

Triptycene-Based Microporous Polymers: Synthesis and Their Gas Storage Properties

Chun Zhang,^{*,†} Ying Liu,[†] Buyi Li,[‡] Bien Tan,^{*,‡} Chuan-Feng Chen,^{*,§} Hui-Bi Xu,[†] and Xiang-Liang Yang^{*,†}

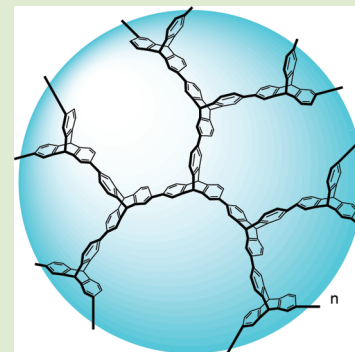
[†]College of Life Science and Technology, Huazhong University of Science and Technology, and National Engineering Research Center for Nanomedicine, Hubei, 430074, China

[‡]School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Hubei, 430074, China

[§]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

S Supporting Information

ABSTRACT: A novel kind of star triptycene-based microporous polymer (STPs) was synthesized efficiently from trihalotriptycenes by nickel(0)-catalyzed Ullmann cross-coupling reactions. STPs display a BET surface area of 1305 m² g⁻¹ and 1990 m² g⁻¹, and reversibly adsorb 1.60 and 1.93 wt % H₂ at 1.0 bar/77 K, 16.15 and 18.20 wt % CO₂ at 1.0 bar/273 K for STP-I and STP-II, respectively.



Organic microporous polymers possessing pores with a diameter <2 nm, have attracted increasing interest because of their potential applications in gas storage,¹ separations,² catalysis,³ and drug delivery.⁴ With a number of advantages, such as composing of light elements, easy functionality, and high stability, organic microporous polymers have been developed into several indispensable types including covalent organic frameworks (COFs),⁵ hyper-cross-linked polymers (HPCs),⁶ polymers of intrinsic microporosity (PIMs),⁷ conjugated microporous polymers (CMPs),⁸ crystalline triazine-based frameworks (CTFs),⁹ and porous aromatic frameworks (PAFs).¹⁰ One of the recent developments in this area is the construction of new materials by using novel building blocks and varying the rigid organic linkers to tune material properties such as density, pore volume, and surface area. Notably, the use of some interesting three-dimensional building blocks has resulted in some 3D porous polymers with high surface area and stability, such as tetraphenyl methane, tetraphenyl silane, and hexaphenylbenzene.^{5,10,11}

Triptycene and its derivatives,¹² with three-dimensional rigid frameworks, have been used as building blocks to construct new supramolecular systems.^{12a,13} More and more applications of microporous polymers, including PIMs, are being reported in materials science.^{14,15} The synthesis of trihalotriptycenes could provide us opportunities to construct novel porous polymers.¹⁶ Herein, we used 2,6,14-trihalotriptycenes as the starting materials to synthesize novel star triptycene-based porous polymers (STP-I and STP-II) by nickel(0)-catalyzed Ullmann

cross-coupling reaction. By combining triptycenes' intrinsic porosity, "internal molecular free volume" (which was put forward by Swager first),^{12b,14d,e} with expanded networks constructed by a triptycene–triptycene coupling reaction, STPs would possess a unique porous structure, which may afford us a new opportunity to find safe and effective gas adsorbents, especially for hydrogen or carbon dioxide.

