



Nitrogen and sulfur-enriched porous bithiophene-melamine covalent organic polymers for effective capture of CO₂ and iodine

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ABSTRACT

Low-cost bithiophene and melamine were constructed into a new nitrogen and sulfur-enriched organic framework (TPFM) by one-pot Schiff-base type reaction without any catalysts and post-treatment procedure. The as-synthesized TPFM exhibits the sphere-like morphology and mesopore-dominated porous structure with 611.3 m² g⁻¹ surface area. Profiting from the pore channels with abundant -NH groups on TPFM, it presents efficient carbon dioxide adsorption capacity with 77.5 cm³ g⁻¹ (about 16 wt%) at 273 K. The donated lone pair electrons in S and N atoms on TPFM contributed to its fast and efficient iodine adsorption capacities of 293.3 mg g⁻¹ in cyclohexane solution within several minutes.

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1. Introduction

Covalent organic polymers (COPs) is a novel type of structure with abundant pores. Various COPs with special functions have been developed with different organic building blocks [1,2]. In particular, because of its unique pore structure and modulable surface functional groups, COPs showed the great potentials in adsorption and captures for gas, iodine (I₂), heavy metal ions etc [3,4].

The efficient and reusable solid trap materials for carbon dioxide (CO₂) are becoming urgent, owing to huge release of CO₂ and thus the caused environmental problems. The boron-based, triazine-based and imine-based COPs with higher surface area (even > 3600 m² g⁻¹) have demonstrated the efficient CO₂ adsorption capacities from 30 to 240 mg g⁻¹ at 273 K and 1 bar [5]. On the other hand, some COPs with tunable heteroatoms showed the unique potentials for radioactive I₂ adsorption [6]. The electron-rich heterocycles and π conjugated system of COPs could remarkably facilitate the uptaking of I₂ on their frameworks [7,8]. Though effective adsorption for CO₂ and I₂ for some COPs, many COPs especially for boron-based COPs are unstable in moist air or water. The COPs often required complicated and harsh synthesis conditions with expensive organic building blocks. Low-cost stable COPs with easily-obtained organic building blocks were still desired for facilitating the potential applications of COPs in CO₂ and I₂ capture.

Herein, the inexpensive N-rich melamine and S-rich thiophene formaldehyde have been used as the raw materials to construct a novel bithiophene-melamine porous organic framework (TPFM) by one-pot Schiff-base type reaction (Fig. 1). The N and S-enriched surface and mesopore-dominated pore structure as well as easily-accessible sphere-like morphology endow it with the impressive capture capacities for CO₂ and I₂.

2. Experimental

2.1. Synthesis of TPFM

2,2'-Bithiophene-5,5'-dicarboxaldehyde (BTCA) was prepared by oxidizing 2-thenaldehyde with ferric chloride. The prepared BTCA (about 0.97 g) and melamine (0.84 g) were added into a three-neck flask with dimethyl sulfoxide (DMSO, 120 mL) under N₂ atmosphere. The resultant mixtures were heated at 160 °C for 72 h. A milky white powdery solid was collected by filtering the cooled mixtures, washing with DMSO in an ultrasonic washing machine and absolute ethanol [9]. The final TPFM product was obtained after being dried in vacuum at 60 °C for 24 h.

2.2. Characteristics of TPFM frameworks

Fourier-transform infrared (FT-IR) spectra were recorded on an infrared spectrophotometer (Bruker Tensor 27 with KBr pellets). Solid-state ¹³C NMR of TPFM was performed on the German Bruker Avance III 400 MHz nuclear magnetic resonance instrument. The

