



# Microporous polymer based on hexaazatriphenylene-fused triptycene for CO<sub>2</sub> capture and conversion

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**ABSTRACT** Chemical conversion of carbon dioxide (CO<sub>2</sub>) to value-added useful chemicals like cyclic carbonates represents one potential solution to climate warming. Here, a kind of porous organic polymer (HAT-TP) with large surface area and excellent carbon dioxide uptake capacity is prepared *via* a condensation reaction to introduce hexaazatriphenylene (HAT) units into triptycene (TP)-based microporous polymer. HAT-TP can coordinate with zinc ions, and the resulting polymer (Zn/HAT-TP) can be utilized as an efficient recyclable catalyst for chemical conversion of CO<sub>2</sub> into cyclic carbonates with epoxides.

**Keywords:** microporous polymer, CO<sub>2</sub> capture, CO<sub>2</sub> conversion, triptycene, hexaazatriphenylene

## INTRODUCTION

Global energy shortage and climate warming have greatly threatened the sustainable development of mankind. Chemical conversion of carbon dioxide (CO<sub>2</sub>) to value-added useful chemicals like cyclic carbonates was recognized as one of the most promising and important pathways to resolve such environmental and energy issues [1–7]. The strategy has been industrialized utilizing homogeneous catalysts [8–11] under high temperature and pressure wherein new energy consumption was required and new CO<sub>2</sub> emission was caused. To overcome these shortcomings, some heterogeneous catalysts based on inorganic porous materials like porous silicon [12,13] have been developed, while the instability under acid or basic conditions limit their large scale applications. Hence, constructing a stable heterogeneous catalytic system for chemical conversion of CO<sub>2</sub> at mild conditions is currently critical.

Porous organic polymers (POPs) have been successfully utilized in CO<sub>2</sub> capture owing to their high surface area,

easy functionality and excellent stability [14]. Among the numerous polymers available, POPs with nitrogen atoms doping have attracted great attention on account of their CO<sub>2</sub>-philic properties which greatly enhance their CO<sub>2</sub> uptake capacity [15,16]. Recently, this kind of materials was also confirmed to be an ideal candidate for chemical conversion of CO<sub>2</sub> after introducing metal catalytic sites or other catalytic active centers. So far, some POPs with high CO<sub>2</sub> uptake capacity have been synthesized and utilized as heterogeneous catalysts for CO<sub>2</sub> conversion [17–25]. However, POPs with good capability of CO<sub>2</sub> capture from easy synthesis still need to be designed by wisely choosing building blocks to obtain ideal heterogeneous catalysts for practical use.

Hexaazatriphenylene (HAT) [26,27], a N-containing polyheterocyclic aromatic system, was used as building blocks in the construction of chemical sensors, nonlinear optical chromophores, liquid crystals, microporous polymers for energy storage and so on. With multiple metal ion chelating sites, HAT has also been recognized as an excellent ligand to load metal ions for homogeneous or heterogeneous catalytic systems [28–30]. Recently, we used triptycene as building block to develop a series of microporous polymers for gas adsorption, water treatment and heterogeneous catalysis [31–37]. Herein, we introduced HAT units into triptycene-based microporous polymer by a condensation reaction of hexaamino-triptycene hexachloride and triquinoyl hydrate to synthesize a HAT-fused triptycene-based microporous polymer (HAT-TP) [38] with high surface area and good CO<sub>2</sub> uptake capacity. HAT-TP could coordinate with zinc ions to prepare zinc(II)-coordinated HAT-TP (Zn/HAT-TP) by a simple treatment of HAT-TP with Zn(OAc)<sub>2</sub>. The synthesized Zn/HAT-TP not only displayed good CO<sub>2</sub> capture capacity, but also served as highly efficient

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heterogeneous catalyst for CO<sub>2</sub> conversion. It is worth noting that Zn/HAT-TP displays an enhanced catalytic efficiency for halogenated epoxides compared with propylene oxide, which might result from the activation of halogen bond interactions between catalysts and halogenated epoxides.

## EXPERIMENTAL SECTION

### Preparation of compounds

2,3,6,7,14,15-Hexaammoniumtriptycene hexachloride **1** was synthesized according to the literature [39,40], and the other chemicals were obtained from commercial sources without further purification.

### Synthesis of HAT-TP

Hexaaminotriptycene hexachloride **1** (168 mg, 0.3 mmol) and triquinoyl hydrate **2** (94 mg, 0.3 mmol) was suspended in the mixture of acetic acid aqueous solution (3 mol L<sup>-1</sup>) and ethylene glycol (1/1 in v/v) (10 mL) in a 25-mL pyrex tube. After being sonicated for 15 min and degassed by three freeze-pump-thaw cycles, the tube was heated at 120°C for 4 days, and then cooled down to room temperature. The precipitate was filtered, washed by water and methanol, and purified by Soxhlet extraction using methanol for 2 days. Subsequent drying in vacuum gave HAT-TP as black powder with a yield of 92%.

