

## Supporting Information

### **Photopolymerization of metal-organic polyhedra: an efficient approach to improve the hydrostability, dispersity, and processability**

Xiao-Yan Xie<sup>†</sup>, Fan Wu<sup>†</sup>, Xin Liu, Wei-Qiang Tao, Yao Jiang, Xiao-Qin Liu, and Lin-Bing Sun\*

State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China.

\*E-mail: lbsun@njtech.edu.cn.

## Experimental Methods

### Chemicals

Glycine tert butyl ester hydrochloride ( $\geq 98\%$ ), 5-aminoisophthalic acid ( $\geq 98\%$ ), methacrylic anhydride (MA,  $\geq 94\%$ ), and butyl methacrylate (BMA,  $\geq 99\%$ ) was supplied by Aladdin Industrial Co., Ltd. Phenylbis (2,4,6-trimethylbenzoyl)phosphine oxide ( $\geq 96\%$ ) was supplied by Tokyo Chemical Industry Co., Ltd.  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  ( $\geq 98\%$ ),  $\text{CH}_2\text{Cl}_2$  ( $\geq 99.5\%$ ), *N,N*-dimethylformamide (DMF,  $\geq 99.5\%$ ), triethylamine ( $\geq 99\%$ ), ethanol (EtOH,  $\geq 95\%$ ), ethyl acetate ( $\geq 99.5\%$ ), hydrochloric acid, and cyclohexane ( $\geq 99.5\%$ ) were offered by Sinopharm Chemical Reagent Co., Ltd.

### Synthesis of MOP-15

The synthesis of MOP-15 was conducted as follows. The ligand 5-aminoisophthalic acid (4 mmol) was dissolved in DMF/EtOH and named as solution A. Glycine tert butyl ester hydrochloride (8 mmol) was dissolved in DMF and trimethylamine (8 mmol) was added to the solution. The white precipitate ( $\text{TEA} \cdot \text{HCl}$ ) was removed by filtration and the filtrate was named as solution B.  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (4 mmol) was dissolved in DMF and named as solution C. Then the solutions A, B, and C were mixed together in a capped vial (20 mL) and maintained at room temperature for 5 days. Green truncated-octahedral crystals were formed. These crystals were washed with  $3 \times 10$  mL of DMF and  $2 \times 5$  mL of cyclohexane.

### Synthesis of MOP-MA

In a typical procedure, 0.04 mmol dried MOP-15 (ca. 1 mmol equiv. of  $\text{NH}_2$ ) were suspended in  $\text{CH}_2\text{Cl}_2$  in a 20 mL vial, and 2.5 mmol MA was then added to the mixture. The vial was capped and left on the bench for 5 days. The reaction was stopped by removing the reaction solution and washing the solids 3-4 times with fresh  $\text{CH}_2\text{CH}_2$ . The solid was then dried under vacuum for 5 h at  $40^\circ\text{C}$ .

### Synthesis of *p*MOP-MA-BMA

MOP-MA (0.1 g, ca. 0.35 mmol equiv. of  $\text{NH}_2$ ) were suspended in BMA (1.0 g, 7mmol) and stirred for 30 min. To the mixture, photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (0.03 g, 0.07 mmol) was added and stirred for another 10 min. The resulting suspension

was dripped into a quartz vessel and photopolymerized under a UV lamp for 1 h to obtain the membrane, which was named as *p*MOP-MA-BMA. The distance between the mould and light was set to 20 cm. Among them, the sample *p*MOP-MA-BMA in the characterization test including IR, <sup>1</sup>HNMR, and UV-vis was post-washed with an excess of dichloromethane to remove the self-polymer of BMA.

### **Synthesis of *p*BMA**

The photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (0.03 g, 0.07 mmol) was added to BMA (1.0 g, 7mmol) and stirred for 3 min. The resulting suspension was dripped into a quartz vessel and photopolymerized under a UV lamp for 1 h to obtain the membrane, which was named as *p*BMA.

