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ARTICLE TYPE

High Surface Area Hypercrosslinked Microporous Organic Polymer Networks Based on Tetraphenylethylene for CO₂ Capture

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A series of hypercrosslinked microporous organic polymer and copolymer networks has been synthesized via Friedel-Crafts alkylation of tetraphenylethylene (TPE) and / or 1,1,2,2-tetraphenylethane-1,2-diol (TPD) using a formaldehyde dimethyl acetal crosslinker promoted by anhydrous FeCl₃. Statistical copolymerization demonstrates that the ratios of the micropore surface area and the micropore volume for the resulting polymer networks could be controlled by adjusting the content of TPD segments. The polymer network with 100% TPE shows high Brunauer-Emmet-Teller specific surface area up to 1980 m² g⁻¹ with a CO₂ uptake ability of 3.63 mmol g⁻¹ (1.0 bar / 273 K), while the polymer network with 100% TPD shows the highest CO₂/N₂ selectivity of 119:1, although it exhibits the lowest CO₂ uptake ability of 1.92 mmol g⁻¹ (1.0 bar / 273 K) among the resulting polymer networks. Increased TPD content in the hypercrosslinked polymer networks led to improved CO₂/N₂ selectivity, suggesting an efficient strategy for the design of microporous organic polymers for post-combustion carbon capture. Due to the high surface area, the outstanding CO₂ sorption performances, and the inexpensive reagents and catalyst employed, these polymer networks are promising candidates for potential applications in post-combustion CO₂ capture and sequestration technology.

Introduction

Porous organic polymers (POPs), combined with high surface area, high chemical and thermal stability, have broad potential in applications such as molecular separation,¹ heterogeneous catalysis^{2,3} and gas storage.⁴ To date, a range of POPs have been developed using various chemical strategies and building blocks: these include polymers of intrinsic microporosity (PIMs),^{5,6} covalent organic frameworks (COFs),^{7,8} conjugated microporous polymers (CMPs),^{9,10} porous polymer networks (PPNs),¹¹ porous aromatic frameworks (PAFs),¹² covalent triazine-based frameworks (CTFs),¹³ porous benzimidazole-linked polymers (BILPs),¹⁴ and hypercrosslinked porous polymers (HCPs).^{15,16} POPs show some advantages such as large specific surface area, high chemical and thermal stability, low skeleton density and synthetic diversity. This could make POPs strong candidates for post-combustion carbon capture and storage (CCS), and have been the subject of intense recent interest.^{17,18} CCS is becoming increasingly important as the excessive CO₂ emissions to the atmosphere result in global warming and environmental issues. Due to the large scale of carbon dioxide emissions, CCS technologies require large quantities of adsorbent at a low cost. However, most POPs are often synthesized using noble metal catalyzed polymerization (e.g. Pd-catalyzed Sonogashira-Hagihara cross coupling,⁹ Ni(0)-catalyzed Yamamoto homocoupling,¹² Pd-catalyzed Suzuki coupling,¹⁹ and Co(0)-catalyzed trimerization of aromatic alkynes),²⁰ which makes the relative higher cost for preparing these sorbent materials to other POPs.²¹ Recently, high nitrogen content triazine-based covalent organic polymers have been synthesized via facile catalyst free C-N coupling polymerization, the low cost for preparing this class

