Electronic supplementary information for:

Surfactant-directed assembly of mesoporous metal-organic framework nanoplates in ionic liquid

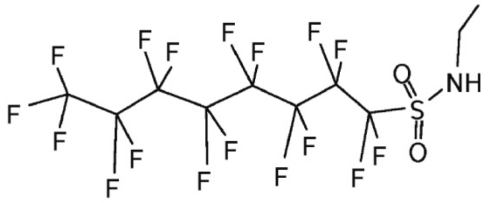
Li Peng, Jianling Zhang*, Jianshen Li, Buxing Han*, Zhimin Xue and Guanying Yang

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences

E-mail: zhangjl@iccas.ac.cn; hanbx@iccas.ac.cn

1. Experimental

Materials. N-EtFOSA (>95%) was purchased from Guangzhou Leelchem Corporation without any further purification. 1,1,3,3-Tetramethylguanidine (TMG) was produced by Alfa Aesar. Trifluoroacetate and triethylamine were provided by Beijing Chemical Reagent Company. Copper(II) acetate monohydrate ($Cu(OAc)_2{\cdot}H_2O$) (A. R. Grade) was purchased from Alfa Aesar. H_3BTC (purity 95%) was provided by Aldrich.



N-EtFOSA

TMGT

Fig. S1 Molecular structures of N-EtFOSA and TMGT.

Synthesis of TMGT The ionic liquid (IL) TMGT was prepared according to the literature method.[1] In a typical experiment, 100 mL ethanol and 23 g TMG (0.2 mol) were loaded into a 250 mL flask in a water bath of 15 ^{o}C. Then 0.2 mol CF_3COOH in 35 mL ethanol was charged into the flask under stirring. The reaction lasted for 2 hours. The reaction mixture was evaporated under reduced pressure. Then, the IL was dried under vacuum at 100 ^{o}C for 48 hours, and product was obtained.

Synthesis of Cu-BTC MOFs The MOFs were synthesized using a similar synthetic protocol reported by Yaghi and coworkers.[2] In a typical experiment, H_3BTC (0.3 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.54 mmol) were added into N-EtFOSA/TMGT solution (5 g), which was loaded in an Teflon-lined stainless-steel autoclave. Then 0.5 mL triethylamine was added into the autoclave to deprotonate the linker. The mixture was stirred at 30 ^{o}C for 23 hours, and then the blue product was washed with ethanol repeatedly using a Soxhlet extractor. The final product was obtained after being dried at 60 ^{o}C under vacuum for 24 hours.

Characterization of Cu-BTC MOFs The resulting products were characterized by wide-angle XRD (Model D/MAX2500, Rigaka) with Cu Kα radiation at a scanning rate of 2°min^{-1} and small-angle XRD on X'Pert PRO MPD with 0.02^{o}min^{-1}. The morphologies of the MOF were characterized by a HITACHI S-4800 scanning electron microscope equipped with EDX and JeoL-1010 transmission electron microscope at 100 kV. The porosity properties of the MOFs were determined by nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 2020M system. FT-IR spectra were determined using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. The TG measurement was carried out using TA Q50 with N_2 flow of 40 mL/min. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The surface tension of the surfactant/IL solutions was performed on Kyowa Cbvp Surface Tensionmeter A3. The elemental analysis of S was performed on CS-344 element analysis instrument. The element S was undetectable, indicating that the surfactant can be removed by repeated washing. The elemental analysis of N was performed on FLASH EA1112 elemental analysis instrument, which shows a content of 0.21 wt%, indicating that a small amount of IL (1.1 wt%) was present in sample.

