ChemPubSoc Europe

DOI: 10.1002/cctc.201701534

CHEMCATCHEM
Full Papers

Porous Organic Polymers Constructed from Tröger's Base as Efficient Carbon Dioxide Adsorbents and Heterogeneous Catalysts

Zhifeng Dai+,[a, b] Yongquan Tang+,[a] Qi Sun,[a] Xiaolong Liu,[c] Xiangju Meng,*[a] Feng Deng,[c] and Feng-Shou Xiao*[a]

Through a radical solvothermal polymerization method, we synthesized two porous organic polymers based on Tröger's base (POP-TB and POP-Me-TB) from the corresponding vinyl-functionalized monomers (2,8-divinyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*]diazocine and 2,8-divinyl-4,10-dimethly-6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*]diazocine; v-TB and v-Me-TB). The structure and porosity of these polymers are verified by using solid-state NMR spectroscopy, elemental analysis, SEM, TEM, N_2 sorption isotherms, and CO_2 sorption tests. They exhibit high surface areas and moderate pore volumes, which give high CO_2 adsorption capacities (90 and 71 $mg_{CO_2}\,g^{-1}$ at 273 K and 60 and 44 $mg_{CO_2}\,g^{-1}$ at 298 K for POP-TB and POP-Me-TB, respectively) under a CO_2 pressure of 1 bar. In addition, they display excellent catalytic activities together with highly stability as heterogeneous catalysts in the benchmark Knoevenagel reactions.

Introduction

Homogeneous organocatalysts have been used widely in organic synthesis and pharmaceutical chemistry because of their unique activity and selectivity.[1] However, the relatively complicated recycling of these organocatalysts is a challenge for their industrial application.[2] The solution for this issue is to support the organocatalysts on zeolites,[2f,3] carbons,[4] magnetic nanoparticles,[2i,5] and metal–organic materials (MOFs).[6] In these cases, the relatively low concentration and easy leaching of organocatalysts influence their applications strongly. To overcome these problems, the preparation of porous organocatalysts has been suggested.[6d,7,8]

Among organocatalysts, base catalysts such as amines[9] have been applied widely in organic reactions such as Knoevenagel, Michael, and transesterification reactions.[9–12] Tröger's base (TB) was first reported by Julius Tröger in 1887, and the recent development of TB-based solid base catalysts has attracted attention because of its interesting stereochemistry, supramolecular chemistry, and strong base properties.[13] Wang and co-workers[14] used the Sonogashira–Hagihara coupling reaction to prepare a TB-functionalized organic nanoporous polymer, which showed an excellent activity in the addition of diethylzinc to 4-chlorobenzaldehyde as a heterogeneous catalyst. Later, Corma et al.[15] showed that the TB active sites in SBA-15 exhibit excellent catalytic activities in Knoevenagel reactions, the S-arylation of aryl halides, and azide–alkyne cycloaddition, although the TB concentration in these catalysts was relatively low. Besides this progress, a series of materials has been functionalized with TB for CO_2 capture and conversion.[16]

Porous organic polymers (POPs), which have stable covalent bonds and always possess an excellent stability, large pore volume, high surface area, and designable structure, are an emerging class of porous materials.[17] Recently, our group has reported a series of porous organic ligands (POLs) synthesized through solvothermal radical polymerization methods from the corresponding vinyl-functionalized ligand monomers themselves, for which the concentration of organic ligands was maximized because of the composition of the porous polymers with pure organic ligands. For example, if we used vinyl-functionalized diphosphine monomers (v-dppe), a POP called POL-dppe was synthesized.[12b] As a result of the high ligand concentration, the supported Rh catalyst shows extraordinary catalytic properties in the heterogeneous hydroformylation of olefins. In particular, the catalytic activity and selectivity of these heterogeneous catalysts even outperform those of their homogeneous counterparts.

---

[a] *Dr. Z. Dai,+ Y. Tang,+ Dr. Q. Sun, Prof. X. Meng, Prof. F.-S. Xiao*
Key Laboratory of Applied Chemistry of Zhejiang Province and
Department of Chemistry
Zhejiang University
Hangzhou, Zhejiang, 310028 (P.R. China)
E-mail: mengxj@zju.edu.cn
fsxiao@zju.edu.cn

[b] *Dr. Z. Dai+*
MOE Key Laboratory of Bioinorganic and Synthetic Chemistry,
School of Chemistry
Sun Yat-Sen University
Guangzhou 510275 (P.R. China)

[c] *Dr. X. Liu, Prof. F. Deng*
State Key Laboratory of Magnetic Resonance and
Atomic and Molecular Physics
Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences,
Wuhan 430071(P.R. China)

[+] *These authors contributed equally to this work.*

Supporting information for this article can be found under: https://doi.org/10.1002/cctc.201701534.

