Supplementary Information

Post-synthetic modification of MOFs with ionic polymer for efficient adsorption removal of methylene blue from water

Hao Fan,[a] Zhufeng Zhang,[a] Yingjie Chen,[a] Ziquan Wang,[a] Huimin Wen,[a] Shilin Tian,[a] Siyu Chen,[a] Huaixia Zhao,*[a] Yiyan He,*[a] and Yangxin Wang*[a]

[a] *College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, P.R. China.*

Materials and Methods

Materials

Unless otherwise noted, all chemicals were purchased from Beijing InnoChem Science & Technology Co., Ltd., and used without further purification. UiO-66-NH$_2$ was prepared according to our previousy reported method.[1] UiO-66-NH-Met was prepared according to literature report.[2]

Characterization methods

^{1}H NMR spectra were recorded by using a Bruker AVANCE III NMR spectrometer at 400 MHz with tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed on Unicube, Elementar. Fourier-transform infrared (FTIR) spectra were obtained using KBr pellets with Nicolet iS 5 FTIR Spectrometer (Thermo Scientific). Powder X-ray diffraction (PXRD) patterns were recorded in the range of $2\theta = 5\sim80°$ on a desktop X-ray diffractometer (SmartLab-9kW, Rigaku Electric Co., Ltd). N$_2$ adsorption was measured volumetrically at 77 K on V-Sorb 2800P gas adsorption instrument. Each sample was degassed under 80 °C for 8 h before measurement. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area based on the adsorption data in the partial pressure of $0.05 < P/P_0 < 0.35$. The pore size distributions were calculated from the desorption data using Barrett-Joyner-Halenda (BJH) method. Scanning electron microscope (SEM) images were recorded Gemini 300 (Carl Zeiss, Germany) system. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 F30 instrument under the accelerating voltage of 300 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping images were recorded on a images were obtained on Ultim Extreme from Oxford Instruments. Zeta potential was measured using a particle electrophoresis instrument (Zetasizer Nano ZS, Malvern Instruments, Worcestershire, U. K.). The Smoluchowsky model was used by the instrument's software program to convert the electrophoretic mobility measurements into zeta potential values. The concentration of dye solutions was determined by Ultraviolet and visible (UV-Vis) spectrophotometer N4S from Shanghai INESA Analytical Instrument

Co., Ltd.

Preparation of UiO-66-PAMPS

UiO-66-NH-Met (100 mg) was added into an aqueous solution (5 mL) containing 2-acrylamide-2-methylpropane sulfonic acid (AMPS, 500 mg) and 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (I2959, 30 mg). The polymerization was carried out under a UV lamp (365 nm, 100 W) irridiation for 20 min at room temperature with magnetic stirring. The solid was isolated by centrifugation and washed with deionized water (3 × 30 mL) and acetone (3 × 30 mL), which was subsequently dried in vacuum at 60°C overnight to yield the target product UiO-66-PAMPS.

^{1}H NMR characterization of digested MOF materials

Solid MOF material (10 mg) was suspended in deuterium DMSO (600 μL) containing hydrofluoric acid (10 μL, 40 wt% aqueous solution). The mixture was ultrasonicated for about 5 min to generate a transparent solution, which was subsequently subjected to the ^{1}H NMR measurement.

General information for MB adsorption experiments

A series of batch adsorption experiments were carried out to evaluate the adsorption performance of MOF material in a water bath constant temperature oscillator. All the adsorption experiments were carried out in triplicate under 25°C. To study the adsorpiton kinetics, MOF adsorbent (10 mg) was suspended in MB solution (200 mg L^{-1}, 5 mL), and the mixture was shaken gently for a predetermined time before measuring the concentration of residual MB. To study the influence of pH on adsorption performances, UiO-66-PAMPS (10 mg) was suspended in MB solution (200 mg L^{-1}, 5 mL) with different pH values ranging from 3 to 11. The pH values of MB solutions were adjusted with HCl (1 M) and NaOH solutions (0.5 M). To obtain the adsorption isotherms, a set of adsorption experiments were conducted by adding MOF adsorbent (10 mg) into MB solution (5 mL, pH = 9) with varying concentrations ranging from 50

