

Hydroxyl-Incorporated Microporous Polymer Comprising 3D Triptycene for Selective Capture of CO₂ over N₂ and CH₄

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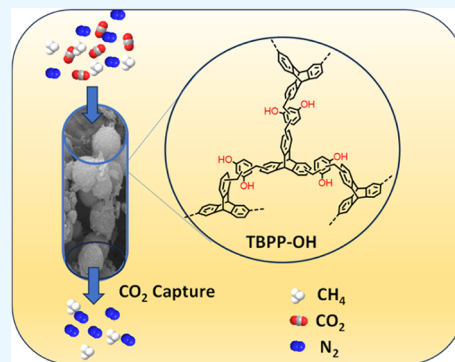


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ABSTRACT: The rising CO₂ concentration in the atmosphere contributes significantly to global warming, necessitating effective carbon capture techniques. Amine-based solvents are widely employed for the chemisorption of CO₂, although they have drawbacks, such as degradation, corrosion, and high regeneration energy requirements. Physical adsorption of CO₂ utilizing microporous adsorbents is a viable alternative that offers excellent efficiency and selectivity for CO₂ capture. This work presents the facile one-pot synthesis of a 3D-triptycene-containing hyper-cross-linked microporous polymer (TBPP-OH) possessing hydroxyl groups. The presence of triptycene units in the TBPP-OH polymeric structure gives several desirable features, such as inherent microporosity, larger surface area, and improved thermal stability. TBPP-OH showed considerable microporosity (%V_{mic} = 70%), a larger BET-specific surface area (S_{BET}) of 838 m² g⁻¹, and good thermal stability (T_d = 372 °C and char yield > 60%) which makes it a promising adsorbent for CO₂ capture. A strong affinity for CO₂ was shown by TBPP-OH with Q_{st} of 32.9 kJ/mol demonstrating a superior CO₂ adsorption capacity of 2.77 mmol/g at 273 K and 1 bar pressure where the volume of the micropore plays a significant role. The selectivity values of CO₂ over N₂ and CH₄ for the polymer TBPP-OH were also estimated to be reasonably high indicating good potential for CO₂ separation in different applications. The mechanism of CO₂ adsorption was investigated by using Langmuir and dual-site Langmuir models.



1. INTRODUCTION

The annual energy consumption is growing due to the continued rise of the world population and industrialization. CO₂ levels in the atmosphere continue to increase because fossil fuels are predominantly being used to produce energy.¹ Rising atmospheric concentration of carbon dioxide (CO₂) is recognized as the significant cause of global warming and its consequences such as climate change.² The latest statistics from 2024 shows that the atmospheric CO₂ content is higher than it has ever been in modern history, topping 420 ppm and continuing to rise. This corresponds to an approximate 50% rise since the start of the industrial age and an upsurge of around 14% since 2000 when the CO₂ concentration was already quite near 370 ppm. Consequently, “carbon capture and sequestration” (CCS) is the subject of extensive research in an attempt to lessen atmospheric CO₂ accumulation and its detrimental impacts on the ecosystem.³ The wet scrubbing method in industry uses monoethanolamine (MEA) for the chemisorption of CO₂. However, there are serious drawbacks associated with this process, such as excessive consumption of energy and high regeneration costs, corrosion of equipments, and formation of harmful products due to chemical degradations of amine-based solvents.⁴ In order to decrease the energy required for the regeneration process in comparison to present technical methods, it is essential that the adsorption of CO₂ is by physisorption with a higher capture efficiency and easy release. The utilization of porous adsorbents for carbon

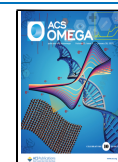
dioxide capture is a viable and efficient approach.^{5,6} In contemporary research, the design of solid porous materials for effective CO₂ capture is of great importance.^{7–9} Various porous materials have been investigated as potential materials for CO₂ capture such as adsorbents based on porous silica,¹⁰ zeolite-based,¹¹ poly(ionic liquids),¹² porous carbons,^{13–17} and metal–organic frameworks (MOFs).¹⁸ Adsorbent design for CO₂ capture continues to advance in contemporary research. Recently, several smart adsorbents have been reported for controlled CO₂ capture, such as light-responsive adsorbents that can demonstrate selective adsorption with efficient regeneration.^{19,20} However, over time, a novel group of polymeric materials known as porous organic polymers (POPs)—which have a persistent pore network and a large specific surface area—emerged for useful applications.^{21–24} POPs have enormous promise for usage in numerous applications, such as catalysis, energy storage, and gas capture and separation, because of their higher porosity, design flexibility, larger surface area, low density, and exceptional

