



Microporous polymer based on hexaazatriphenylene-fused triptycene for CO₂ capture and conversion

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ABSTRACT Chemical conversion of carbon dioxide (CO₂) 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 CO₂ into cyclic carbonates with epoxides.

Keywords: microporous polymer, CO₂ capture, CO₂ conversion, triptycene, hexaazatriphenylene

INTRODUCTION

Global energy shortage and climate warming have greatly threatened the sustainable development of mankind. Chemical conversion of carbon dioxide (CO₂) 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 CO₂ 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 CO₂ at mild conditions is currently critical.

Porous organic polymers (POPs) have been successfully utilized in CO₂ 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 CO₂-philic properties which greatly enhance their CO₂ uptake capacity [15,16]. Recently, this kind of materials was also confirmed to be an ideal candidate for chemical conversion of CO₂ after introducing metal catalytic sites or other catalytic active centers. So far, some POPs with high CO₂ uptake capacity have been synthesized and utilized as heterogeneous catalysts for CO₂ conversion [17–25]. However, POPs with good capability of CO₂ 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 CO₂ 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)₂. The synthesized Zn/HAT-TP not only displayed good CO₂ capture capacity, but also served as highly efficient

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heterogeneous catalyst for CO₂ 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⁻¹) 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 CO₂

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 CO₂ (1 atm=1.01325×10⁵ Pa) using a balloon, the mixture was stirred at room temperature for 48 h and the yields were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Gas sorption analysis

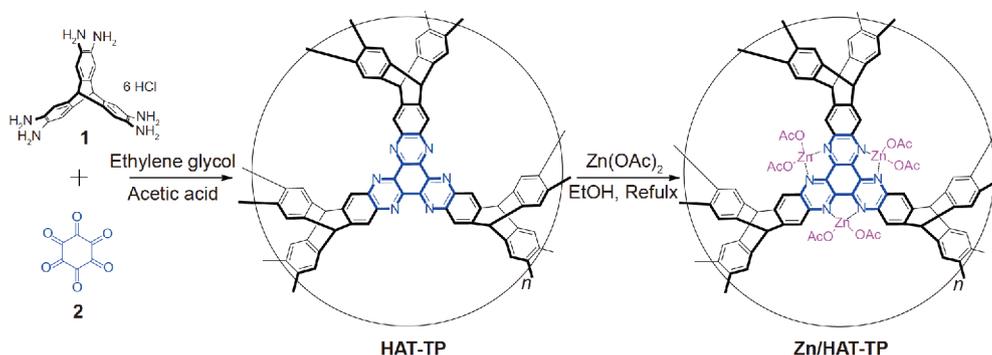
Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. The sample was degassed at 120°C for 8 h under vacuum before analysis. CO₂ isotherms were measured at 273 and 298 K up to 1.0 bar using 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}C cross-polarization magic-angle spinning (CP/MAS) NMR experiments. The ^{13}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 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°C under nitrogen (Fig. S2b). The slight mass drop before 100°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 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 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 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 CO_2 and facilitated local-dipole/quadrupole interactions with 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

