

# Tröger's base-derived microporous organic polymer: design and applications in CO<sub>2</sub>/H<sub>2</sub> capture and CO<sub>2</sub> hydrogenation into formic acid

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## **1. General experimental methods**

### **Materials**

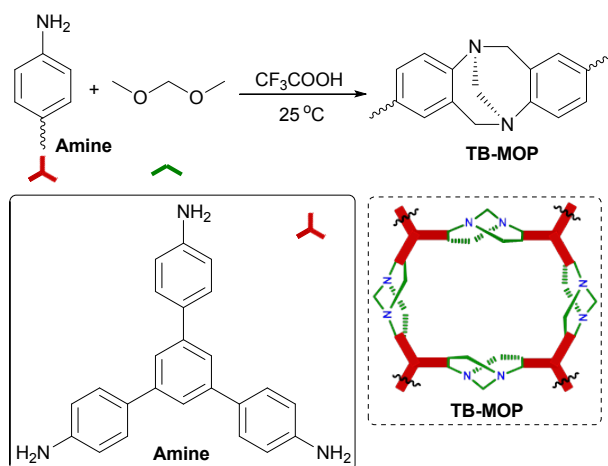
All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise.

### **Instrumentation**

Liquid  $^1\text{H}$  NMR spectra was recorded at Bruker 400 spectrometer in  $\text{CDCl}_3$  and  $\text{CDCl}_3$  (7.26 ppm) was used as internal reference, Liquid  $^{13}\text{C}$  NMR was recorded at 100.6 MHz in  $\text{CDCl}_3$  and  $\text{CDCl}_3$  (77.0 ppm) was used as internal reference. Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The  $^{13}\text{C}$  CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of  $2\text{ cm}^{-1}$ . The elemental analysis of the polymer was determined using a Flash EA1112 analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were outgassed at  $120\text{ }^\circ\text{C}$  for 8 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 15.0 kV. Transmission electron microscope (TEM) images were obtained with a JEOL JEM-1011 instrument operated at 200 kV. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25 to  $600\text{ }^\circ\text{C}$  under nitrogen and air atmosphere with a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$ . X-ray photoelectron spectroscopy (XPS) data was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of  $\sim 3 \times 10^{-9}$  mbar (1 mbar = 100 Pa) using Al K $\alpha$  as the excitation source ( $h\nu=1486.6\text{ eV}$ ) and operated at 15 kV and 20 mA. The binding energies were referenced to the  $\text{C}_{1s}$  line at 284.8 eV from adventitious carbon. The loading content of Pd in the catalysts was determined by ICP-AES (VISTA-MPX).

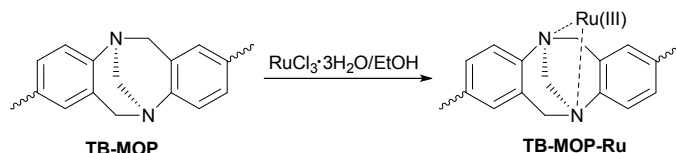
## **2. Synthetic procedures**

### **(1) Synthesis of TB-functionalized MOP (TB-MOP)<sup>1</sup>**



Under  $N_2$  atmosphere, amine (1 mmol) was dissolved in dimethoxymethane (1 mL) and the solution was cooled in an ice bath. Trifluoroacetic acid (10 mL) was added dropwise over 20 min and the mixture was stirred for 48 h at room temperature. The viscous brown mixture was slowly poured into aqueous ammonium hydroxide solution and stirred vigorously for 2 h during which a brown solid was formed. The solid was collected by filtration, washed with distilled water, THF,  $CH_3OH$  and acetone until the washings were clear. The product was then dried at 120 °C under vacuum for 12 h to give **TB-MOP** as a slight brown solid (Yield: 79%). Elemental analysis: C 76.57%, H 8.41%, N 6.11%.

### (2) Synthesis of TB-MOP-Ru



$RuCl_3 \cdot 3H_2O$  (260 mg) was dissolved in 25 mL of EtOH, and then **TB-MOP** (1 g) was added. The mixture was kept stirring for 24 h at room temperature. The resulting solid was isolated by filtration and washed with EtOH, and then purified using Soxhlet extraction (EtOH) for 24 h. **TB-MOP-Ru** was obtained as a brown powder after drying at 80 °C under vacuum for 12 h. The Ru content in **TB-MOP-Ru** was 4.87 wt% as determined by ICP. Elemental analysis for **TB-MOP-Ru**: C 60.33%, H 4.59%, N 7.35%.

