectance spectra were measured using a SHIMADZU UV-2700 spectrophotometer, with BaSO<sub>4</sub> plates as references (100% reflection). Fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorometer. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope. GC analysis was obtained on a SHIMADZU GC-2014 gas chromatograph, with n-dodecane as internal standard. Nitrogen adsorption and desorption isotherm measurements were performed on a Micromeritics ASAP2020 analyzer at 77K.

## References

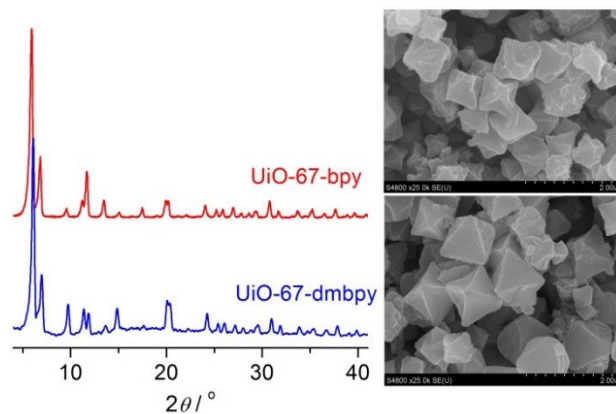
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- 2 G. Nickerl, M. Leistner, S. Helten, V. Bon, I. Senkowska and S. Kaskel, *Inorg. Chem. Front.*, 2014, **1**, 325.
- 3 (a) Q. Zhang, J. Yu, J. Cai, L. Zhang, Y. Cui, Y. Yang, B. Chen and G. Qian, *Chem. Commun.*, 2015, 51, 14732; (b) L. Xu, Y. Luo, L. Sun, S. Pu, M. Fang, R. X. Yuan and H. B. Du, *Dalton Trans*, 2016, 45, 8614.



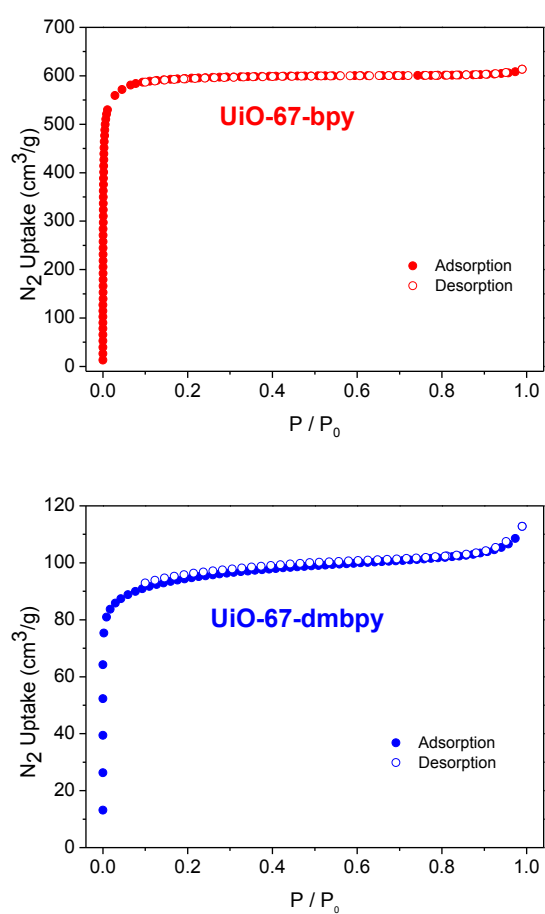
**Fig. S1** IR spectra of the MOFs before and after N-methylation modification.



**Fig. S2**  $^1\text{H}$  NMR spectra of the MOFs before and after N-methylation modification. The spectra were recorded with the solutions obtained by digesting the solids with  $\text{HF}(\text{aq.})/\text{d}_6\text{-DMSO}$  (1/40, v/v).