to 4000 mg L^{-1}. The resulting mixture was shaken for sufficient time to ensure the achievment of adsorption equilibrium. The concentrations of MB were determined by UV-Vis spectrophotometer. The calibration curves were established using 5 standards between 0 and 5 mg L^{-1} and had a coefficient of determination R^2 above 0.99. The adsorption capacities were calculated by Equation (1) as follows:

$$q_e = (c_0 - c_e) \cdot V/m \qquad (1)$$

where q_e (mg g^{-1}) is the adsorption capacity, c_0 (mg L^{-1}) and c_e (mg L^{-1}) are initial and equilibrium concentration of dyes, respectively. m (g) is the quality of added adsorbent, and V (L) represents the solution volume.

Pseudo-first- and pseudo-second-order model are used to analyze the adsorption kinetics, which are usually described by Equation (2) and (3), respectively.

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad (2)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (3)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption capacity at equilibrium and adsorption time t (min), respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) represent the constant of pseudo-first- and pseudo-second-order model, respectively.

Langmuir and Freundlich adsorption isotherm models are used to fit the adsorption isotherm data. These two adsorption isotherm models can be described by the Equation (4) and (5), respectively.

$$c_e/q_e = 1/q_m K_L + c_e/q_m \qquad (4)$$

$$lgq_e = lg K_F + 1/n \cdot lgc_e \qquad (5)$$

In Equation (4) and (5), q_e (mg g^{-1}) and c_e (mg L^{-1}) represent the adsorption capacity and the concentration of MB at equilibrium, respectively. q_m (mg g^{-1}) is the theoretical maximum adsorption capacity. K_L (L mg^{-1}) is the constant of the Langmuir model which relates to the energy of the binding sites and affinity to adsorption. K_F (mg g^{-1}) is a constant related to adsorption capacity and adsorption intensity, and 1/n is the Freundlich constant indicating the extent of nonlinearity between the solution concentration and adsorption capacities.