### (3) Reference

1. M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli and N. B. McKeown, *Science*, 2013, **339**, 303-307.

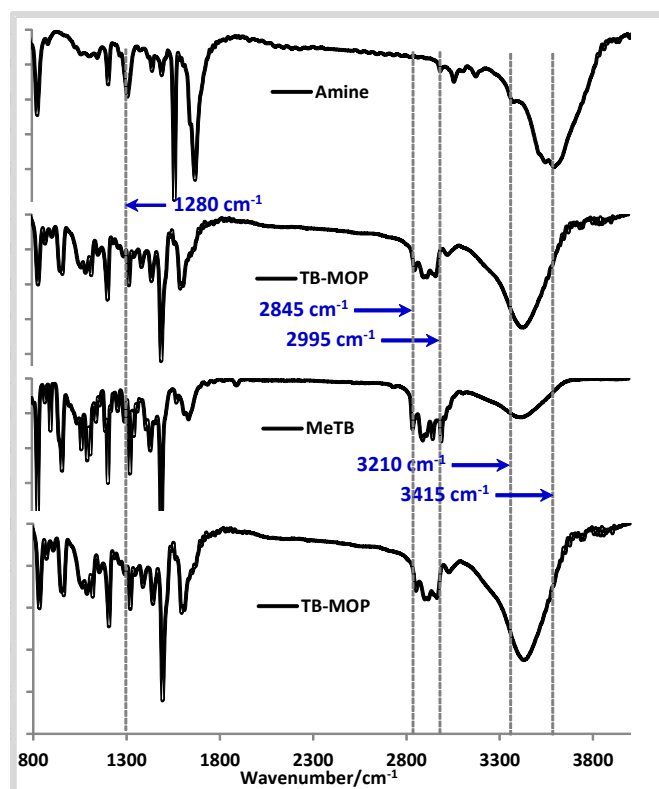
### 3. Typical procedure of the hydrogenation of $CO_2$ catalyzed by TB-MOP-Ru

A stainless steel autoclave with a Teflon tube (25 mL inner volume) was purged with  $CO_2$  to evacuate air, and then **TB-MOP-Ru** (0.05 g),  $PPh_3$  (1 mmol) and  $Et_3N$  (5 mL) were added successively.  $H_2$  (6 MPa) was charged in the reactor at room temperature, and then  $CO_2$  was charged until the total pressure reaching 12 MPa. The autoclave was stirred at 40 °C for 24 h. After reaction, then the excess of gas was vented. The product yield was determined by  $^1H$  NMR

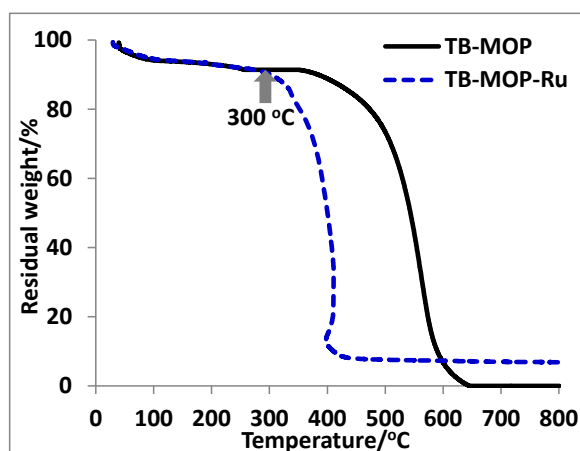
(CDCl<sub>3</sub>, 400 MHz) using 1,4-bis(chloromethyl)-benzen as an internal standard.

For catalyst recycling, the catalyst was recycled by filtration, washed with ethanol and CH<sub>2</sub>Cl<sub>2</sub>, and then dried under vacuum at 40 °C for 24 h, followed by being reused for the next run.