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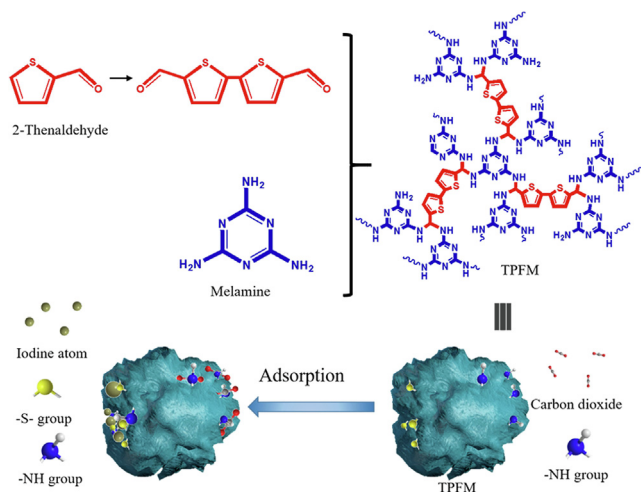


Fig. 1. Schematic representation for the synthesis of TPFM COP.

pore structures were analyzed on a Quadrasorb evo analyzer at 77 K. The morphology was observed by JEM-2100F transmission electron microscope (TEM) operated at 200 kV and Hitachi S-4800 scanning electron microscope (SEM).

2.3. Capture of I_2 in solution

10 mg TPFM was added to 5 mL I_2 -cyclohexane solution of 200 to 1000 mg L^{-1} . The mixture was filtered after standing at room temperature for 2 h. The ultraviolet–visible spectrophotometer was used to detect the concentration of I_2 in the adsorbed I_2 -cyclohexane solution (523 nm). The adsorption amount and removal efficiency can be calculated according to the Lambert-Beer law.

3. Results and discussion

The $-NH_2$ groups of melamine reacted with the $-CHO$ groups in BTCA by Schiff-base type reaction. In the FT-IR spectrum of TPFM (Fig. 2B), two new IR adsorption peaks at 1564 and 1343 cm^{-1} were identified. These corresponded to the typical stretching modes of C-N heterocycles, suggesting the successful condensation of $-NH_2$ and $-CHO$. The appearances of absorption bond at 2971 cm^{-1} (C-H bond stretching) and at 1195 cm^{-1} (N-H bond stretching) indicate the formation of aminal linkages. The absorptions bond in 1649 cm^{-1} (C = C bond stretching of thiophene rings) and 812 cm^{-1} (C-S bond stretching of thiophene rings) announce the existence of thiophene units in TPFM [10–11]. Moreover, there are four peaks in the ^{13}C NMR spectrum (Fig. 2A), located in 51.1, 112.3, 151.2 and 163.2 ppm. The signals at 112.3 and 151.2 ppm could be signed for C_2 and C_1 carbons of the thiophene rings. The triazine ring carbons were assigned to 163.2 ppm [11]. The presence of sp^3 hybrid carbon at 51.1 ppm also affirmed the linkage between these two raw materials (More information see Fig. S1, Supplementary figure 1).

SEM images showed sphere morphology of TPFM (Fig. 3E). A clearer observation from TEM images (Fig. 3A, B and D) also demonstrated the similar spheres with a diameter about 30–40 nm. The sphere morphology that could avoid the serious particle-stacking is different from the usual two-dimension plate morphology of the reported COPs. The enlarged TEM images could find its abundant porous textures. The morphology and pores help it to possess the better mass-transportation properties in adsorption process.

The N_2 -sorption analysis exhibited an atypical type I or type IV isotherm curve of TPFM. It can be seen that the adsorption volume rises sharply in the region of $P/P_0 < 0.001$ and $P/P_0 > 0.95$ (Fig. 2C), characteristic of Type I isotherms. However, there is a remarkable increase of N_2 -uptaking in the whole middle pressure of P/P_0 . Like the type IV isotherm, a broad insignificant loop was also observed. It illustrated the existence of abundant mesopores with a wide pore distribution. The pore size distribution of TPFM is around