### Synthesis of Zn/HAT-TP

The synthesized HAT-TP (100 mg), zinc acetate dihydrate (200 mg for 17.7 wt% Zn content, 100 mg for 12.47 wt% Zn content, 50 mg for 9.76 wt% Zn content and 30 mg for 6.29 wt% Zn content) and ethyl alcohol (90 mL) were refluxed under Ar for 24 h. After cooling down to room temperature, the black solid was filtered and purified by Soxhlet extraction using methanol for

another 24 h. Zn/HAT-TP was obtained by vacuum drying then.

### General procedure for the catalytic cycloaddition of epoxides with atmospheric CO<sub>2</sub>

Epoxide (5 mmol), tetrabutyl ammonium bromide (TBAB, 116 mg) and the catalysts (7.2 mg) were mixed together in the reactor. After being sealed and purged with CO<sub>2</sub> (1 atm=1.01325×10<sup>5</sup> Pa) using a balloon, the mixture was stirred at room temperature for 48 h and the yields were determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

### Gas sorption analysis

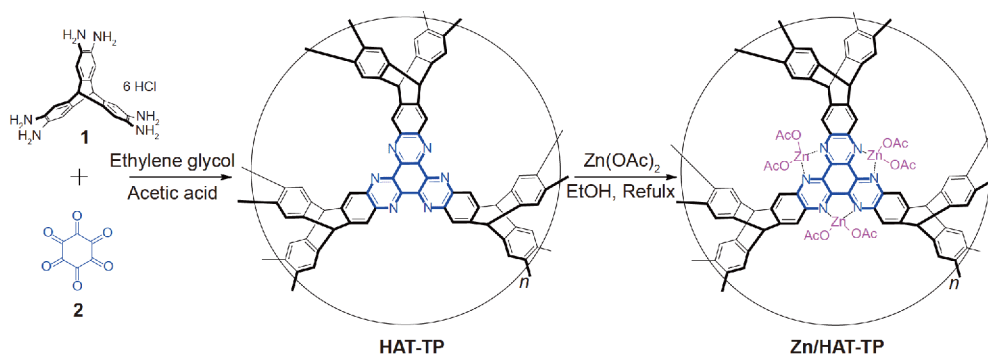
Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. The sample was degassed at 120°C for 8 h under vacuum before analysis. CO<sub>2</sub> isotherms were measured at 273 and 298 K up to 1.0 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure.

## RESULTS AND DISCUSSION

### Fabrication and characterization of HAT-TP

As illustrated in Scheme 1, HAT-TP was synthesized by the condensation reaction of hexaaminotriptycene hexachloride **1** with triquinoyl hydrate **2** under solvothermal conditions. Typically, a mixture of the two precursors in ethylene glycol and acetic acid aqueous solution was degassed and then heated at 120°C for 4 days. After reaction, the precipitated solid was filtrated and washed by water and methanol. After being extracted by Soxhlet extraction in methanol and dried in vacuum, the product HAT-TP was obtained with yield of 92%.

The formation of HAT-TP was demonstrated by



**Scheme 1** Synthesis of Zn/HAT-TP.

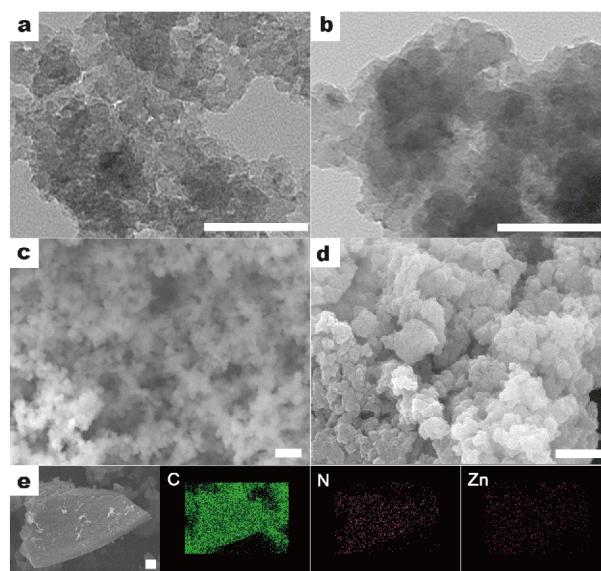
Fourier-transform infrared (FT-IR) and  $^{13}\text{C}$  cross-polarization magic-angle spinning (CP/MAS) NMR experiments. The  $^{13}\text{C}$  CP/MAS NMR spectrum of HAT-TP displayed four major carbon signals with the chemical shifts of 53, 124, 143, and 145 ppm, which could be assigned to the methylidyne bridge carbon (a), and the aromatic carbons (c, e, b and d), respectively (Fig. S1). The FT-IR spectrum (Fig. S2a) shows a strong signal at  $1624\text{ cm}^{-1}$ , confirming the formation of C=N bonds.