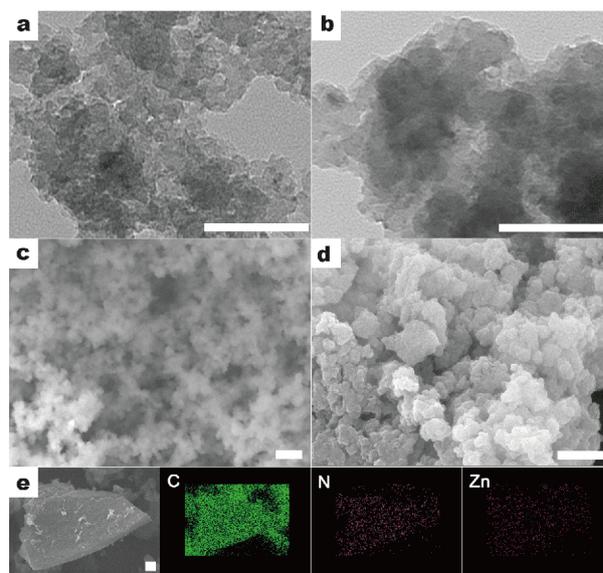


Figure 1 Electron microscopy images of HAT-TP and Zn/HAT-TP. Representative TEM images of HAT-TP (a) and Zn/HAT-TP (b). Representative SEM images of HAT-TP (c) and Zn/HAT-TP (d). (e) Another SEM image of Zn/HAT-TP and the corresponding EDX mappings for C, N and Zn atoms. Scale bar: 100 nm (a, b), $1\ \mu\text{m}$ (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 cm^{-1} could be assigned to the $-\text{C}=\text{O}$ signal of 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}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 (OAc)₂ (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],

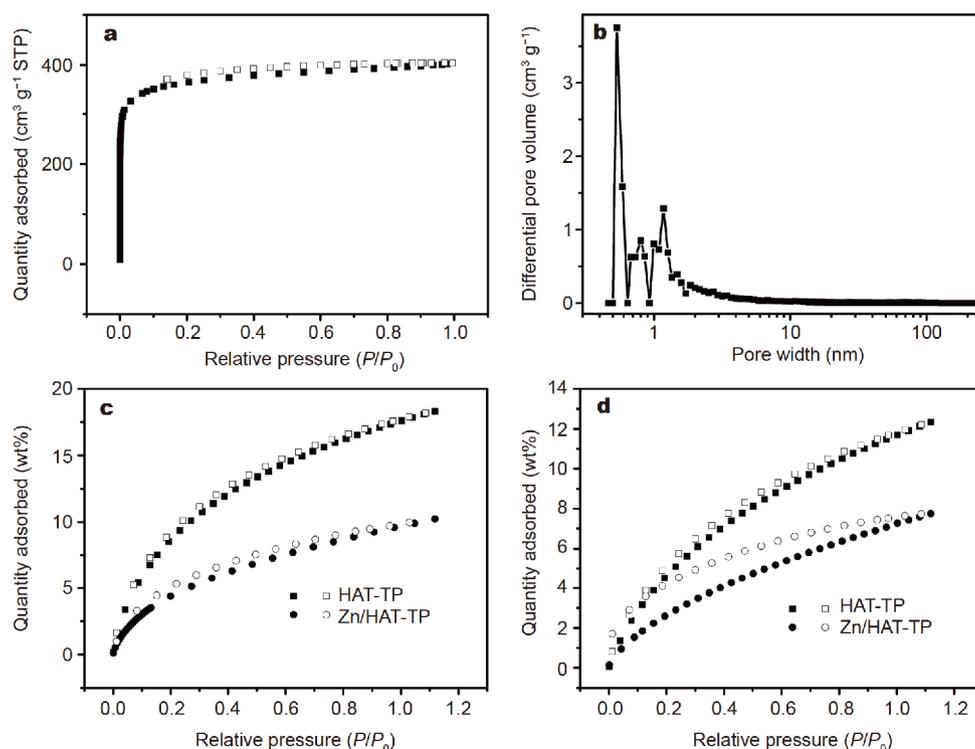


Figure 2 Gas sorption test of HAT-TP and Zn/HAT-TP. (a) Nitrogen sorption and desorption isotherms of HAT-TP at 77 K. (b) Pore size distribution calculated for HAT-TP. CO₂ adsorption and desorption isotherms of HAT-TP and Zn/HAT-TP at 273 K (c) and 298 K (d). In (a), (c), and (d), filled symbols denote gas adsorption and empty symbols denote desorption.

implying that Zn²⁺ 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 m² g⁻¹ (Langmuir surface area was 520 m² g⁻¹) 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 CO₂ 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 CO₂ capture. The isosteric enthalpy (Q_{st}) of Zn/HAT-TP toward CO₂ calculated from the adsorption isotherms (Fig. S5) and the CO₂/N₂ selectivity calculated for Zn/HAT-TP using the slopes at low pressure in the Henry's law region for both CO₂ and N₂ at 273 K (Fig. S6) were both lower than those of HAT-TP.