### **Materials Characterization**

The Fourier transform infrared (IR) spectra were conducted using a Nicolet Nexus 470 spectrometer with KBr wafer. <sup>1</sup>H NMR spectra of samples were recorded on a 400 MHz nuclear magnetic resonance instrument (Bruker Avance). Approximately 50 mg of pristine MOP-15, MOP-MA, and *p*MOP-MA-BMA were degraded in a solution of HCl and extracted by ethyl acetate respectively. Then the dried organic ligands were dissolved in D<sub>[6]</sub>DMSO. The TG curves were obtained with a thermobalance (STA-499C, NETZSCH) at the temperature range from 50 to 800 °C under the constant Air flow (20.0 mL·min<sup>-1</sup>). The crystalline structures of the samples were analyzed using X-ray diffraction (XRD) measurements on a Bruker D8 Avance diffractometer with Cu K $\alpha$  at 40 kV and 40 mA.

The amounts of copper in the composites were measured by inductively coupled plasma-atomic emission spectrometer (ICP-AES). A PerkinElmer sequential ICP spectrometer (Optima 2000 DV) was used for measurement. Samples were dissolved in nitric acid before measurement. The amounts of copper in MOP-15, MOP-MA, and *p*MOP-MA-BMA can be calculated. The C, H, and N element analyses were performed by a Vario Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). UV-vis spectra were performed using the SHIMADZU UV-2600 in the region of 200–850 nm.

## Adsorption Experiments

Methylene blue (MB) was used as the adsorbate for adsorption study. The concentration of MB in aqueous solution was  $25 \text{ mg}\cdot\text{L}^{-1}$ . Adsorption experiment was performed in the quartz cuvette directly in the cell holder of UV-vis spectrophotometer under ambient conditions. Then in a typical adsorption experiment, 2 mg of the adsorbent was statically dispersed in the aqueous solution (3 mL) containing  $25 \text{ mg}\cdot\text{L}^{-1}$  of guest molecule, until the adsorption equilibrium was reached.<sup>1</sup> The contents of guest molecules in the treated solutions were determined at regular intervals using the UV-vis spectrophotometer.

Before the adsorption tests, standard curves of absorbance vs concentration of aqueous methylene blue (MB) solution was plotted using the Beer–Lambert law, from which the linear equation was obtained. The equation was then applied to determine the amount of dye molecules adsorbed from the solutions. Prior to the addition of dye solution (MB), an adsorbent was weighted precisely and added to a cuvette. A UV–vis spectrophotometer was used to measure the adsorption curve after exposure to various irradiation conditions. The dye concentration was determined at appropriate time intervals, and adsorption amount ( $Q_e$ ) was calculated using equation 1.

$$Q_e = \frac{(c_i - c_0)V}{m} \quad (1)$$

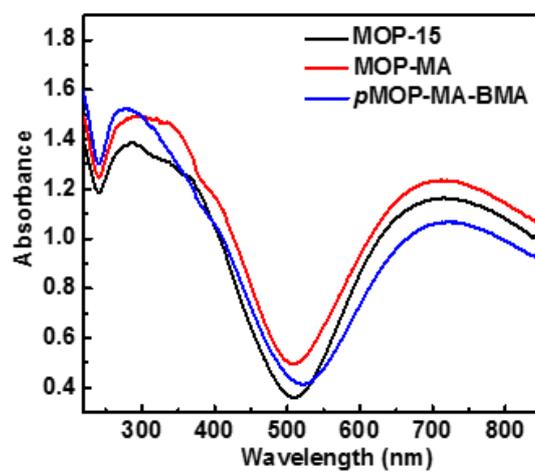
Where  $c_i$  and  $c_0$  represent the initial concentration and the equilibrium concentration, respectively,  $V$  represents the volume of solution, and  $m$  represents the mass of adsorbent. Desorption experiment was performed by using saturated adsorbents in ethanol under various irradiation conditions.

