SUPPORTING INFORMATION

Supporting Information

Electronic supplementary information (ESI)

Polyether Amine Modified Metal Organic Framework Enhanced CO_2 Adsorption Capacity of Room Temperature Porous Liquid

*Xuemei Zhao[a], Yihui Yuan[a], Peipei Li[*b], Zenjun Song[c], Chunxin Ma[*a], Duo Pan,[d,e,f] Shide Wu,[g] Tao Ding,[h,*] Zhanhu Guo[*e], Ning Wang[*a]*

a. State Key Laboratory of Marine Resources Utilization in South China Sea, Hainan University, Haikou, Hainan, 570228, P.R. China
Email: machunxin@hainu.edu.cn, wangn02@foxmail.com
b. School of Advanced Materials and Nanotechnology, Xidian University, Xi'an, 710071, China
Email: lip@xidian.edu.cn
c. School of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou, Zhejiang, 318000, P.R. China
d. College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, Shandong 266590, China
e. Integrated Composites Laboratory, Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996 USA.
Email: zguo10@utk.edu
f. Key Laboratory of Materials Processing and Mold (Zhengzhou University), Ministry of Education, National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou, China
g. Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou, 450001, China
h. College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China
Email: dingtao@henu.edu.cn

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Experimental Section

Materials

Isophthalic acid (IPA) (99%), terephthalic acid (TPA) (99%), dimethylformamide (DMF, 99.9%) and methanol (99.5%) were purchased from Macklin. $ZrCl_4$ (99.9%) was purchased from Aladdin. CH_3COOH (99.5%) was purchased from Xilong Scientific Co., Ltd. Polyether amine of D2000 and M2070 were purchased from Suzhou Changke new material technology Co., Ltd.

Characterization

Attenuated total reflectance-infrared spectra (ATR-IR) were performed with a Nicolet 7199 spectrometer. Thermo-gravimetric analysis (TGA) measurements were obtained at a heating rate of 10 °C / min through TGA Q50 TA instrument under N_2 atmosphere. Nitrogen adsorption isotherms were taken at 77 K using an ASAP2460 volumetric adsorption analyser, the sample was dried and degassed in vacuum at 200 °C for 12 h before measurements. The specific surface area and pore size distributions of the UIO-66 and D2000@UIO-66 were evaluated by the obtained N_2 adsorption-desorption isotherms at 77 K under the relative pressure (P/P_0) range from 0.01 to 0.1, through the Brunauer Emmett-Teller method (BET, Beckman Coulter SA3100). Rheological properties were obtained on the AR-G2 instrumentation through a steel cone and a steel plate geometry with 2° cone angle and a 40 mm diameter plate respectively. The temperature-dependent modulus was measured at the angle was fixed at 10.0 $rad \cdot s^{-1}$ and the strain amplitude was 2.0%. The Differential scanning calorimetry (DSC) was measured under N_2 atmosphere at a heating rate of 10 °C /min through the DSC Q 100 TA instrument. XRD tests were performed by using an X-ray diffractometer (AXIS SUPRA, Kratos) with a Cu-Kα radiation source (λ = 1.5406 Å). Micro-structures and morphologies of the UIO-66, D2000@UIO-66 and UIO-66-liquid were observed by a high resolution transmission electron microscope (TEM, JEM 2100, JOEL) and a field emission scanning electron microscope (SEM, S-4800, Hitachi). X-ray photoelectron spectroscopy (XPS) measurements were obtained with a Thermo Scientific Escalab 250Xi spectrometer. Gas (CO_2 and N_2) adsorption-desorption isotherms were calculated by a high-precision Intelligent Gravimetric Analyser (IGA, Hiden Isochema) according to previous report,[1] after the samples were dried and degassed at 80 °C in a vacuum for 24 h. Firstly, the samples were loaded within a quartz vessel and sealed completely in a chamber; then the mass measurements were calculated accurately at specific bars. All the tests were conducted at a constant temperature of 298 K via a recirculating water bath.

Synthesis of UIO-66 NPs

The UIO-66 NPs were synthesized according to the previous reports.[2,3] $ZrCl_4$ (1.165 g), TPA (0.665 g), IPA (0.166 g), CH_3COOH (9.006 g) was dissolved within DMF (37.64 g) by ultrasonic (at a molar ratio of 1 $ZrCl_4$/ 0.8 TPA/ 0.2 IPA/ 30 CH_3COOH/ 103 DMF), and then the mixed precursor was transferred to a 100 mL Teflon-lined autoclave and reacted for 24 h at 120 °C. After cooled, the as-synthesized solid product was obtained through centrifugation (8000 rpm, 15 min), washed with DMF and methanol in turn, and finally dried under vacuum (12 h, 60 °C).

Synthesis of D2000@UIO-66 NPs

The D2000@UIO-66 NPs were fabricated according to the previous report.[4] 1.0 g of UIO-66 was dissolved in a mixture of deionized water and methanol. Then the polyether amine of D2000 was slowly added until the PH of the mixture at 7.0, and evaporated by plate heating (80 °C). The product of D2000@UIO-66 was obtained after the solution was dried under vacuum at 60 °C for at least 12 h.

Synthesis of ionic liquid ([M2070][IPA])

A new ionic liquid ([M2070][IPA]) was prepared according to the previous report.[5] 3.0 g of the polyether amine of M2070 was dissolved in a mixture of deionized water and methanol. Then the IPA was slowly added until the PH of the mixture is 7.0, and evaporated by plate heating (80 °C). The product of ionic liquid ([M2070][IPA] was achieved after the solution was dried under vacuum at 60 °C for at least 12 h.

Synthesis of UIO-66-liquid/[M2070][IPA]

A novel porous liquid of UIO-66-liquid/[M2070][IPA] was prepared according to the previous report.[5] To begin with, D2000@UIO-66 (0.5 g) was dispersed in 3.0 mL methylbenzene solution and stirring for 10 min and ionic liquid ([M2070][IPA]) (0.5 g) was dispersed in 3.0 mL methylbenzene solution and stirring for 10 min. Then, ionic liquid ([M2070][IPA]) mixture was slowly added to the D2000@UIO-66 suspension under stirring for 24 h. The resulting porous liquid of UIO-66-liquid was achieved after the mixture was dried on a hot plate with stirring at 80 °C. The UIO-66-liquid was kept at 45 °C under vacuum for use.