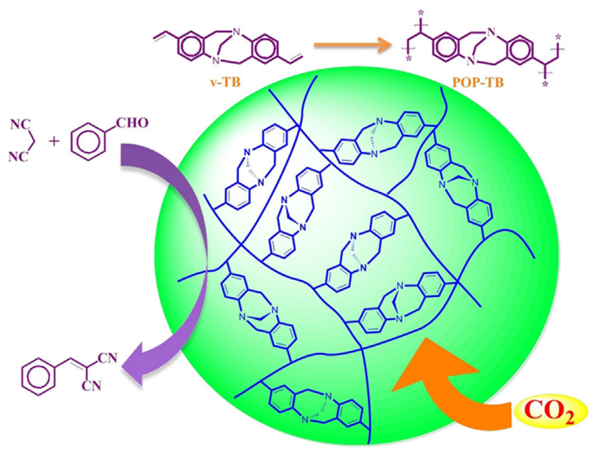
This manuscript is part of a Special Issue on "Supported Molecular Catalysts".

The solid base materials are potentially important for gas sorption, separation, and catalysis and it is interesting to develop stable and porous solid base materials. In this work, we synthesized two TB-derived porous organic polymers (POP-TB and POP-Me-TB) from a simple radical polymerization of the corresponding vinyl-functionalized TB monomers (v-TB and v-Me-TB) under solvothermal conditions. In particular, the POPs were obtained quantitatively, and the TB ligands were retained fully in the frameworks. The combination of the basic properties of TB and the high concentration of the ligands in the framework offer a good opportunity to obtain solid base materials for gas sorption (CO_2) and base-catalyzed reactions. CO_2 sorption tests indicate that these porous polymers have a high CO_2 capture capacity (90 and 71 $\mathrm{mg_{CO_2}\,g^{-1}}$ of CO_2 at 273 K and 60 and 44 $\mathrm{mg_{CO_2}\,g^{-1}}$ at 298 K for POP-TB and POP-Me-TB, respectively). Knoevenagel tests show that these porous polymers are highly efficient catalysts with both high activities and excellent stabilities.

Results and Discussion

To demonstrate the "proof-of-concept", we first prepared the vinyl-functionalized TB monomers 2,8-divinyl-6*H*,12*H*-5,11-methanodibenzo[b,f]diazocine (v-TB) and 2,8-divinyl-4,10-dimethyl-6*H*,12*H*-5,11-ethanodibenzo[*b*,*f*]diazocine (v-Me-TB; Schemes S1 and S2). After radical solvothermal polymerization, two TB-based POPs (POP-TB and POP-Me-TB) were obtained in quantitative yields (Scheme 1). Notably, the radical solvothermal synthesis of POPs is facile and efficient compared with metal-catalyzed cross-coupling reactions and self-assembly.[17]

The synthesis of the TB-functionalized polymers was verified by using ^{13}C magic-angle spinning (MAS) NMR spectroscopy, elemental analysis, SEM, and TEM. The ^{13}C solid-state NMR spectrum of POP-TB is shown in Figure 1 A. Compared with the spectrum of the v-TB monomer, the disappearance of the peaks at $\delta = 110$–120 ppm that correspond to the vinyl bonds and the simultaneous appearance of two new peaks at $\delta = 28.0$ and 40.9 ppm assigned to alkyl carbon atoms indicate that the polymerization of the double bonds is complete in the spectrum of POP-TB. The overlapped peaks at $\delta = 46.5$ and 64.4 ppm are attributed to the methylene carbon atom linked to the N atoms, whereas the peaks at $\delta = 127.8$–146.4 ppm are related to the aryl backbones. Similarly, POP-Me-TB exhibits almost the same spectrum (Figure S1). Elemental analysis of the polymers shows that the compositions of POP-TB (C 74.7 %, N 9.7 %, H 6.8 %) and POP-Me-TB (C 80.4 %, N 9.3 %, H 7.3 %) are consistent with the molecular structures of the monomers v-TB and v-Me-TB, which indicates that the structure of TB in POP-TB and POP-Me-TB remained after solvothermal polymerization. Further experiments show that these polymers are insoluble in most organic solvents, which include DMF, THF, toluene, and DMSO.



Scheme 1. Proposed structure of POP-TB.