## Tables

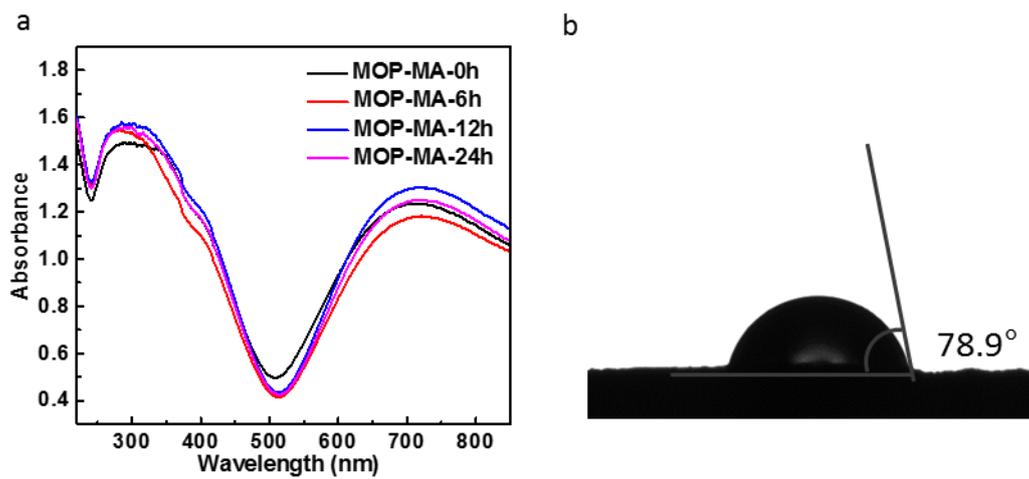
**Table S1.** Elemental analyses data and ICP data of MOP-15, MOP-MA, and *p*MOP-MA-BMA

Sample	Elemental composition (wt%)			ICP (wt%)
	C	H	N	Cu
MOP-15	40.02	2.52	6.50	24.83
MOP-MA	44.73	2.66	4.90	22.41
<i>p</i> MOP-MA-BMA	66.46	9.00	0.51	2.28

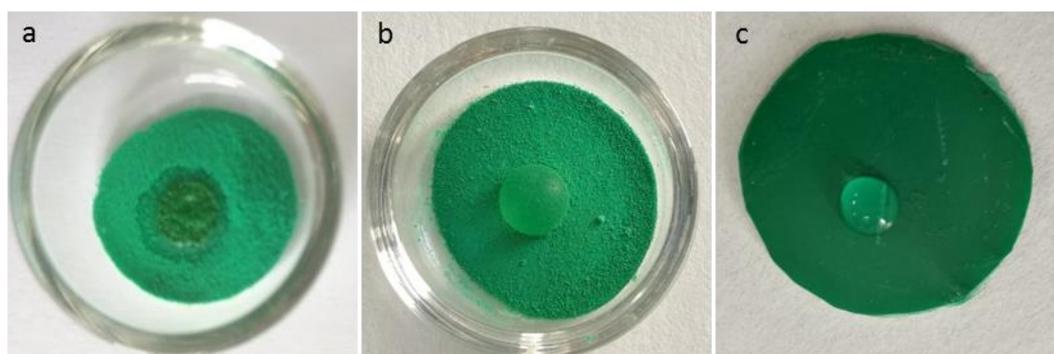
## Figures



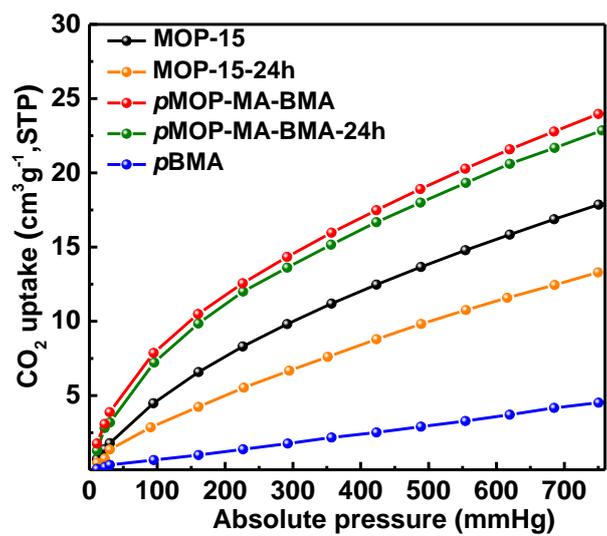
**Fig. S1** UV-vis spectra of MOP-15, MOP-MA, and pMOP-MA-BMA.



