# **Electronic Supplementary Information**

## Tröger's-base-functionalised organic nanoporous polymer

## for heterogeneous catalysis

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- A: Experimental procedures
- **B:** Analysis equipments
- C: FT-IR spectra for fresh (polymer 3) and recycled catalysts
- **D:** <sup>13</sup>C CP/MAS NMR spectra for fresh (polymer **3**) and recycled catalysts
- **E:** EDX sum spectrum for polymer **3**
- **F:** HR-TEM images for polymer **3**
- G: Atomistic simulations for polymer 3
- **H:** TGA and DSC analyses for polymer **3**

### A: Experimental procedures

Synthesis of (±)-2,8-diiodo-6H,12H-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (1):<sup>1</sup> A mixture of 4-iodoaniline (6.59 g, 30 mmol) and paraformaldehyde (1.81 g, 60 mmol) was added in portions under vigorous stirring to TFA (50 mL) at -15 °C under nitrogen atmosphere. The resulting mixture was allowed to reach 0 °C and stirred for 7 days, then slowly added to a stirred mixture of ice and an excess of concentrated aqueous NH<sub>3</sub>. Extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL), drying of the organic layer over MgSO<sub>4</sub>, and removal of the solvent in vacuum gave a crude product, which was purified by flash chromatography (AcOEt/CH<sub>2</sub>Cl<sub>2</sub> 1:10) to give product **1** (3.98 g, 56%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.46 (dd, *J* = 8.4, *J* = 1.6 Hz, 2H), 7.23 (d, *J* = 1.6 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.63 (d, *J* = 16.8 Hz, 2H), 4.23 (s, 2H), 4.09 (d, *J* = 16.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 147.55, 136.42, 135.70, 130.13, 126.99, 87.58, 66.48, 58.08; ESI-MS: 475 (100, [MH]<sup>+</sup>). In Figs. S1 and S2 are shown the <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of (±)-**1**.



**Fig. S1** <sup>1</sup>H NMR spectrum of  $(\pm)$ -2,8-diiodo-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]-diazocine,  $(\pm)$ -1.



180 170 160 150 140 130 120 110 100 90 80 70 60 50 30 20 ppm Fig. S2 <sup>13</sup>C NMR spectrum of  $(\pm)$ -2,8-diiodo-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine, (±)-1.

#### Synthesis of polymer 3:

1,3,5-triethynylbenzene (185 mg, 1.2 mmol), (±)-2,8-diiodo-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (400 mg), bis(triphenylphosphine)palladium dichloride (40 mg), and copper iodide (16 mg) were dissolved in the mixture of dried dimethylformamide (50ml) and Et<sub>3</sub>N (50 ml). The reaction mixture was heated to 80 °C, stirred for 72 h under nitrogen atmosphere.<sup>2</sup> The mixture was cooled to room temperature and the precipitate was filtered and washed four times with chloroform, water, methanol, and acetone. Further purification of the precipitate was carried out by Soxhlet extraction from methanol for 48 h to remove any unreacted monomer or catalyst residues. The product was dried in vacuum for 24 h at 70 °C (421 mg, yield of 72 %. Since the homo-coupling side reaction, *i.e.*, alkyne dimerization are also contributed, the yield of polymer 3 was calculated according to the sum of triethynylbenzene and diazocine). IR (KBr cm<sup>-1</sup>): 3428 (−C≡C−H), 3060 (Ph−H), 2903 (-H-C-H-), 2205 (-C=C-), 1490 (Ph), 1321 (C-N), (see Fig. S4). Elemental combustion analysis (%) Calcd for C<sub>23</sub>H<sub>14</sub>N<sub>2</sub>: C 86.79, H 4.40, N 8.81; Found: C 81.42, H 4.70, N 7.21. Found by EDX analysis (wt. %): C 96.23, Pd 0.92, I 2.85 (see Fig. S6).

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#### Typical procedure (Entry 4 in Table 1) for Catalytic Test

To a reaction vial charged with 4-chlorobenzaldehyde **5** (70 mg, 0.5 mmol), polymer **3** used as the catalyst (77 mg, 0.2 mmol), under argon was added anhydrous toluene (2.5 mL), and diethylzinc **4** (1.5 mL, 1 M in hexane, 1.5 mmol). The mixture was stirred at 40 °C for 24 h, then quenched with saturated NH<sub>4</sub>Cl solution (2 mL). The mixture was isolated by centrifugal sedimentation and purified by silica gel chromatography (silica gel hexane/ethyl acetate 6:1) to give 1-(4-chlorophenyl)-propan-1-ol **6** as a slightly white solid (51 mg, 60%). Fig. S3 shows the <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **6**. The used catalyst (polymer **3** after catalytic reaction) was washed with toluene and non-ion water for three times, respectively. Finally, the used catalyst was dried in vacuum under 80 °C for 24 h for next catalytic run.



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**Fig. S3** <sup>1</sup>H NMR spectrum of 1-(4-chlorophenyl)-propan-1-ol, 6.