The thermal stability of HAT-TP was examined by the thermogravimetric analysis (TGA). The TGA curve indicated that HAT-TP was stable and its thermal degradation started at about  $500^\circ\text{C}$  under nitrogen (Fig. S2b). The slight mass drop before  $100^\circ\text{C}$  was attributed to trapped solvent within the micropores. HAT-TP was amorphous and showed a broad peak in powder X-ray diffraction (PXRD) pattern (Fig. S2c). The results of field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images (Fig. 1a, c) display that HAT-TP is in loose and irregular topography, similar to other triptycene-based porous polymers.

To evaluate the surface area and porous properties of HAT-TP, nitrogen sorption isotherm was measured at 77 K. The Brunauer-Emmett-Teller (BET) surface area was then calculated to be  $1224\text{ m}^2\text{ g}^{-1}$  (Langmuir surface area was  $1439\text{ m}^2\text{ g}^{-1}$ ) for HAT-TP (Fig. S2d). As shown in Fig. 2a, HAT-TP exhibited typical type I reversible sorption profile, displaying a steep nitrogen gas uptake at low relative pressure ( $P/P_0 < 0.001$ ), which reflected abundant micropore structure. The pore size distribution calculated using density functional theory (DFT) (Fig. 2b) also confirmed the presence of plentiful primary micropores. The  $\text{CO}_2$  sorption properties of HAT-TP were measured by volumetric methods at 273 and 298 K (Fig. 2c, d), and it showed a high  $\text{CO}_2$  uptake of 17.6 wt% at 1.0 bar and 273 K, surpassing most POPs as well as some porous cages [41–43]. The excellent  $\text{CO}_2$  adsorption performance of HAT-TP could benefit from the presence of abundant micropores and the electron rich properties of nitrogen atoms in the HAT units, which provided pores with appropriate size to adsorb  $\text{CO}_2$  and facilitated local-dipole/quadrupole interactions with  $\text{CO}_2$ .

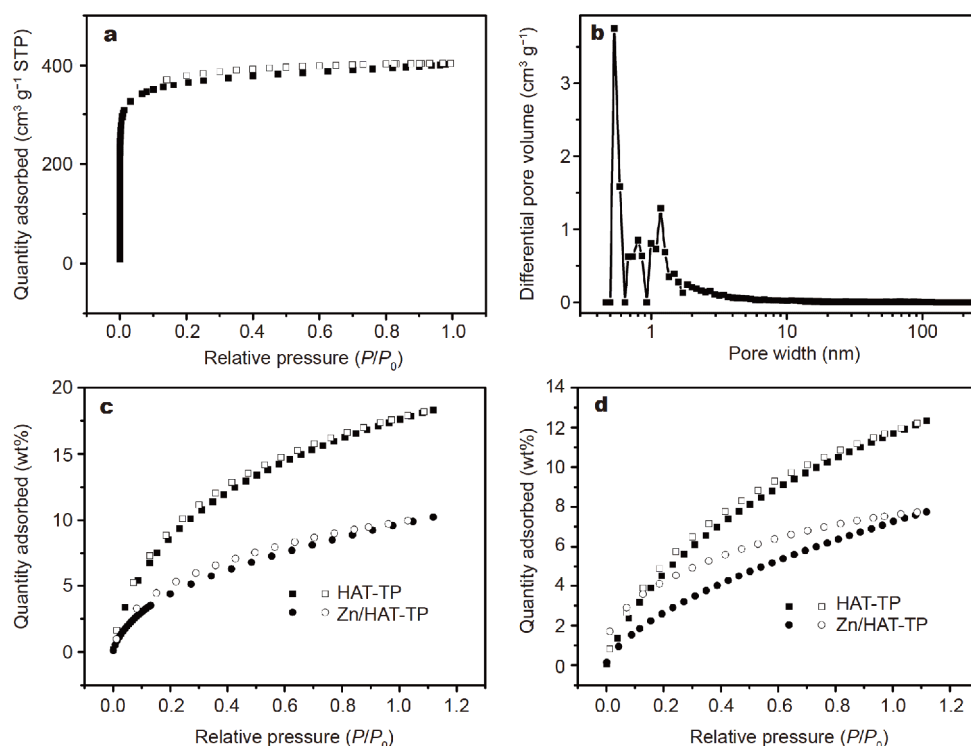
#### Fabrication and characterization of Zn/HAT-TP

By a simple post-treatment of HAT-TP with zinc acetate in ethanol solution, Zn(II)-containing HAT-TP, namely Zn/HAT-TP, was facily obtained. From the comparisons of FT-IR spectra and PXRD patterns of HAT-TP and Zn/HAT-TP, it was apparent that the structure of



**Figure 1** Electron microscopy images of HAT-TP and Zn/HAT-TP. Representative TEM images of HAT-TP (a) and Zn/HAT-TP (b). Representative SEM images of HAT-TP (c) and Zn/HAT-TP (d). (e) Another SEM image of Zn/HAT-TP and the corresponding EDX mappings for C, N and Zn atoms. Scale bar: 100 nm (a, b),  $1\ \mu\text{m}$  (c–e).

