Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Enhancing the Hydrostability and Processability of Metal–Organic Polyhedra by Self-polymerization or Copolymerization with Styrene

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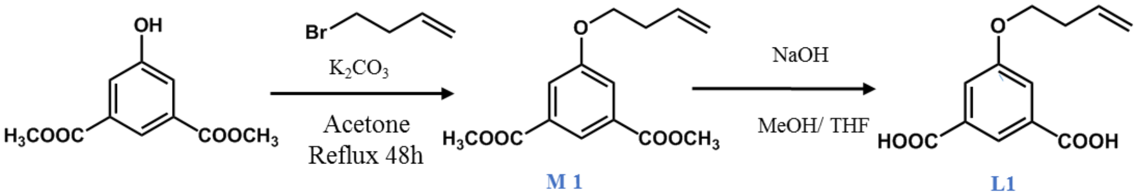
Experimental Methods

Chemicals

Dimethyl 5-hydroxyisophthalate (≥ 98%), 4-bromo-1-butene (≥ 97%), 2,2'-azobis(2-methylpropionitrile) (AIBN, ≥ 98%) was supplied by Tokyo Chemical Industry Co., Ltd. *N,N*-diethylformamide (DEF, ≥ 99%) and styrene (≥ 99%) was supplied by Aladdin Industrial Co., Ltd. Hydrochloric acid (HCl), acetone (≥ 99%), tetrahydrofuran (THF, ≥ 96%), CH_2Cl_2 (≥ 99.5%), ethanol (EtOH, ≥ 95%), methanol (MeOH, ≥ 99.5%), NaOH (≥ 99%), K_2CO_3 (≥ 99.99%) were offered by Sinopharm Chemical Reagent Co., Ltd. $Cu(NO_3)_2(2.5H_2O)$ (≥ 98%) was offered by Shanghai Adamas Reagent Co., Ltd. Deionized water was utilized throughout the experiments.

Synthesis of 5-(3-buten-1-yloxy)isophthalic acid (L1)

Ligand L1 was synthesized as follows.[1] A mixture of dimethyl 5-hydroxyisophthalate (1.05 g, 5.0 mmol), 4-bromo-1-butene (1 mL, 10.0 mmol), and K_2CO_3 (0.7 g, 5.0 mmol) were mixed in acetone (110 mL) and refluxed for 48 h under argon atmosphere. The reaction mixture was filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel, the obtained mid product was donated as M1.



M1 (2.0 g, 7.6 mmol) was stirred in a mixed solution of THF/MeOH/H_2O (60 mL, 20/20/20), then NaOH (2 g, 50 mmol) was added. The solution became clear and was allowed to stir for 24 at room temperature. Then the solution was acidified with 2M HCl solution until the pH reached about 3. The formed precipitate was washed with deionized water 5 times and dried to give a white powder, which was designated as L1.

Synthesis of MOP-Bt

L1 (0.06 g, 0.25 mmol) was dissolved in DEF/EtOH (6 mL, 3.6/2.4) and named as solution A.

$Cu(NO_3)_2(2.5H_2O)$ was dissolved in DEF/EtOH (6 mL, 3.6/2.4) and named as solution B. The solutions A and B were mixed together and transformed into a 50 mL Teflon autoclave, and then heated up to 100 °C for 24 h. Finally, the autoclave was cooled at room temperature. The blue rhombic plate-shaped crystals named as MOP-Bt were formed, and the crystals were washed with 3 × 10 mL of DMF and 2 × 5 mL of cyclohexane.[2]

Synthesis of *p*MOP

MOP-Bt (0.1 g, 0.014 mmol) and AIBN (2.3mg, 0.014 mmol) was dispersed in EtOH (10 mL) in a two-necked flask. After the mixture was sealed and deoxygenated by bubbling argon for 30 min to remove air, the mixture was subsequently stirred at 65 °C for 24 h for polymerization. After that, the product was collected by centrifugation and washed with EtOH for 2 times and dried under vacuum at 40 °C, leading to the formation of *p*MOP.