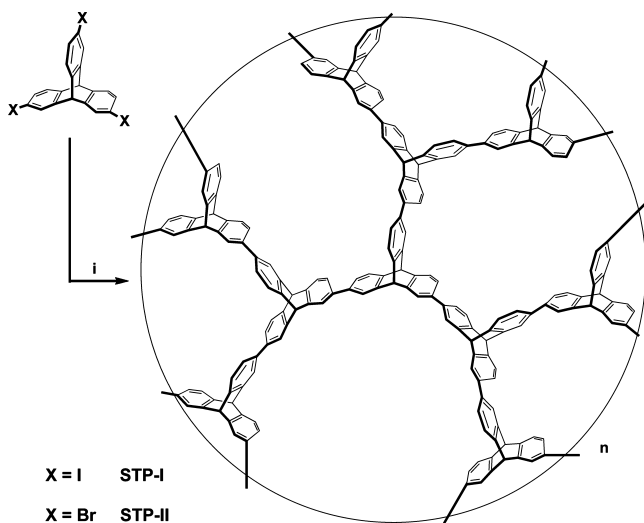
The synthesis was carried out by nickel(0)-catalyzed Ullmann cross-coupling reaction, as outlined in Scheme 1. Typically, a mixture of 2,6,14-trihalotriptycenes (0.85 mmol), 1,5-cyclooctadiene (3.5 mmol), bis(1,5-cyclo-octadiene)-nickel(0) (3.5 mmol), and 2,2'-bipyridyl (3.5 mmol) in dehydrated DMF (40 mL) was heated at 85 °C under argon for 96 h. After the reaction, concentrated hydrochloric acid was added to the reaction mixture. The precipitated solid was filtrated and washed successively with CHCl₃, THF, and H₂O. After drying in vacuum, the products STP-I (200 mg) and STP-II (190 mg) were obtained as off-white solids with 94 and 88% yields, respectively. The products were found to be insoluble in any common organic solvent.

Formation of STPs was confirmed by the FTIR analysis. The disappearance of C–I and C–Br bonds in spectra of STP-I and STP-II compared with that of their precursors 2,6,14-triiodotriptycene and 2,6,14-tribromo-triptycene demonstrated

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Scheme 1. Synthesis of STPs^a

^aReagents and conditions: (i) 1,5-cyclooctadiene, bis(1,5-cyclooctadiene)nickel(0), 2,2'-bipyridyl, DMF, 85 °C, 96 h.

the success of triptycene–triptycene coupling (Supporting Information, Figures S1 and S2). The ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR confirmed the successful growth of a microporous network with triptycene units furthermore. As shown in Figure 1 and Figure S3, the

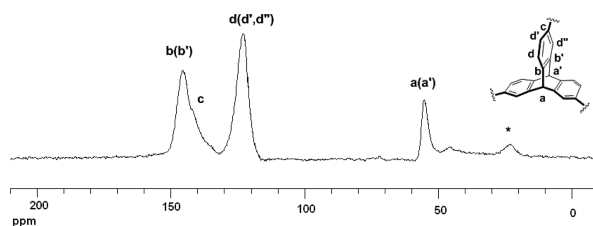


Figure 1. Cross-polarization (CP) ¹³C MAS NMR spectrum of STP-I. Asterisks denote spinning sidebands.

resonance peaks at $\delta = 145$, 142, 122, and 55 ppm can be assigned to the aromatic carbon b (b'), c, d (d',d''), and the methylidyne bridge carbon a (a'), respectively. Field-emission scanning electron microscopy (FE-SEM; Supporting Information, Figure S4) and transmission electron microscopy (TEM; Supporting Information, Figure S5) were utilized to investigate the morphology of STPs. The results of FE-SEM and TEM show that STPs adopted a sphere shape with particle size ~ 100 nm. Powder X-ray diffraction spectrum displayed the broad peaks in noncrystalline (Supporting Information, Figure S6), which results in part from the irreversible covalent reaction. Moreover, the STPs were found to have good thermal stability as a result of their stable C–C bonds. The thermogravimetric analysis (TGA) of STPs (Supporting Information, Figure S7) showed that they are stable up to 450 °C under air condition.