HAT-TP did not change when HAT-TP coordinated with Zn ions. In the IR spectrum of Zn/HAT-TP, the new peak at  $1526\text{ cm}^{-1}$  could be assigned to the  $-\text{C}=\text{O}$  signal of  $\text{OAc}^{-1}$  (Fig. S3a). While the PXRD pattern of Zn/HAT-TP was almost the same with that of HAT-TP, which suggested the amorphous property of Zn/HAT-TP (Fig. S3b). The  $^{13}\text{C}$  CP/MAS NMR spectrum of Zn/HAT-TP was also nearly identical to that of HAT-TP in the phenyl areas, offering more evidence for the structural preservation of HAT-TP after the zinc-treatment. Two additional peaks at 180 and 27 ppm were assigned to the carbonyl and methyl groups of the incorporated Zn ( $\text{OAc}$ )<sub>2</sub> (Fig. S1). SEM and TEM images indicated the morphology preservation after zinc-treatment (Fig. 1b, d). The corresponding elemental maps (C, N, and Zn) of Zn/HAT-TP were measured by energy dispersive X-ray (EDX) analysis, as shown in Fig. 1e. It was very clear that Zn and N atoms were homogeneously distributed on the polymer framework. X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the incorporation of zinc in HAT-TP (Fig. 3 and Fig. S3c). The C 1s spectra of HAT-TP and Zn/HAT-TP were almost identical, consisting of the signals of C–C (284.8 eV), C=N (285.7 eV), C–N (287.6 eV) and C=O (289.0 eV) (Fig. 3a, c). Compared with the spectrum of HAT-TP, a new peak at 399.8 eV in the N 1s XPS spectrum of Zn/HAT-TP could be assigned to  $-\text{N}-\text{Zn}$  [44],



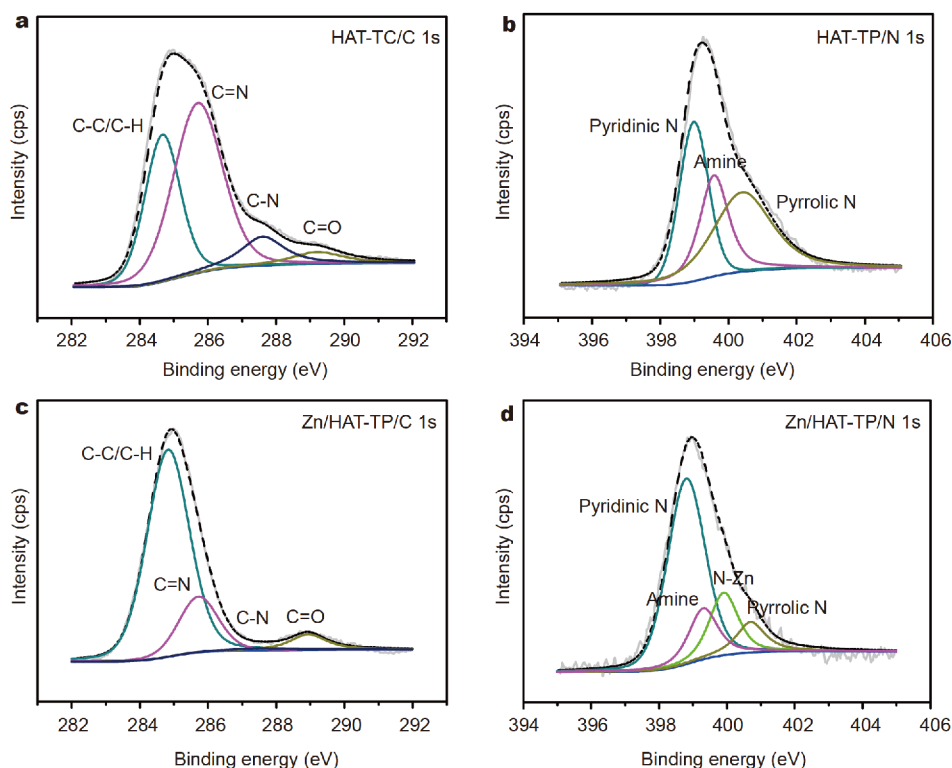
**Figure 2** Gas sorption test of HAT-TP and Zn/HAT-TP. (a) Nitrogen sorption and desorption isotherms of HAT-TP at 77 K. (b) Pore size distribution calculated for HAT-TP. CO<sub>2</sub> adsorption and desorption isotherms of HAT-TP and Zn/HAT-TP at 273 K (c) and 298 K (d). In (a), (c), and (d), filled symbols denote gas adsorption and empty symbols denote desorption.