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physiochemical stability.²⁵ Hyper-cross-linked polymers (HCPs) are members of the POP family, which has garnered significant interest in recent years.^{26–32} The Friedel–Crafts polymerization technique is typically used to design HCPs, which are amorphous polymers with strong cross-linking. Because of their facile synthesis, a large variety of aromatic monomers can be used to synthesize HCPs with different pore sizes and polymer properties. High chemical and thermal stability, larger surface area and microporosity, low density, efficient adsorption capabilities, simplicity in synthesis, affordability, and reusability are just a few of the many positive attributes of HCPs.³² These unique features of HCPs, apart from other polymers, make them excellent choices for addressing environmental contamination³³ and energy issues.^{30,34} In contemporary research, the design of efficient HCPs with desired adsorbent properties for CO₂ capture application is important. Some representative examples are as follows: Chen and co-workers reported the enhanced CO₂ capture in the hyper-cross-linked resin integrated microporous polymer where the adsorption capacity of CO₂ reaches 35.7 cm³/g at 298 K;³⁵ Wang and colleagues reported the selective CO₂ capture in the presence of N₂ and CH₄ by triphenylamine-derived microporous HCPs;³⁶ and Zhang et al. also reported several benzyl alcohols-derived HCPs with a CO₂ uptake capacity of 1.86–1.96 mmol/g at 298 K and 1 bar. The desired adsorbent properties such as thermal and physiochemical stability, microporosity, and surface area may be obtained by employing 3D rigid robust motifs as monomers for the synthesis of high-performance HCPs. Triptycene is such a rigid robust and distinctive three-dimensional (3D) organic monomer comprising three phenyl rings arranged in a paddle wheel manner.³⁷ Internal free volume (IFV) and excellent thermal stability are known characteristics of its unique rigid and sturdy structure.³⁸ In recent decades, the utilization of materials comprising triptycene has been investigated for sensing,³⁹ electronics,³⁸ liquid crystal displays,⁴⁰ gas capture and separation,^{41,42} host–guest chemistry,⁴³ and molecular machines.⁴⁴ In this work, we report the synthesis, characterization, and adsorption properties of a microporous polymer (TBPP-OH) comprising 3D triptycene motifs with ample hydroxyl group which was obtained via a facile one-step Friedel–Crafts cross-linking polymerization. TBPP-OH is predominantly microporous (pore size of less than 2 nm) with a larger BET-specific surface area of 838 m²/g. The carbon dioxide adsorption capacity of TBPP-OH outperforms several porous polymeric adsorbents reported in the literature. We have also evaluated the CO₂/CH₄ and CO₂/N₂ selectivity values at different temperatures (273 and 298 K) up to 1 bar pressure. The selective capture of carbon dioxide over N₂ is essential for post-combustion CO₂ removal from flue gases, which typically contain more than 70% N₂ and around 10–15% CO₂. Additionally, it is crucial to separate CO₂ from CH₄ to increase the efficiency of natural and landfill gases which are richer in CH₄. TBPP-OH showed promising ability to selectively capture CO₂ at different temperatures. This showed that TBPP-OH is an efficient microporous polymer, with applications in selective CO₂ capture.

2. EXPERIMENTAL PART

2.1. Materials. Triptycene (98%), dimethoxymethane (99%), resorcinol (99%), and anhydrous FeCl₃ (99.99%) were purchased from Sigma-Aldrich. The following chemicals were obtained from Sigma-Aldrich and used without further

purification: Anhydrous dichloroethane (DCE) (99.8%), methanol (99.6%), acetone (99.5%), and tetrahydrofuran (THF, 99.9%).

2.2. Synthesis of TBPP-OH. In a three-neck round-bottom flask (100 mL), triptycene (254 mg, 1 mmol), dimethoxymethane (348 μ L, 3 mmol), resorcinol (110 mg, 1 mmol), and anhydrous FeCl₃ (648 mg, 4 mmol) were taken and subsequently, anhydrous DCE (30 mL) was added and refluxed for 24 h at constant stirring under an inert N₂ atmosphere. Then, the resulting residue solid thus formed was subjected to filtration and washed with DCE, distilled water, methanol, tetrahydrofuran (THF), and acetone. MeOH was used for 24 h to further purify the solid polymer using the Soxhlet apparatus. The resulting solid powder was then heated to 110 °C inside a vacuum oven for 24 h, yielding the desired polymer TBPP-OH (brown solid). Yield: 91%; FTIR: 3446 (broad, –OH), 3012, 2926 (–CH–), (Ar–C=C–, 1615–1467), 1378, 1262, 1223, 1183, 1097, 891, 822, 765 cm^{–1}.

2.3. Structural Characterizations. Using a Thermo Fisher Scientific (Nicolet 6700) instrument, we did Fourier transform infrared spectroscopy (FTIR) investigations to gain insight into the presence of different functional groups in TBPP-OH. A Thermo Scientific EscaLab 250Xi, system consisting of an Al K α (1486.6 eV) source, was used for the X-ray photoelectron spectroscopy (XPS) analysis of TBPP-OH. Powder X-ray diffraction analysis (PXRD) was performed using a Rigaku Miniflex-II diffractometer that was connected to a Cu K α anode (wavelength = 1.5416 Å). A 400 MHz Bruker instrument functioning at 125.65 MHz was used to perform the solid-state ¹³C cross-polarization magic angle spinning (CP-MAS) NMR analysis. Thermogravimetric analysis (TGA) was done on a TA Q500 instrument under a N₂ flow (20 mL/min) at a 10 °C min^{–1} heating rate. The morphological properties of TBPP-OH were examined using a TESCAN-LYRA-3 (Czech Republic) field emission scanning electron microscopy (FESEM) instrument. A JEOL-JEM2100F instrument (Japan) was used to perform transmission electron microscopy (TEM) analysis at 200 kV acceleration voltage. Textural properties of TBPP-OH such as porosity and pore volumes were evaluated from N₂ isotherm data collected by utilizing a (Quantachrome Instruments) Quadrasorb SI instrument.

2.4. Gas Adsorption Experiment. Quantachrome Instrument (Quadrasorb SI) was used to obtain unary N₂, CO₂, and CH₄ isotherms at various temperatures. A dynamic vacuum (10^{–5} bar) at 120 °C for 12 h was used to pretreat about 0.2 g of the polymer samples prior to the isotherm measurements. The isotherm temperatures were maintained within the accuracy of ± 1 °C by utilizing a circulation bath having an equimolar mixture of ethylene glycol and H₂O. The mechanism of CO₂ adsorption was elucidated by using the Langmuir model and dual-site Langmuir model (DSL), eqs 1 and 2, respectively, to fit the experimentally obtained isotherm data points.^{45,46}