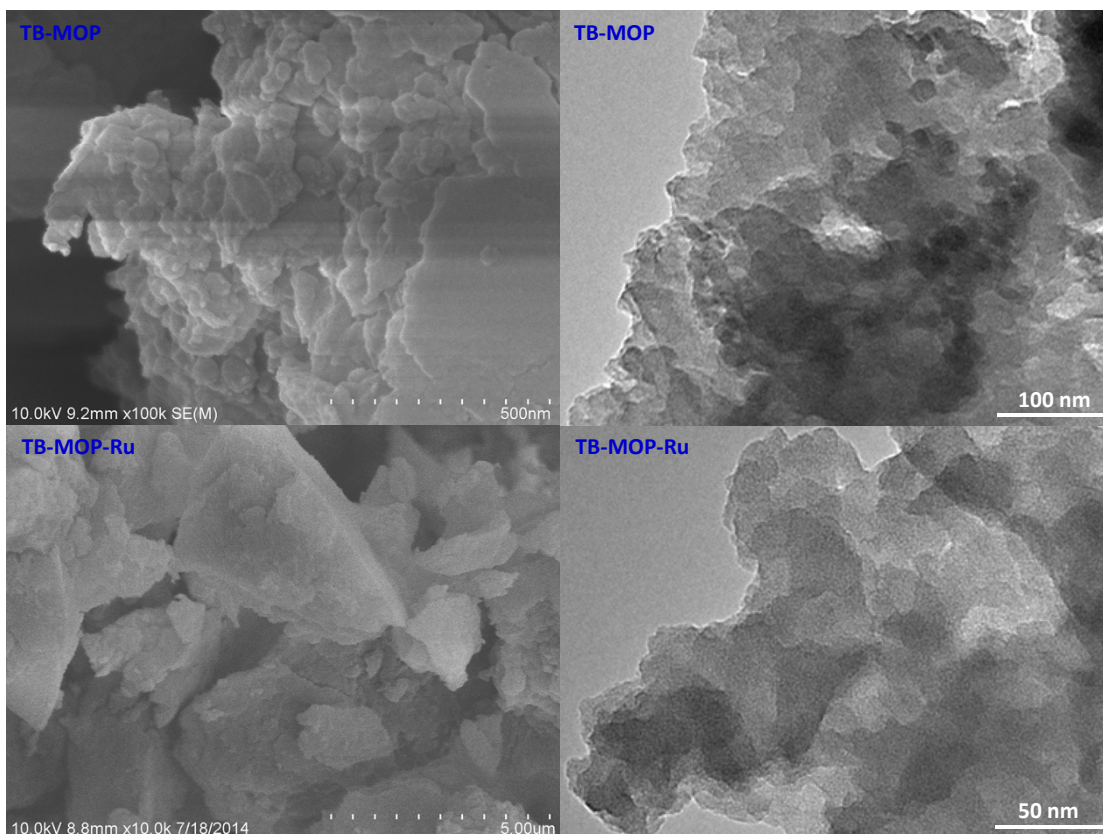
For reloading Ru(III) species to the recycled catalyst, the procedure was similar to that for the preparation of TB-MOP-Ru, and the content of Ru species was detected by ICP, which was very close to that of the original TB-MOP-Ru. The newly prepared TB-MOP-Ru was reused for the next run.



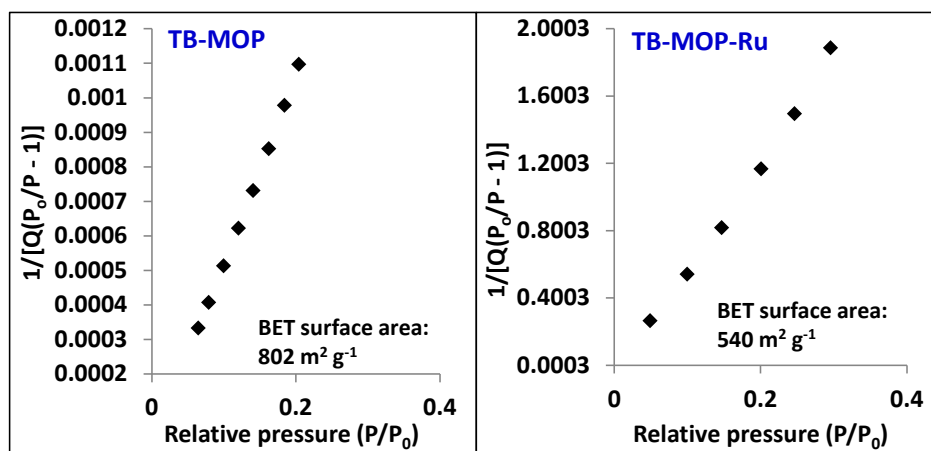
**Fig. S1** FTIR spectra of **TB-MOP** and the monomers. The spectra were recorded as KBr pellets. 3415 (free N-H), 3210 (hydrogen-bonded N-H), 2845-2995 (CH<sub>2</sub>), 1280 (C-N), 1600, 1580, 1500 and 1450 (aromatic C=C) cm<sup>-1</sup>. MeTB: 2,8-dimethyl-troeger's base (CAS: 529-81-7). DMM: dimethoxymethane.