implying that Zn<sup>2+</sup> may coordinate with the nitrogen atoms in HAT units (Fig. 3b, d). The nitrogen sorption and desorption isotherms of Zn/HAT-TP were measured at 77 K (Fig. S4a) and the BET surface area of Zn/HAT-TP dropped to 396 m<sup>2</sup> g<sup>-1</sup> (Langmuir surface area was 520 m<sup>2</sup> g<sup>-1</sup>) for the reason that some porous channel and nitrogen atoms were occupied by Zn complex. As shown in Fig. S4b, the pore size distribution calculated using DFT method also demonstrated that the pore volume of micropores decreased. The CO<sub>2</sub> uptake ability of Zn/HAT-TP was measured to be 9.9 wt% at 1.0 bar and 273 K (Fig. 2c), which was lower than that of HAT-TP as well, but still made Zn/HAT-TP an ideal material for CO<sub>2</sub> capture. The isosteric enthalpy (Q<sub>st</sub>) of Zn/HAT-TP toward CO<sub>2</sub> calculated from the adsorption isotherms (Fig. S5) and the CO<sub>2</sub>/N<sub>2</sub> selectivity calculated for Zn/HAT-TP using the slopes at low pressure in the Henry's law region for both CO<sub>2</sub> and N<sub>2</sub> at 273 K (Fig. S6) were both lower than those of HAT-TP.

#### Catalytic performance of Zn/HAT-TP

The ideal CO<sub>2</sub> capture capacity of Zn/HAT-TP inspired us to investigate its performance as catalyst for cycloadd-

dition of epoxide with CO<sub>2</sub> (Figs S7–S11). Typically, the reactions were conducted in the presence of Zn/HAT-TP with epoxide and CO<sub>2</sub>, using TBAB as co-catalyst under mild reaction condition (25°C, 1 atm). Zn/HAT-TP exhibited moderate catalytic activity in the cycloaddition of propylene oxide with a yield of 70% (Table 1, entry 1), inferior to some other POPs catalysts [15–18]. Under the same condition, HAT-TP with co-catalyst could only afford a yield of 22% for such reaction (Table 1, entry 3) (Fig. S12) which was similar to the yield of 24% (Table 1, entry 2) when TBAB was used alone (Fig. S13), suggesting the importance of Zn species for catalytic activity. Consistent with the mechanism established by previous studies [45–47], the proposed catalytic processes of Zn/HAT-TP (Fig. S14) could be hypothesized: Lewis acid activated epoxide toward nucleophilic ring opening by Br<sup>-</sup>, and facilitated subsequent insertion of CO<sub>2</sub>, in which the zinc ions could play the role of Lewis acid. Other epoxides were also used as substrates to validate the catalytic activity of Zn/HAT-TP. As shown in Table 2, the cycloaddition of epichlorohydrin catalyzed by Zn/HAT-TP yields about 97% carbonate (Table 2, entry 3). When 1,2-epoxybutane or styrene oxide was used, the catalyst



**Figure 3** XPS analysis on HAT-TP and Zn/HAT-TP. The C 1s spectra of HAT-TP (a) and Zn/HAT-TP (c). The N 1s spectra of HAT-TP (b) and Zn/HAT-TP (d).

**Table 1** Catalytic data of cycloaddition of propylene oxide with CO<sub>2</sub><sup>a)</sup>

Entry	Catalyst	Yield (%)
1	Zn/HAT-TP + TBAB	70
2	TBAB	24
3	HAT-TP + TBAB	22

a) Reaction conditions: 5 mmol epoxides with 7.2 mg catalyst and 116 mg TBAB, CO<sub>2</sub> pressure 1 atm, room temperature, reaction time 48 h. Isolated yields determined by <sup>1</sup>H NMR

afforded the reactions with yields of only 78% (Table 2, entry 2) and 55% (Table 2, entry 5), respectively. Interestingly, it seemed that epichlorohydrin afforded the highest conversion rate when Zn/HAT-TP was used as catalyst. Although volatility of substrates could influence the yields of carbonate to some extent, in similar research, propylene oxide usually afforded higher conversion rate or at least was similar to other epoxides [15–18]. A plausible explanation appeared to be that weak interactions between epichlorohydrin and catalyst influenced the

**Table 2** Different substituted epoxides coupled with CO<sub>2</sub>, catalyzed by Zn/HAT-TP at room temperature and atmospheric pressure<sup>a)</sup>

Entry	Epoxides	Products	Yields (%)
1			70
2			78
3			97
4			99
5			55

a) Reaction conditions: 5 mmol epoxides with 7.2 mg catalyst and 116 mg TBAB, CO<sub>2</sub> pressure 1 atm, room temperature, reaction time 48 h. Isolated yields determined by <sup>1</sup>H NMR

catalytic efficiency. Since HAT was one of the smallest 2D N-containing polyheterocyclic aromatic systems, it was hypothesized that halogen bonds (C–Cl⋯π) could occur between halogen atoms of epichlorohydrin and HAT

units of Zn/HAT-TP and then facilitate the cycloaddition of epichlorohydrin with CO<sub>2</sub>. Another halogenated substrate, epibromohydrin, was also used as reactant under the same condition. It was found that epibromohydrin could easily be converted into carbonate with a yield of 99% (Table 2, entry 4), which offered additional evidence in support of the hypothesis.