Data analysis

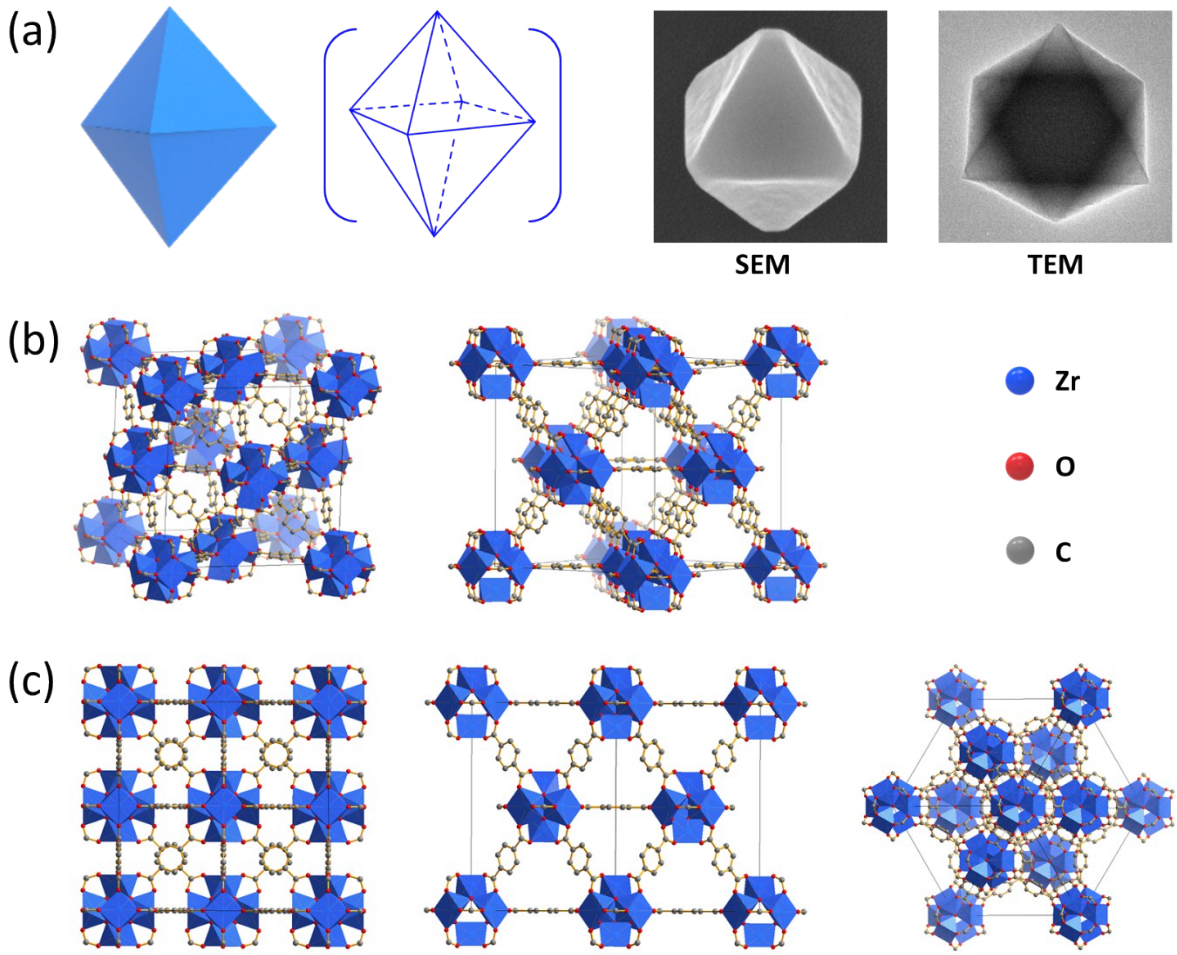

Fig. S1 (a) The Octahedral crystal morphology and the (b) 3D, (c) 2D Crystal unit illustration of the UIO-66 NP.

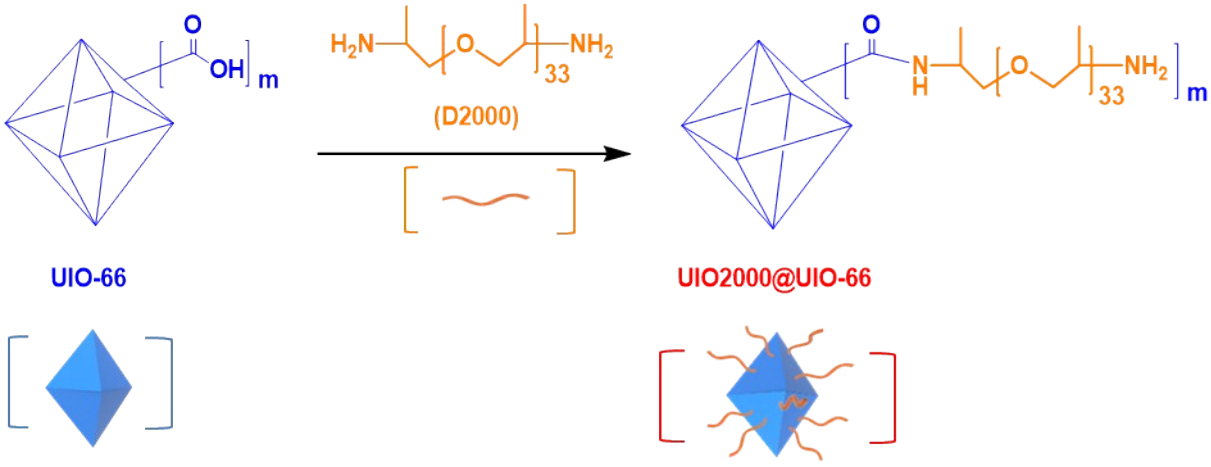

Fig. S2 Synthesis of D2000@UIO-66 and the illustration of surface change of UIO-66.

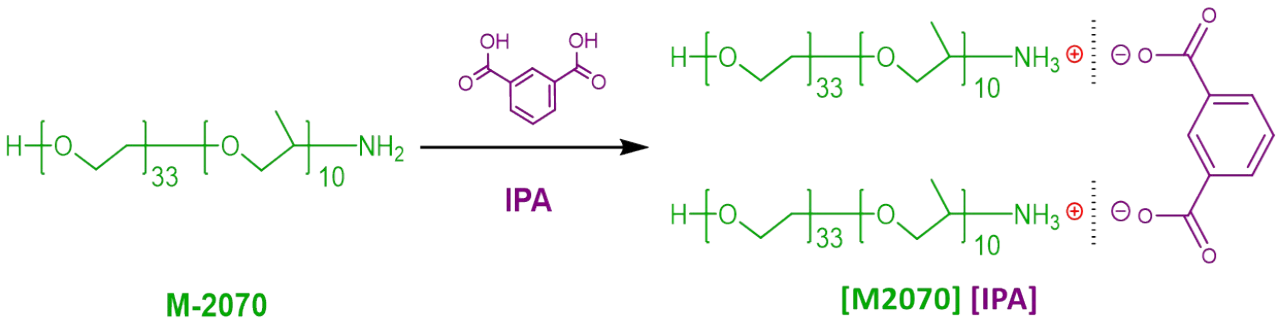

Fig. S3 Synthesis of the ionic liquid ([M2070][IPA]).