of sorbent materials making them promising candidates for applications in CCS.²¹

HCPs, produced from bulk chemicals such as benzene and linked together via Friedel-Crafts alkylation promoted by anhydrous FeCl₃,²² represent a subclass of porous materials which are low cost and can be facily prepared. This avoids the use of noble metal coupling catalysts, and also avoids the need for monomers with specific polymerisable groups when an external linker such as formaldehyde dimethyl acetal is employed. As thus, HCPs can be considered as promising porous materials for carbon dioxide capture.²³ For example, benzene-based HCPs showed high surface area up to 1391 m² g⁻¹ with a CO₂ uptake capacity of 3.61 mmol g⁻¹ (1.0 bar/273K).²² Tetraphenylmethane-based HCP with higher surface area of 1470 m² g⁻¹ exhibited the CO₂ uptake capacity of 2.95 mmol g⁻¹ (1.0 bar / 273K).²⁴ Binaphthol-based HCPs showed an improved CO₂ uptake capacity as high as 3.96 mmol g⁻¹ (1.0 bar / 273K) because the incorporation of polar hydroxyl groups enhanced the interaction between the pore wall and the CO₂ molecules.²⁵ To satisfy the requirements of CCS technologies, the selectivity of the porous material for CO₂ over other permanent gases such as nitrogen will need to be improved as well, besides the low cost. Common strategy to improve the selectivity for CO₂ is to incorporate polar functional groups (such as hydroxyl²⁵ and amine²⁶) into the polymer network to enhance the interaction between the material and the CO₂ molecules. For example, polyamine-tethered PPNS showed exceptionally high CO₂/N₂ adsorption selectivity up to 442 for PPN-6-CH₂DETA under ambient conditions,²⁷ amine functionalized POPs synthesized by post-synthetic approach showed a high CO₂/N₂ adsorption selectivity of 155.²⁸

We describe here the production of high surface area

hypercrosslinked microporous organic polymer network from the rigid tetraphenylethylene building block with formaldehyde dimethyl acetal as a crosslinker promoted by anhydrous FeCl_3 . As statistical copolymerization has been used as a means of tuning the properties of POPs,^{29, 30} it is possible to use a statistical mixture of monomers in HCP systems to vary properties systematically. We hypothesized that the statistical copolymerization of tetraphenylethylene with its derivative of 1,1,2,2-tetraphenylethane-1,2-diol with polar hydroxyl groups would be an effective strategy for generating HCPs with improved CO_2 sorption performances.

Experimental section

Materials

Tetraphenylethylene (TPE) and 1,1,2,2-tetraphenylethane-1,2-diol (TPD) were purchased from Adamas. Formaldehyde dimethyl acetal (FDA), anhydrous FeCl_3 , 1,2-dichloroethane (DCE) and other chemicals were obtained from J & K Scientific Ltd. All chemicals were used as received.

Synthesis of hypercrosslinked tetraphenylethylene-containing microporous organic polymer networks

All of the tetraphenylethylene-containing microporous organic polymer networks were synthesized by Friedel-Crafts alkylation of tetraphenylethylene and/or 1,1,2,2-tetraphenylethane-1,2-diol using a formaldehyde dimethyl acetal external crosslinker promoted by anhydrous FeCl_3 . All polymerization reactions were carried out at a fixed total molar monomer concentration (50 mmol/L) and a fixed reaction temperature and reaction time (80 °C/24 h). Both the molar ratios of FeCl_3 and FDA to the total monomer were set at 4:1. A typical experimental procedure for **network-1** is given as an example: To the mixture of tetraphenylethylene (1.0 mmol, 0.332 g), FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, FeCl_3 (4.0 mmol, 0.649 g) was added at room temperature. The mixture was heated to 80 °C and stirred for 24 h under a nitrogen atmosphere. The mixture was then cooled down to room temperature and the precipitated polymer network was filtered and washed with methanol, distilled water, dichloromethane and acetone successively, until the filtrate was nearly colorless. The further purification of the network was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C to give dark brown powder (Yield: 99.5%). Elemental combustion analysis (%) Calcd for $(\text{C}_{28}\text{H}_{20})_n$ (based on the 1.0 mmol starting material of TPE completely reacted with 2.0 mmol FDA) C 94.34, H 5.66; Found: C 88.15, H 7.61.

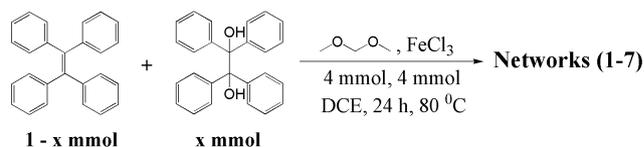
Characterization

The FT-IR spectra were collected in transmission on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. The thermal properties of the polymer networks were evaluated using a thermogravimetric analysis (TGA) – differential thermal analysis instrument (Q1000DSC+LNCS+FACS Q600SDT) over the temperature range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C/min. Elemental analysis was carried

out on a EURO EA3000 Elemental Analyzer. Surface areas and pore size distributions of the polymer networks were measured by nitrogen adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. The surface areas were calculated in the relative pressure range (P/P_0) from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory. Samples were degassed at 120 °C for 15 hours under vacuum (10^{-5} bar) before analysis. Hydrogen adsorption isotherms were measured on the ASAP 2420-4 at 77.3 K up to 1.0 bar. Carbon dioxide adsorption isotherms were also collected on the ASAP 2420-4 at 273 K, 283 K and 298 K, respectively.