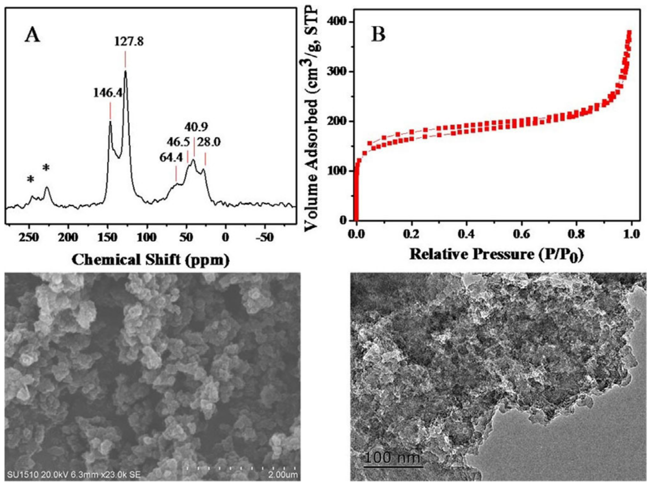


Figure 1. A) ^{13}C MAS NMR spectrum, B) N_2 sorption isotherm, C) SEM image, and D) TEM image of POP-TB.

The porosity of the polymers was investigated by measuring the N_2 sorption isotherms at 77 K. The N_2 sorption isotherms of POP-TB are shown in Figure 1 B. The deep step at a low relative pressure ($P/P_0 < 0.1$) reveals the presence of the microporosity in the polymer framework. The hysteresis loop at $P/P_0 = 0.4$–0.7 suggests the presence of a mesoporous structure in the sample. The pore size distribution of POP-TB calculated by using nonlocal density function theory (NLDFT) was mainly 0.5–3 and 2.6–30 nm (Figure S2). The BET surface area and pore volume of POP-TB are estimated at 568 $\mathrm{m^2\,g^{-1}}$ and 0.49 $\mathrm{cm^3\,g^{-1}}$, respectively. The N_2 sorption isotherms of POP-Me-TB (Figure S3 A) indicate a hierarchical porous polymer, which has a high BET surface area (575 $\mathrm{m^2\,g^{-1}}$) and large pore volume (0.36 $\mathrm{cm^3\,g^{-1}}$). The pore size distribution of POP-Me-TB is mainly at 1.8 and 4.1 nm (Figure S3 B).

Thermogravimetric analysis (TGA; Figure S4) indicates that the decomposition temperature of POP-TB and POP-Me-TB under N_2 is approximately 643 K, which reflects their high thermal stability. We used SEM and TEM to further confirm the presence of large mesopores (Figure 1 C and D and Figure S5).

Solid base materials have attracted much attention because of their excellent adsorption capacity for acidic CO_2 and might be good candidates to replace methods based on amine solution wet scrubbing used widely in industry. As a result of the basic properties of TB (pK_{HB}(N) $= 1.15$) and the resulting CO_2-philicity of the materials, we propose that POP-TB and POP-

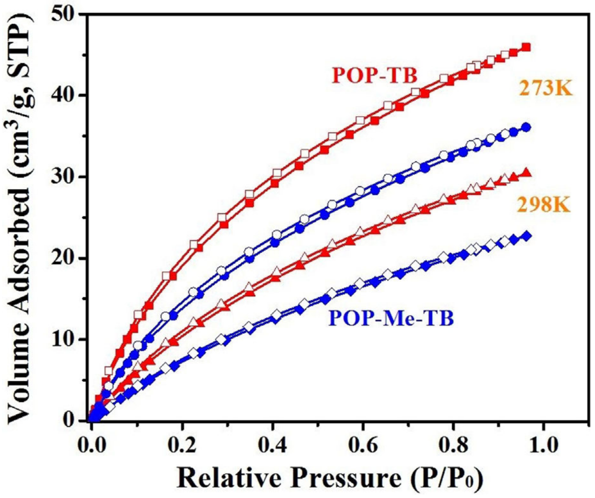
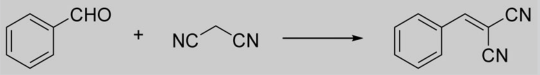


Figure 2. CO_2 sorption isotherms of POP-TB and POP-Me-TB.

Me-TB should have a high CO_2 uptake. Thus, we tested the CO_2 sorption capacity of POP-TB and POP-Me-TB. At 273 K, POP-TB and POP-Me-TB can absorb 90 and 71 $mg_{CO_2}\,g^{-1}$ of CO_2 at a pressure up to 1 bar of pure CO_2, and the uptake is reduced to 60 and 44 $mg_{CO_2}\,g^{-1}$, respectively, if the temperature is increased to 298 K (Figure 2). These values are comparable to those reported previously (Table S1).[17c,18] The relatively higher adsorption capacity of POP-TB than that of POP-Me-TB is reasonably attributed to the higher pore volume of POP-TB (0.49 $cm^3\,g^{-1}$) than that of POP-Me-TB (0.36 $cm^3\,g^{-1}$), as demonstrated by the N_2 sorption isotherm. The isosteric heat of CO_2 adsorption (Qst) for POP-TB and POP-Me-TB is 25.8 and 24.8 $kJ\,mol^{-1}$, respectively, calculated from the Clausius–Clapeyron equation. The relatively low Qst values of POP-TB and POP-Me-TB are favorable for the desorption of CO_2 from the polymers with a low energy penalty.