To evaluate the stability of the catalyst, Zn/HAT-TP was filtered after catalysis, washed by methanol, and dried for next cycle directly. It was clear that the product yields exhibited no manifest decrease after 5 runs which means that Zn/HAT-TP could be reused for at least 5 times without loss of catalytic activity (Fig. S15a). The FT-IR spectra (Fig. S15b) of Zn/HAT-TP catalysts after different reaction runs indicated that the structure of Zn/HAT-TP was almost maintained, and the TEM images of the catalysts before and after recycle tests were basically the same, confirming that irregular topography of Zn/HAT-TP remained consistent during the process (Fig. S16). The PXRD pattern and the nitrogen adsorption isotherm at 77 K of Zn/HAT-TP after catalysis were also obtained, which were almost the same with those of Zn/HAT-TP before catalysis (Fig. S17), further confirming that the porous structure of Zn/HAT-TP did not change during the catalytic process. XPS analysis on the used Zn/HAT-TP for 5 runs indicated a similar Zn content on the surface (1.9 atomic percent) with the initial amount (1.73 atomic percent). Inductively coupled plasma mass spectrometry (ICP-MS) analysis suggested moderately leaching of Zn species from 8.8 wt% to 4.9 wt%. But the catalytic activity did not change. We further investigated the catalytic performance of Zn/HAT-TP with different zinc ions loading (17.70 wt%, 12.47 wt%, 9.76 wt% and 6.29 wt%) and there was no obvious difference between them. Since the polymer could be metalized again by a simple post-treatment, the leaching of metal may not affect the use of the catalyst.

## CONCLUSIONS

In summary, we introduced HAT units into polymer skeleton based triptycene to construct a kind of organic microporous polymer named HAT-TP. With high surface area and abundant nitrogen atoms, HAT-TP was an ideal candidate for CO<sub>2</sub> capture and storage. Concurrently, HAT-TP could coordinate with Zn complex, and the synthesized Zn/HAT-TP could catalyze the reaction between epoxide and CO<sub>2</sub> to obtain cyclic carbonate with high activity under the mild conditions. Since a variety of organic microporous polymers with HAT units could be designed and synthesized with little cost, the study of

such materials could facilitate the development of chemical conversion of CO<sub>2</sub>.

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- Otto A, Grube T, Schiebahn S, *et al.* Closing the loop: Captured CO<sub>2</sub> as a feedstock in the chemical industry. *Energy Environ Sci*, 2015, 8: 3283–3297
- Kar S, Sen R, Goeppert A, *et al.* Integrative CO<sub>2</sub> capture and hydrogenation to methanol with reusable catalyst and amine: Toward a carbon neutral methanol economy. *J Am Chem Soc*, 2018, 140: 1580–1583
- Rao H, Schmidt LC, Bonin J, *et al.* Visible-light-driven methane formation from CO<sub>2</sub> with a molecular iron catalyst. *Nature*, 2017, 548: 74–77
- Trickett CA, Helal A, Al-Maythaly BA, *et al.* The chemistry of metal-organic frameworks for CO<sub>2</sub> capture, regeneration and conversion. *Nat Rev Mater*, 2017, 2: 17045
- Shaikh RR, Pornpraprom S, D'Elia V. Catalytic strategies for the cycloaddition of pure, diluted, and waste CO<sub>2</sub> to epoxides under ambient conditions. *ACS Catal*, 2018, 8: 419–450
- Liang J, Chen RP, Wang XY, *et al.* Postsynthetic ionization of an imidazole-containing metal-organic framework for the cycloaddition of carbon dioxide and epoxides. *Chem Sci*, 2017, 8: 1570–1575
- Liu TT, Liang J, Xu R, *et al.* Salen-Co(III) insertion in multivariate cationic metal-organic frameworks for the enhanced cycloaddition reaction of carbon dioxide. *Chem Commun*, 2019, 55: 4063–4066
- Castro-Osma JA, Lamb KJ, North M. Cr(salophen) complex catalyzed cyclic carbonate synthesis at ambient temperature and pressure. *ACS Catal*, 2016, 6: 5012–5025
- Kreider-Mueller A, Quinlivan PJ, Owen JS, *et al.* Synthesis and structures of cadmium carboxylate and thiocarboxylate compounds with a sulfur-rich coordination environment: Carboxylate exchange kinetics involving tris(2-mercapto-1-*t*-butylimidazolyl) hydroborato cadmium complexes, [Tm<sup>Buu</sup>]Cd(O<sub>2</sub>CR). *Inorg Chem*, 2015, 54: 3835–3850
- Buchard A, Kember MR, Sandeman KG, *et al.* A bimetallic iron(III) catalyst for CO<sub>2</sub>/epoxide coupling. *Chem Commun*, 2011, 47: 212–214
- North M, Quek SCZ, Pridmore NE, *et al.* Aluminum(salen) complexes as catalysts for the kinetic resolution of terminal epoxides via CO<sub>2</sub> coupling. *ACS Catal*, 2015, 5: 3398–3402
- Baleizão C, Gigante B, Sabater MJ, *et al.* On the activity of chiral chromium salen complexes covalently bound to solid silicates for the enantioselective epoxide ring opening. *Appl Catal A-General*, 2002, 228: 279–288
- Lu XB, Wang H, He R. Aluminum phthalocyanine complex covalently bonded to MCM-41 silica as heterogeneous catalyst for the synthesis of cyclic carbonates. *J Mol Catal A-Chem*, 2002, 186: 33–42
- Das S, Heasman P, Ben T, *et al.* Porous organic materials: Strategic design and structure-function correlation. *Chem Rev*, 2017, 117: 1515–1563
- Chen Q, Luo M, Hammershøj P, *et al.* Microporous polycarbazole with high specific surface area for gas storage and separation. *J Am Chem Soc*, 2012, 134: 6084–6087
- Luo Y, Li B, Wang W, *et al.* Hypercrosslinked aromatic heterocyclic microporous polymers: A new class of highly selective CO<sub>2</sub>