**Fig. S2** Thermogravimetric analysis (TGA) of **TB-MOP** and **TB-MOP-Ru** under air up to 800 °C at a rate of 10 °C min<sup>-1</sup>.



**Fig. S3** Scanning Electron Microscopy (SEM) (left) and Transmission Electron Microscopy (TEM) (right) images of **TB-MOP** and **TB-MOP-Ru**.



**Fig. S4** BET plot ( $P/P_0 = 0.06-0.2$ ) from  $N_2$  isotherms at 77 K of **TB-MOP** and **TB-MOP-Ru**.

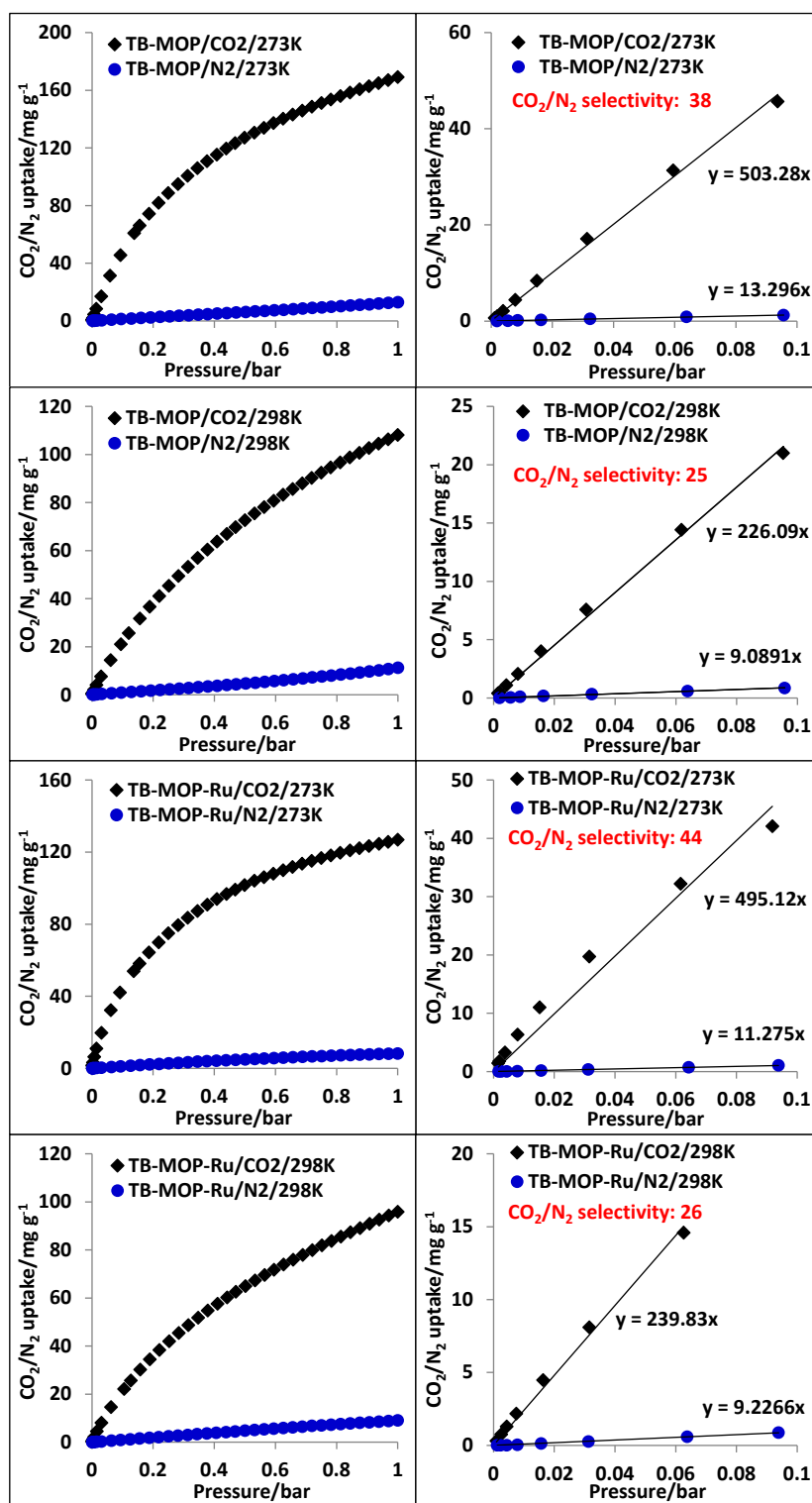
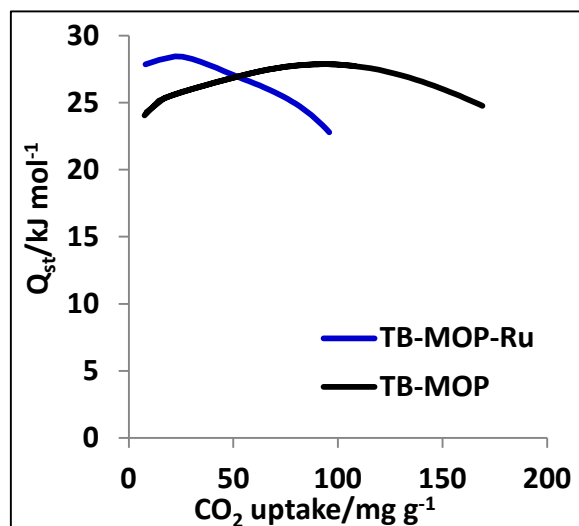