To investigate the heterogeneous catalytic properties, Knoevenagel reactions were chosen as a benchmark reaction. At 313 K and under solvent-free reaction conditions, POP-TB could catalyze the condensation reaction of benzaldehyde and malononitrile efficiently with the conversion of the benzaldehyde at 96.5 % (Table 1, entry 1), which is comparable to that of the homogeneous catalyst TB of 99.0 % (Table 1, entry 2). If the catalyst was removed from the reaction system, the conversion of the reaction is relatively low (19.6 %; Table 1, entry 3). If the catalyst loading was reduced from 1.7 to 0.5 mol %, an increase of the reaction time from 3 to 5 h is required to achieve a conversion of 86.1 % (Table 1, entry 4). We also tested the catalytic activity of POP-TB at room temperature (300 K). Under the typical conditions, the heterogeneous catalyst POP-TB could be used to obtain a conversion of 84.9 % in 5 h (Table 1, entry 5), which is comparable to that of TB immobilized on mesoporous SBA-15.[15b] The catalytic properties of POP-Me-TB were also tested under similar conditions and can be used to obtain a conversion of 74.0 % (Table 1, entry 6) under the same reaction conditions. The lower activity of POP-Me-TB than POP-TB may be attributed to their different characteristics, as indicated by the N_2 sorption isotherms.

Table 1. Catalytic performance of POP-TB in the Knoevenagel reaction.[a]



Entry	Catalyst	Catalyst ratio [%]	*T* [K]	Conversion [%][b]
1	POP-TB	1.7	313	96.5
2[c]	TB	1.7	313	99.0
3	–	0	313	19.6
4	POP-TB	0.5	313	86.1
5	POP-TB	1.7	300	84.9
6	POP-Me-TB	1.7	313	74.0
7[d]	POP-TB	1.7	313	91.8

[a] Reaction conditions: 10 mmol benzaldehyde, 10 mmol malononitrile, catalyst, solvent-free condition at 313 K for 3 h. [b] Determined by using GC. [c] Homogeneous catalyst TB was used. [d] Recycled for 4 times.

In addition, the higher CO_2 uptake capacity of the catalyst is more favorable to obtain higher catalytic activity. This phenomenon might be related to the higher CO_2 uptake capacity of the POP-TB, which has a relatively larger pore volume and pore size that plays an important role in the catalytic activity in Knoevenagel reactions.

The recyclability of the POP-TB catalyst is shown in Figure 3. Notably, after simple centrifugation and washing with EtOAc under ultrasound, POP-TB could be reused readily four times without a significant decrease in the activity (91.8 %; Table 1, entry 7), which indicates the robustness of the POP. Furthermore, we tested the substrate scope of the aldehyde in the Knoevenagel reaction over heterogeneous POP-TB and POP-Me-TB and homogeneous TB. If the substrates possess electron-donating or -withdrawing groups such as *p*-methylbenzaldehyde and 4-bromobenzaldehyde, the reactions could be finished in 3 h with quantitative yields (Table 2, entries 1 and 2) over the three catalysts. Impressively, POP-TB is compatible with long-chain alkylaldehydes, which include phenylpropyl aldehyde and octanal, to reach a conversion of 90.5 and 88.0 %, respectively (Table 2, entries 3 and 4). These catalytic activities are superior to those of homogeneous TB (83.5 and 85.7 %;

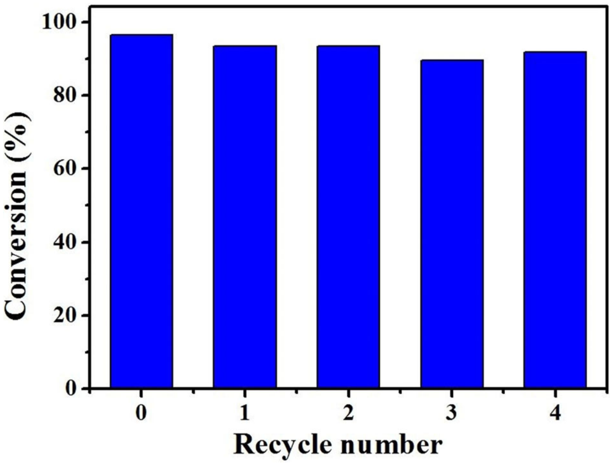
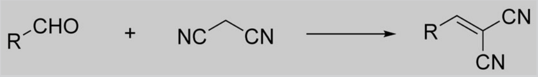
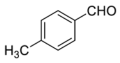
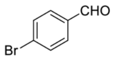
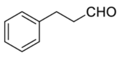
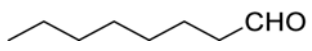
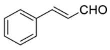
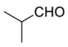
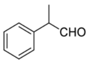


Figure 3. Recycling test in the Knoevenagel reaction over POP-TB.