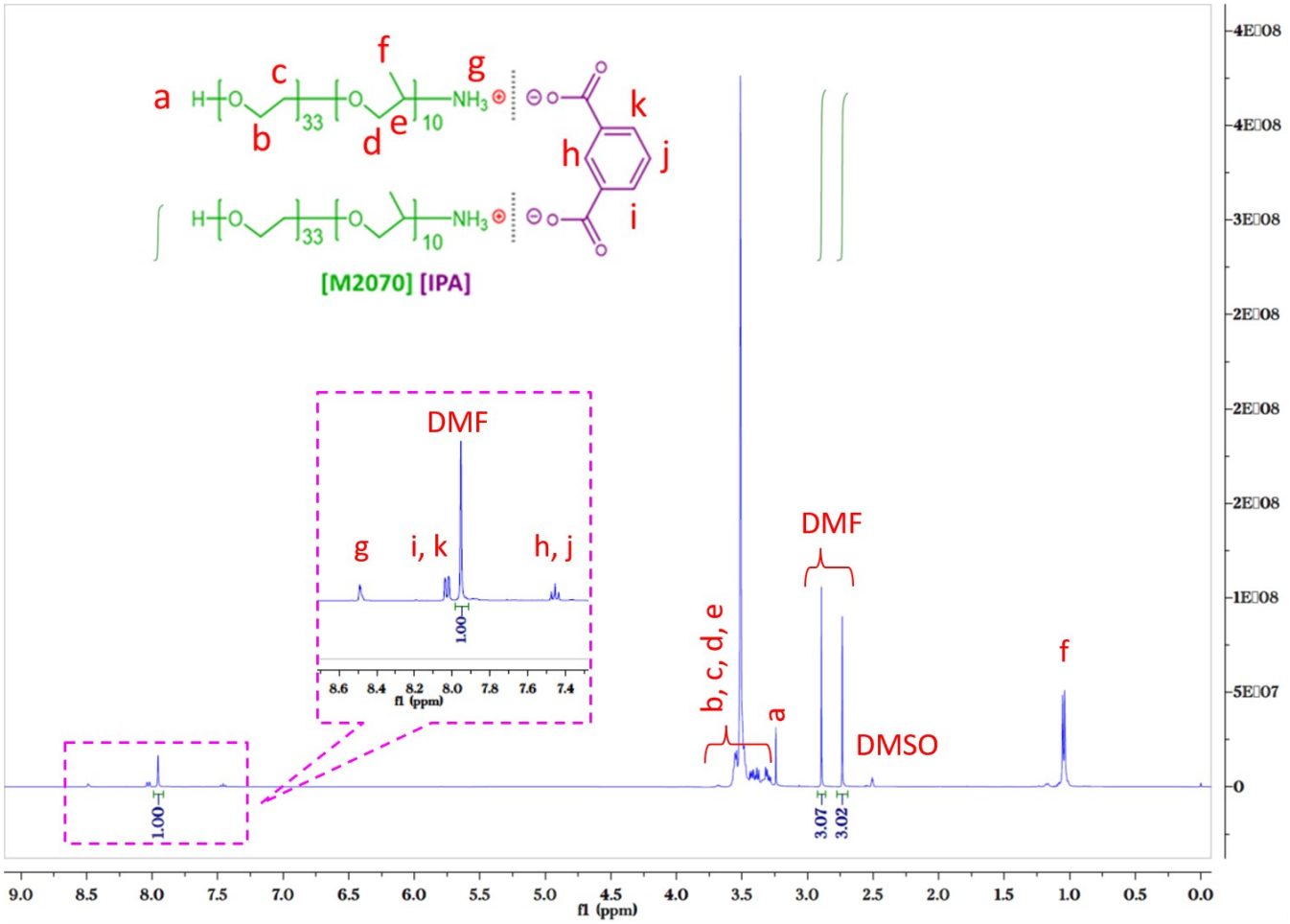

Fig. S4 ^{1}H-NMR spectrum of the ionic liquid ([M2070][IPA]) in DMSO-D_6.

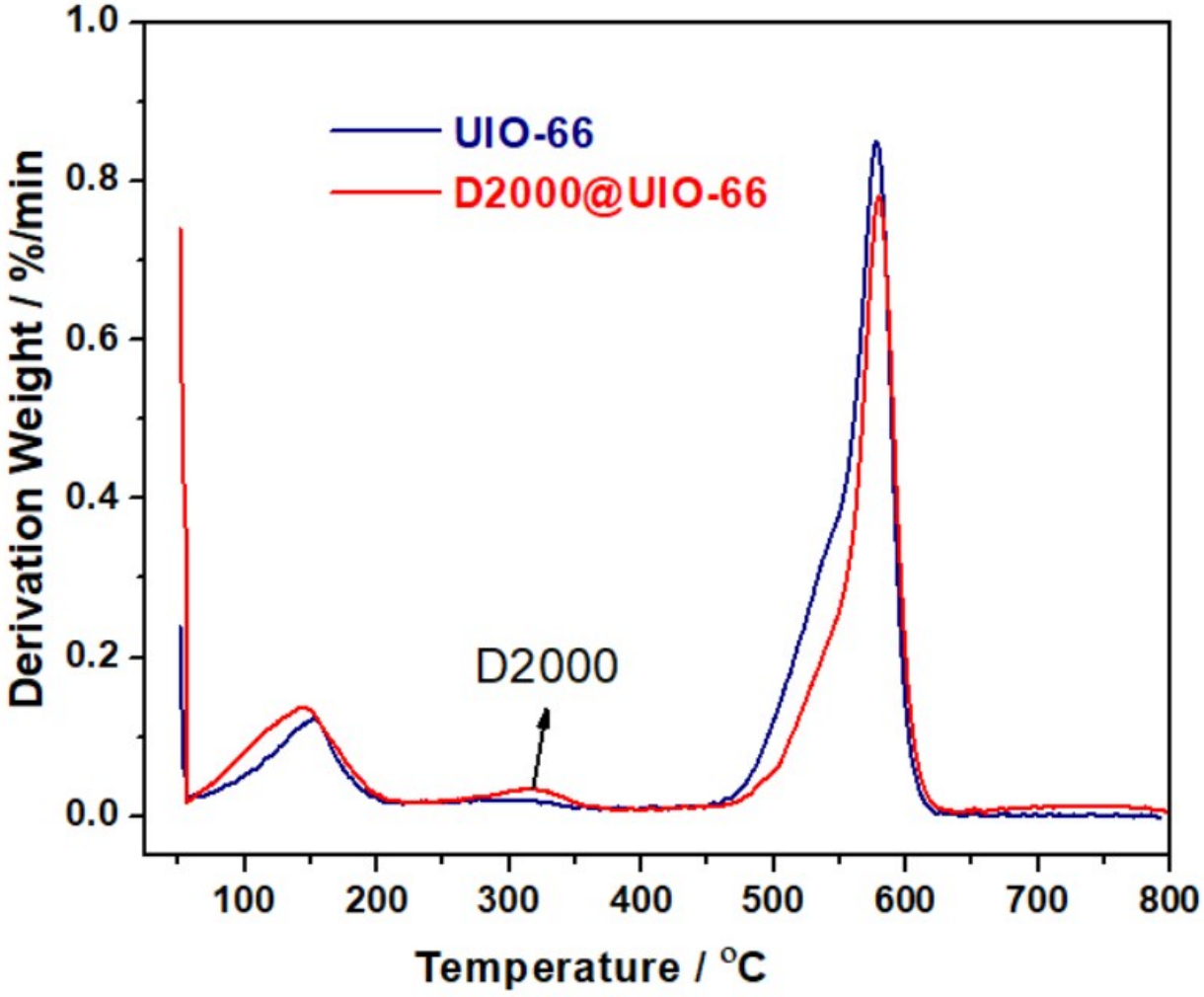

Fig. S5 DTG curves of UIO-66 and D2000@UIO-66 under N_2 atmosphere.