Synthesis of *p*MOP-ST powder

MOP-Bt (0.1 g, 0.014 mmol), styrene (57 µL, 0.5 mmol), and AIBN (2.3mg, 0.014 mmol) was dispersed in EtOH (10 mL) in a two-necked flask. After the mixture was sealed and deoxygenated by bubbling argon for 30 min to remove air, the mixture subsequently stirred at 65 °C for 24 h for polymerization. After that, the product was collected by centrifugation and washed with CH_2Cl_2 for 3 times to remove unreacted monomers as well as self-polymerization of styrene. Finally the obtained solid dried under vacuum at 40 °C, leading to the formation of *p*MOP-ST. The characterization data are exclusively for the power sample and no further characterization was performed on the gel as shown below.

Synthesis of *p*MOP-ST gel

MOP-Bt (0.05 g, 0.007 mmol), styrene (285 µL, 2.5 mmol), and AIBN (1.2 mg, 0.007 mmol) were dispersed in customized cylindrical, conical and square strains. After the mixture was sealed and deoxygenated by bubbling argon for 30 min to remove air, the mixture subsequently stirred at 65 °C for 24 h for polymerization. After that, *p*MOP-ST with cylindrical, tapered, and cubic shapes were collected.

Materials Characterization

The Fourier transform infrared (IR) spectra were conducted using a Nicolet Nexus 470 spectrometer with KBr wafer. ^1H NMR spectra of samples were recorded on a 400 MHz nuclear magnetic resonance instrument (Bruker Avance). Approximately 5 mg of M1 or L1 was dissolved in $CDCl_3$ and $D_{[6]}DMSO$, respectively. At the same time, approximately 50 mg of pristine MOP-Bt, *p*MOP-MA, and *p*MOP-ST were degraded in a solution of HCl and extracted by ethyl acetate respectively. Then the dried organic ligands were dissolved in $D_{[6]}DMSO$. The crystalline structures of the samples were analyzed using X-ray diffraction (XRD) measurements on a Bruker D8 Avance diffractometer with Cu Kα at 40 kV and 40 mA. The TG curves were obtained with a thermosbalance (STA-499C, NETZSCH) at the temperature range from 50 to 800 °C under the constant Air flow (20 $mL \cdot min^{-1}$). The N_2 adsorption-desorption isotherms were measured by a Micromeritics ASAP 2020 instrument at 77 K. The Brunauer–Emmett–Teller (BET) model was chosen to evaluate the surface areas (at the p/p_0 range from 0.04 to 0.20). 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-Bt, *p*MOP-MA, and *p*MOP-ST can be calculated. The C and H element analyses were performed by a Vario Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). UV–vis spectra were collected using the Shimadau UV-2600 in the region of 200–850 nm. Solid state samples were directly used for UV-vis measurement. The static contact angle test was measured on a Drop Meter Model A-100P contact angle meter. Before the test, the sample was pressed into a piece having a diameter of about 13 mm and a thickness of about 10 mm with a resolution of 0.01°.

Gas Adsorption Experiments

Static gas adsorption measurements of CO_2, N_2, and CH_4 over the samples at 273 K were performed using the ASAP 2020 analyzer. The pretreatment of samples was carried out at 60 °C for 6 h before the testing. Helium (99.999%) was used to measure the free space on the basis of the assumption that helium was not adsorbed at the measured temperature. The IAST (ideal adsorption solution theory) based on the dual-site Langmuir-Freundlich mode was exploited to evaluate the adsorption selectivities of the samples, as follows,

$$S = \frac{x_i/x_j}{y_i/y_j}$$

where *x* and *y* refer to the molar fractions in the adsorbed and bulk phases, and *i* and *j* represent component 1 and component 2, respectively.