Regeneration and recycling of UiO-66-PAMPS

The reusablity study of UiO-66-PAMPS was conducted using the sample which was recovered after adsorption experiment carried out with UiO-66-PAMPS (50 mg) in MB solution (500 mg L^{-1}, 25 mL, pH = 9). The separated UiO-66-PAMPS was washed thoroughly with HCl (1 M) and ethanol. Afterwards, it was further washed with acetone (3 × 10 mL), and dried in vaccume at 60 °C overnight. The regenerated UiO-66-PAMPS was used again for adsorption experiment under the same conditions.
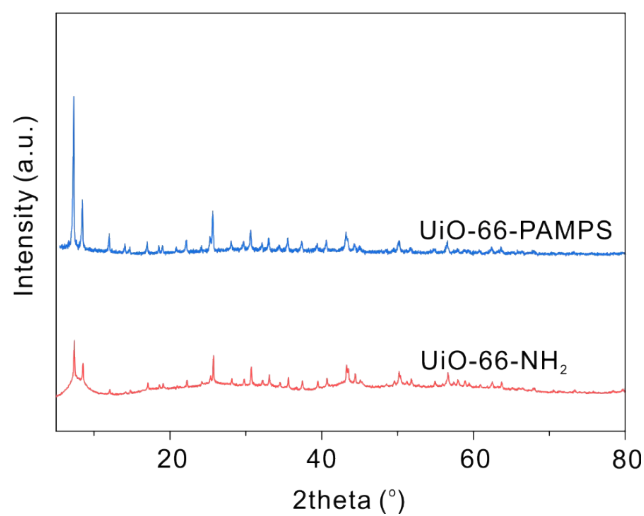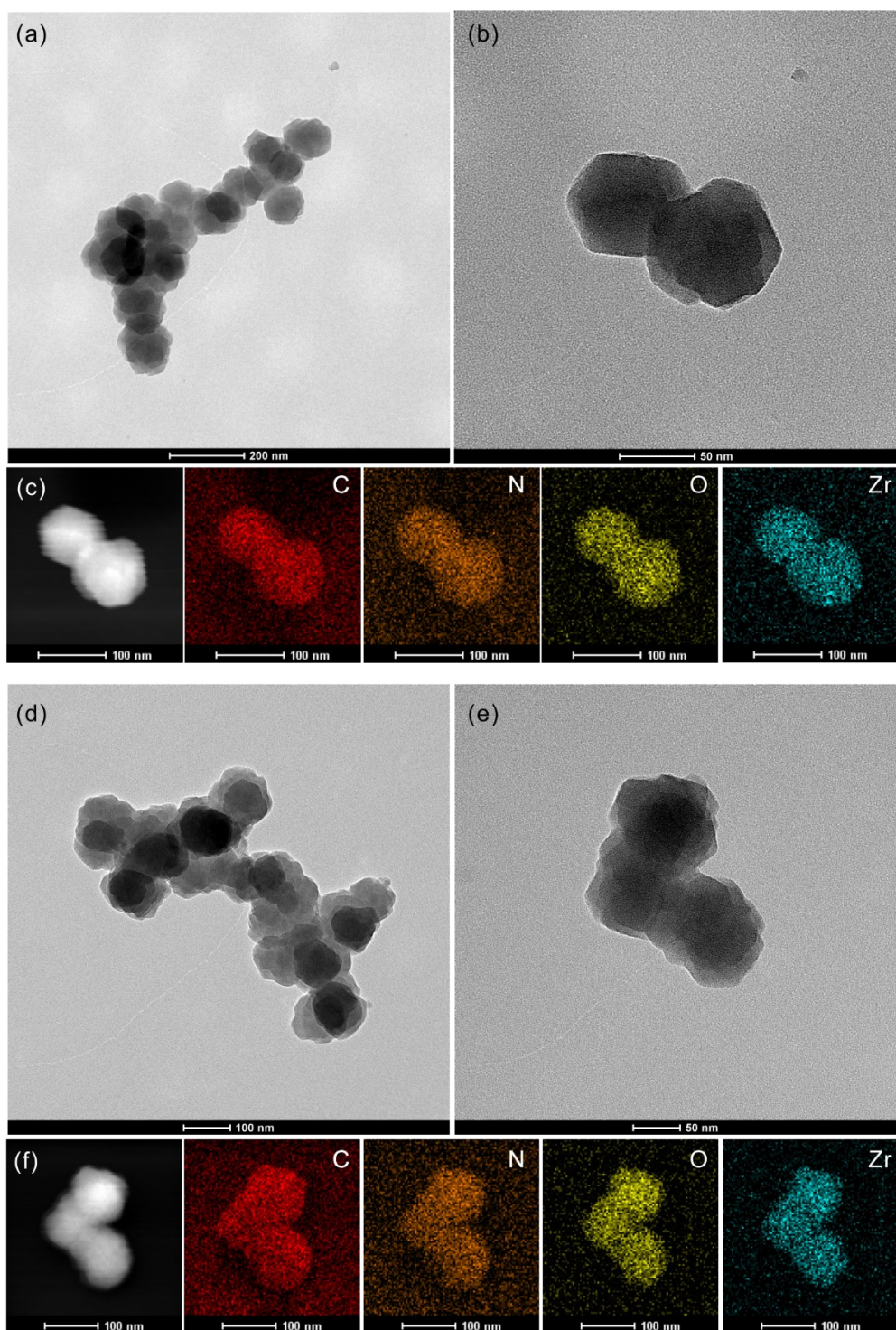
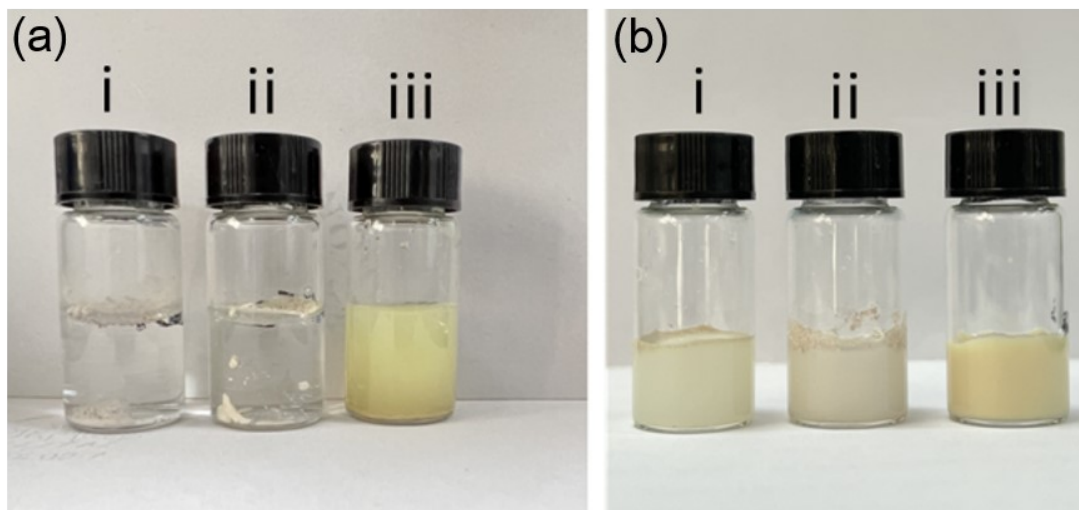**Fig. S1**   PXRD patterns for UiO-66-NH$_2$ and UiO-66-PAMPS.
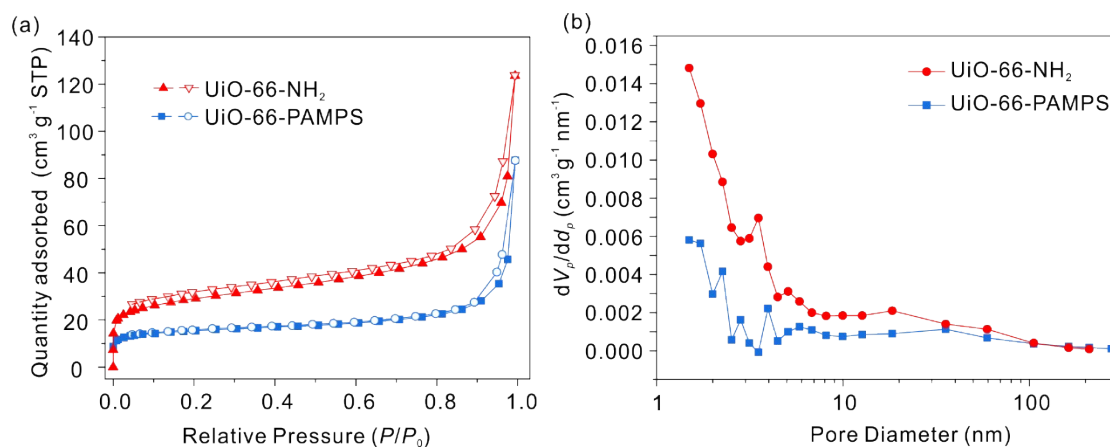
Fig. S2   (a) N$_2$ adsorption and desorption isotherms of UiO-66-NH$_2$ and UiO-66-PAMPS; (b) Pore size distribution of UiO-66-NH$_2$ and UiO-66-PAMPS.
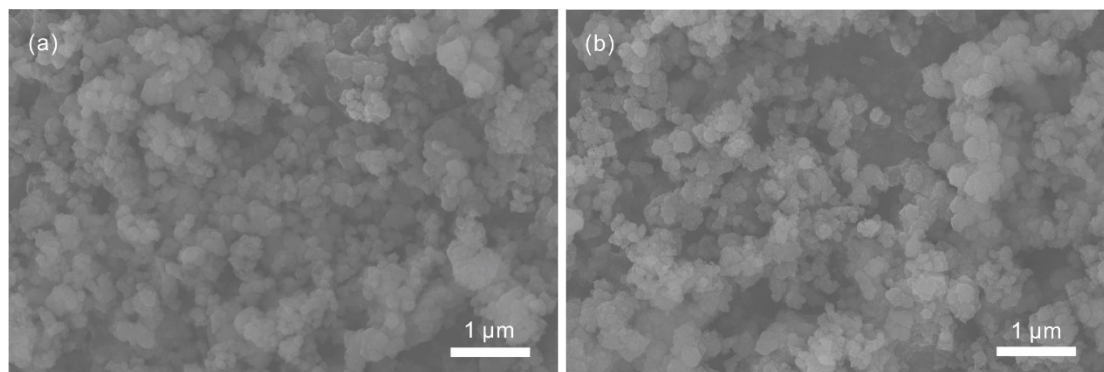