Catalytic performance of Zn/HAT-TP

The ideal CO₂ capture capacity of Zn/HAT-TP inspired us to investigate its performance as catalyst for cycloadd-

dition of epoxide with CO₂ (Figs S7–S11). Typically, the reactions were conducted in the presence of Zn/HAT-TP with epoxide and CO₂, 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⁻, and facilitated subsequent insertion of CO₂, 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

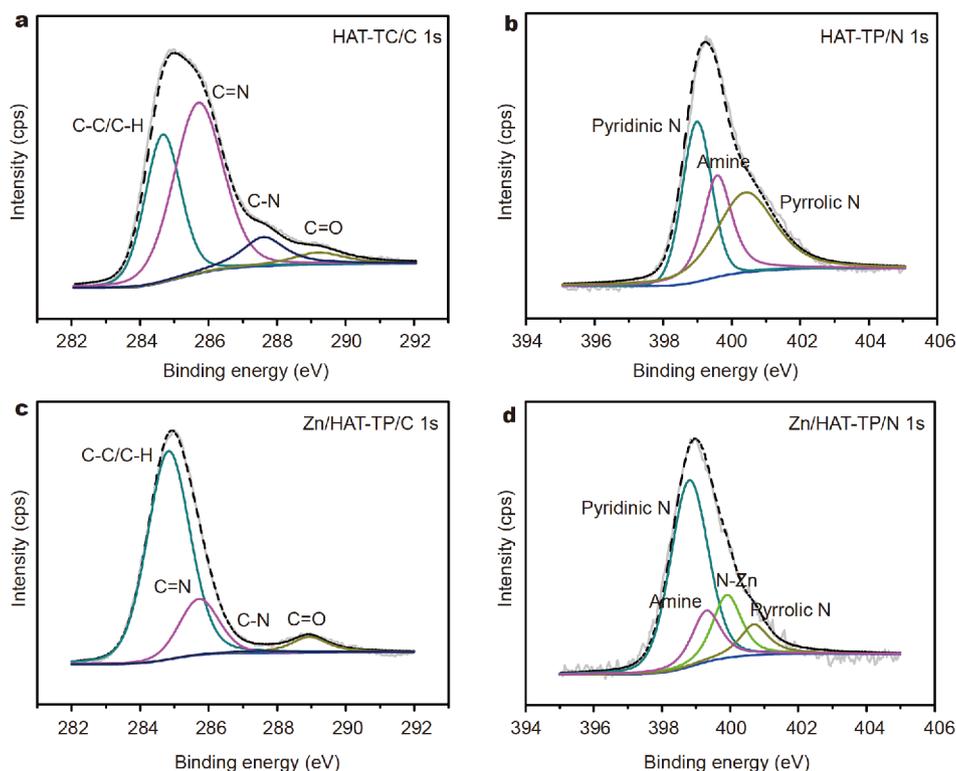


Figure 3 XPS analysis on HAT-TP and Zn/HAT-TP. The C 1s spectra of HAT-TP (a) and Zn/HAT-TP (c). The N 1s spectra of HAT-TP (b) and Zn/HAT-TP (d).

Table 1 Catalytic data of cycloaddition of propylene oxide with CO₂^{a)}

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, CO₂ pressure 1 atm, room temperature, reaction time 48 h. Isolated yields determined by ¹H 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 CO₂, catalyzed by Zn/HAT-TP at room temperature and atmospheric pressure^{a)}

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, CO₂ pressure 1 atm, room temperature, reaction time 48 h. Isolated yields determined by ¹H 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 CO₂. 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 CO₂ capture and storage. Concurrently, HAT-TP could coordinate with Zn complex, and the synthesized Zn/HAT-TP could catalyze the reaction between epoxide and CO₂ 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 CO₂.

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Author contributions Zhang C and Ma H conceived, coordinated the research, and designed the experiments. Zhang C acquired funding. Ma H conducted all experiments, analyzed the data and wrote the manuscript. Zhang C supervised the whole project. All the authors participated in discussions of the research.

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.