Results and discussion

Scheme 1 shows the synthetic route for the series of polymer networks by statistical copolymerization of tetraphenylethylene and/or 1,1,2,2-tetraphenylethane-1,2-diol in a number of ratios (Table 1). All of the copolymerizations produced brown to black powders. Yields of the most polymer networks were quantitative, as observed for most other reported HCPs.^{22, 25} All of these polymer networks are insoluble in conventional organic solvents because of their highly crosslinked structures. The polymer networks show less thermal stability, as revealed by TGA (up to 250 °C, Fig. S1) in nitrogen atmosphere, compared with other types of POPs (e.g. CMPs showed high thermal stability up to 400 °C,⁹ and covalent organic polymer, COP-3 showed superior thermal stability up to 370 °C in nitrogen atmosphere owing to its robust aromatic nature of the framework),³¹ which could be attributed to the presence of cross-linker of methylene groups in the HCPs which reduced their thermal stability. The FT-IR spectra of the networks (Fig. S2) were consistent with the expected networks showing unsaturated C=C vibration bands at 1500 and 1600 cm^{-1} , and C–H stretching vibrations originating from $-\text{CH}_2-$ at 2920 cm^{-1} , and the O–H vibrations at around 3450 cm^{-1} for networks (2–6) which was not observed in the FT-IR spectrum for network-1 without TPD. Powder X-ray diffraction measurements indicated that the polymer networks are amorphous in nature (Fig. S3).



Scheme 1 Synthetic route for the polymer networks.

The porous properties of the copolymer networks were investigated by nitrogen adsorption analyses at 77.3 K. As shown in Fig. 1a, the polymer network-1 with 100% TPE showed broadly a Type II nitrogen gas sorption isotherm in nature with evidence of some Type IV character showing a steep rise in the nitrogen adsorption at high relative pressures ($P/P_0 > 0.8$), indicating that the material consists of micro- and mesopores. As a sharp contrast, network-7 homocoupled from TPD showed a typical Type I nitrogen gas sorption isotherm, indicating that it is a typical microporous material. All the other copolymer networks

(network 2–6) gave rise to Type I nitrogen gas sorption isotherm with a steep nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$). Significant hysteresis was observed in the desorption branch of the isotherm for all samples, particularly for network-1, which is consistent with elastic deformations or swelling as a result of gas sorption.³² Fig. 1b shows the pore size distribution (PSD) curves for the series of polymer networks as calculated

using nonlocal density functional theory (NL-DFT). All samples exhibited abundant micropore structures with micropore diameters centered at around 1.11 and 1.65 nm with a spot mesopores peaked at around 2.12 and 4.92 nm. Along with the increase molar ratio of TPD (from network-1 to 7), the intensity of the mesopore peaks decreases gradually, and these peaks almost could not be observed for network-7 with 100% TPD.