Fig. S3   SEM images of (a) UiO-66-NH$_2$ and (b) UiO-66-PAMPS.

Fig. S4 (a, b) TEM images of UiO-66-NH$_2$; (c) HAADF-STEM and elemental mapping images of UiO-66-NH$_2$; (d, e) TEM images of UiO-66-PAMPS; (f) HAADF-STEM and elemental mapping images of UiO-66-PAMPS.
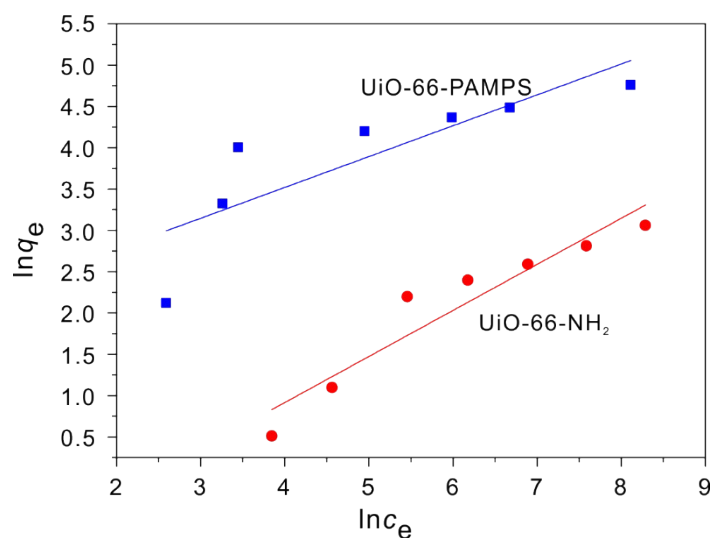
Fig. S5 Digital photos of (i) UiO-66-NH$_2$, (ii) UiO-66-Met, and (iii) UiO-66-PAMPS dispersed in deionzied water: (a) Before ultrasonication; (b) After ultrasonication.
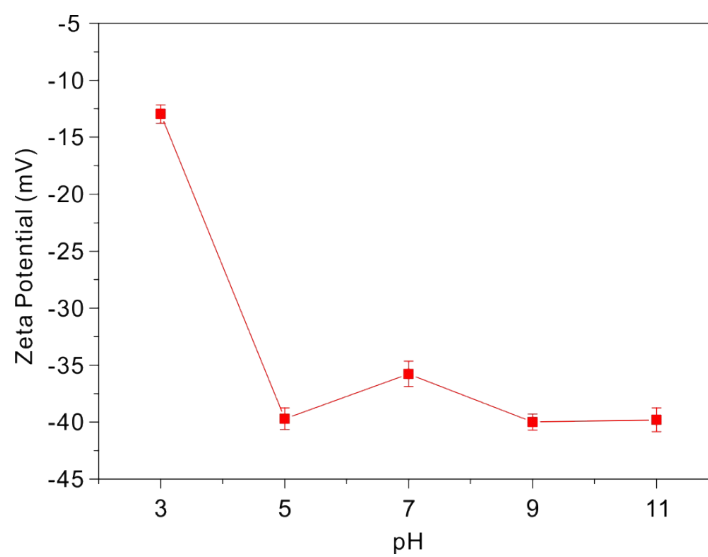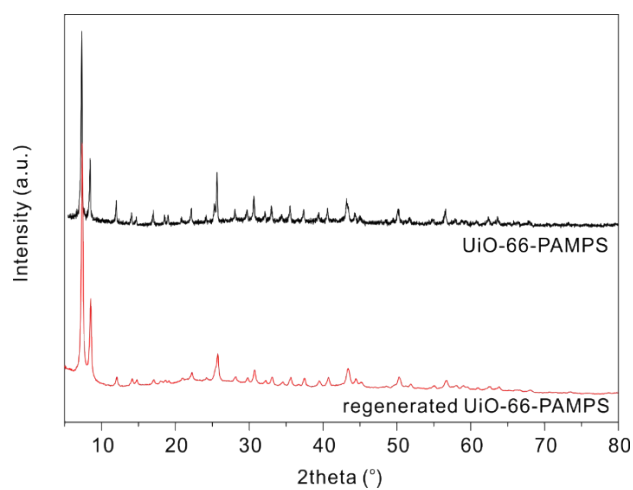