2. Results

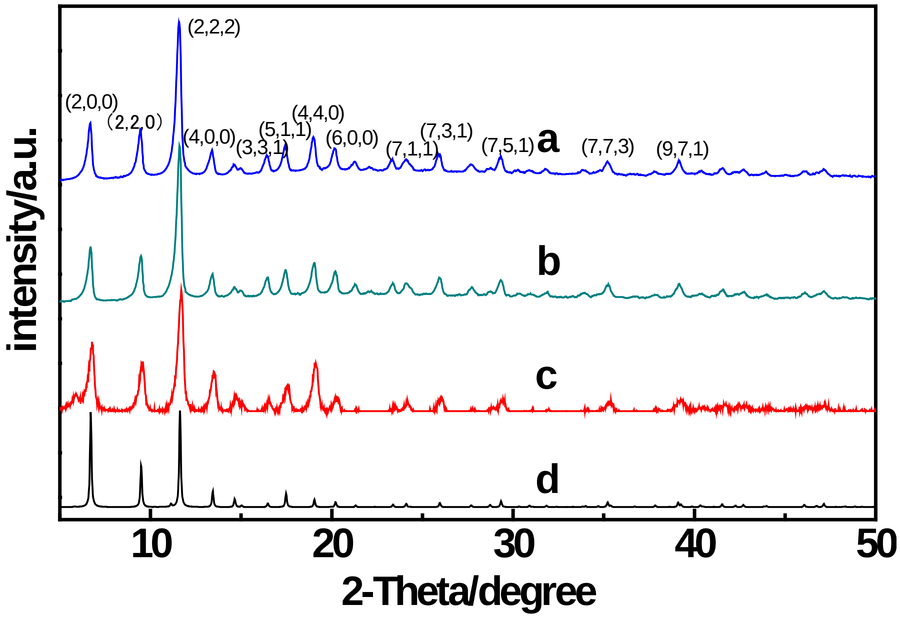


Fig. S2 Wide-angle XRD patterns of the MOFs synthesized in 0.05 wt% (a), 2 wt% (b), and 5 wt% (c) N-EtFOSA/TMGT solutions and the simulated XRD pattern of HKUST-1 (d). The XRD pattern of the MOF is in nice agreement with the reported and simulated XRD patterns of HKUST-1.[3] The broad diffraction peaks indicate that the samples are constructed with small nanocrystals. It is notable that reflections attributed by CuO (2θ=35.5° and 38.7°) or Cu_2O (2θ=36.43°) are absent from the XRD pattern, indicating the high quality of the samples prepared under ambient conditions.