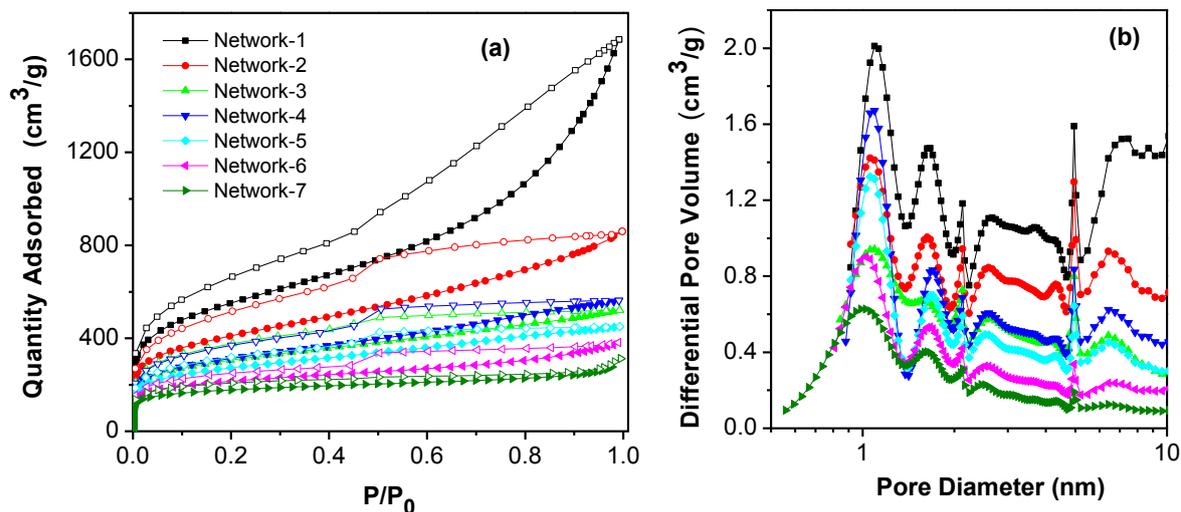


Fig. 1 a) Nitrogen adsorption/desorption isotherms (the adsorption branch is labeled with filled symbols and desorption branch is labeled with open symbols); b) Pore size distribution curves calculated by NL-DFT for the networks (the symbols are same as Fig. 1a).

In addition, the ratio of micropore surface area over the total BET surface area increases from network-1 to network-7 with increase the molar ratio of TPD, although the total BET surface areas for these polymer networks were found to decrease successively from 1980 $\text{m}^2 \text{g}^{-1}$ for network-1 to 618 $\text{m}^2 \text{g}^{-1}$ for network-7, as measured by nitrogen sorption (Table 1). These results demonstrate that the ratios of micropore surface area and the micropore volume for the resulting polymer networks could be controlled by adjusting the content of TPD segments, which is similar to CMPs, where both the surface area and the pore size

could be fine controlled by the strut length of the employed monomer linkers.²⁹ A reasonable explanation for this result could be: (i) the segment of TPD is much more flexible than TPE because the $-\text{C}-\text{C}-$ (ethane) in TPD shows more flexibility than the $-\text{C}=\text{C}-$ (ethene) in TPE, which leads to the decrease of surface area with the increase content of TPD; (ii) The hydroxyl groups in TPD will occupy some pores, resulting in again the decrease of surface area and making the pore size narrower with the increase content of TPD.

Table 1 Summary of pore properties for the networks

Network	TPE [mol %]	TPD [mol %]	S_{BET} [$\text{m}^2 \text{g}^{-1}$] ^a	S_{Micro} [$\text{m}^2 \text{g}^{-1}$] ^b	V_{Total} [$\text{cm}^3 \text{g}^{-1}$] ^c	V_{Micro} [$\text{cm}^3 \text{g}^{-1}$] ^d	$S_{\text{Micro}}/S_{\text{BET}}$ [%]	$V_{\text{Micro}}/V_{\text{Total}}$ [%]
Network-1	100	0	1980	988	2.61	0.72	49.9	27.6
Network-2	80	20	1463	940	1.33	0.54	64.2	40.6
Network-3	60	40	1159	810	0.86	0.42	69.9	48.8
Network-4	50	50	1014	750	0.79	0.43	73.9	54.4
Network-5	40	60	962	713	0.69	0.37	74.1	53.6
Network-6	20	80	754	564	0.59	0.27	74.8	45.7
Network-7	0	100	618	519	0.43	0.25	83.9	58.1

^a Surface area calculated from N_2 adsorption isotherm in the relative pressure (P/P_0) range from 0.05 to 0.20; ^b Micropore surface area calculated from the N_2 adsorption isotherm using t-plot method based on the Harkins-Jura Equation. ^c Total pore volume at $P/P_0 = 0.988$. ^d The micropore volume derived from the t-plot method.