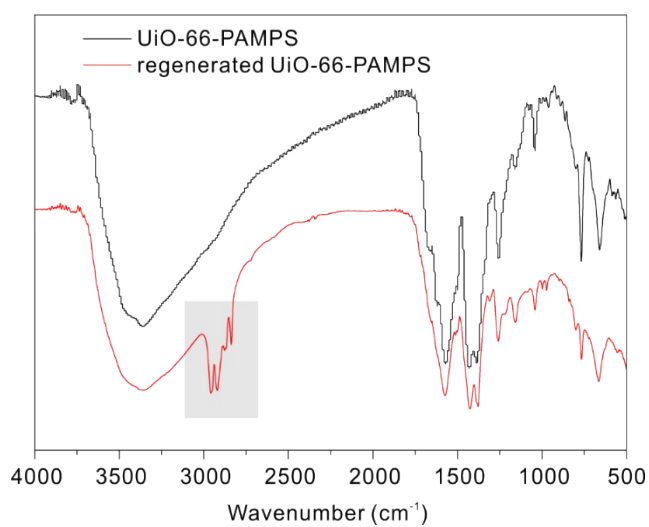**Fig. S6** Zeta potential of UiO-66-PAMPS under different pH.

Fig. S7 Freundlich adsorption isotherm plots of UiO-66-NH$_2$ and UiO-66-PAMPS.

Fig. S8 PXRD patterns for UiO-66-PAMPS before and after recycling experiment.

Fig. S9 FTIR spectra of UiO-66-PAMPS before and after reclcying experiment.

Table S1. Elemental analysis of UiO-66-NH$_2$, UiO-66-NH-Met, and UiO-66-PAMPS.

Sample	N (%)	C (%)	H (%)	S (%)
UiO-66-NH$_2$	5.24	30.19	3.320	0.191
UiO-66-NH-Met	3.03	27.56	3.683	0.130
UiO-66-PAMPS	3.50	27.78	3.842	1.858

Table S2. Porosity parameters of UiO-66-NH$_2$ and UiO-66-PAMPS.

Sample	Maximum adsorption quantity (cm^3 g^{-1} STP)	BET surface area (m^2 g^{-1})	Total Pore volume (cm^3 g^{-1})
UiO-66-NH$_2$	123.52	104.41	0.1778
UiO-66-PAMPS	87.732	57.16	0.1213

Table S3. Adsorption kinetic parameters for MB adsorption on UiO-66-NH$_2$ and UiO-66-PAMPS

Sample	Pseudo-first order			Pseudo-second order		
	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
UiO-66-PAMPS	44.94	0.113	0.951	48.70	3.51×10^{-3}	0.986
UiO-66-NH$_2$	15.32	0.012	0.979	22.88	3.82×10^{-4}	0.977

Reference:

1. Y. Wang, N. Zhang, E. Zhang, Y. Han, Z. Qi, M. B. Ansorge-Schumacher, Y. Ge and C. Wu, *Chem. Eur. J.*, 2019, **25**, 1716-1721.

2. Y. Zhang, X. Feng, H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang and B. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 4259-4263.