$$n^* = \frac{m_1 k_1 P}{1 + k_1 P} \quad (1)$$

$$n^* = \frac{m_1 k_1 P}{1 + k_1 P} + \frac{m_2 k_2 P}{1 + k_2 P} \quad (2)$$

Scheme 1. Synthesis of TBPP-OH

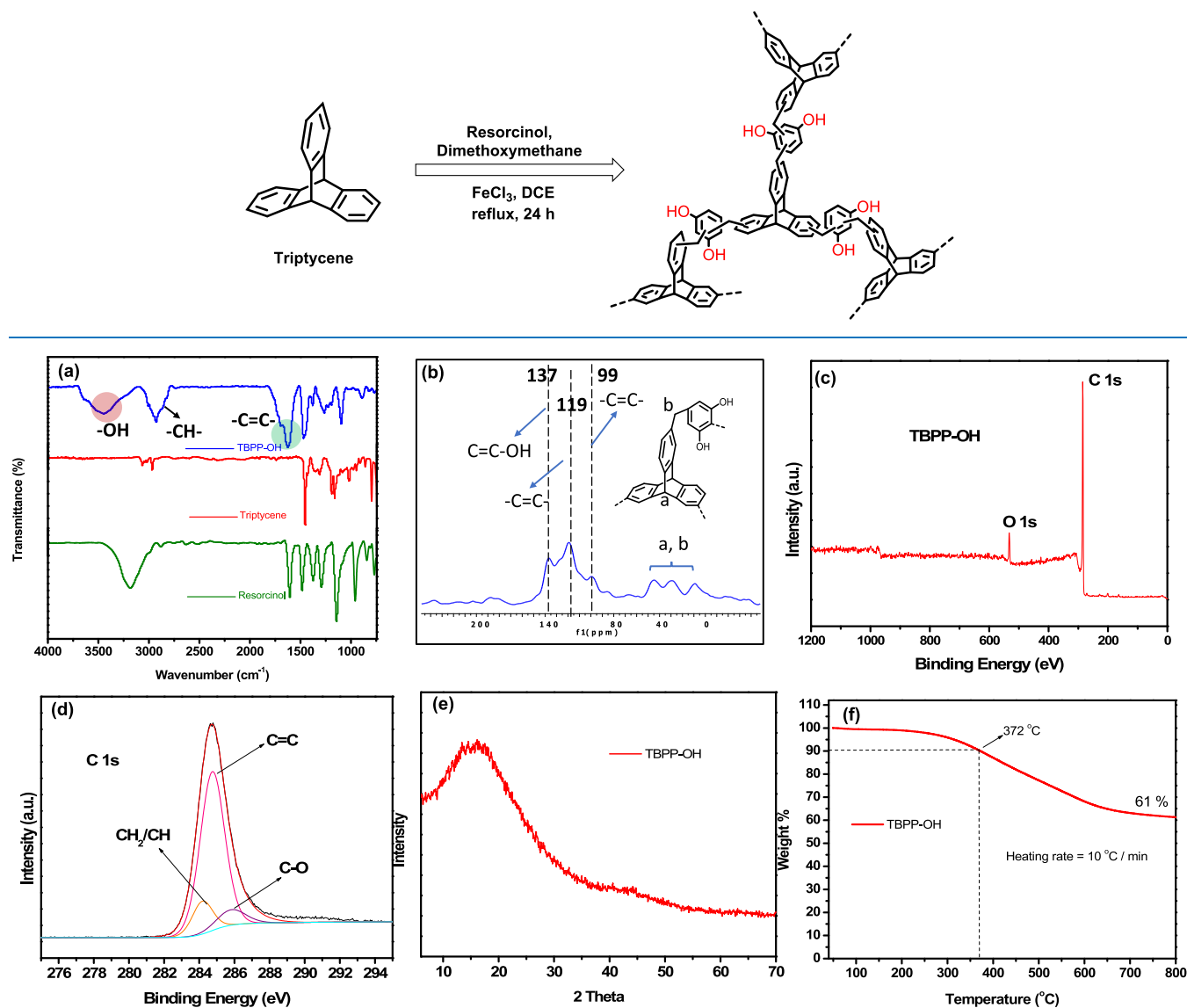


Figure 1. FTIR analysis (a), ^{13}C CP/MAS NMR (b), full-scan XPS spectrum (c), high-resolution C 1s spectrum (d), PXRD pattern (e), and TGA (f) of TBPP-OH.

where n^* is the predicted capacity (mmol/g), k_1 and k_2 are equilibrium constants (bar^{-1}) for sites of type 1 and type 2, respectively, and P is the pressure (bar).

Further, these isotherm results were used to calculate selectivity by ideal adsorbed solution theory (IAST selectivity) ($S_{1/2}$) for representative post-combustion flue gas (carbon dioxide = 15%) (nitrogen = 85%)⁴⁷ and biogas mixtures (50% CO_2 and 50% CH_4)⁴⁸ mixtures using eq 3.⁴⁹

$$S_{1/2} = \frac{n_1}{n_2} \times \frac{p_2}{p_1} \quad (3)$$

where n_1 and n_2 are, respectively, the adsorption capacities (mmol/g) of component 1 and component 2 at p_1 and p_2 , which represent the partial pressures of component 1 and component 2 in feed gas.

3. RESULTS AND DISCUSSION

3.1. Synthesis of TBPP-OH and Characterizations.

TBPP-OH polymer was prepared by Friedel–Crafts polymerization reaction using triptycene and resorcinol as monomers (Scheme 1). The polymer TBPP-OH is a brown-colored solid. The solubility analysis was performed in different solvents, and it was observed that TBPP-OH was insoluble in most of the common solvents like dichloromethane, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide (solubility analysis shown in Table S1). Structural characterizations of TBPP-OH were performed using ^{13}C CP/MAS NMR, FTIR, and XPS. FTIR analysis is shown in Figure 1a. The broad peak in the FTIR spectrum, which appears at around 3446 cm^{-1} , is ascribed to the polymer's $-\text{OH}$ -functional groups.^{42,50} Additionally, the peak observed at 2926 cm^{-1} corresponds to the characteristic $-\text{C}-\text{H}$ stretching vibration of the aliphatic $-\text{CH}_2-$ groups, indicating successful cross-linking. Peaks resulting from characteristics aromatics' $-\text{C}=\text{C}-$ stretching vibrations were observed at 1615 and 1467 cm^{-1} .³⁷