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It is worth noting that the surface area of $1980 \text{ m}^2 \text{ g}^{-1}$ for the network-1 with 100% TPE is much higher than that of other HCPs produced from the external crosslinker of formaldehyde dimethyl acetal, such as the benzene-based HCPs ($S_{\text{BET}} = 1391 \text{ m}^2 \text{ g}^{-1}$),²² tetraphenylmethane-based HCPs ($S_{\text{BET}} = 1470 \text{ m}^2 \text{ g}^{-1}$),²⁴

binaphthol-based HCPs ($S_{\text{BET}} = 1015 \text{ m}^2 \text{ g}^{-1}$),²⁵ and heterocyclic-based HCPs (e.g. $726 \text{ m}^2 \text{ g}^{-1}$ for thiophene-based HCP),³³ but lower than the porous aromatic frameworks (e.g. PPN-4, $S_{\text{BET}} = 6461 \text{ m}^2 \text{ g}^{-1}$) produced from nickel-catalyzed Yamamoto cross-coupling reaction.¹¹

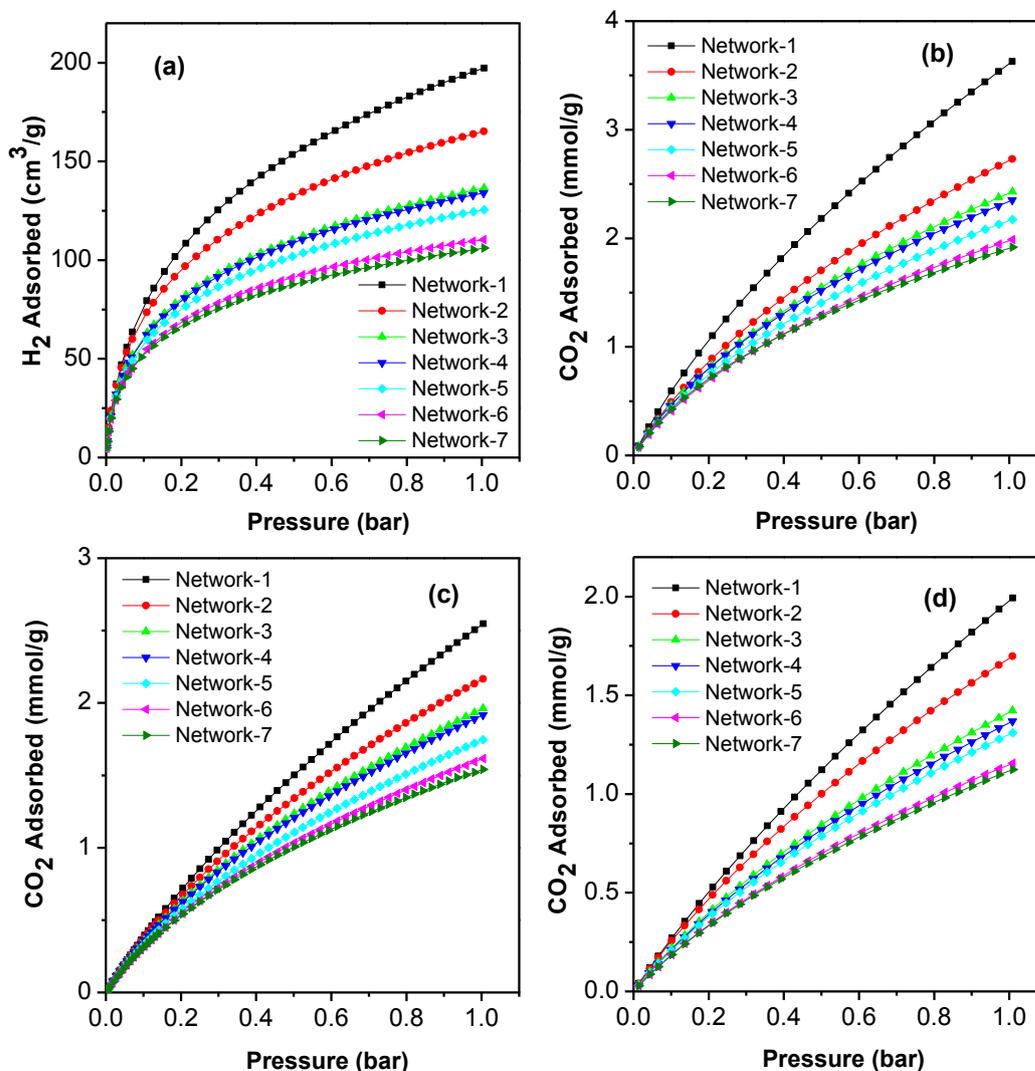


Fig. 2 a) Volumetric H_2 sorption curves collected at 77.3 K up to 1.0 bar for the Networks 1–7; b) CO_2 adsorption isotherms collected at 273 K; c) CO_2 adsorption isotherms collected at 283 K; d) CO_2 adsorption isotherms collected at 298 K.

The high specific surface area and the microporous nature of the polymer networks inspired us to investigate their gas uptake capacities. Fig. 2a shows the volumetric hydrogen sorption curves of the polymer networks at 77.3 K up to a pressure of 1.0 bar. Network-1 (with 100% TPE), possessing the highest apparent BET surface area, exhibited the largest H_2 uptake ($197 \text{ cm}^3 \text{ g}^{-1}$, $\sim 1.76 \text{ wt} \%$), while network-7 (with 100% TPD) showed the

lowest H_2 uptake ($106 \text{ cm}^3 \text{ g}^{-1}$, $\sim 0.95 \text{ wt} \%$). In general, there was a systematic change in H_2 uptake as a function of the surface area for these polymer networks (Fig. 2a), which was also observed in CMP copolymer networks.²⁹ The hydrogen uptake capacity of network-1 is comparable to or higher than that of some previously reported HCPs under the same conditions, such as the benzene-based HCPs ($1.58 \text{ wt} \%$),²² the heterocyclic-based