Table S1. Strutural characteristics and elemental compositions of MOP-Bt, *p*MOP, and *p*MOP-ST.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_P ($cm^3 \cdot g^{-1}$)	Elemental composition (wt%)[a]		
			C	H	Cu
MOP-Bt	151	0.27	48.55	3.98	21.07
*p*MOP	283	0.60	48.28	4.04	21.69
*p*MOP-ST	174	0.42	53.99	4.40	18.86

[a] C and H were obtained by elemental analysis while Cu was detected by ICP.

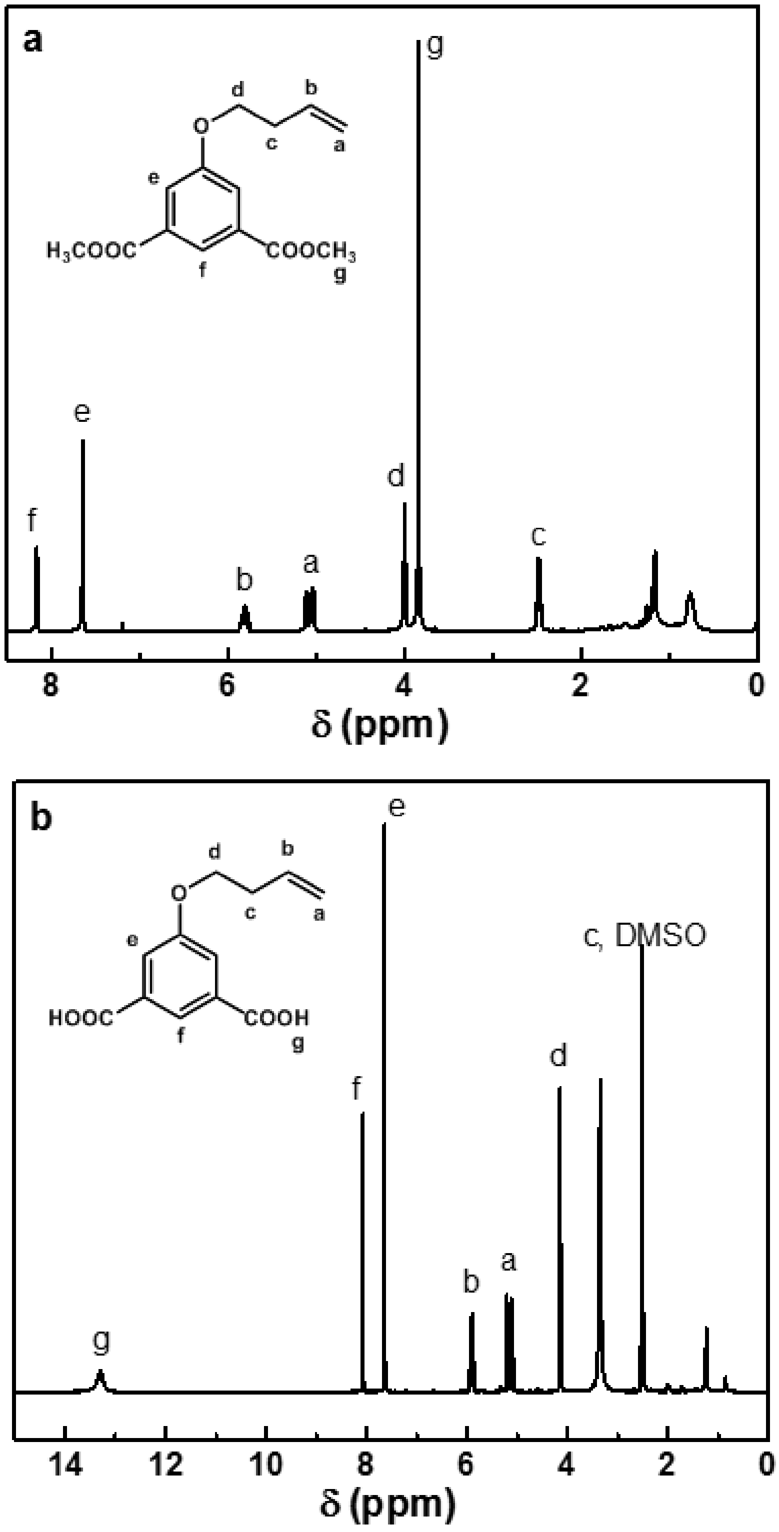


Fig. S1 ^{1}H NMR of (a) the intermediate M1 and (b) the ligand L1.