#### **References:**

- [1] S. Sergeyev, M. Schär, P. Seiler, O. Lukoyanova, L. Echegoyen and F. Diederich, Chem. Eur. J., 2005, 11, 2284.
- [2] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, Angew. Chem., Int. Ed., 2007, 46, 8574.

## **B:** Analysis equipments

The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system.

Elementar Analysensysteme GmbH VarioEL V3.00 was used to characterise the elemental compositions of the samples.

FT-IR spectra were recorded by Nicolet NEXUS 670 (results shown in Fig. S4).

Solid-state NMR spectra were obtained on a WB 400 MHz Bruker Avance II spectrometer. The <sup>13</sup>C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and pulse delay of 3 s (results shown in Fig. S5).

An Oxford Instruments 7200 EDX detector was used to conduct elemental analysis of polymer composition (results shown in Fig. S6).

Surface morphologies and microstructures of the materials were examined by a scanning electron microscope (SEM, JEOL, JSM-6701F, Japan), and by transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) operated at 200 KV. For TEM analysis, the samples were dispersed in ethanol, and then dipped and dried on Cu grid coated with transparent graphite (results shown in Fig. S7).

The thermal properties of polymer **3** were evaluated using a thermogravimetric analysis (TGA) – differential scanning calorimetry (DSC) instrument (STA 449C Jupiter) over the temperature range of 25 to 800 °C under air atmosphere with a heating rate of 10 °C/min (results shown in Fig. S9).



### C: FT-IR spectra for fresh (polymer 3) and recycled catalysts

**Fig. S4** FT-IR spectra of polymer **3** as fresh catalyst (in black) and the catalyst recycled after three-time catalytic reactions (in red). It is evident that the structure of polymer **3** was maintained after catalytic reactions.





**Fig. S5** Solid-state NMR spectra of polymer **3** as fresh catalyst (in black) and the catalyst recycled after three-time catalytic reactions (in red). <sup>13</sup>C CP/MAS spectra was recorded at an MAS rate of 10.0 kHz and reported relative to Me<sub>4</sub>Si. Asterisks denote spinning sidebands. It was evident that the structure of polymer **3** used as catalyst was not destroyed after catalytic reactions. However, little change in the high-field region (0 to 50 ppm) of <sup>13</sup>C solid-state NMR spectra should not be overlooked. Our BET analyses on the recycled catalysts also showed that BET surface areas could decrease to a certain extent (79 m<sup>2</sup> g<sup>-1</sup> as minimum). These results imply that the decrease of catalytic activity of the recycled catalysts may come from partial blocking of polymeric nanopores.

## **E: EDX** sum spectrum for polymer 3



Fig. **S6** EDX sum spectrum of organic nanoporous polymer 3. In Sonogashira-Hagihara cross-coupling reactions, the homo-coupling side reaction which involves the Glaser-type oxidative dimerization of alkynes cannot be avoided (for detailed discussion, see, for example: P. Siemsen, R. C. Livingston and F. Diederich, Angew. Chem., Int. Ed., 2000, 39, 2632; R. Chinchilla and C. Najera, Chem. Rev., 2007, 107, 874). Therefore, excess of alkynes are often applied in the reaction in order to reach a higher conversion for cross-coupling between alkyne and aryl halide. The low iodine content in EDX sum spectrum is probably accounted for avoidless homocoupling of ethynyl monomer, while the low palladium content is due to the incomplete washing after Sonogashira- Hagihara cross-coupling reaction.

## F: HR-TEM images for polymer 3



Fig. S7 TEM images of the synthesized polymer 3.

### G: Atomistic simulations for polymer 3

The procedure of atomistic simulation for polymer **3** is similar to those described by Cooper and co-workers.<sup>2</sup> Molecular models for the network components were calculated with the Materials Studio Modeling 4.0 package (Accelrys Inc., San Diego, CA, 2005). The network was generated by adding the repeating unit in a stepwise manner. All models fully relaxed using the *Discover* molecular mechanics and dynamics simulation module with the COMPASS forcefield.<sup>2</sup> A seed molecule was constructed by fully substituting the 1,3,5-triethynylbenzene monomer with three of the corresponding Tröger's base monomers. The network model of polymer **3** was built to contain a total of 25 repeat units (see Fig. S8).



**Fig. S8** (a) Atomistic simulation for a unit of 1,3,5-triethynylbenzene linker connecting three Tröger's-base monomers; (b) Topology for the simulated network of polymer 3; (c) Molecular structure of Tröger's base as functional moieties in polymer 3. The dihedral angel in the central bicyclic aliphatic unit fused with two benzene rings is about 124°.



H: TGA and DSC analyses for polymer 3

**Fig. S9** TGA (in black) and DSC (in red) measurements for polymer **3**. There is no evidence for structural change in the material until 350 °C. The TGA measurement was performed under air atmosphere. At the given onset of polymer decomposition, the system may react with trace of  $CO_2$  or  $O_2$  in the air and gain some weight, which causes the slightly ascent curve. Same phenomena were also observed for other functionalized conjugated microporous polymers (see, for example, in the Supporting Information: R. Dawson, A. Laybourn, R. Clowes, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Macromolecules*, 2009, ASAP. DOI: 10.1021/ma901801s).