The surface area and porous properties of STPs (Table 1) were analyzed by nitrogen sorption analysis. The BET surface areas were obtained to be 1305 and 1990 m²/g (Langmuir surface area are 1760 and 2695 m² g⁻¹) and the total volumes were 1.015 and 1.553 cm³ g⁻¹ (micropore volume calculated from the nitrogen isotherm at $P/P_0 = 0.0500$ are 0.48 and 0.72 cm³ g⁻¹) for STP-I and STP-II, respectively. For STPs, as shown in Figure 2a, the nitrogen adsorption isotherms indicate

Table 1. Comparison of Porosity and Gas Uptake Capacities of Triptycene-Based Porous Polymers

polymers	S_{BET} (m ² g ⁻¹)	H ₂ uptake (wt %)	CO ₂ uptake (wt %)	ref
STP-I	1305	1.60	16.15	
STP-II	1990	1.92	18.20	
Trip-PIM(Et)	1065 ^a	1.65		15a
Trip-PIM(Me)	1760	1.83		15b

^aThe BET surface area of 1065 m² g⁻¹ for Trip-PIM(Et) had been modified to 1416 m² g⁻¹.^{15b}

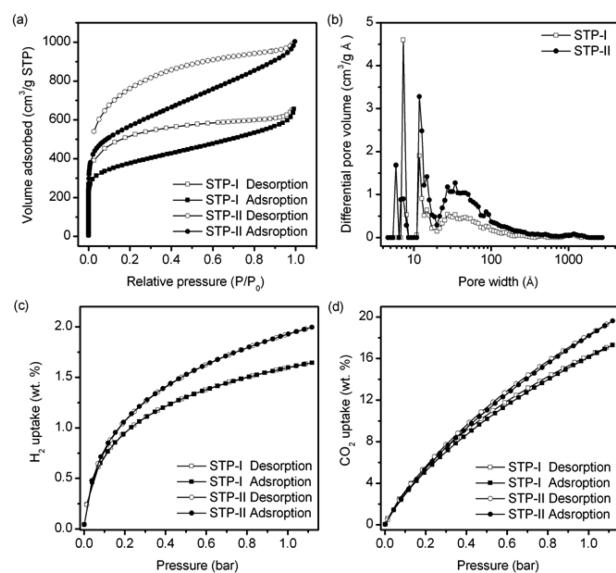


Figure 2. Nitrogen sorption isotherms at 77.3 K (a), pore distribution, and pore size distributions calculated using DFT methods, slit pore models, differential pore volumes and pore width (b), volumetric H₂ adsorption isotherms and desorption isotherms up to 1.13 bar at 77.3 K (c), and volumetric CO₂ adsorption isotherms and desorption isotherms up to 1.13 bar at 273.15 K (d) of STP-I and STP-II.

a steep nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$), thus, reflecting abundant micropore structure; a sharp rise at medium and high pressure region ($P/P_0 = 0.8–1.0$) implies the presence of macropores in the material; low pressure hysteresis is extending to the lowest attainable pressures, this phenomenon is associated with the irreversible uptake of gas molecules in the pores (or through pore entrances). It probably means a swelling of polymer matrix at 77 K by nitrogen. The pore size distribution (Figure 2b, calculated using DFT methods, slit pore models, differential pore volumes, and pore width) also confirmed the presence of primary micropore and a spot of meso- and macro-pore, which may result from the intrinsic porosity and expanded networks of triptycenes. The difference between STPs' porous properties may result from the different polymerization degree because of the different reactivity of iodide and bromide.^{14b24}

Atomistic simulation^{17,18} results (details described in Supporting Information) of STP-I shown in Figure 3 are consistent with experimental data. This model simulated only microporosity in the material and did not account for the meso- or macroporosity; mesopores in STP-I possess the dimensions that are larger than those of the simulation cell (3.6912 nm), as shown in pore size distributions (Figure 2b). The Connolly surface area¹⁹ (2600 m²/g) is higher than the Langmuir surface area, while the simulated micropore volume (0.5283 cm³/g) is