Table 2. Catalytic performance of POP-TB in the Knoevenagel reaction with various substrates.[a]



Entry	Substrate	Catalyst	Conversion [%][b]
1		POP-TB	98.5
		POP-Me-TB	99.0
		TB	99.0
2		POP-TB	99.0
		POP-Me-TB	99.0
		TB	99.0
3		POP-TB	90.5
		POP-Me-TB	56.4
		TB	83.5
4		POP-TB	88.0
		POP-Me-TB	68.3
		TB	85.7
5		POP-TB	51.4
		POP-Me-TB	28.8
		TB	99.0
6		POP-TB	54.1
		POP-Me-TB	62.7
		TB	87.0
7		POP-TB	53.5
		POP-Me-TB	7.5
		TB	87.5

[a] Reaction conditions: 10 mmol aldehyde, 10 mmol malononitrile, 1.7 % mol POP-TB catalyst, solvent-free conditions at 40 °C for 3 h. [b] Determined by using GC.

Table 2, entries 3 and 4). However, if cinnamaldehyde, which has a rotation-prohibiting double bond in the α position, was employed the conversion decreased to approximately 51.4 % (Table 2, entry 5), which is much lower than that of TB (99.0 %; Table 2, entry 5). This might be because the hindered rotation of the double bonds could increase the steric hindrance of cinnamaldehyde, which would reduce the catalytic activity for condensation. In addition, this conversion is almost the same as that of substrates with stronger steric effects, which include isobutyraldehyde (54.1 %; Table 2, entry 6) and 2-phenylpropionaldehyde (53.5 %; Table 2, entry 7), whereas homogeneous TB maintains almost the same activity (87.0 and 87.5 %, respectively; Table 2, entries 6 and 7). If these substrates are reacted over POP-Me-TB, which has a relatively small pore volume, much lower conversions were observed (Table 2, entries 3–7) except for isobutyraldehyde. Possibly, if the relatively small isobutyraldehyde substrate is employed, the stronger basicity of POP-Me-TB than POP-TB would dominate in the condensation reaction rather than the pore volume. In this case, POP-Me-TB shows a slightly higher conversion with isobutyraldehyde than POP-TB. These results indicate that the heterogeneous POP-TB and POP-Me-TB catalysts promote substrate adaptation and size selectivity in Knoevenagel reactions.

Conclusions

We have synthesized two porous organic polymers based on Tröger's base (POP-TB and POP-Me-TB) by radical solvothermal polymerization from the corresponding vinyl-functionalized monomers. As a result of the high surface area and moderate porosity of the structures, the porous organic polymers show high CO_2 adsorption capacity and excellent catalytic properties in the Knoevenagel reaction as heterogeneous catalysts.

Experimental Section

General

Solvents were purified according to standard laboratory methods. Other commercially available reagents were purchased in high purity and used without further purification.

Synthesis of POP-TB

Typically, v-TB (1 g) was dissolved in DMF (10 mL), and azobisisobutyronitrile (AIBN; 50 mg) was added. The mixture was transferred into an autoclave and heated at 100 °C for 24 h. After washing with EtOAc and drying under vacuum, a white solid was obtained, which was denoted as POP-TB.

Synthesis of POP-Me-TB

Typically, v-Me-TB (1 g) was dissolved in DMF (10 mL), and AIBN (50 mg) was added. The mixture was transferred into an autoclave and heated at 100 °C for 24 h. After washing with EtOAc and drying under vacuum, a white solid was obtained, which was denoted as POP-Me-TB.

Catalytic tests

Typically, the catalyst was added to a 25 mL Schlenk tube equipped with benzaldehyde (10 mmol) and malononitrile (10 mmol). After stirring at 40 °C for 3 h under solvent-free conditions, EtOAc was added, and the catalyst was removed by centrifugation. The reaction conversion was determined by using GC. For the recycling test, the catalyst was washed thoroughly with EtOAc with ultrasonication, dried in air, and used directly for the next run.

Characterization

N_2 sorption isotherms at 77 K were measured by using Micromeritics ASAP 2020M and Tristar systems. The samples were outgassed for 10 h at 100 °C before the measurements. SEM was performed by using a Hitachi SU 1510 and SU 4800. TEM was performed by using a Hitachi HT-7700. TGA was performed by using a SDT Q600 V8.2 Build100 thermogravimetric analyzer under N_2 flow. ^{1}H NMR spectra were recorded by using a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from $Si(CH_3)_4$ at $\delta = 0$ ppm, and J values are given in Hz. ^{13}C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS) NMR spectra were recorded by using a Varian infinity plus 400 spectrometer equipped with a MAS probe in a 4 mm ZrO_2 rotor.