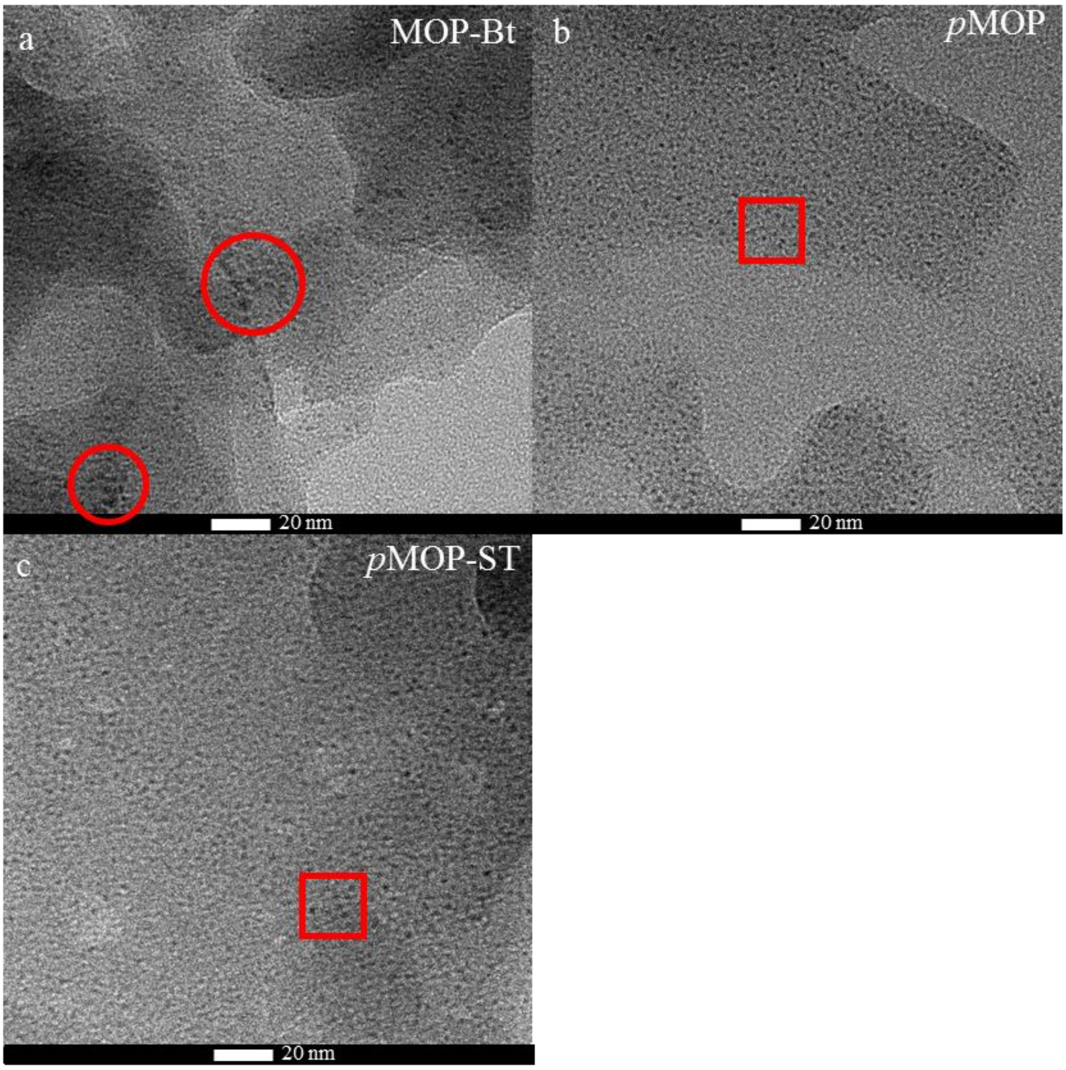


Fig. S2 TEM images of (a) MOP-Bt, (b) *p*MOP, and (c) *p*MOP-ST. The circles and squares in panels show some examples of aggregated and dispersed MOPs, respectively.