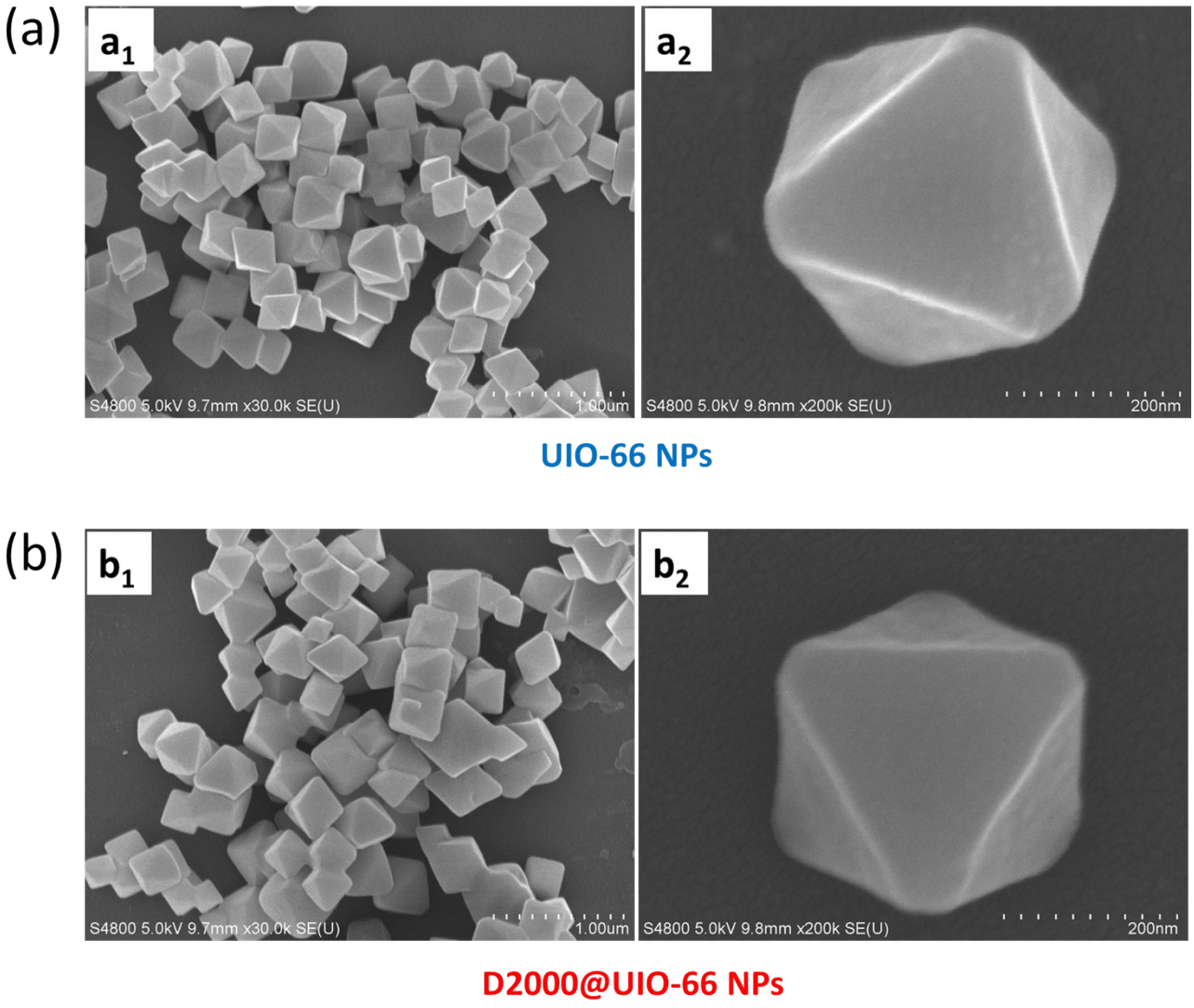

Fig. S6 SEM images of (a) UIO-66 and (b) D2000@UIO-66, respectively.

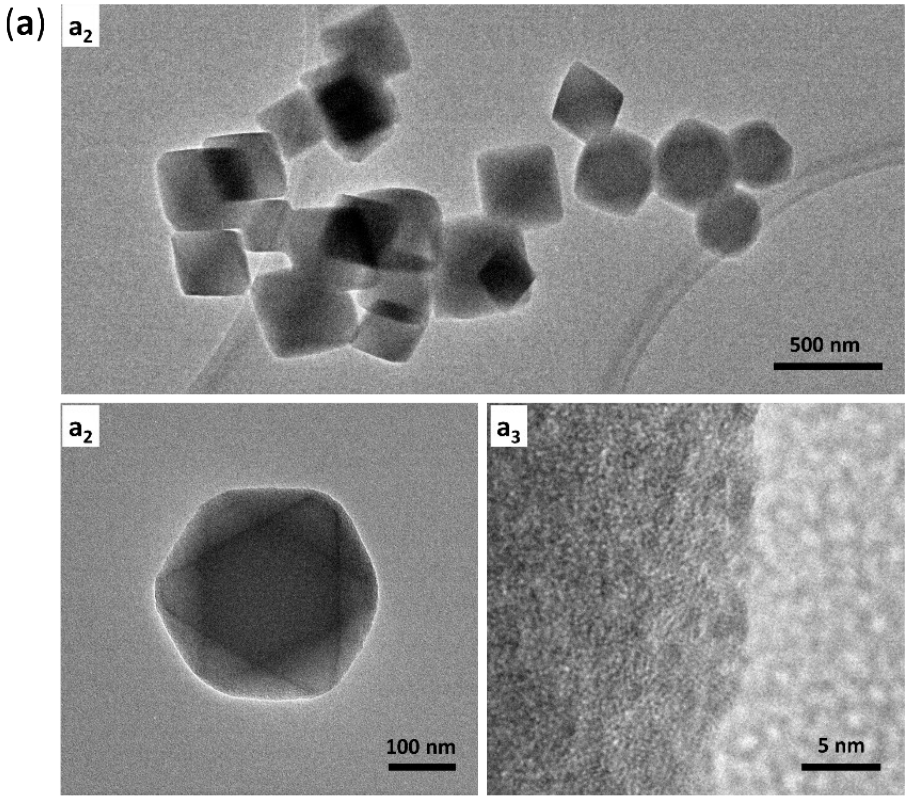

Fig. S7 TEM images of (a) UIO-66 and (b) D2000@UIO-66, respectively.

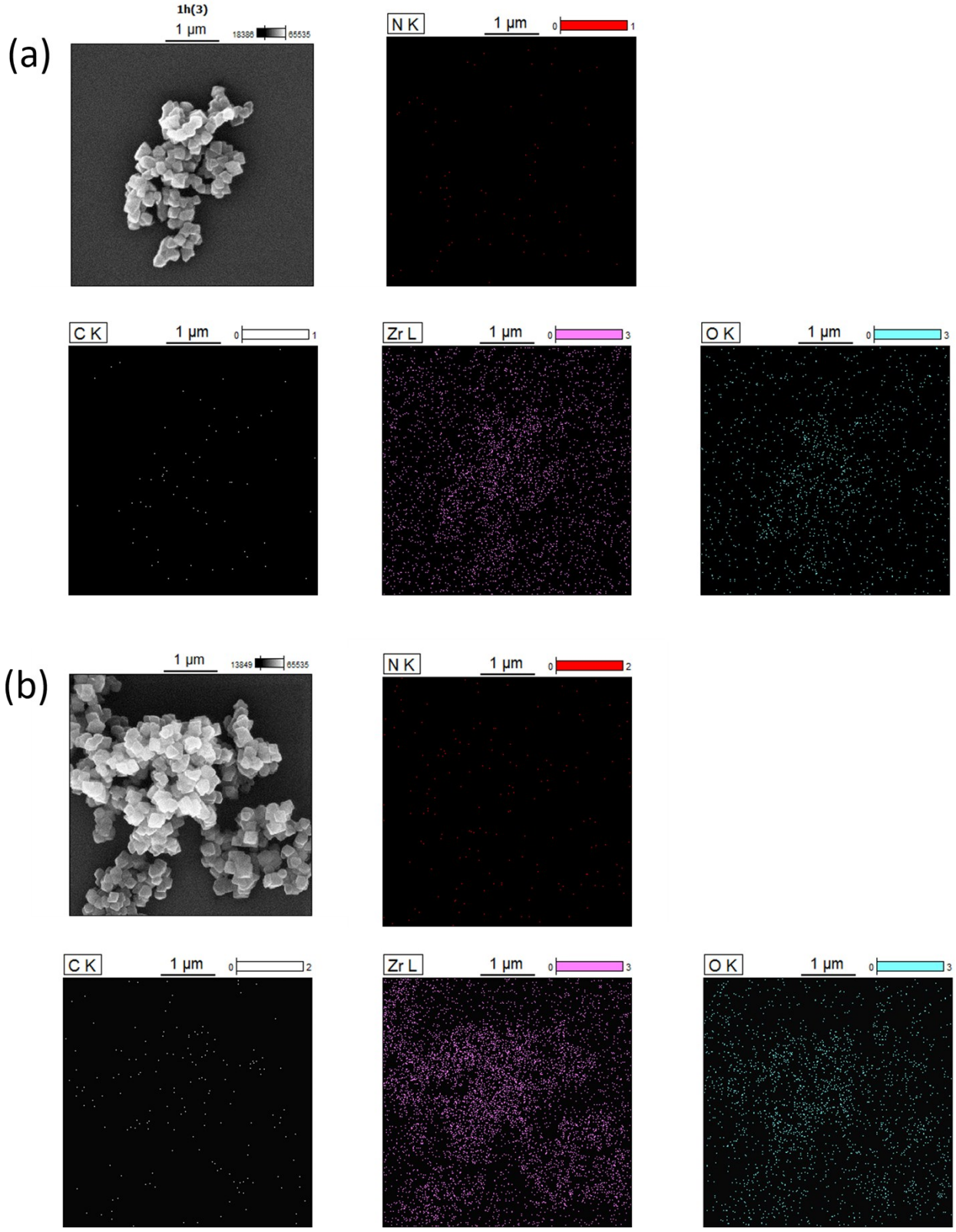

Fig. S8 C, N, O, Zr EDS mapping of (a) UIO-66 and (b) D2000@UIO-66, respectively.