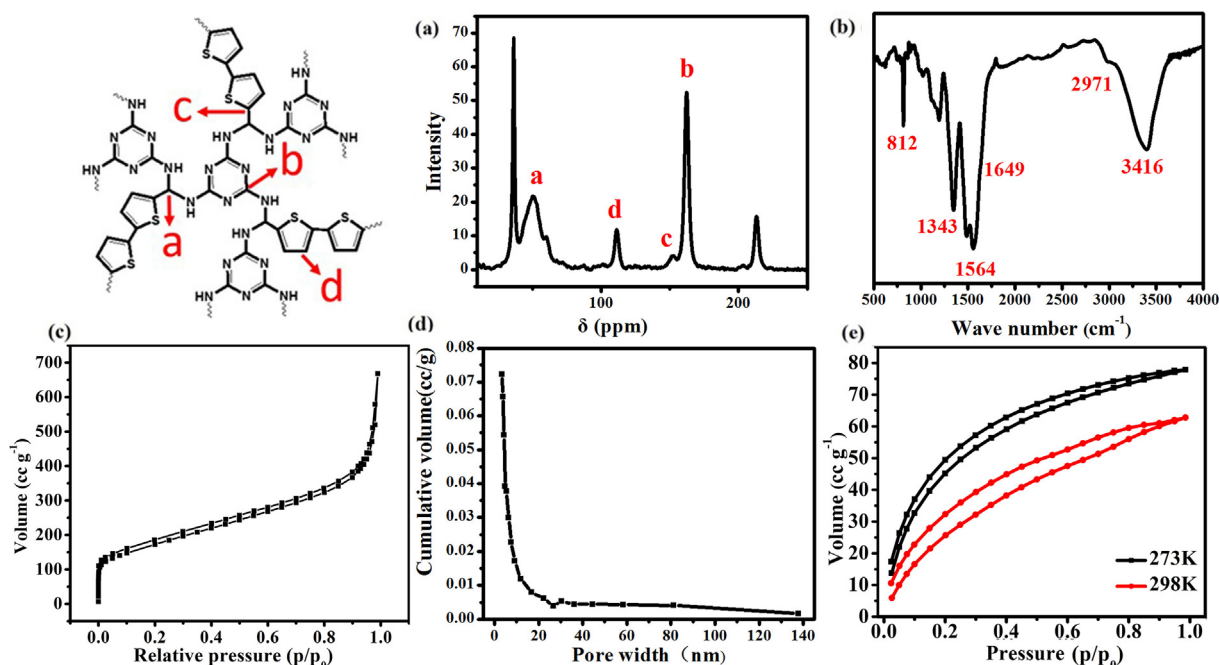


Fig. 2. Solid-state ^{13}C NMR (a), FT-IR spectrum (b), N_2 -sorption isotherms (c), and mesopore pore size distribution curves (d) and CO_2 -sorption isotherms (e) of TPFM.