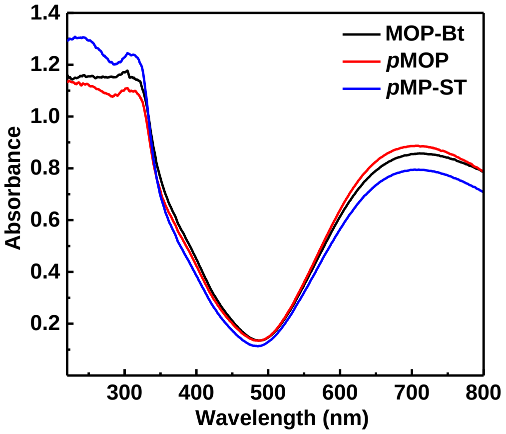


Fig. S3 UV-vis spectra of the samples MOP-Bt, *p*MOP, and *p*MOP-ST.

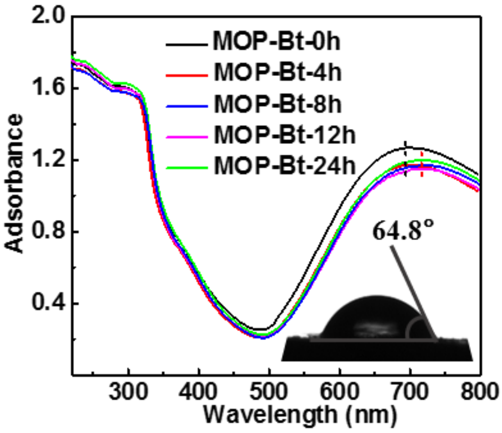


Fig. S4 UV-vis spectra and water contact angle of MOP-Bt after exposure to humid atmosphere (relative humidity = 75%) for 24 h.

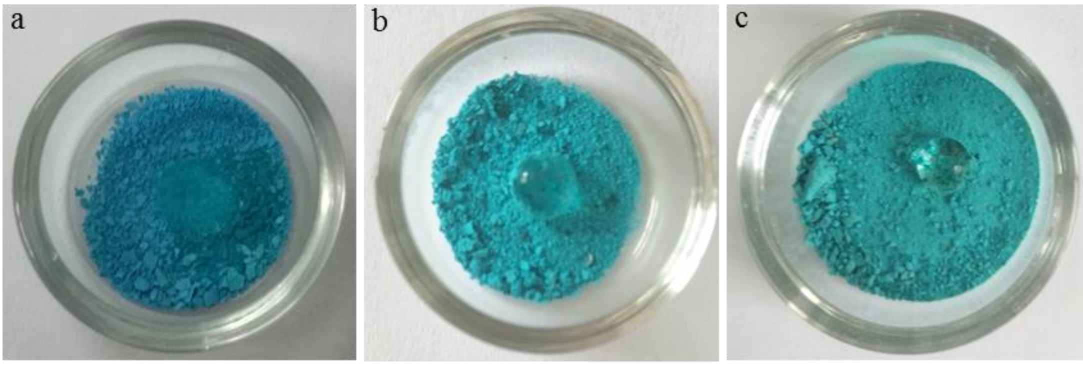


Fig. S5 The wettability photos of the samples (a) MOP-Bt (b) *p*MOP, and (c) *p*MOP-ST.