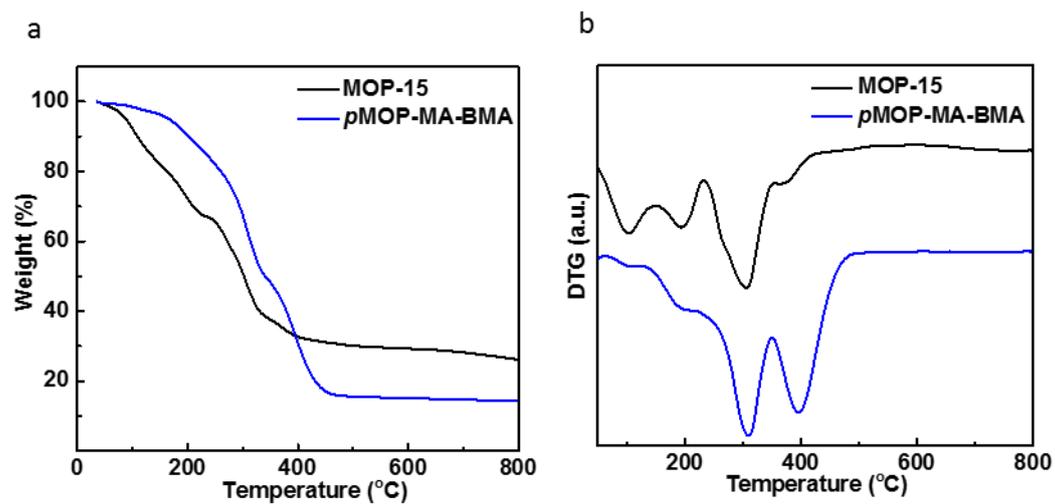
**Fig. S2** (a) UV-vis spectra of MOP-MA after exposure to humid atmosphere (relative humidity = 75%) for 24h. (b) Water contact angle image of MOP-MA.



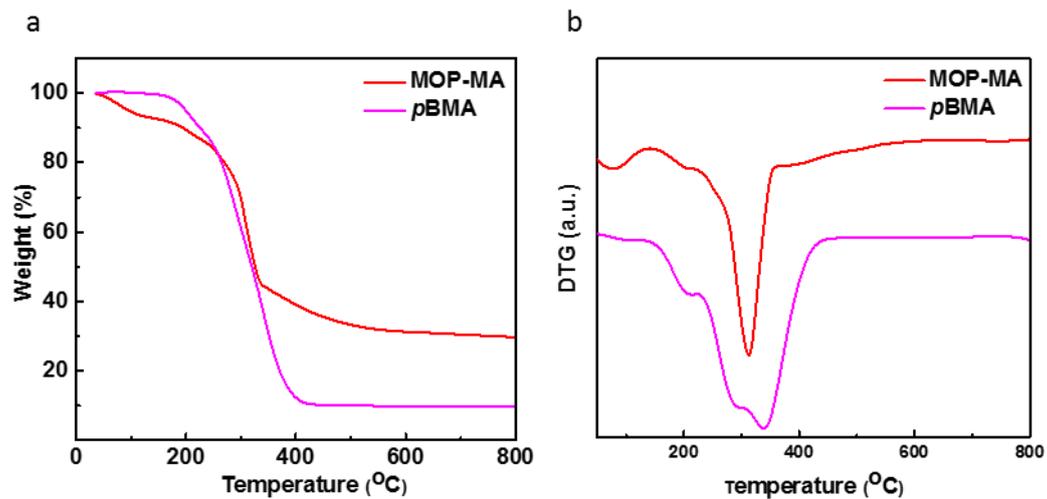
**Fig. S3** The wettability of (a) MOP-15, (b) MOP-MA, and (c) *p*MOP-MA-BMA.