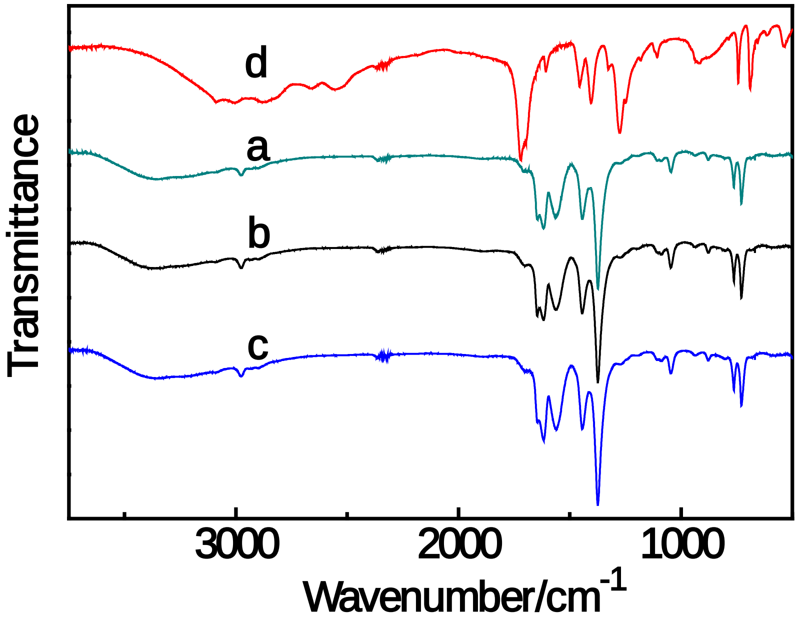


Fig. S3 FTIR spectra of MOFs synthesized in 0.05 wt% (a), 2 wt% (b), and 5 wt% (c) N-EtFOSA/TMGT solutions and H_3BTC (d). The FT-IR spectra of the three MOFs (curves a, b, and c) display the characteristic asymmetric (1630 cm^{-1}, 1562 cm^{-1}) and symmetric vibration (1443 cm^{-1}, 1373 cm^{-1}) of carboxylate anions in deprotonated H_3BTC, which is consistent with that in literature.[4] In comparison with the IR spectrum of H_3BTC (curve d), the wavenumber difference of asymmetric and symmetric vibration of carboxylate anions is narrowed. This indicates that carboxylate groups of BTC are coordinated to Cu (II) ions.[5]

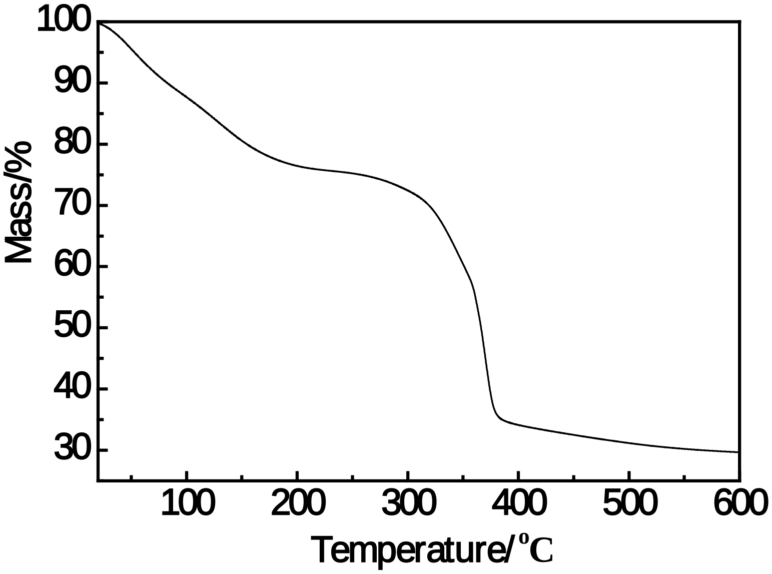
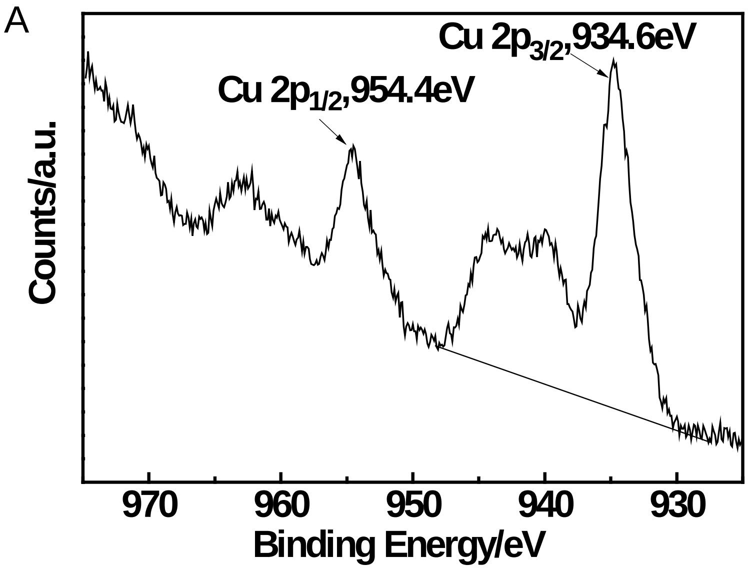


Fig. S4 Thermogravimetric curve of MOF synthesized in 2 wt% N-EtFOSA/TMGT solution. In the temperature range below 170 °C, the weight loss (about 25 wt%) is assigned to the desorption of water and ethanol both adsorbed on surface and located inside the pores of MOF. A sudden weight loss of about 40% takes place after 300 °C, corresponding to the decomposition of HKUST-1 to CuO and volatile compounds.[3a,3c,6]