- capturing materials. *Adv Mater*, 2012, 24: 5703–5707
- 17 Ji G, Yang Z, Zhang H, *et al.* Hierarchically mesoporous *o*-hydroxyazobenzene polymers: Synthesis and their applications in CO<sub>2</sub> capture and conversion. *Angew Chem Int Ed*, 2016, 55: 9685–9689
- 18 Xie Y, Wang TT, Liu XH, *et al.* Capture and conversion of CO<sub>2</sub> at ambient conditions by a conjugated microporous polymer. *Nat Commun*, 2013, 4: 1960–1966
- 19 Wang S, Song K, Zhang C, *et al.* A novel metalporphyrin-based microporous organic polymer with high CO<sub>2</sub> uptake and efficient chemical conversion of CO<sub>2</sub> under ambient conditions. *J Mater Chem A*, 2017, 5: 1509–1515
- 20 Chen J, Zhong M, Tao L, *et al.* The cooperation of porphyrin-based porous polymer and thermal-responsive ionic liquid for efficient CO<sub>2</sub> cycloaddition reaction. *Green Chem*, 2018, 20: 903–911
- 21 Liang J, Huang YB, Cao R. Metal-organic frameworks and porous organic polymers for sustainable fixation of carbon dioxide into cyclic carbonates. *Coord Chem Rev*, 2019, 378: 32–65
- 22 Liu TT, Liang J, Huang YB, *et al.* A bifunctional cationic porous organic polymer based on a Salen-(Al) metalloligand for the cycloaddition of carbon dioxide to produce cyclic carbonates. *Chem Commun*, 2016, 52: 13288–13291
- 23 Liu TT, Xu R, Yi JD, *et al.* Imidazolium-based cationic covalent triazine frameworks for highly efficient cycloaddition of carbon dioxide. *ChemCatChem*, 2018, 10: 2036–2040
- 24 Yi JD, Xu R, Wu Q, *et al.* Atomically dispersed iron-nitrogen active sites within porphyrinic triazine-based frameworks for oxygen reduction reaction in both alkaline and acidic media. *ACS Energy Lett*, 2018, 3: 883–889
- 25 Zhao D, Kong C, Du H, *et al.* A molecular-templating strategy to polyamine-incorporated porous organic polymers for unprecedented CO<sub>2</sub> capture and separation. *Sci China Mater*, 2019, 62: 448–454
- 26 Segura JL, Juárez R, Ramos M, *et al.* Hexaazatriphenylene (HAT) derivatives: From synthesis to molecular design, self-organization and device applications. *Chem Soc Rev*, 2015, 44: 6850–6885
- 27 Gould CA, Darago LE, Gonzalez MI, *et al.* A trinuclear radical-bridged lanthanide single-molecule magnet. *Angew Chem Int Ed*, 2017, 56: 10103–10107
- 28 Tsuji Y, Yamamoto K, Yamauchi K, *et al.* Near-infrared light-driven hydrogen evolution from water using a polypyridyl triruthenium photosensitizer. *Angew Chem Int Ed*, 2018, 57: 208–212
- 29 Yuan F, Li J, Namuangruk S, *et al.* Microporous, self-segregated, graphenel polymer nanosheets prepared by dehydrogenative condensation of aza-PAHs building blocks in the solid state. *Chem Mater*, 2017, 29: 3971–3979
- 30 Ibáñez S, Poyatos M, Peris E. A D<sub>3h</sub>-symmetry hexaazatriphenylene-tris-*N*-heterocyclic carbene ligand and its coordination to iridium and gold: Preliminary catalytic studies. *Chem Commun*, 2017, 53: 3733–3736
- 31 Chen JJ, Zhai TL, Chen YF, *et al.* A triptycene-based two-dimensional porous organic polymeric nanosheet. *Polym Chem*, 2017, 8: 5533–5538
- 32 Ma H, Chen JJ, Tan L, *et al.* Nitrogen-rich triptycene-based porous polymer for gas storage and iodine enrichment. *ACS Macro Lett*, 2016, 5: 1039–1043