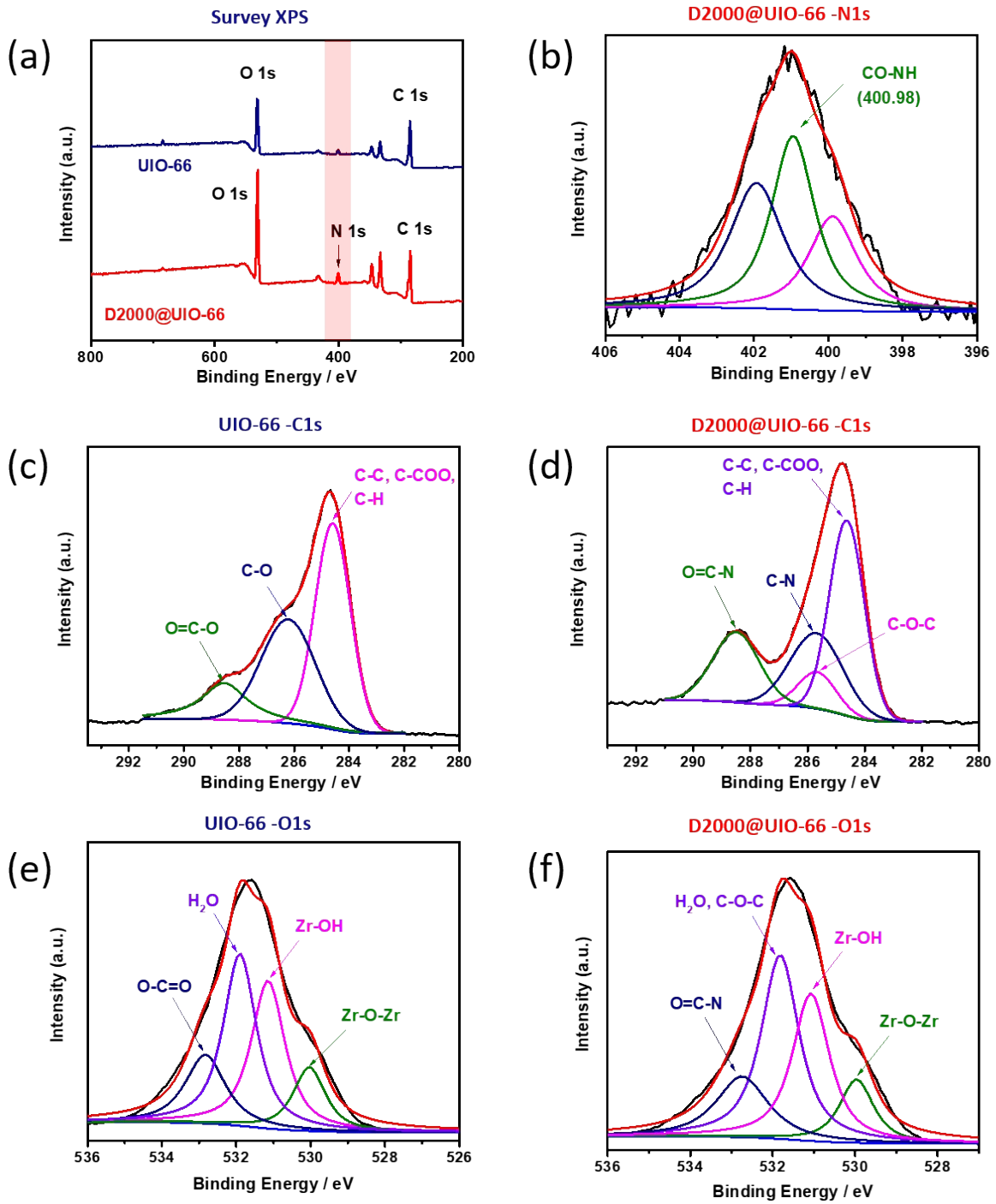

Fig. S9 XPS spectra of UIO-66 and D2000@UIO-66. (a) Survey XPS spectra of UIO-66 and D2000@UIO-66; (a-f) high-resolution XPS spectra of the UIO-66 and D2000@UIO-66, respectively.

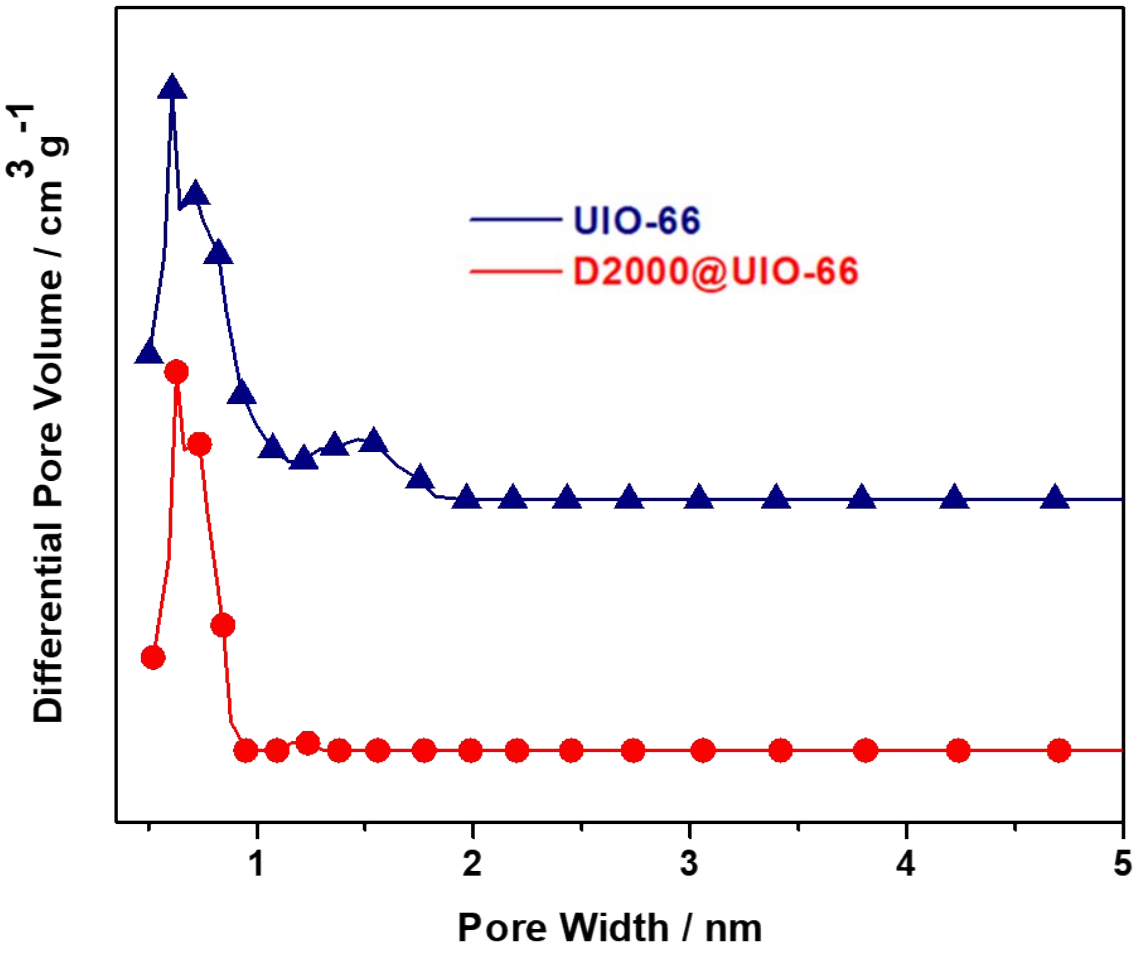

Fig. S10 Pore size distributions of UIO-66 and D2000@UIO-66.