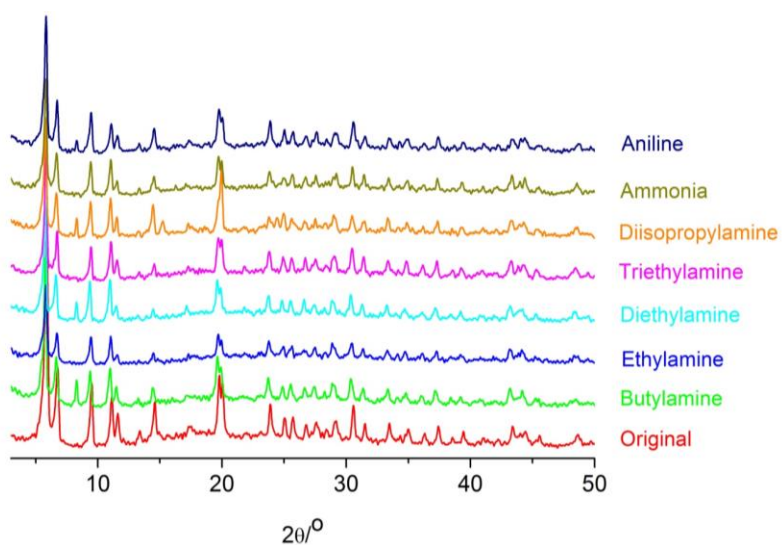
**Fig. S3** PXR profiles (left) and SEM pictures (right) of the MOFs before and after N-methylation.



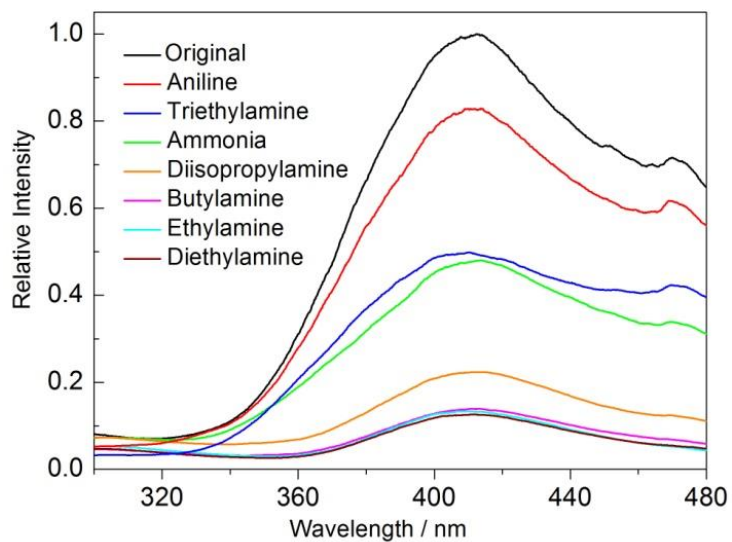
**Fig. S4**  $N_2$  adsorption/desorption isotherms of UiO-67-bpy (top) and UiO-67-dmbpy (bottom).



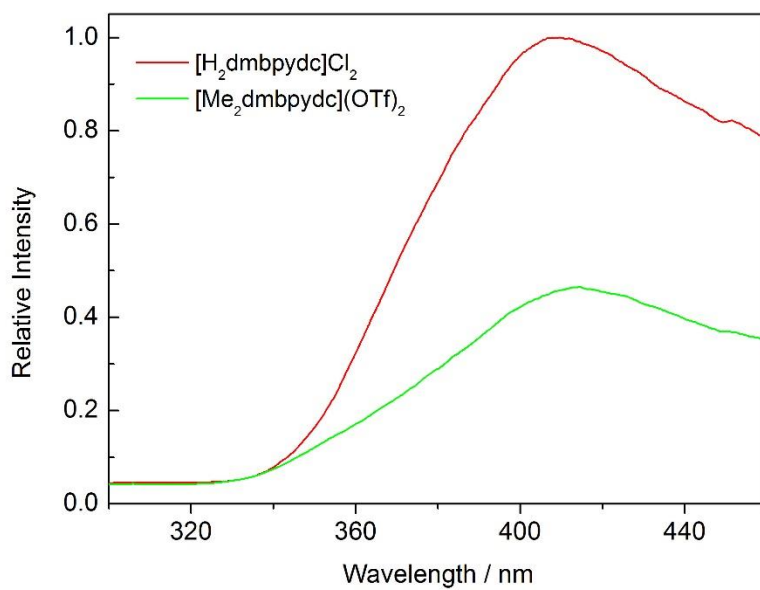
**Fig. S5** Pictures showing the color change of powder samples of the UiO-67-dmbpy when exposed to ammonia/amine vapors. BA = butylamine, EA = ethylamine, DEA = diethylamine, TEA = triethylamine, DiPA = diisopropylamine, AN = aniline.