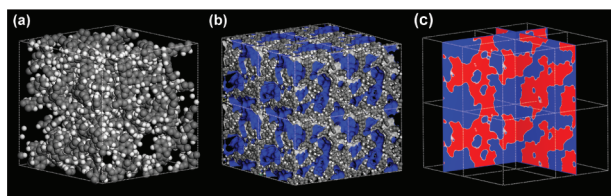


Figure 3. (a) Simulated STP-I, dimension of simulation box (the “amorphous cell”) = 3.6912 nm. Carbon atom was gray and Hydrogen atom was white. (b) Three-dimensional array of eight ($2 \times 2 \times 2$) amorphous cells with periodic boundary conditions. A Connolly surface was shown in blue/gray. Connolly surface area = $2600 \text{ m}^2/\text{g}$, simulated micropore volume = $0.5283 \text{ cm}^3/\text{g}$. (c) Two-dimensional “slices” through the simulated pore structure. The occupied and unoccupied volume is shown in red and blue, respectively.

larger than the experimental micropore volume. The overestimation of surface area and micropore volume is assigned to noninterconnected pockets of occluded free volume.¹⁷ In reality, this occluded free volume would not be accessible to the sorbate molecules. A two-dimensional “slice” through the simulated pore structure simulates the micropore dimensions quite well and exhibits the noninterconnected pockets of occluded free volume; the majority of the pore channels in width are 10 \AA , which is consistent with pore size distribution (Figure 2b).

It was demonstrated that the triptycene structure was suitable to the adsorption of H_2 from the theoretical study.²⁰ To estimate the hydrogen storage ability of STPs with all-triptycene units, hydrogen sorption and desorption measurements at low pressure were carried out at 77 K , which displayed type I behavior. As shown in Figure 2c, STP-I can absorb $1.60 \text{ wt } \% \text{ H}_2$ at 1.0 bar . While STP-II can absorb $1.92 \text{ wt } \% \text{ H}_2$ at 1.0 bar , which is larger than that had been found for another triptycene-based polymer (Trip-PIM)^{15a} and CTFs^{9b} with BET surface area of $1065 \text{ m}^2 \text{ g}^{-1}$ and $2475 \text{ m}^2 \text{ g}^{-1}$, respectively. Moreover, STPs performs well in comparison to most MOFs, mesoporous carbon materials, and zeolites with similar surface area.²¹

The CO_2 sorption properties of STPs were measured by volumetric methods at 273 K . As shown in Figure 2d, STP-I can absorb $16.15 \text{ wt } \%$ (161.5 mg g^{-1}) CO_2 at 1.0 bar . STP-II can uptake $18.20 \text{ wt } \%$, which is larger than the highest CO_2 uptake of $18 \text{ wt } \%$ or $85 \text{ cm}^3 \text{ g}^{-1}$ ($\sim 17 \text{ wt } \%$) observed for the POF 1B²² or covalent organic framework COF-6,^{5c} respectively. With the characterization of high CO_2 adsorption capacity and high thermal stability, STPs may be used as a CO_2 adsorbent, like some porous polyimides.²³

In summary, we synthesized two novel star triptycene-based porous polymers, STP-I and STP-II, from 2,6,14-triiodotriptycene and 2,6,14-tribromotriptycene, respectively. These STPs display the BET surface area up to $1990 \text{ m}^2 \text{ g}^{-1}$ and reversibly adsorb $1.92 \text{ wt } \% \text{ hydrogen}$ at $1.0 \text{ bar}/77 \text{ K}$ and $18.20 \text{ wt } \% \text{ CO}_2$ at $1.0 \text{ bar}/273 \text{ K}$. These materials are promising gas adsorbent candidates with high thermal stability. Optimization of the properties of these new triptycene-based porous polymers by utilizing new building blocks to control pore dimension and surface area is undergoing in our lab.

■ ASSOCIATED CONTENT

Supporting Information

Details of experimental materials and measurements, synthetic procedures of STPs, FT-IR spectra of STPs and trihalotripty-

cene, FE-SEM images, TEM images, and TGA data of STPs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chunzhang@hust.edu.cn; bien.tan@hust.edu.cn; cchen@iccas.ac.cn; yangxl@hust.edu.cn.

Notes

The authors declare no competing financial interest.

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