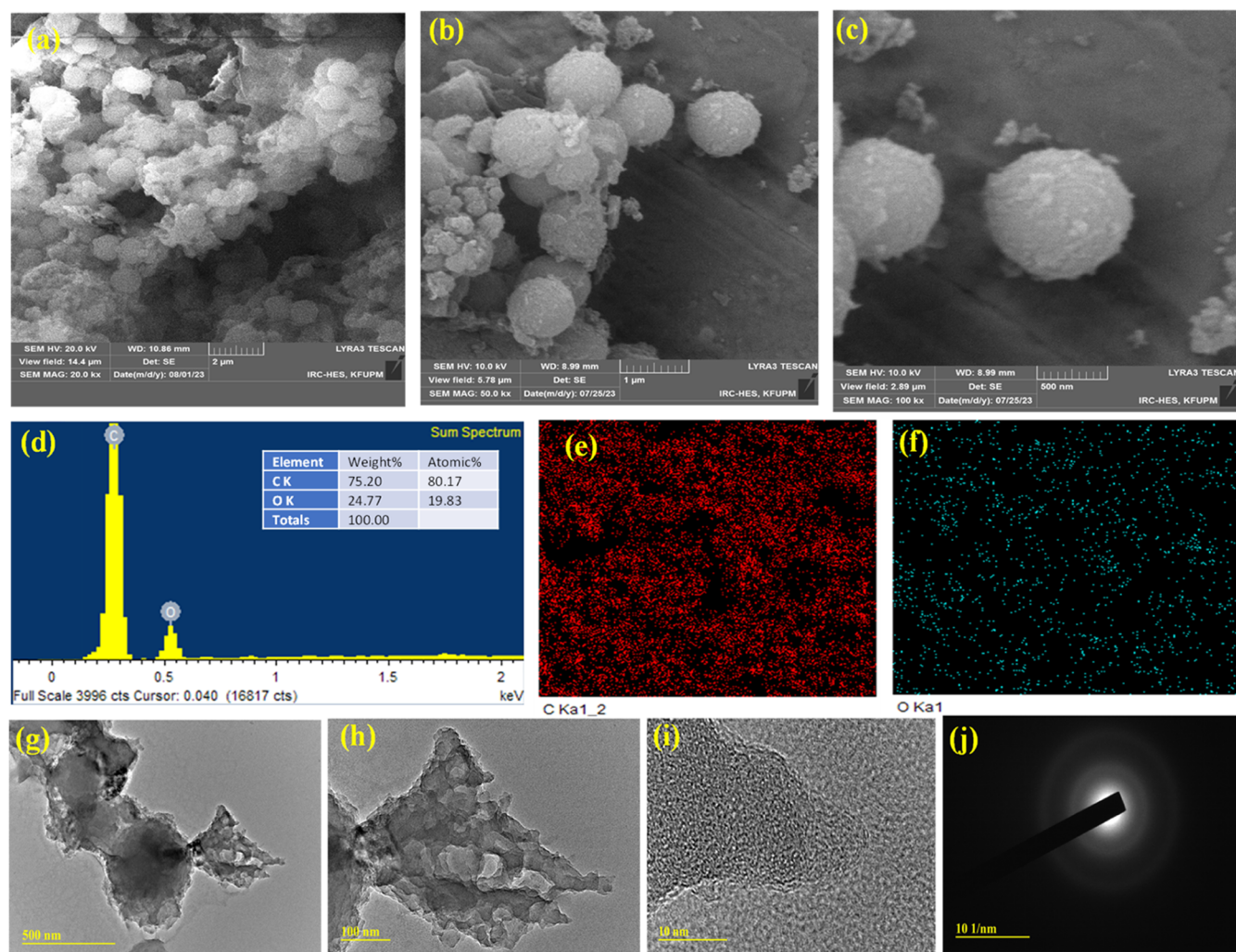


Figure 2. FESEM micrographs (a–c), EDS analysis (d), elemental mapping (e, f), and TEM images (g–j) of TBPP-OH.

Figure 1b displays the ^{13}C CP/MAS NMR spectrum of TBPP-OH. As expected, the broad peaks in the region of 140–99 ppm were attributed to the carbons of the aromatic rings. The peak observed at 137 ppm was assigned to hydroxyl-substituted aromatic carbon ($\text{C}=\text{C}-\text{OH}$). The peaks due to the bridgehead carbon of triptycene ($-\text{CH}-$) motifs and methylene carbons ($-\text{CH}_2-$) appeared at about 50–15 ppm. Therefore, ^{13}C CP/MAS NMR analysis clearly revealed the successful incorporation of resorcinol and triptycene units in the framework of the polymer TBPP-OH. TBPP-OH was also characterized by XPS analysis; the XPS analysis results are displayed in Figures 1c,d and S1. As can be seen in Figure 1c, the full-scan XPS spectrum of TBPP-OH exhibited two distinctly identifiable peaks at around 284 and 532 eV for C 1s and O 1s, respectively, indicating successful incorporation of resorcinol and triptycene. This conclusion was further supported by the high-resolution C 1s and O 1s photoemission spectra of TBPP-OH (Figures 1d and S1). The deconvoluted C 1s spectrum (Figure 1d) displays three distinct peaks at 285.81, 285.41, and 284.75 eV, respectively, ascribed to $\text{C}-\text{O}$, $\text{C}=\text{C}$, and CH_2/CH of TBPP-OH. The deconvoluted O 1s spectrum (Figure S1) shows one distinct peak at 532.52 attributed to hydroxyl oxygen of $\text{C}=\text{C}-\text{OH}$ present in TBPP-OH.