Acknowledgements

This work was supported by National Key Research and Development Program of China (2017YFC0211101), National Natural Science Foundation of China (21422306, 21720102001 and

91634201), and Zhejiang Provincial Natural Science Foundation under Grant No. LR15B030001.

Conflict of interest

The authors declare no conflict of interest.

Keywords: heterogeneous catalysis · mesoporous materials · organocatalysts · polymers · radical reactions

[1] a) T. Akiyama, J. Itoh, K. Yokota, K. Fuchibe, *Angew. Chem. Int. Ed.* **2004**, *43*, 1566–1568; *Angew. Chem.* **2004**, *116*, 1592–1594; b) K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244; c) D. L. Silverio, S. Torker, T. Pilyugina, E. M. Vieira, M. L. Snapper, F. Haeffner, A. H. Hoveyda, *Nature* **2013**, *494*, 216–221; d) S. Bertelsen, K. A. Jorgensen, *Chem. Soc. Rev.* **2009**, *38*, 2178–2189.

[2] a) M. Benaglia, A. Puglisi, F. Cozzi, *Chem. Rev.* **2003**, *103*, 3401–3429; b) M. Gruttadauria, F. Giacalone, R. Noto, *Chem. Soc. Rev.* **2008**, *37*, 1666–1688; c) J. Lu, P. H. Toy, *Chem. Rev.* **2009**, *109*, 815–838; d) A. Dewaele, F. Verpoort, B. Sels, *ChemCatChem* **2016**, *8*, 3010–3030; e) C. Van Doorslaer, J. Wahlen, P. Mertens, K. Binnemans, D. De Vos, *Dalton Trans.* **2010**, *39*, 8377–8390; f) A. E. Fernandes, O. Riant, K. F. Jensen, A. M. Jonas, *Angew. Chem. Int. Ed.* **2016**, *55*, 11044–11048; *Angew. Chem.* **2016**, *128*, 11210–11214; g) S. Ding, Y. Xing, M. Radosz, Y. Shen, *Macromolecules* **2006**, *39*, 6399–6405; h) S. Ghosh, S. S. Acharyya, T. Sasaki, R. Bal, *ACS Sustainable Chem. Eng.* **2015**, *3*, 2823–2830; i) C. Ó. Dálaigh, S. A. Corr, Y. Gun'ko, S. J. Connon, *Angew. Chem. Int. Ed.* **2007**, *46*, 4329–4332; *Angew. Chem.* **2007**, *119*, 4407–4410; j) K. Kamata, K. Yonehara, Y. Sumida, K. Hirata, S. Nojima, N. Mizuno, *Angew. Chem. Int. Ed.* **2011**, *50*, 12062–12066; *Angew. Chem.* **2011**, *123*, 12268–12272; k) F. H. Richter, Y. Meng, T. Klasen, L. Sahraoui, F. Schuth, *J. Catal.* **2013**, *308*, 341–351.

[3] a) Q.-H. Fan, Y.-M. Li, A. S. C. Chan, *Chem. Rev.* **2002**, *102*, 3385–3466; b) S. Minakata, M. Komatsu, *Chem. Rev.* **2009**, *109*, 711–724; c) D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, *Chem. Rev.* **2002**, *102*, 3615–3640; d) F. Rajabi, D. Schaffner, S. Follmann, C. Wilhelm, S. Ernst, W. R. Thiel, *ChemCatChem* **2015**, *7*, 3513–3518; e) P. Li, S. Kawi, *Catal. Today* **2008**, *131*, 61–69.

[4] a) X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu, A. Vinu, *Angew. Chem. Int. Ed.* **2009**, *48*, 7884–7887; *Angew. Chem.* **2009**, *121*, 8024–8027; b) M. Kawaguchi, S. Yagi, H. Enomoto, *Carbon* **2004**, *42*, 345–350; c) Q.-Y. Bi, J.-D. Lin, Y.-M. Liu, H.-Y. He, F.-Q. Huang, Y. Cao, *Angew. Chem. Int. Ed.* **2016**, *55*, 11849–11853; *Angew. Chem.* **2016**, *128*, 12028–12032; d) L. Geng, X. Zhang, W. Zhang, M. Jia, G. Liu, *Chem. Commun.* **2014**, *50*, 2965–2967.

[5] a) A. Schätz, R. N. Grass, W. J. Stark, O. Reiser, *Chem. Eur. J.* **2008**, *14*, 8262–8266; b) O. Gleeson, R. Tekoriute, Y. K. Gun'ko, S. J. Connon, *Chem. Eur. J.* **2009**, *15*, 5669–5673; c) M. Nazish, S. Saravanan, N. H. Khan, P. Kumari, R. I. Kureshy, S. H. R. Abdi, H. C. Bajaj, *ChemPlusChem* **2014**, *79*, 1753–1760.