- 33 Zhai TL, Tan L, Luo Y, *et al.* Microporous polymers from a carbazole-based triptycene monomer: Synthesis and their applications for gas uptake. *Chem Asian J*, 2016, 11: 294–298
- 34 Zhang C, Zhu PC, Tan L, *et al.* Synthesis and properties of organic microporous polymers from the monomer of hexaphenylbenzene based triptycene. *Polymer*, 2016, 82: 100–104
- 35 Zhang C, Zhu PC, Tan L, *et al.* Triptycene-based hyper-cross-linked polymer sponge for gas storage and water treatment. *Macromolecules*, 2015, 48: 8509–8514
- 36 Zhang C, Wang JJ, Liu Y, *et al.* Main-chain organometallic microporous polymers based on triptycene: Synthesis and catalytic application in the Suzuki-Miyaura coupling reaction. *Chem Eur J*, 2013, 19: 5004–5008
- 37 Zhang C, Liu Y, Li B, *et al.* Triptycene-based microporous polymers: Synthesis and their gas storage properties. *ACS Macro Lett*, 2012, 1: 190–193
- 38 Mahmood J, Kim SJ, Noh HJ, *et al.* A robust 3D cage-like ultramicroporous network structure with high gas-uptake capacity. *Angew Chem Int Ed*, 2018, 57: 3415–3420
- 39 Chong JH, MacLachlan MJ. Robust non-interpenetrating coordination frameworks from new shape-persistent building blocks. *Inorg Chem*, 2006, 45: 1442–1444
- 40 Mastalerz M, Sieste S, Cenic M, *et al.* Two-step synthesis of hexammonium triptycene: An air-stable building block for condensation reactions to extended triptycene derivatives. *J Org Chem*, 2011, 76: 6389–6393
- 41 Zhang C, Wang Z, Tan L, *et al.* A porous tricyclooxacalixarene cage based on tetraphenylethylene. *Angew Chem Int Ed*, 2015, 54: 9244–9248
- 42 Wang Z, Luo Y, Zhai TL, *et al.* Porous triphenylbenzene-based bicyclooxacalixarene cage for selective adsorption of CO<sub>2</sub>/N<sub>2</sub>. *Org Lett*, 2016, 18: 4574–4577
- 43 Wang Z, Ma H, Zhai TL, *et al.* Networked cages for enhanced CO<sub>2</sub> capture and sensing. *Adv Sci*, 2018, 5: 1800141
- 44 Dzara MJ, Artyushkova K, Shulda S, *et al.* Characterization of complex interactions at the gas-solid interface with *in situ* spectroscopy: The case of nitrogen-functionalized carbon. *J Phys Chem C*, 2019, 123: 9074–9086
- 45 Yamaguchi K, Ebitani K, Yoshida T, *et al.* Mg-Al mixed oxides as highly active acid-base catalysts for cycloaddition of carbon dioxide to epoxides. *J Am Chem Soc*, 1999, 121: 4526–4527
- 46 Sit WN, Ng SM, Kwong KY, *et al.* Coupling reactions of CO<sub>2</sub> with neat epoxides catalyzed by PPN salts to yield cyclic carbonates. *J Org Chem*, 2005, 70: 8583–8586
- 47 Sun Q, Aguila B, Perman J, *et al.* Flexibility matters: Cooperative active sites in covalent organic framework and threaded ionic polymer. *J Am Chem Soc*, 2016, 138: 15790–15796

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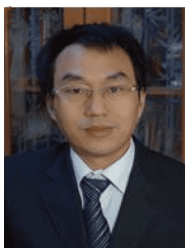
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**Conflict of interest** The authors declare that they have no conflict of interest.

**Supplementary information** Supporting data are available in the online version of the paper.



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## 六氮杂苯并菲扩环三蝶烯微孔聚合物的合成及其在二氧化碳捕获与催化转化领域的应用

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**摘要** 作为二氧化碳化学转化的研究热点, 利用二氧化碳作为原料合成有机小分子化合物被认为是解决温室效应的有效途径之一. 本文合成了一种基于六氮杂苯并菲扩环三蝶烯的有机微孔聚合物 (HAT-TP). 该多孔聚合物表现出较高比表面积以及较好的二氧化碳吸附能力. 通过与锌离子配位, Zn/HAT-TP聚合物还能够作为一类良好的非均相催化剂催化二氧化碳与环氧化物反应生成对应的环状碳酸酯.