Powder X-ray diffraction analysis (PXRD) of TBPP-OH shows a broad spectrum (Figure 1e), exhibiting its amorphous nature, which can be ascribed to the existence of rigid robust, and bulky triptycene motifs in the framework of polymer TBPP-OH.⁴² The thermal characterization of TBPP-OH was determined by performing thermogravimetric analysis (TGA) (Figure 1f). Under an inert nitrogen environment, a given amount of sample of TBPP-OH was heated to 800 °C at a heating rate of 10 °C/min. TBPP-OH exhibited high thermal stability as indicated by its TGA experiment. The thermal degradation temperature (T_d) for TBPP-OH was 372 °C at which only 10% weight loss was registered. The char yield at 800 °C was observed to be 61%. The bearing of stiff, robust 3D triptycene molecules in TBPP-OH is attributed to the excellent thermal stability.^{50–52}

Further to study the morphology of TBPP-OH, field emission scanning electron microscopy (FESEM) analysis was carried out. As shown in Figure 2a–c, FESEM micrographs reveal the formation of spherical shape aggregates that are roughly 0.5–1 μm in size. Similar morphology has been exhibited by other porous polymers made using Friedel-Crafts cross-linking polymerizations.^{22,53} EDS and elemental mapping of TBPP-OH are also shown in Figure 2d–f. It is evident from SEM-EDS mappings of the polymer sample that TBPP-OH has a significantly higher O content of around 24% indicating

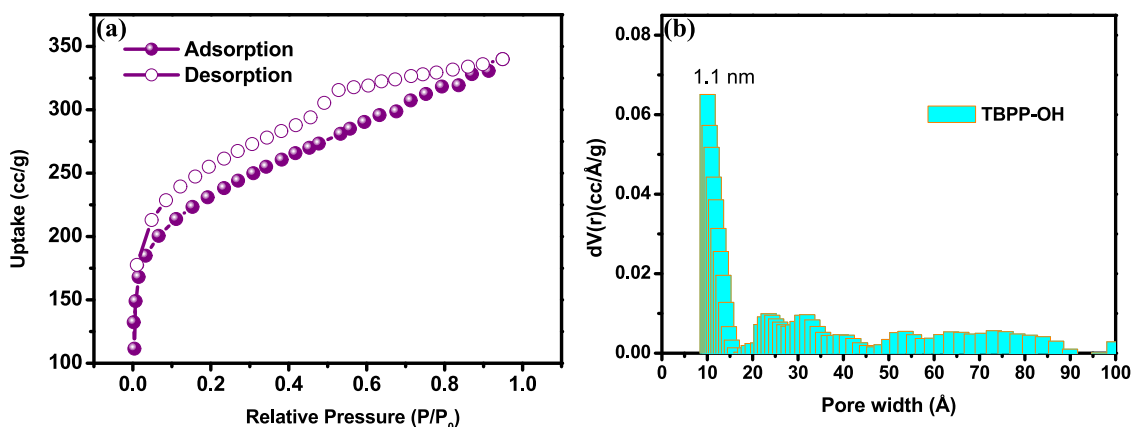


Figure 3. N_2 isotherm measured at 77 K (a) and PSD plot (b) of TBPP-OH.

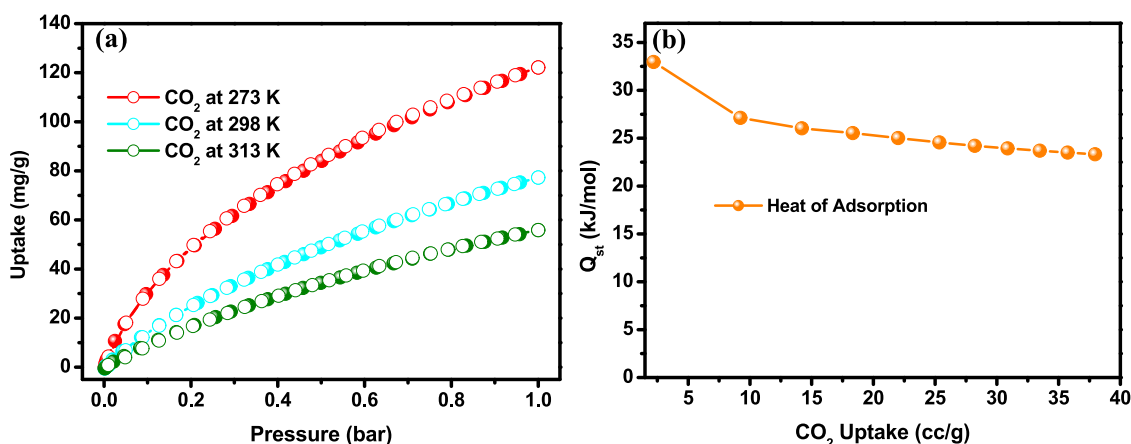


Figure 4. (a) Carbon dioxide uptake isotherms at different temperatures, filled sphere (adsorption) and empty sphere (desorption), and Q_{st} (heat of adsorption) (b) of TBPP-OH.