[6] a) L. C. Li, R. Matsuda, I. Tanaka, H. Sato, P. Kanoo, H. J. Jeno, M. L. Foo, A. Wakamiya, Y. Murata, S. Kitagawa, *J. Am. Chem. Soc.* **2014**, *136*, 7543–7546; b) L. Q. Ma, C. Abney, W. B. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248–1256; c) D. T. Genna, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *J. Am. Chem. Soc.* **2013**, *135*, 10586–10589; d) F. Song, C. Wang, W. Lin, *Chem. Commun.* **2011**, *47*, 8256–8258; e) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563–2565; f) H. Fei, S. M. Cohen, *Chem. Commun.* **2014**, *50*, 4810–4812; g) M. Zheng, Y. Liu, C. Wang, S. Liu, W. Lin, *Chem. Sci.* **2012**, *3*, 2623–2627; h) S. A. Burgess, A. Kassie, S. A. Baranowski, K. J. Fritzsching, K. Schmidt-Rohr, C. M. Brown, C. R. Wade, *J. Am. Chem. Soc.* **2016**, *138*, 1780–1783.

[7] a) J. Park, D. Feng, S. Yuan, H.-C. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 430–435; *Angew. Chem.* **2015**, *127*, 440–445; b) A. B. Powell, Y. Suzuki, M. Ueda, C. W. Bielawski, A. H. Cowley, *J. Am. Chem. Soc.* **2011**, *133*, 5218–5220; c) K. Manna, T. Zhang, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 6566–6569; d) D. Yang, S. O. Odoh, J. Borycz, T. C. Wang, O. K. Farha, J. T. Hupp, C. J. Cramer, L. Gagliardi, B. C. Gates, *ACS Catal.* **2016**, *6*, 235–247; e) Z. Dai, Q. Sun, F. Chen, S. Pan, L. Wang, X. Meng, J. Li, F.-S. Xiao, *ChemCatChem* **2016**, *8*, 812–817; f) C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, *J. Am. Chem. Soc.* **2012**, *134*, 8058–8061; g) H. Q. Yang, L. Zhang, L. Zhong, Q. Yang, C. Li, *Angew. Chem. Int. Ed.* **2007**, *46*, 6861–6865; *Angew. Chem.* **2007**, *119*, 6985–6989; h) B. Li, S. Bai, X. Wang, M. Zhong, Q. Yang, C. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 11517–11521; *Angew. Chem.* **2012**, *124*, 11685–11689.

[8] a) Q. Sun, M. Jiang, Z. Shen, Y. Jin, S. Pan, L. Wang, X. Meng, W. Chen, Y. Ding, J. Li, F.-S. Xiao, *Chem. Commun.* **2014**, *50*, 11844–11847; b) Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F.-S. Xiao, *J. Am. Chem. Soc.* **2015**, *137*, 5204–5209; c) Q. Sun, B. Aguila, G. Verma, X. Liu, Z. Dai, F. Deng, X. Meng, F.-S. Xiao, S. Ma, *Chem* **2016**, *1*, 628–639; d) Y. Huangfu, Q. Sun, S. Pan, X. Meng, F.-S. Xiao, *ACS Catal.* **2015**, *5*, 1556–1559.

[9] a) A. C. Cope, *J. Am. Chem. Soc.* **1937**, *59*, 2327–2330; b) N. Martin, C. Seoane, J. L. Soto, *Tetrahedron* **1988**, *44*, 5861–5868; c) G. Jenner, *Tetrahedron Lett.* **2001**, *42*, 243–245; d) S. Fioravanti, L. Pellacani, P. A. Tardella, M. C. Vergari, *Org. Lett.* **2008**, *10*, 1449–1451.

[10] a) U. Schuchardt, R. M. Vargas, G. Gelbard, *J. Mol. Catal. A* **1995**, *99*, 65–70; b) A. Horváth, *Tetrahedron Lett.* **1996**, *37*, 4423–4426; c) D. Simoni, F. P. Invidiata, S. Manfredini, R. Ferroni, I. Lampronti, M. Roberti, G. P. Pollini, *Tetrahedron Lett.* **1997**, *38*, 2749–2752.

[11] G. Gelbard, F. Vielfaure-Joly, *Tetrahedron Lett.* **1998**, *39*, 2743–2746.

[12] a) A. Solladié-Cavallo, M. Roje, T. Isarno, V. Sunjic, V. Vinkovic, *Eur. J. Org. Chem.* **2000**, 1077–1080; b) D. Bensa, J.-M. Brunel, G. Buono, J. Rodriguez, *Synlett* **2001**, 0715–0717.