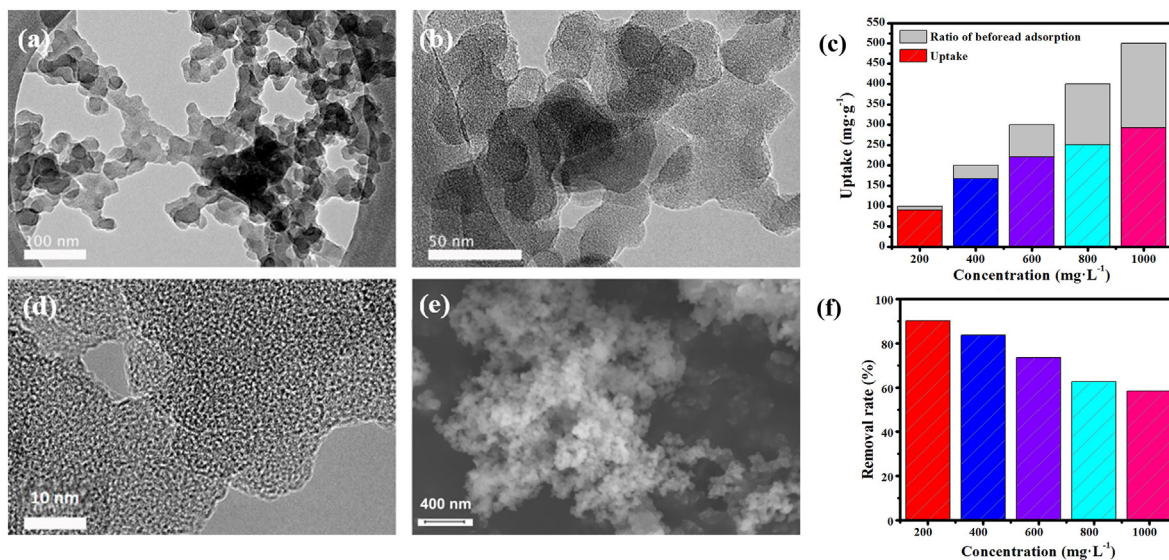


Fig. 3. TEM images (a, b and d) and SEM image (e) of TPFM. (c and f) Adsorption capacity and removal efficiency of I₂ in cyclohexane.

0.41 nm for micropores (Fig. S2, Supplementary figure 2) and mesopores ranging from 2 to 40 nm (Fig. 2D). The Brunauer-Emmett-Teller (BET) surface area of TPFM is calculated to be 611.3 m² g⁻¹, consisted of the mesopore-dominated external surface area of 523.4 m² g⁻¹ and micropore area of 87.9 m² g⁻¹ calculated from T-plot method. These results indicated that the prepared TPFM is a mesopore-dominated porous polymer.

The exposed -NH groups could serve as the Lewis-base to graft CO₂ molecules. The CO₂-adsorption isotherm of TPFM reveals that the CO₂ uptake capability on it is 77.5 cm³ g⁻¹ (about 3.5 mmol g⁻¹ or 16.2 wt%, 1 atm, 273 K) and 60.1 cm³ g⁻¹ (about 2.5 mmol g⁻¹ or 11.1 wt%, 1 atm, 298 K) (Fig. 2E). When compared the S_{BET} value of TPFM with about 1000–2000 cm³ g⁻¹ of the reported COPs [11], the CO₂ uptake capacity of TPFM is among the better COP-based materials [12]. The sphere morphology and unique porosity of TPFM contributed to fast transportation of CO₂, while the exposed -NH provided the efficient catching groups for CO₂ molecules.

It can be seen that the color of the solution changes significantly before and after adsorption (Fig. S5, Supplementary figure 5). To achieve the color changes of I₂-cyclohexane solution, the COP powder of 10 mg was only required to shake with I₂-cyclohexane solution for about 2–5 min. The fast adsorption rate made the kinetically adsorption curve been difficult to be obtained. The calculated adsorption amount in Fig. 3C are positively correlated with the I₂ concentration in solution. The adsorption amount (292.3 mg g⁻¹) of TPFM is the largest in 1000 mg L⁻¹ solution. The removal efficiency generally showed a negative correlation to the I₂ concentration in solution (Fig. 3F). Among them, the removal efficiency of TPFM is highest in the 200 mg L⁻¹ solution, up to about 90%. The FT-IR and the fluorescence emission spectra of I₂@TPFM testified that the weak electron transfer interactions between S and N heteroatoms with lone pair electrons and electron-deficient I₂ contributed to the I₂ adsorption on porous TPFM polymers (Fig. S3 and Fig. S4, Supplementary figure 3 and Supplementary figure 4) [13].

4. Conclusion

A novel porous covalent organic framework was synthesized by one-pot Schiff-base type reaction using BTCA and melamine as the building blocks. The synthesized TPFM presented the effective CO₂ adsorption capacity with 77.5 cm³ g⁻¹ (about 16 wt%) at

273 K. It also exhibited fast capture capacity for I₂ in cyclohexane, up to 292.3 mg g⁻¹. The special sphere-like morphology and porous structure as well as the exposed -NH and C-S groups contributed to its impressive adsorption capacity for CO₂ and I₂.

CRedit authorship contribution statement

Luyao Liu: Investigation, Methodology, Writing - original draft. **Chunmei Song:** Conceptualization, Supervision. **Aiguo Kong:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.128291>.

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