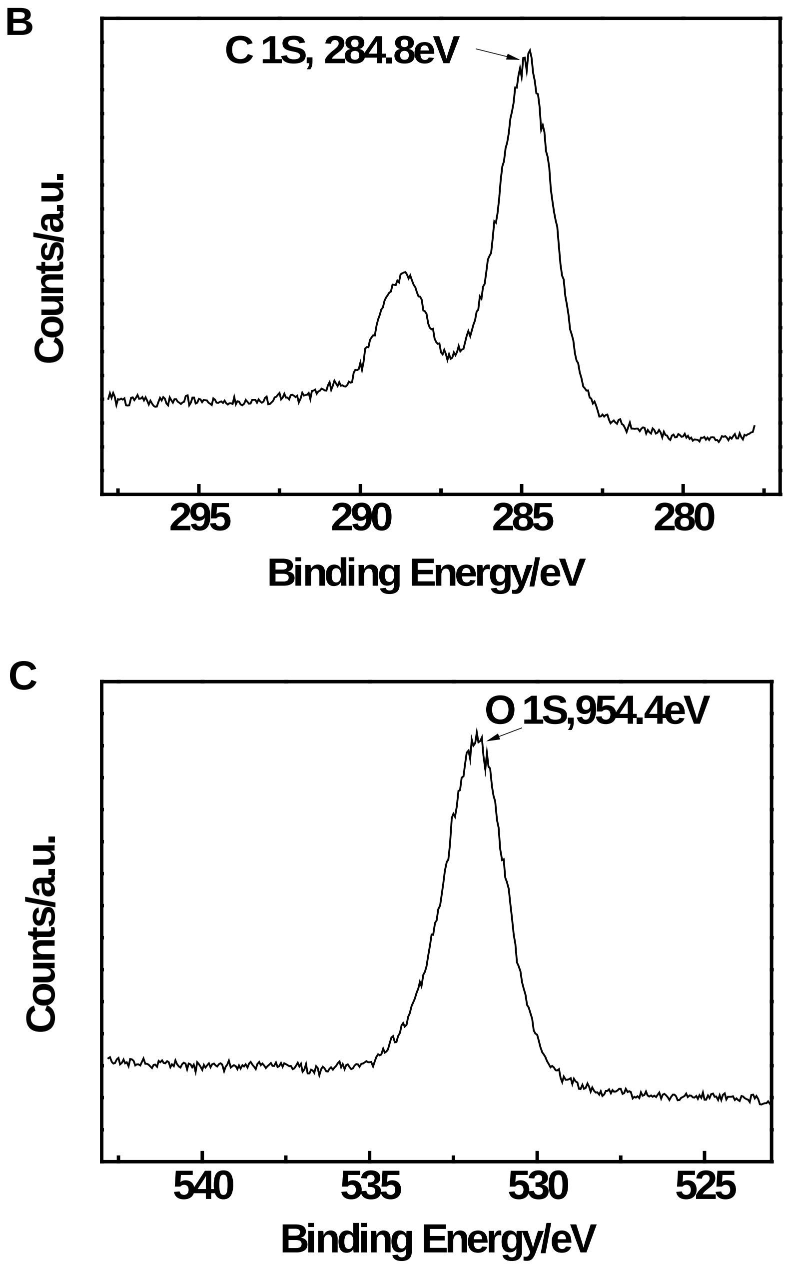


Fig. S5 X-ray photoelectron spectroscopy (XPS) of MOF synthesized in 2 wt% N-EtFOSA/TMGT solution. The binding energies of copper element are 934 eV and 954 eV, characteristic of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^{2+}, respectively. The binding energies of carbon element and oxygen element are 284.8 eV and 954.4 eV respectively. The atom percentages in MOF gained from the areas of peaks for copper element, carbon element and oxygen element are 7.86%, 59.99% and 25.56%. Thus the atomic ratio of C to Cu is 7.63, higher than the calculated value 6 of $Cu_3(BTC)_2$. This can be attributed to the existence of ethanol adsorbed in MOF, which was revealed by TG determination.