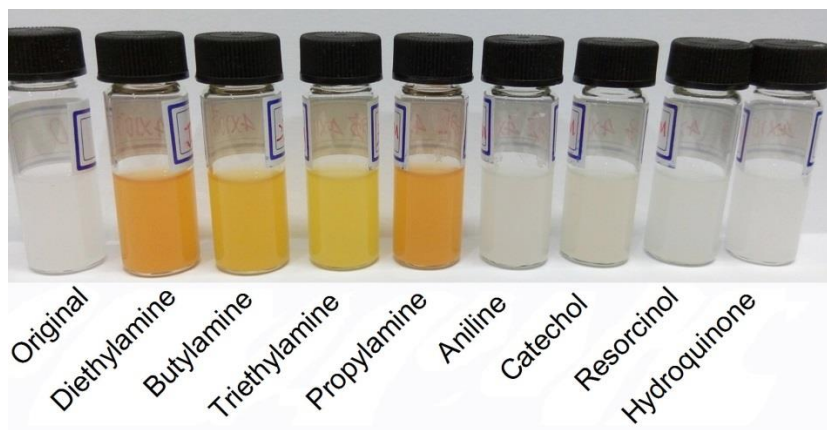
**Fig. S6** PXR D profiles of UiO-67-dmbpy before and after exposition to different amine vapors.



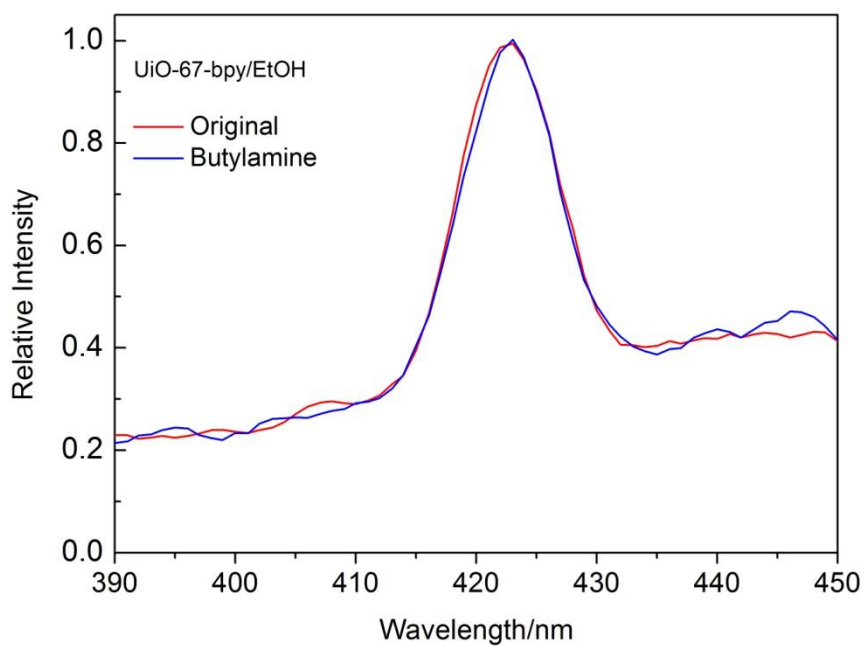
**Fig. S7** Fluorescence spectra of UiO-67-dmbpy before and after exposition to different amine vapours.