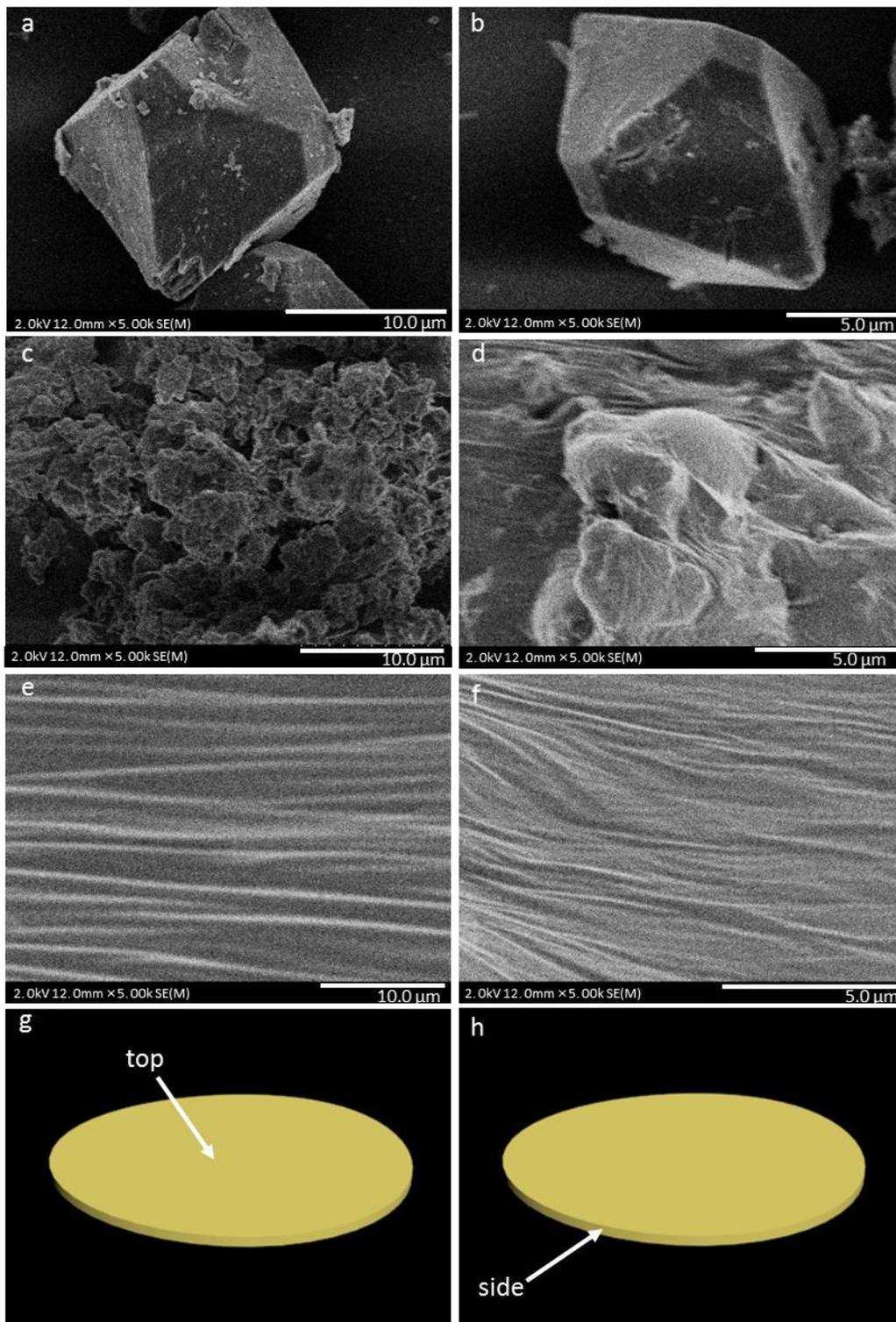
**Fig. S4.** CO<sub>2</sub> adsorption isotherms of MOP-15, pMOP-MA-BMA, and pBMA before and after exposure to humid atmosphere for 24 h.



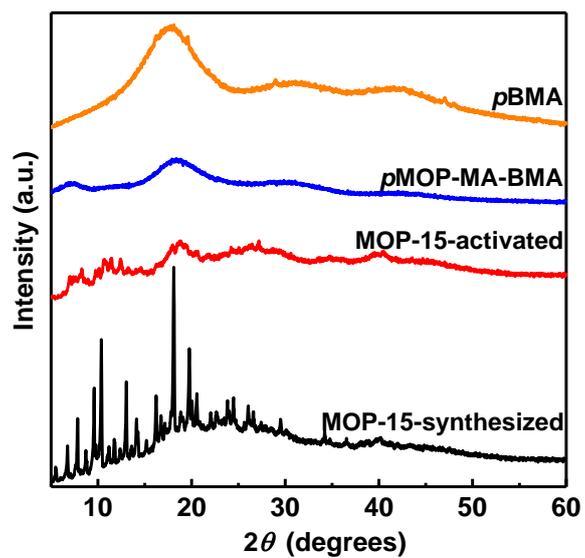
**Fig. S5** (a) TG and (b) DTG curves of MOP-15 and pMOP-MA-BMA.