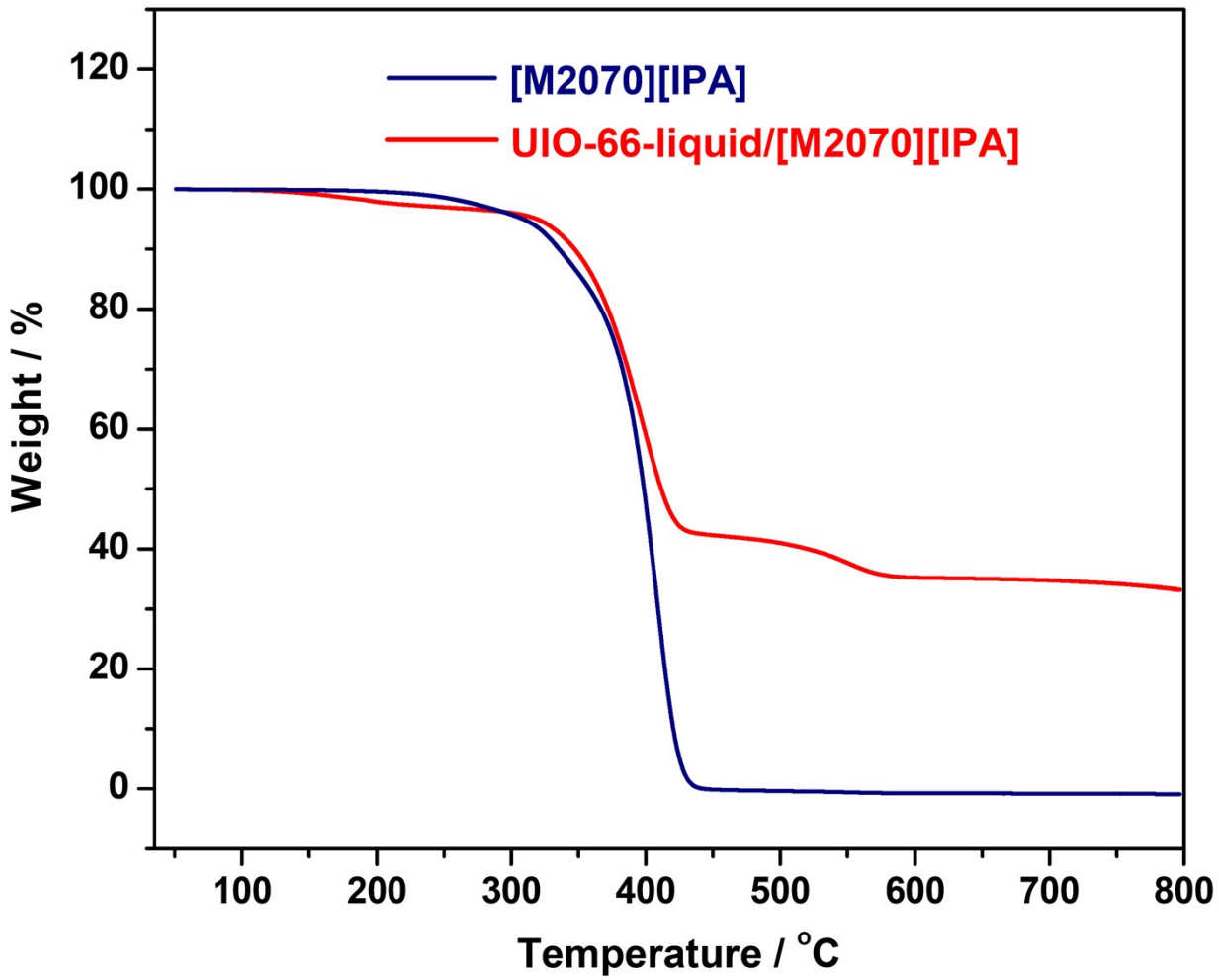

Fig. S11 TGA curves of the [M2070][IPA] and UIO-66-liquid/[M2070][IPA].

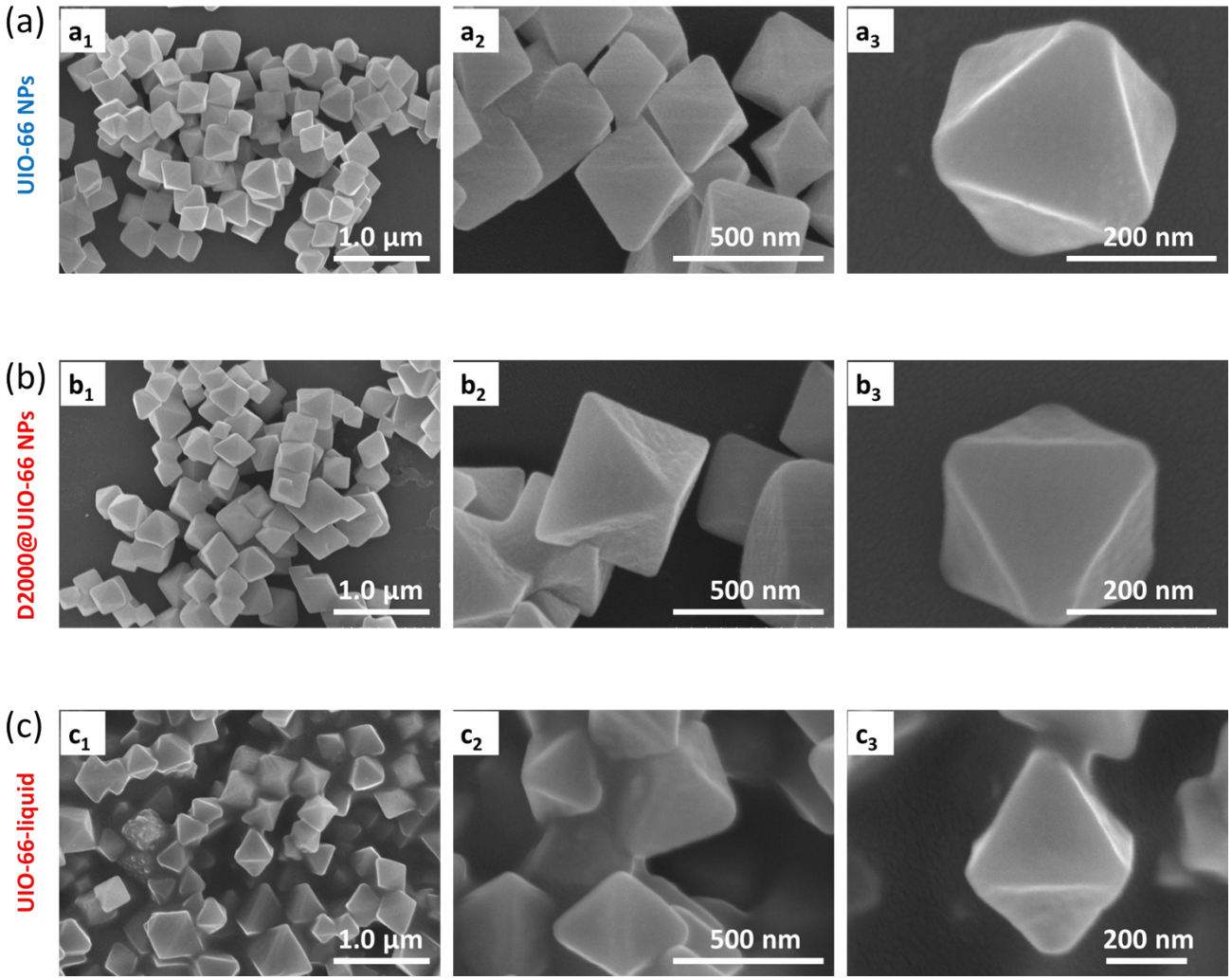

Fig. S12 SEM images of (a) UIO-66, (b) D2000@UIO-66 and (c) UIO-66-liquid, respectively.