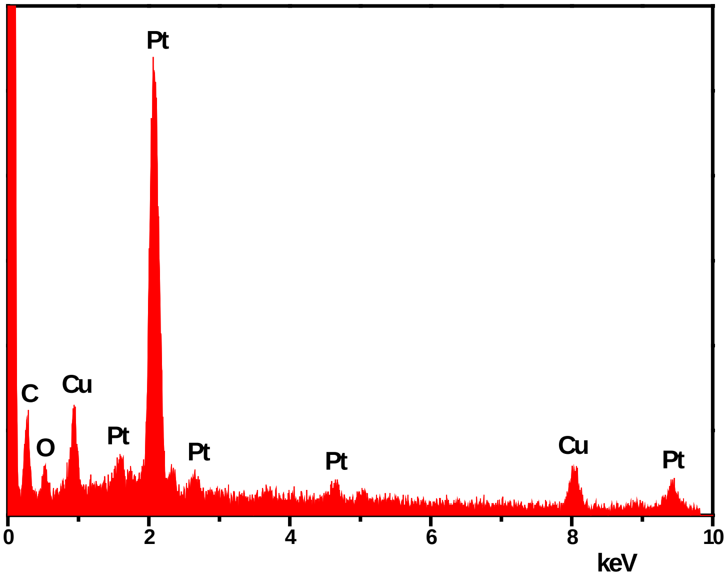


Fig. S6 Energy dispersive X-ray (EDX) spectrum of the MOF synthesized in 2 wt% N-EtFOSA/TMGT solution. It demonstrates the presence of copper, oxygen and carbon in the prepared MOF. The Pt results from sample spraying for better conductivity, in order to gain better SEM images.

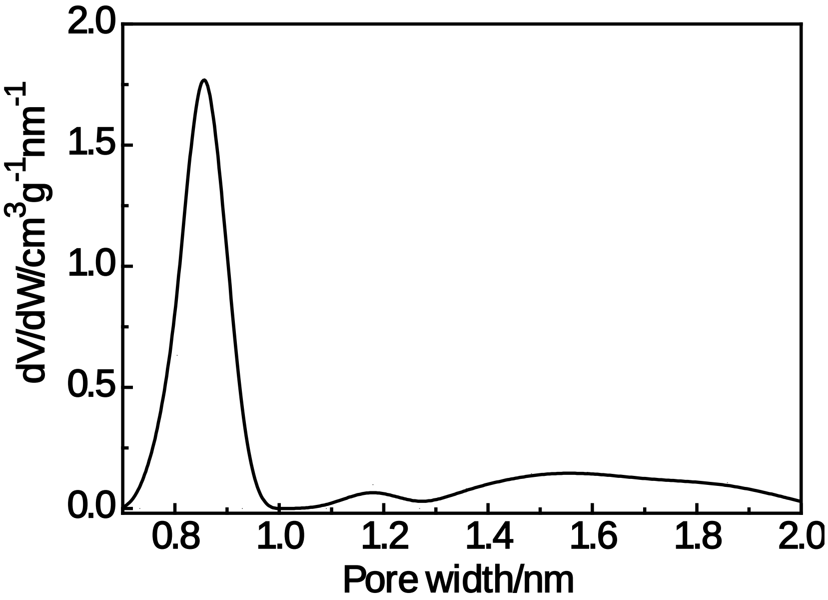


Fig. S7 The micropore size distribution of MOF synthesized in 2 wt % N-EtFOSA/TMGT solution.