Figure S5 CO<sub>2</sub>/N<sub>2</sub> selectivities for TB-MOP and TB-MOP-Ru calculated using the Henry's Law constants in the linear low pressure (< 0.1 bar) range.



**Figure S6** Isosteric heats of adsorption ( $Q_{st}$ ) for  $\text{CO}_2$ . Isosteric heats of adsorption were calculated from the adsorption data at 273 and 298 K using Clausius-Clapeyron equation.

**Table S1** Reaction conditions screening for the hydrogenation of  $\text{CO}_2$  to produce HCOOH catalyzed by **TB-MOP-Ru<sup>a</sup>**

Entry	$\text{H}_2$ /MPa	Total /MPa	T/°C	$\text{Et}_3\text{N}$ /mL	$\text{PPh}_3$ /mmol	Time/h	HCOOH/mmol <sup>b</sup>	TON <sup>c</sup>
1	3	6	60	1	0.5	24	0.77	32
2	4	8	60	1	0.5	24	2.69	112
3	5	10	60	1	0.5	24	7.95	331
4	6	12	60	1	0.5	24	10.88	453
5	7	14	60	1	0.5	24	9.02	376
6	6	12	25	1	0.5	24	11.62	484
7	6	12	40	1	0.5	24	12.97	540
8	6	12	80	1	0.5	24	0.47	20
9	7	12	40	1	0.5	24	12.75	531
10	5	12	40	1	0.5	24	12.54	523
11	6	12	40	1	1	24	13.39	558
12	6	12	40	2	1	24	29.4	1225
13	6	12	40	3	1	24	43.83	1826
14	6	12	40	4	1	24	48.27	2011
15	6	12	40	5	1	24	54.09	2254
16	6	12	40	6	1	24	38.45	1602
17	6	12	40	7	1	24	32.23	1343
18	6	12	40	5	1.5	24	39.85	1660
19	6	12	40	5	1	16	40.07	1670
20	6	12	40	5	1	32	54.31	2263

<sup>a</sup> Reaction conditions: **TB-MOP-Ru** 0.05 g (0.024 mmol Ru based on ICP). <sup>b</sup> The yield of HCOOH was determined by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) using 1,4-bis(chloromethyl)-benzene as an internal standard. <sup>c</sup> Turnover number (TON) was obtained as mmol of HCOOH obtained/mmol of Ru added.