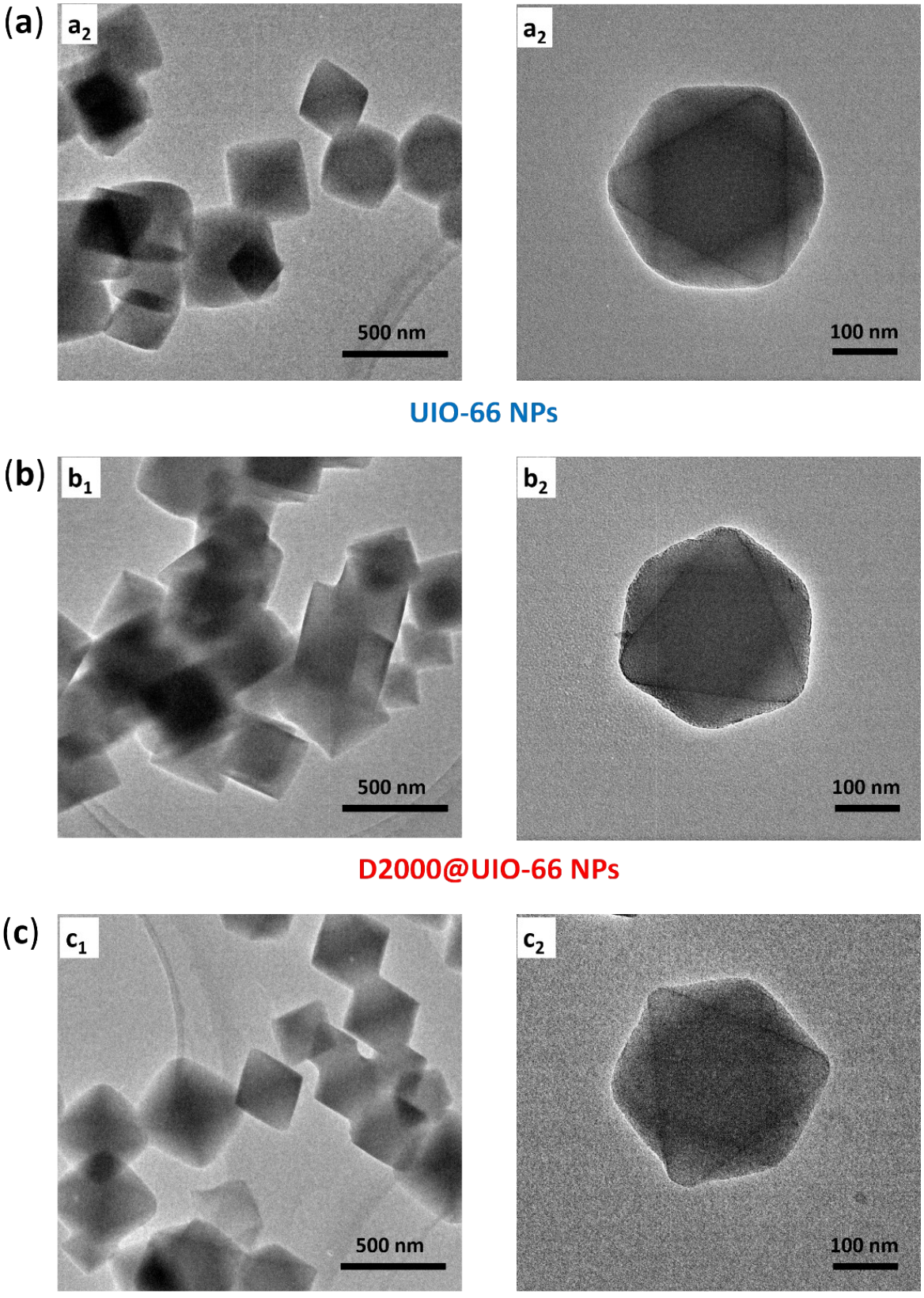

Fig. S13 TEM images of (a) UIO-66, (b) D2000@UIO-66 and (c) UIO-66-liquid, respectively.

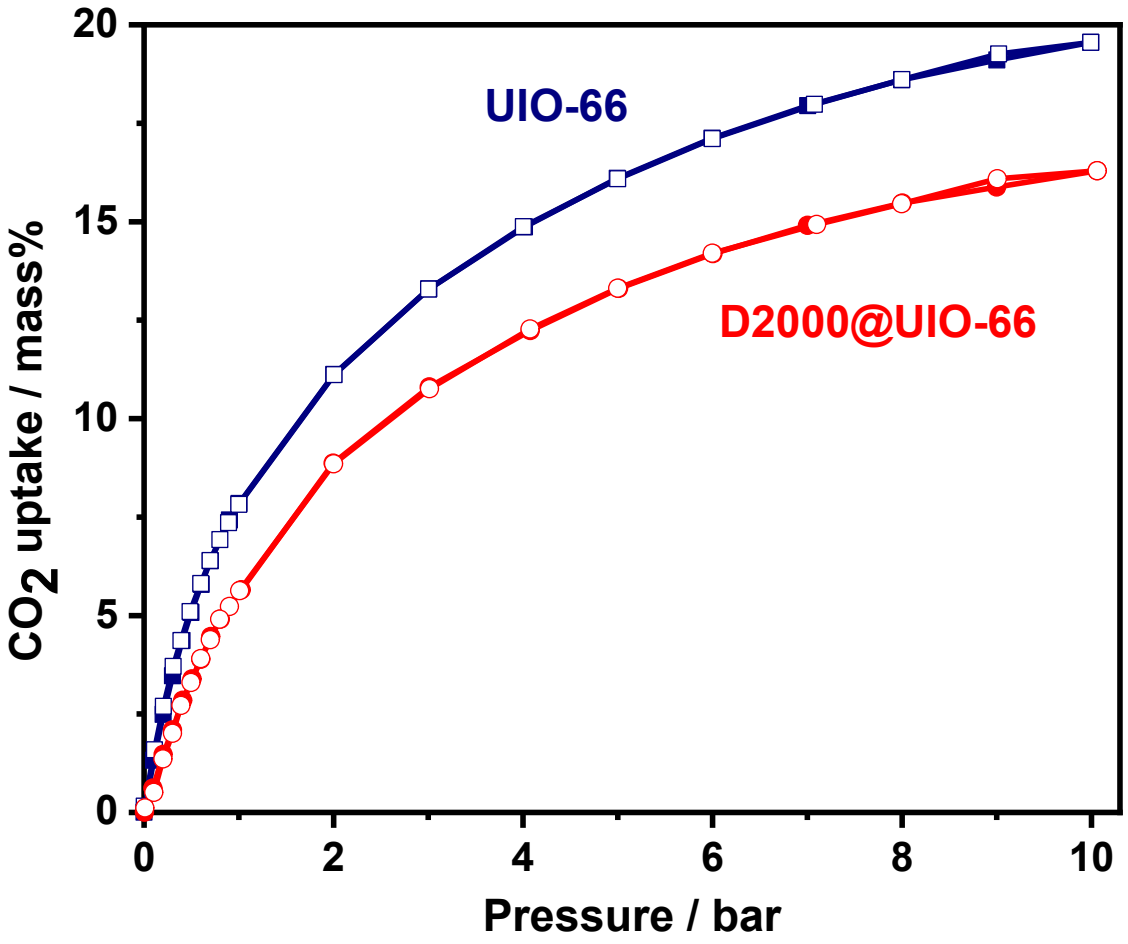

Fig. S14 CO_2 adsorption-desorption isotherms of UIO-66 and D2000@UIO-66 at 298 K.