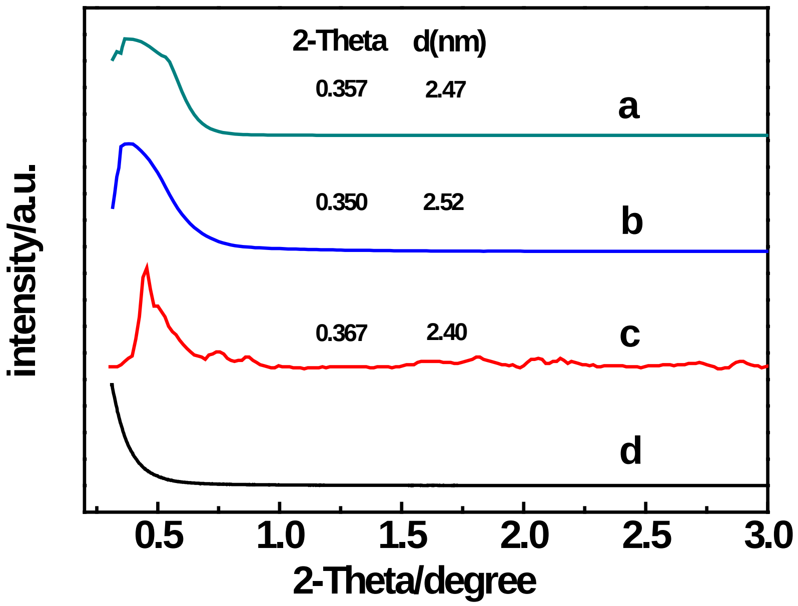
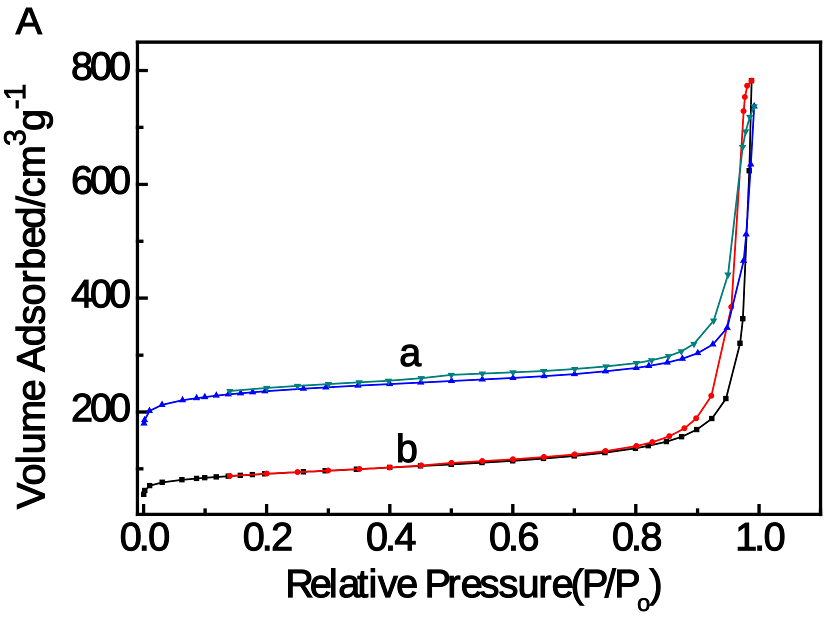


Fig. S8 Small-angle X-ray diffraction patterns of the MOFs synthesized in 5 wt% (a), 2 wt% (b), 0.05 wt% (c) N-EtFOSA/TMGT solution and MOF synthesized in pure TMGT (d).