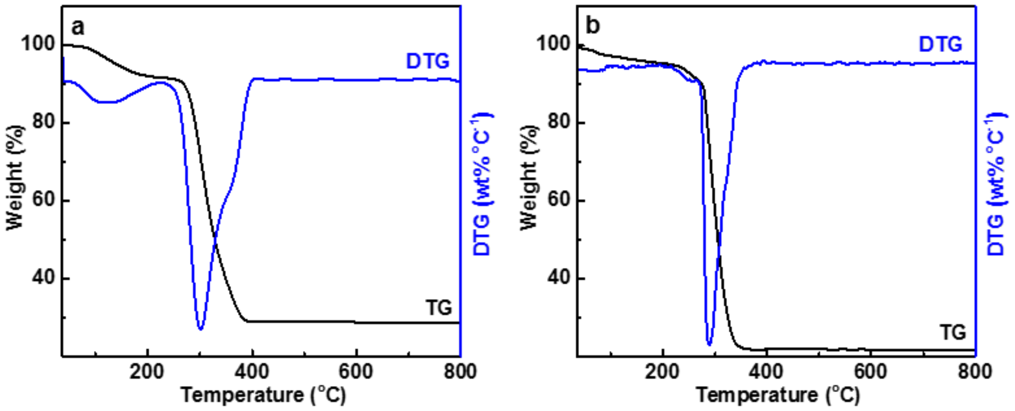


Fig. S6 TG and DTG curves of the sample MOP-Bt (a) before and (b) after degass.

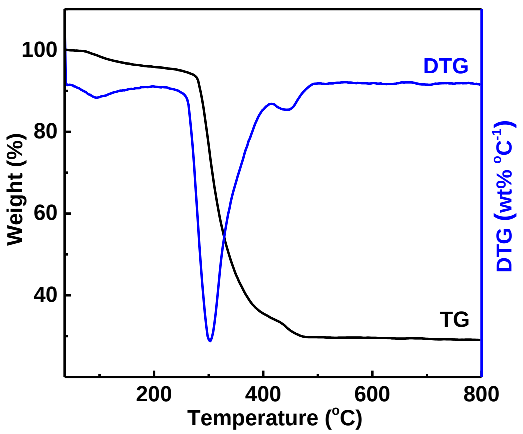


Fig. S7 TG and DTG curves of the sample *p*MOP.

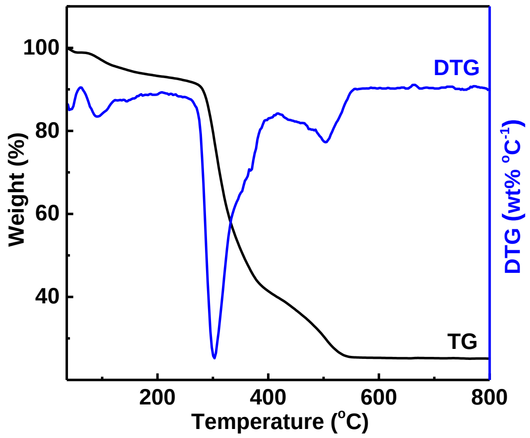


Fig. S8 TG and DTG curves of the sample *p*MOP-ST.

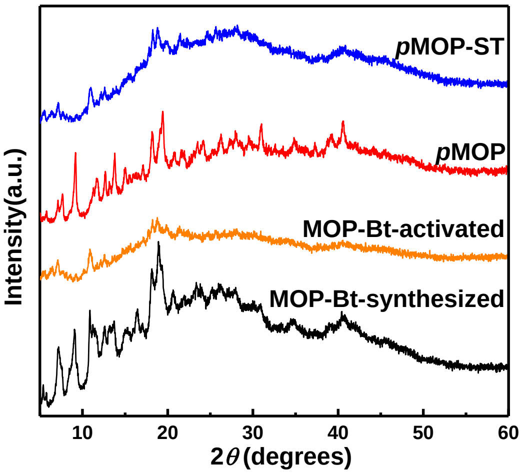


Fig. S9 XRD patterns of synthesized MOP-Bt, activated MOP-Bt, *p*MOP, and *p*MOP-ST.