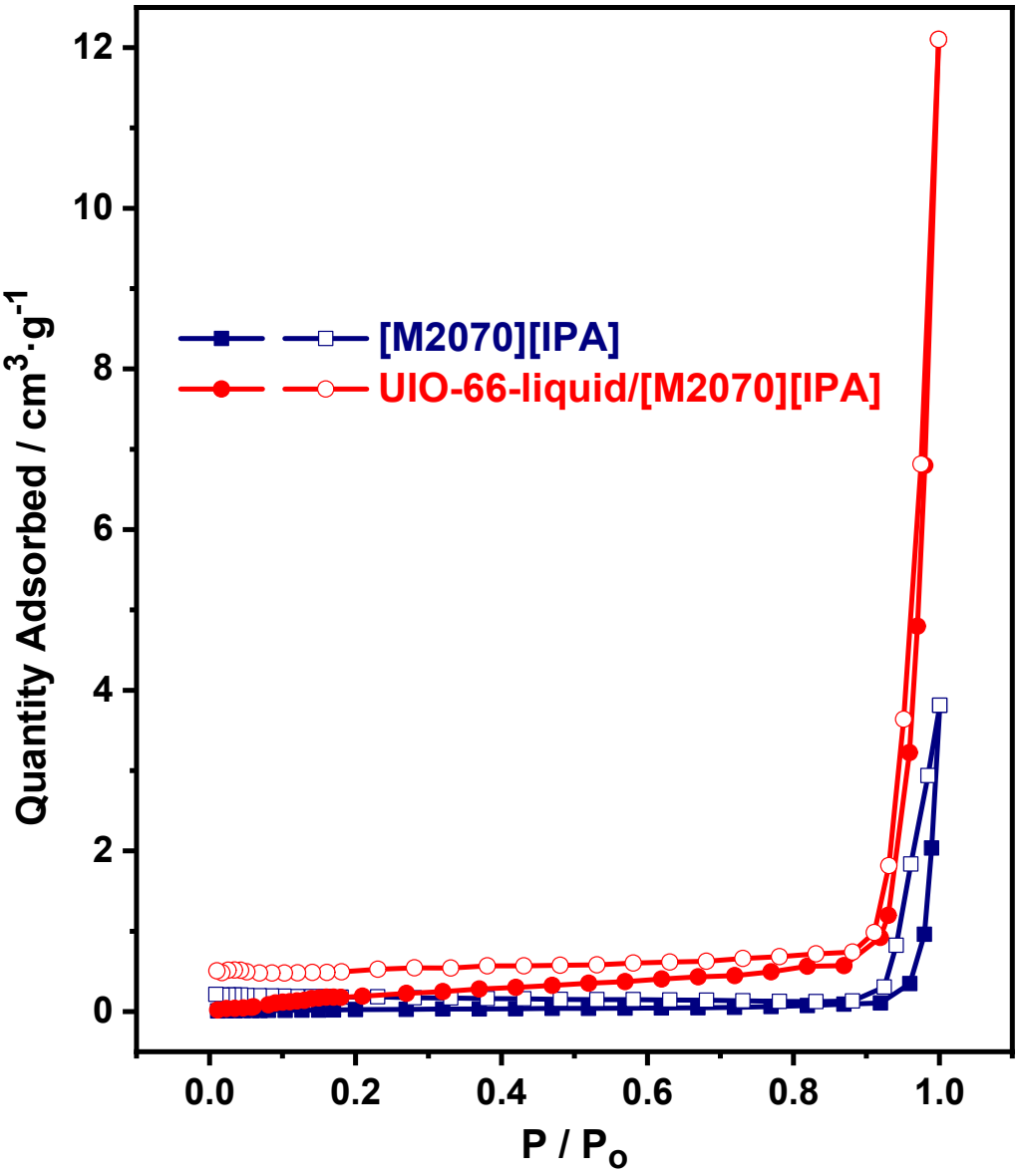

Fig. S15 N_2 adsorption-desorption isotherms of UIO-66-liquid and the ionic liquid ([M2070][IPA]) by BET at 77 K.

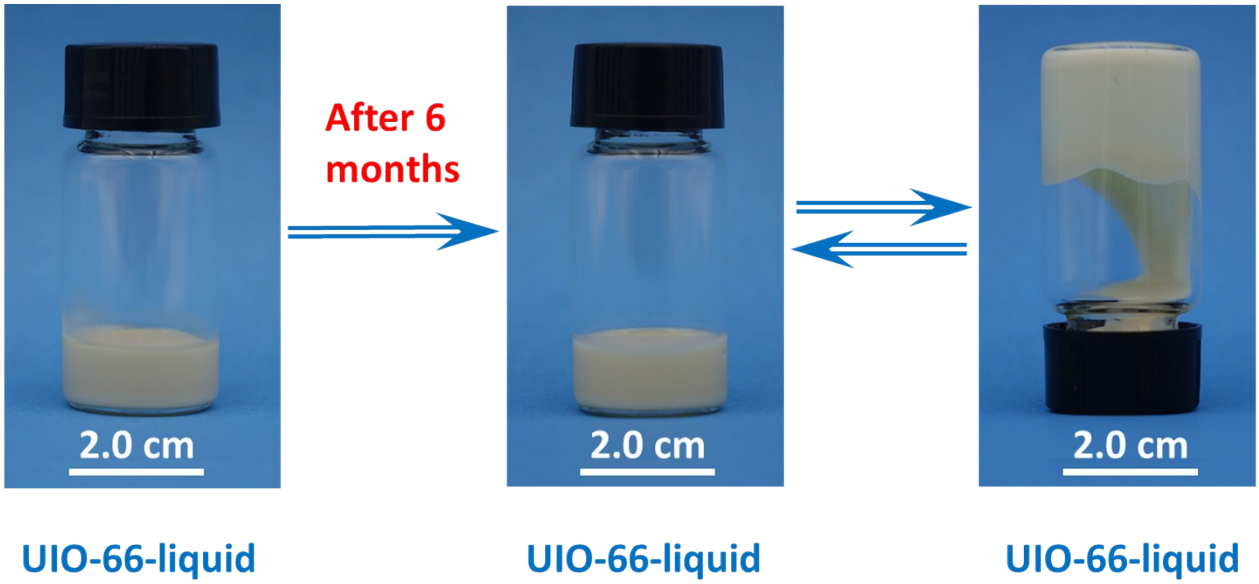

Fig. S16 Fluidity of this UIO-66-liquid after setting for six months in a vacuum oven at 45 °C.

Table S1. Comparison of the CO_2 uptake capacity of the UIO-66-liquid to coexisting porous liquids

Material	Adsorption Condition	Adsorption Capacity	Reference
UIO-66-liquid/[M2070][IPA] (50 wt% UIO-66)	10 bar 25 ℃	7.32 wt. %	This work
HCS-liquid	10 bar 25 ℃	1.9 wt. %	[4]
ZIF-8-PL (30 wt% ZIF-8)	10 bar 25 ℃	6.86 wt. %	[5]
ZIF-8/[Bpy][NTf_2]	10 bar 25 ℃	2.5 wt. %	[6]
H-ZSM-5-liquid/[P66614][Br]	10 bar 25 ℃	2.95 wt. %	[7]
UIO-66-liquid/[M2070][IPA] (50 wt% UIO-66)	5 bar 25 ℃	4.99 wt. %	This work
ZIF-8/[$P_{6,6,6,14}$][NTf_2]	5 bar 25 ℃	2.112 wt. %	[8]
UIO-66-liquid/[M2070][IPA] (50 wt% UIO-66)	1 bar 25 ℃	1.95 wt. %	This work
15 wt% ZIF-8+34 wt% mIm+ 51 wt% glycol	1 bar 30 ℃	5.5 g/L	[9]

Notes and references

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