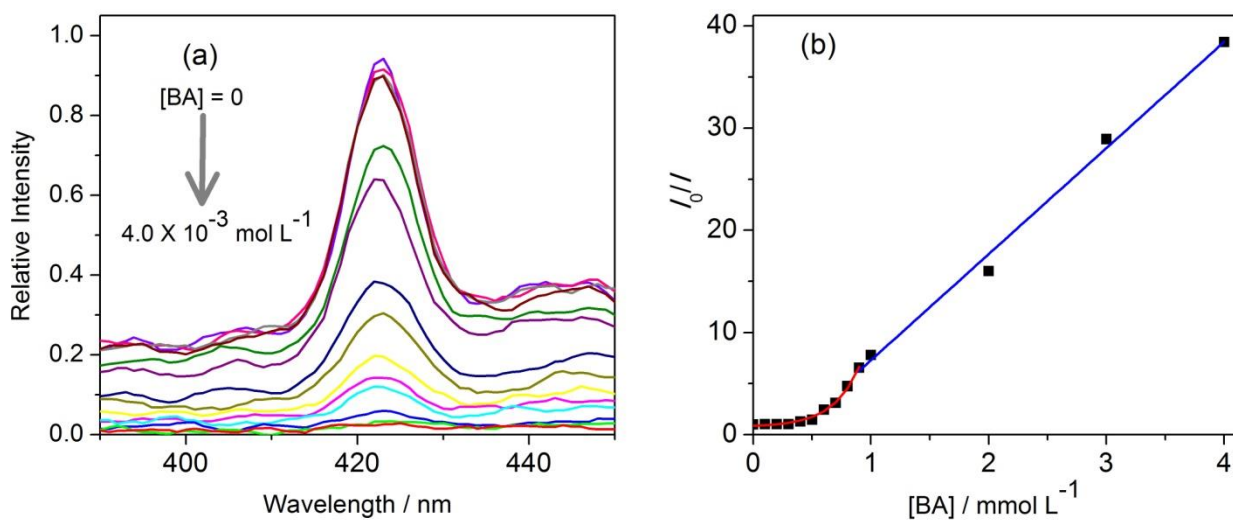
**Fig. S8** Fluorescence spectra of [H<sub>2</sub>dmbpydc]Cl<sub>2</sub> and [Me<sub>2</sub>dmbpydc](OTf)<sub>2</sub> (excited at 245 nm).



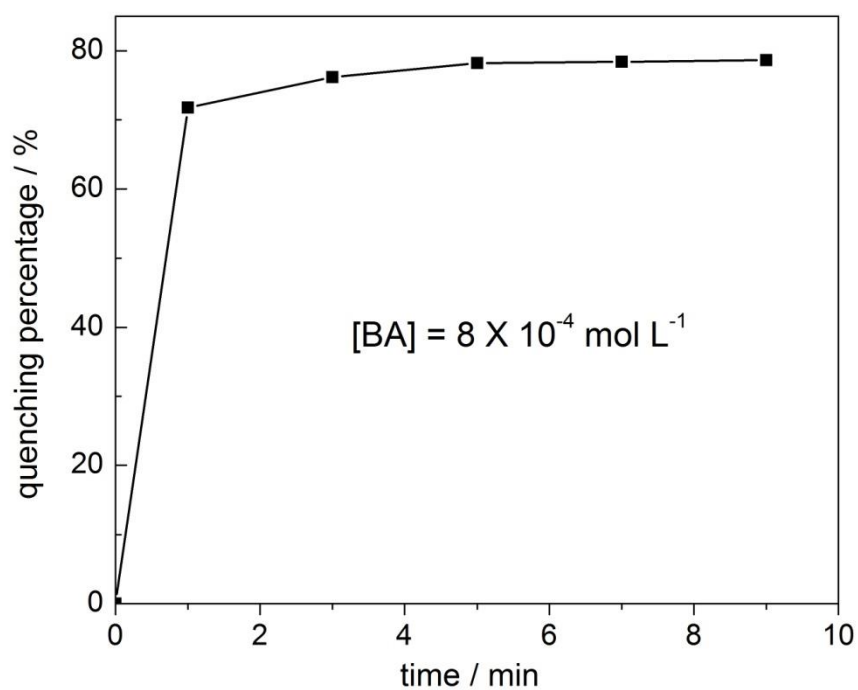
**Fig. S9** Pictures of UiO-67-dmbpy/EtOH dispersions after addition of different amines and dihydroxybenzene ( $4 \times 10^{-3} \text{ mol L}^{-1}$ ).



**Fig. S10** Fluorescence spectra of the UiO-67-bpy/EtOH dispersion before and after addition of butylamine ( $4 \times 10^{-3} \text{ mol L}^{-1}$ ).



**Fig. S11** Fluorescent emission spectra of the UiO-67-dmbpy/EtOH dispersion in response to butylamine (excitation wavelength: 235 nm).



**Fig. S12** The quenching percentage at different time after adding butylamine ( $8 \times 10^{-4} \text{ mol L}^{-1}$ ) to the UiO-67-dmbpy/EtOH dispersion.