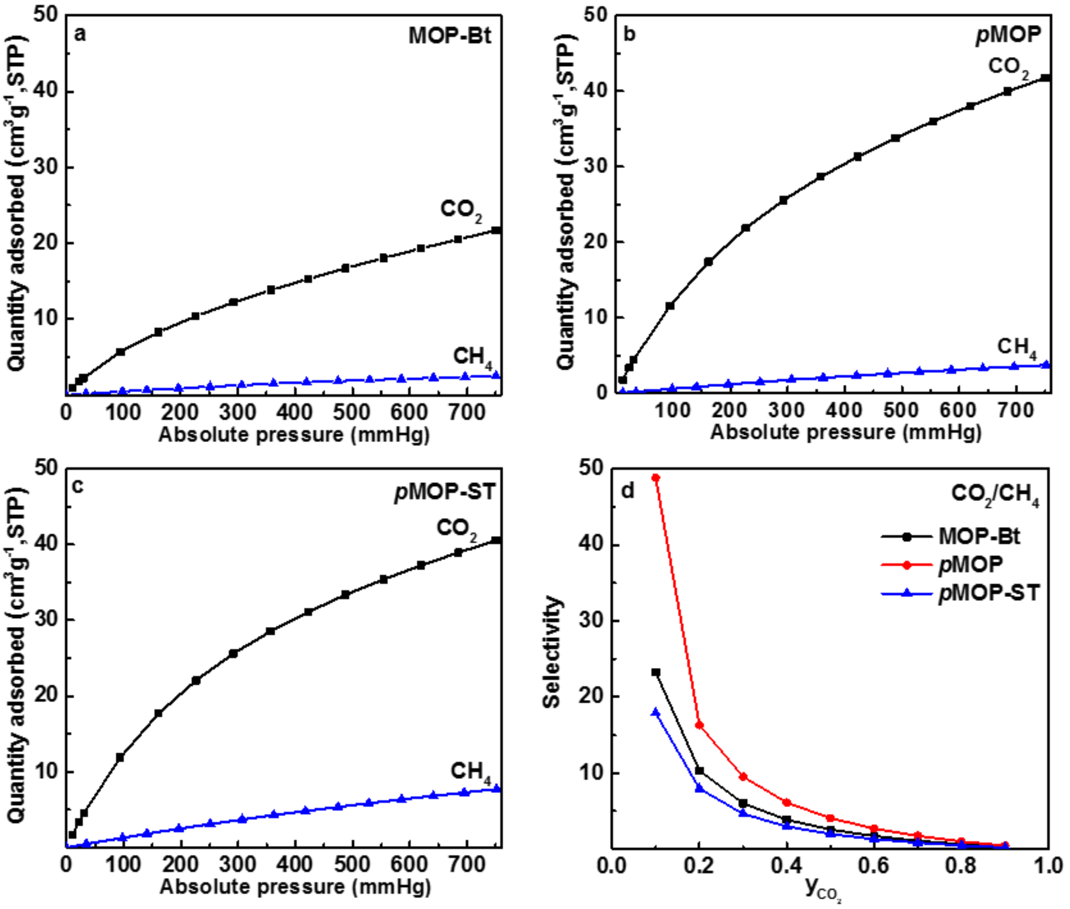


Fig. S10 CO$_2$ and CH$_4$ adsorption isotherms of (a) MOP-Bt, (b) *p*MOP, and (c) *p*MOP-ST as well as (d) IAST selectivity of CO$_2$/CH$_4$ on MOP-Bt, *p*MOP, and *p*MOP-ST.

Notes and references

1. Y. Sha, S. Bai, J. Lou, D. Wu, B. Liu and Y. Ling, *Dalton transactions*, 2016, **45**, 7235-7239.
2. H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 11650-11661.