Table 1. Comparison of CO_2 Uptake and Selectivity of TBPP-OH with Other Reported Porous Polymers

material	CO_2 uptake at 1 bar (mg/g) 273 K	CO_2 uptake at 1 bar (mg/g) 298 K	CO_2 (Q_{st}) isosteric heat of adsorption (kJ/mol)	CO_2/N_2 selectivity 273 K (298 K) (IAST)	CO_2/N_2 selectivity 273 K (298 K) (Henry's law)	CO_2/CH_4 selectivity 273 K (298 K) (IAST)	CO_2/CH_4 selectivity 273 K (298 K) (Henry's law)	ref
TBPP-OH	122	77	32.9	37 (18)	33.7 (14)	4.2 (4.1)	7.4 (5.3)	this work
HCP1b	36.1	23.5	38.2	32.8				53
An-CPOP-1	61.5	57.1						59
PAF32	73	40	26					69
HCP-BA	84.6		27.4	28 (19)				70
HPIL-Cl-2	79	44	45	37				71
PCP-Cl	101.7	61.4	28.5	42 (34)				72
HCP-B	64.2	55.4						73
CB-PCP-1	90	53	35					74
TBP-1	51	35	33.7					75
STNP3	86	50	22					76
HMP-3	104	47						77
HPP-3	61	29.9	35					78

the presence of abundant hydroxyl groups. Additionally, this also demonstrates that resorcinol was successfully incorporated into the polymeric network of TBPP-OH. To further examine the morphology of TBPP-OH, TEM studies were performed, as shown in Figure 2g–j. TEM analysis of TBPP-OH showed nanosheet-like morphology and amorphous structure as evident from its HRTEM and SAED analysis.

3.2. Porous Properties of TBPP-OH. The nitrogen adsorption–desorption isotherm collected at 77 K and up to 1 bar pressure was used to evaluate the textural features, such as surface area, porosity, and pore volumes. As shown in Figure 3a, TBPP-OH displayed sharp uptake of N_2 at low pressures ($P/P_0 = 0–0.01$), indicating its microporous nature, while at high pressures, the isotherms slightly increased. This indicated the microporous nature of TBPP-OH. The pore size

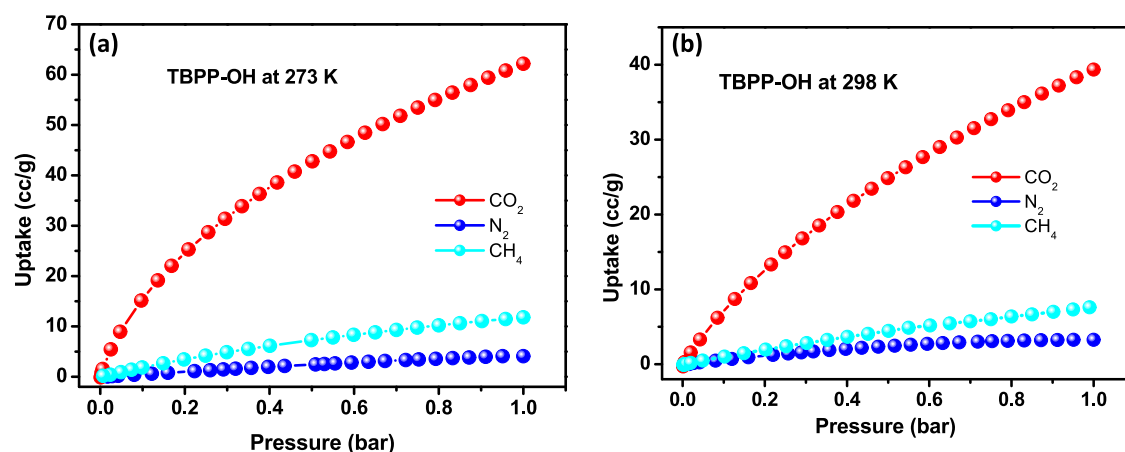


Figure 5. CO₂, N₂, and CH₄ adsorption isotherms at 273 K (a) and 298 K (b).

distribution plot (PSD) further confirms that TBPP-OH is considerably microporous ($\%V_{\text{mic}} = 70\%$) with the majority of pores in the region of 1.1 nm (Figure 3b). The microporous features of TBPP-OH may be ascribed to the existence of triptycene units with internal free volumes (IFV) and extensive cross-linking in the polymeric network. With a micropore volume of (V_{mic}) 0.346 cm³ g⁻¹ and a total pore volume (V_{tot}) of 0.491 cm³ g⁻¹, TBPP-OH demonstrated a larger BET-specific surface area (SA_{BET}) of 838 m² g⁻¹ (BET plot, Figure S2). The observed SA_{BET} of TBPP-OH is higher compared to several other porous polymers such as oxygen-rich HCPs (up to 246.9 m² g⁻¹),⁵³ HCTIn hyper-cross-linked networks (445–560 m² g⁻¹),⁵⁴ phenanthroimidazole-based POPs (CPPs, 49–285 m² g⁻¹),⁵⁵ HCPs based on pyrrolidinone (584 m² g⁻¹),⁵⁶ nitrogen-rich POPs (POP101-104, 205–436 m² g⁻¹),⁵⁷ and triazine-based porous polymers (308–456 m² g⁻¹).⁵⁸

3.3. CO₂ Capture Properties of TBPP-OH. To assess the CO₂-adsorption property of TBPP-OH, we performed CO₂ adsorption–desorption isotherms at various temperatures as displayed in Figure 4a. The hysteresis-free features of the CO₂ adsorption–desorption isotherms demonstrate the reversible CO₂ uptake capability of TBPP-OH (Figure 4a). The CO₂ uptake capacities of TBPP-OH are 122, 77, and 56 mg g⁻¹ at 273, 298, and 313 K, respectively, and 1 bar of pressure (Table 1). The CO₂ capture efficiency at 273 K demonstrated by TBPP-OH is comparatively better than that of various other porous materials reported for CO₂ capture. A few representative examples are the capture capacities of tetraphenyl anthraquinone-based porous polymers (61.6–66.8 mg/g),⁵⁹ nitrogen-rich porous material (97.8 mg/g),⁶⁰ triphenylamine- and triphenyl triazine-based COFs (92.38 mg g⁻¹),⁶¹ triazine-based covalent imine framework (77.3 mg/g),⁶² phthalazine-based CTFs (84–103 mg/g),⁶³ microporous polymer network (6FA-PI-CL, 72.8 mg g⁻¹),⁶⁴ and bicarbazole-based porous polymers (CMPs, 92.3–93.5 mg g⁻¹).⁶⁵ Table 1 also displays the comparison of the CO₂ uptake performance of TBPP-OH with other literature-reported porous polymers. The carbon dioxide adsorption capacity of TBPP-OH at 298 K is also comparable or superior to many other porous polymers such as POP101-104 (40.65–38.49 mg g⁻¹),⁵⁷ An-CPOPs (57–61.6 mg g⁻¹),⁵⁹ TPT-COF-6 (65.65 mg g⁻¹),⁶¹ TPA-TCIF(BD) (50.2 mg g⁻¹),⁶² and CMPs (54.2–54.7 mg g⁻¹).⁶⁵