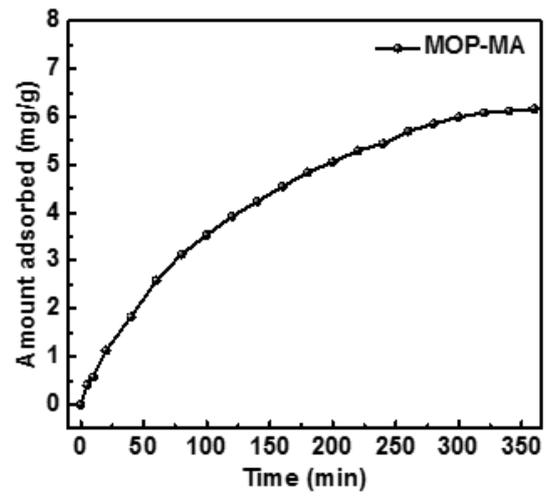
**Fig. S6** (a) TG and (b) DTG curves of MOP-MA and pBMA.



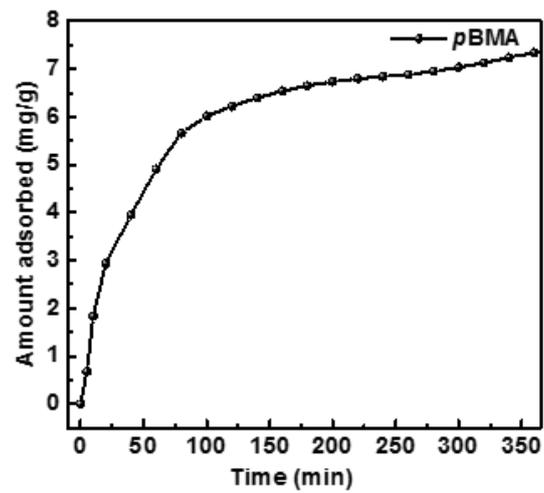
**Fig. S7** SEM images of (a, b) MOP-15, (c, d) *p*MOP-MA-BMA and (e, f) *p*BMA. The images (c) and (e) are scanned from the top of the membrane and the scanning angle can be seen from the schematic diagram (g); the images (d) and (f) are scanned from the side of the membrane and the scanning angle can be seen from the schematic diagram (h).



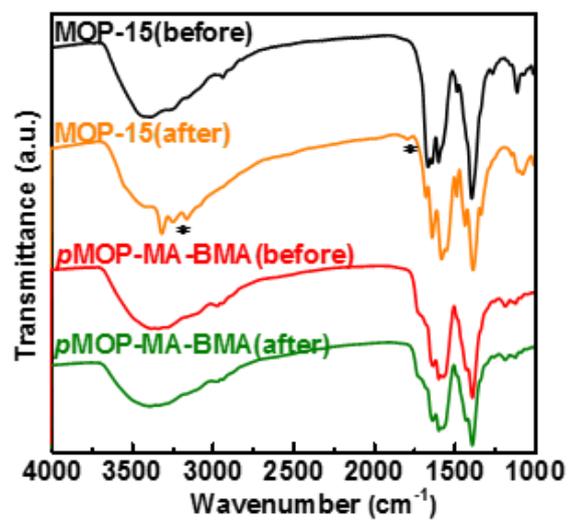
**Fig. S8** Wide-angle XRD patterns of synthesized MOP-15, activated MOP-15, pMOP-MA-BMA, and pBMA.



**Fig. S9** Adsorption curve of MB on the sample MOP-MA.



**Fig. S10** Adsorption curve of MB on the sample pBMA.



**Fig. S11** IR spectra of MOP-15 and *p*MOP-MA-BMA before and after the adsorption and desorption of MB.

## Notes and references

1. J. Zhu, J. J. Ding, X. Q. Liu, P. Tan and L. B. Sun, *Chem. Commun.*, 2016, **52**, 4006.