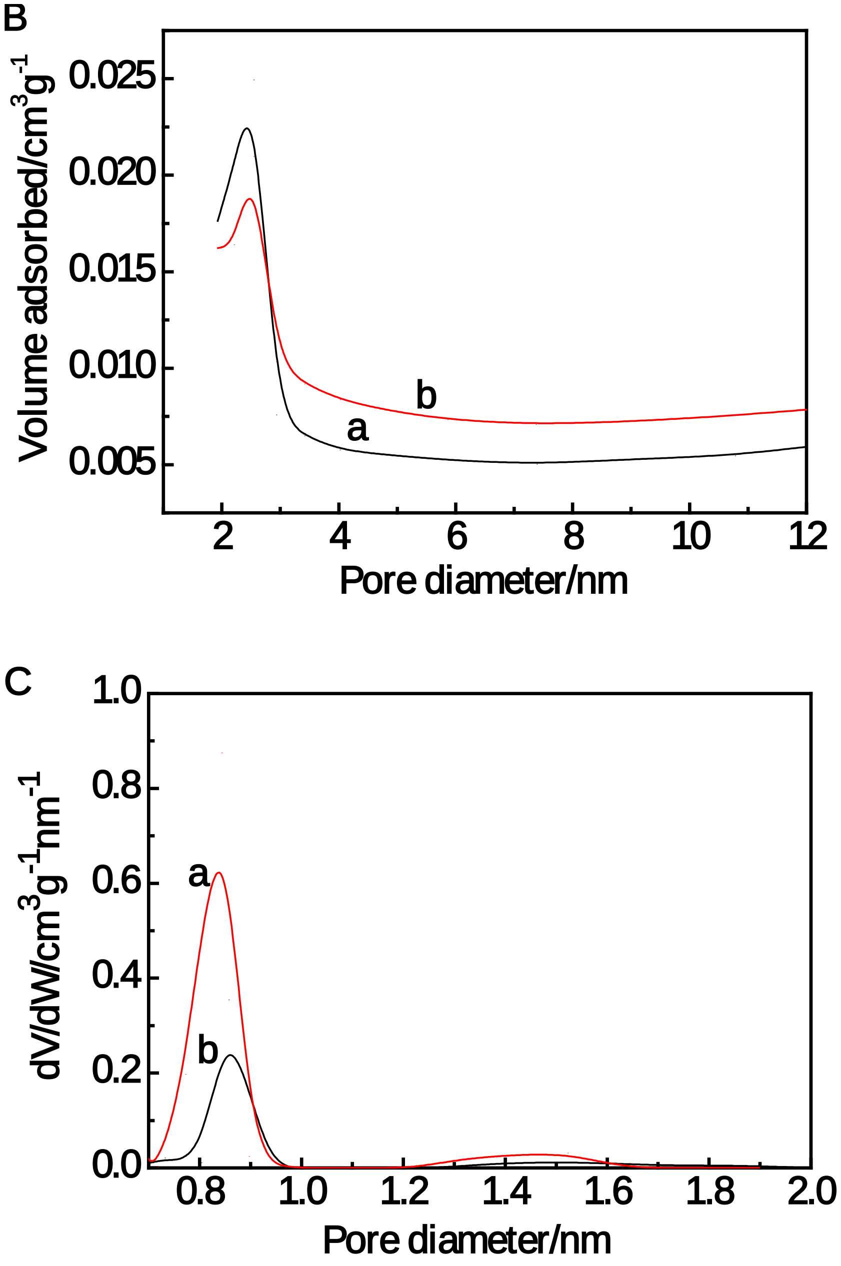


Fig. S9 N_2 adsorption–desorption isotherms (A), mesopore size distribution curves (B), and micropore size distribution curves (C) for MOFs synthesized in 0.05 wt% (a) and 5 wt% (b) N-EtFOSA/TMGT solutions.