The excellent CO₂ uptake exhibited by TBPP-OH may be attributed to its highly microporous network formed by 3D

tritycene and the presence of CO₂-philic –OH groups. The value of the isosteric heat of adsorption (Q_{st}) was also determined from the carbon dioxide uptake isotherms of TBPP-OH to further understanding of the CO₂-capturing mechanism (Figure 4b). The magnitude of Q_{st} was observed to be 32.9 kJ mol⁻¹, which suggested that the CO₂ adsorption by TBPP-OH is through physisorption. The observed Q_{st} is comparable to many other heteroatoms containing porous organic polymers, for instance, TF-PI-CL (28.6–30.2 kJ mol⁻¹),⁶⁴ melamine-based porous polyamides PTPAs (29.5–34.2 kJ mol⁻¹),⁶⁶ TPA-TCIF(BD) covalent imine frameworks (33.7 kJ mol⁻¹),⁶² triazine-based nanoporous polymer (29.2–34.1 kJ mol⁻¹),⁶⁷ imine-based porous polymer, and PIN1–2 (30 kJ mol⁻¹).⁶⁸

3.4. Selective Uptake of CO₂ over CH₄ and N₂ by TBPP-OH. After the successful CO₂ capture performance of TBPP-OH, we were further interested in gauging the CO₂/N₂ and CO₂/CH₄ selectivity for TBPP-OH at different temperatures. CO₂/N₂ separation is a crucial component for the capture of CO₂ from flue gases after combustion, which typically comprises more than 70% nitrogen and around 10–15% carbon dioxide. Further, it is important to separate CO₂ from CH₄ for the treatment of CH₄-rich gases, including biogas, which are often equimolar mixture of CO₂ and CH₄. Therefore, we assessed TBPP-OH's capability for the separation of landfill gas containing a CO₂/CH₄ mixture (50% CO₂:50% CH₄) and flue gas containing a CO₂ and N₂ mixture (15/85, v/v). Subsequently, to evaluate the selective CO₂ capture performance of TBPP-OH, the carbon dioxide, methane, and nitrogen uptake isotherms were collected at two different temperatures (273 and 298 K) and 1 bar pressure as displayed in Figure 5a,b. It was observed that TBPP-OH exhibited a significantly higher efficiency in capturing CO₂ compared to CH₄ and N₂; as a result, a higher uptake of CO₂ was accomplished in the two adsorption isotherms at temperatures 273 and 298 K. The CO₂/N₂ and CO₂/CH₄ selectivity curves of the adsorbent for feed gas simulating post-combustion CO₂ capture and biogas upgrading are given in Figure 6. The IAST method (Figure 6) was employed to measure the selectivity values for CO₂/CH₄ and CO₂/N₂. This method is commonly utilized to predict the selectivity for separation of a gas mixture by using experimental single-component adsorption isotherms. TBPP-OH displayed promising CO₂/N₂ selectivity of 37 at 273 K and 1 bar pressure (Table 1). In comparison to several porous polymers reported

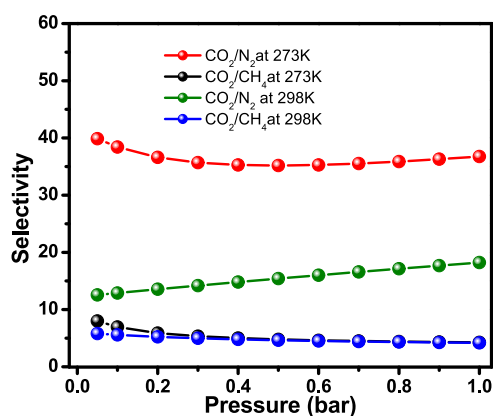


Figure 6. IAST selectivity curves for CO₂ (15%):N₂ (85%) and 50% CO₂:50% CH₄ composition.

in the literature, the observed selectivity of CO₂/N₂ is either comparable to or better than, for example, HCP-0 (16.9),⁷⁹ HCP1b (32.8),⁵³ polyethyleneimine-grafted porous polymer (TCP-PEI, 34)⁸⁰ and porous polyamides PTPA-3 (31.6).⁶⁶

At 298 K, the IAST selectivity value for CO₂/N₂ was 18 (Table 1). The selectivity values for CO₂/N₂ and CO₂/CH₄ were also measured using the Henry's law ratio of the initial slope method (Figure 7). The CO₂/N₂ and CO₂/CH₄ selectivities were, respectively, 33.7 and 7.4 at 273 K (Table 1). At a given temperature, the selectivity for CO₂/N₂ is better than CO₂/CH₄ selectivity, as CO₂ and N₂ show a greater difference in polarizability as compared to CO₂ and CH₄. Further, the decrease in selectivity with increasing temperature for both CO₂ over N₂ and CH₄ indicates that the adsorbent shows both better selectivity and capacity at 273 K. Moreover, the adsorption mechanism was elucidated by fitting the experimental adsorption data points with the Langmuir and dual-site Langmuir models (Figure 8). The experimental data can be predicted more appropriately using the dual-site Langmuir model, indicating two types of adsorption sites in the adsorbent. The adsorption and desorption isotherms are overlapping for all gases, indicating weak physisorption-type interactions and the possibility of adsorbent regeneration by a simple pressure/vacuum swing. Further, at both investigated temperatures, CO₂ capacity is the highest followed by CH₄ and N₂ is the least adsorbed. This is attributed to the highest polarizability (2.507 Å³ vs 2.448 Å³ for CH₄ and 1.710 Å³ for