[13] a) M. J. Schultz, C. C. Park, M. S. Sigman, *Chem. Commun.* **2002**, 3034–3035; b) M. S. Sigman, D. R. Jensen, *Acc. Chem. Res.* **2006**, *39*, 221–229.

[14] X. Du, Y. Sun, B. Tan, Q. Teng, X. Yao, C. Su, W. Wang, *Chem. Commun.* **2010**, *46*, 970–972.

[15] a) J. R. Cabrero-Antonino, T. García, P. Rubio-Marqués, J. A. Vidal-Moya, A. Leyva-Pérez, S. S. Al-Deyab, S. I. Al-Resayes, U. Díaz, A. Corma, *ACS Catal.* **2011**, *1*, 147–158; b) E. Poli, E. Merino, U. Díaz, D. Brunel, A. Corma, *J. Phys. Chem. C* **2011**, *115*, 7573–7585.

[16] a) X. Zhu, C.-L. Do-Thanh, C. R. Murdock, K. M. Nelson, C. Tian, S. Brown, S. M. Mahurin, D. M. Jenkins, J. Hu, B. Zhao, H. Liu, S. Dai, *ACS Macro Lett.* **2013**, *2*, 660–663; b) Z.-Z. Yang, H. Zhang, B. Yu, Y. Zhao, G. Ji, Z. Liu, *Chem. Commun.* **2015**, *51*, 1271–1274; c) Y. Zhuang, J. G. Seong, Y. S. Do, W. H. Lee, M. J. Lee, M. D. Guiver, Y. M. Lee, *J. Membr. Sci.* **2016**, *504*, 55–65; d) Z. Wang, D. Wang, F. Zhang, J. Jin, *ACS Macro Lett.* **2014**, *3*, 597–601; e) Z. Wang, D. Wang, J. Jin, *Macromolecules* **2014**, *47*, 7477–7483; f) Y. Zhuang, J. G. Seong, Y. S. Do, H. J. Jo, Z. Cui, J. Lee, Y. M. Lee, M. D. Guiver, *Macromolecules* **2014**, *47*, 3254–3262; g) J. G. Seong, Y. Zhuang, S. Kim, Y. S. Do, W. H. Lee, M. D. Guiver, Y. M. Lee, *J. Membr. Sci.* **2015**, *480*, 104–114; h) M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli, N. B. McKeown, *Science* **2013**, *339*, 303–307.

[17] a) Q. Sun, Z. Dai, X. Meng, F.-S. Xiao, *Chem. Soc. Rev.* **2015**, *44*, 6018–6034; b) Q. Sun, Z. Dai, X. Meng, L. Wang, F.-S. Xiao, *ACS Catal.* **2015**, *5*, 4556–4567; c) Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng, F.-S. Xiao, *J. Catal.* **2016**, *338*, 202–209.

[18] a) Z. Dai, Q. Sun, X. Liu, L. Guo, J. Li, S. Pan, C. Bian, L. Wang, X. Hu, X. Meng, L. Zhao, F. Deng, F.-S. Xiao, *ChemSusChem* **2017**, *10*, 1186–1192; b) M. G. Rabbani, H. M. El-Kaderi, *Chem. Mater.* **2011**, *23*, 1650–1653; c) Y. Huang, Z. Lin, H. Fu, F. Wang, M. Shen, X. Wang, R. Cao, *ChemSusChem* **2014**, *7*, 2647–2653; d) R. Dawson, D. J. Adams, A. I. Cooper, *Chem. Sci.* **2011**, *2*, 1173–1177; e) G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma, Z. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*, 9685–9689; *Angew. Chem.* **2016**, *128*, 9837–9841; f) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, *Nat. Commun.* **2013**, *4*, 1960.

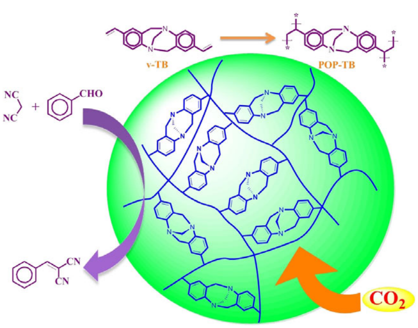
Manuscript received: September 22, 2017
Revised manuscript received: October 14, 2017

Version of record online: ■■ ■■, 0000

*Z. Dai, Y. Tang, Q. Sun, X. Liu, X. Meng,**
*F. Deng, F.-S. Xiao**

■■ – ■■

Porous Organic Polymers Constructed from Tröger's Base as Efficient Carbon Dioxide Adsorbents and Heterogeneous Catalysts



Basic instinct: Porous organic polymers constructed from Tröger's base are highly efficient for CO_2 capture and Knoevenagel reactions.