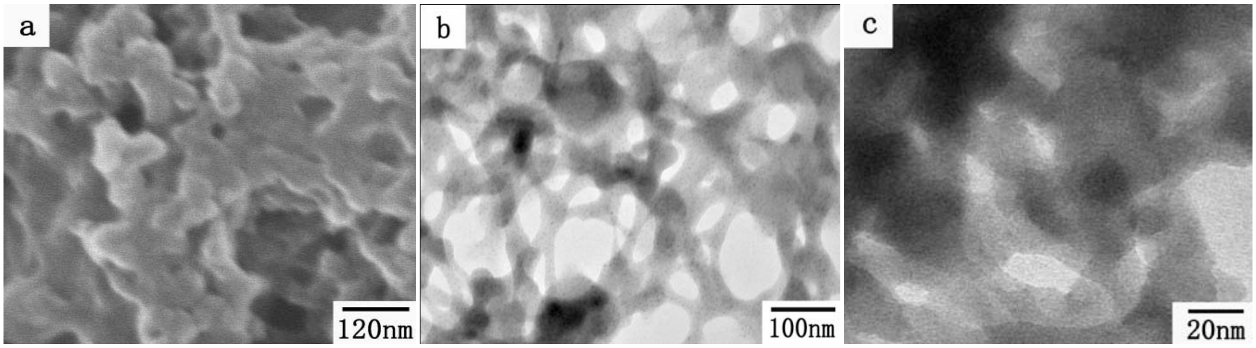


Fig. S10 SEM and TEM images of MOF synthesized in pure TMGT.

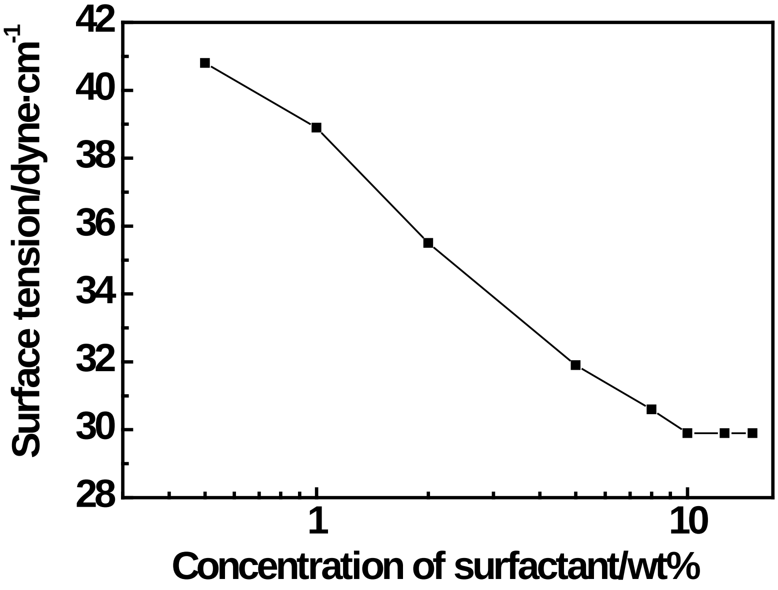


Fig. S11 Surface tensions of N-EtFOSA/TMGT solutions with different surfactant weight fractions.

References

1 H. X. Gao, B. X. Han, J. C. Li, T. Jiang, Z. M. Liu, W. Z. Wu, Y. H. Chang and J. M. Zhang, *Synth. Commun.*, 2004, **34**, 3083.

2 D. J. Tranchemontagne, J. R. Hunt and O. M. Yaghi, *Tetrahedron*, 2008, **64**, 8553.

3 (a) M. Hartmann, S. Kunz, D. Himsl, and O. Tangermann, *Langmuir*, 2008, **24**, 8634; (b) S. Diring, S. Furukawa, Y. Takashima, T. Tsuruoka and S. Kitagawa, *Chem. Mater*., 2010, **22**, 4531; (c) H. Q. Du, J. F. Bai, C. Y. Zuo, Z. F. Xin and J. B. Hu, *CrystEngComm*, 2011, **13**, 3314; (d) S. S. -Y. Chui, S. M. -F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

4 M. -H. Pham, G. -T. Vuong, F. -G. Fontaine and T. -O. Do, *Cryst. Growth Des.*, 2012, **12**, 1008.

5 (a) G. B. Deacon and R. Philips, *Coord. Chem. Re*v. 1980, **33**, 227; (b) Y. J. Zhao, J. L. Zhang, B. X. Han, J. L. Song, J. S. Li and Q. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 636.

6 (a) L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. D. Vos, *Chem. Eur. J.*, 2006, **12**, 7353; (b) J. Liu, J. T. Culp, S. Natesakhawat, B. C. Bockrath, B. Zande, S. G. Sankar, G. Garberoglio and J. K. Johnson, J. *Phys. Chem. C*, 2007, **111**, 9305.