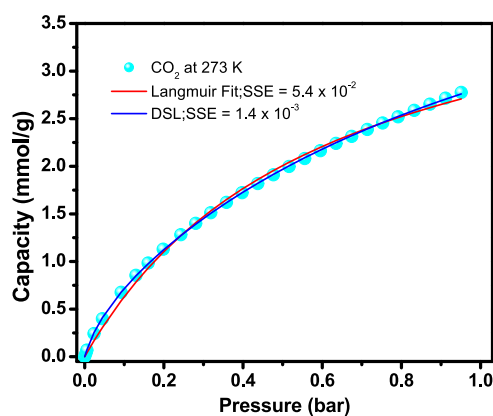


Figure 8. Langmuir and DSL model fit of the CO₂ isotherm at 273 K.

N₂) and quadrupole moment (4.30 DÅ for CO₂ vs 1.54 DÅ and 0.02 DÅ for N₂ and CH₄) of CO₂ among the three gases which favors stronger physisorption interactions of CO₂ than the other two adsorbents. Further, CO₂ is a weakly acidic gas and may interact with the basic OH groups of the TBPP-OH through weak acid–base interactions. Moreover, though N₂ has a higher quadrupole moment than CH₄, CH₄ has higher polarizability than N₂, which favors its adsorption over N₂. For any gas, the adsorption decreases with increasing temperature also pointing to weak physisorption interactions existing between the adsorbate and adsorbent.

Estimating the recyclability of an adsorbent is essential for its practical use. As illustrated in Figure 9, the CO₂ uptake isotherms at 273 K and 1 bar for a maximum of 10 cycles were measured to evaluate the recyclability test. TBPP-OH showed promise as an adsorbent for CO₂ capture by adsorbing 120 mg/g of CO₂ without exhibiting any discernible reduction, even after 10 cycles without any activation treatment showing its potential for efficient CO₂ adsorption applications.

4. CONCLUSIONS

In summary, we presented the facile and one-pot preparation and characterization of a novel hyper-cross-linked microporous polymer based on 3D triptycene (TBPP-OH) adorned with hydroxyl functional groups. The presence of 3D stiff triptycene units in polymer TBPP-OH provides desirable features such as microporosity, higher surface area, and thermal stability. All of these properties in TBPP-OH render it a promising porous

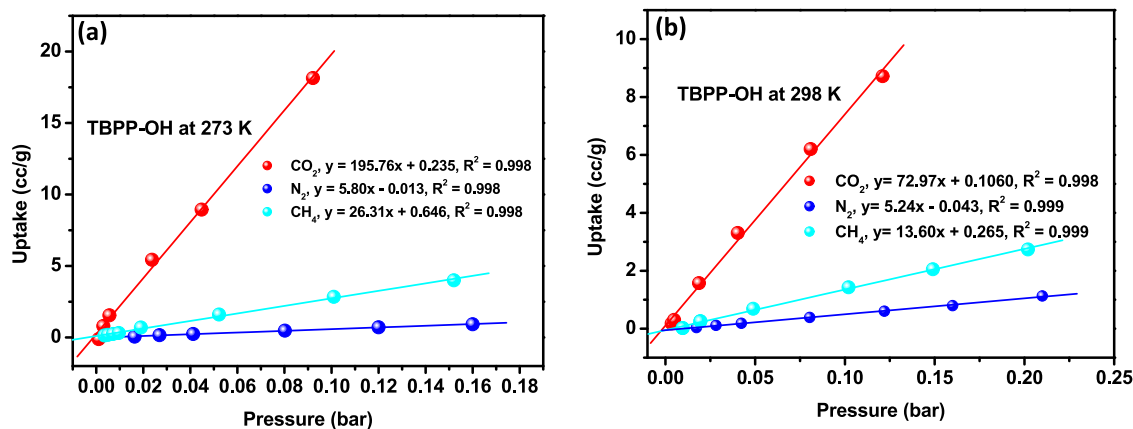


Figure 7. Initial gas uptake slopes of CO₂, N₂, and CH₄ for TBPP-OH at 273 K (a) and 298 K (b).

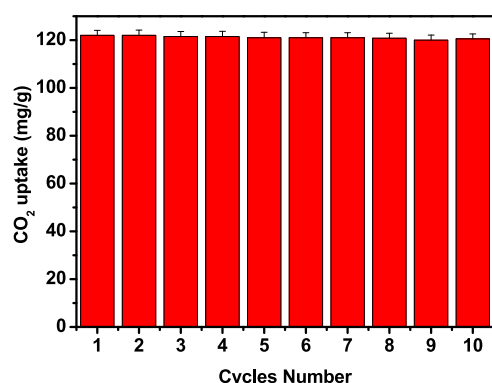


Figure 9. Recyclability performance of TBPP-OH as an adsorbent for capturing CO₂ at 273 K and 1 bar of pressure.

polymer for effective and selective CO₂ uptakes. TBPP-OH demonstrated a higher CO₂ uptake capacity of 122 mg g^{−1} at 273 K. The selectivity values for CO₂/N₂ were also observed to be reasonably high (up to 40). Considering the facile synthesis and ability to effectively and selectively adsorb CO₂ over CH₄ and N₂, TBPP-OH can be considered a potentially valuable material for environmental remediation applications. This work further motivates us and others to explore and synthesize OH-incorporated porous polymers connected with other stiff and aromatic motifs to improve the sorbent characteristics for practical applications given the desired structural features of TBPP-OH.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c08460>.

BET-linear plot of polymer TBPP-OH, solubility test of polymer TBPP-OH, and high-resolution O 1s photoemission spectrum of TBPP-OH (PDF)

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Notes

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