HCPs (1.11 wt %),³³ but lower than the carbazole-based CMP with the hydrogen uptake capacity of 2.80 wt % at 77 K / 1.13 bar.³⁴

The CO₂ uptakes of the polymer networks were also measured up to 1.0 bar at 273, 283 and 298 K, respectively (Fig. 2b–2d). The most porous polymer network–1 (100% TPE) showed a CO₂ uptake of 3.63 mmol g⁻¹ at 1.0 bar / 273 K. When TPD is copolymerized with TPE, the absolute CO₂ uptake capacity of the copolymers decreases from 3.63 mmol g⁻¹ for network–1 to 1.92 mmol g⁻¹ for network–7 with increasing TPD content. This could be explained by the decrease of pore volume and surface area for the series of networks as discussed above (Table 1). The CO₂ uptake of 3.63 mmol g⁻¹ for network–1 is comparable to benzene-based HCPs (3.61 mmol g⁻¹ at 1.0 bar / 273 K),²² binaphthol-based HCPs (3.96 mmol g⁻¹ at 1.0 bar / 273 K),²⁵ and much higher than that of the tetraphenylmethane-based HCPs (2.27 mmol g⁻¹ at 1.0 bar / 273 K),³⁵ the porous aromatic framework PAF-1 (2.65 mmol g⁻¹ at 1.0 bar / 273 K) with much higher surface area of 4077 m² g⁻¹,²⁴ and the covalent organic framework COF-102 (1.56 mmol g⁻¹ at 1.0 bar / 273 K) with a surface area of 3620 m² g⁻¹,³⁶ but still lower than that of the imine-linked porous polymer frameworks (e.g. 6.1 mmol g⁻¹ for PPF-1).³⁷ These results prove that, besides the specific surface area, the molecular structure and chemical nature of the monomer also play crucial roles in the CO₂ uptake capacity for MOPs. Therefore, selection of proper building blocks is an important basis for synthetic porous polymer designing.

Table 2 Summary of gas uptakes for the polymer networks

Network	H ₂ uptake ^a [wt.%]	CO ₂ uptake ^b [mmol g ⁻¹]	CO ₂ uptake ^c [mmol g ⁻¹]	CO ₂ /N ₂ ^d Selectivity
Network–1	1.76	3.63	1.99	33
Network–2	1.47	2.73	1.70	26
Network–3	1.22	2.42	1.42	28
Network–4	1.19	2.35	1.37	27
Network–5	1.12	2.17	1.31	50
Network–6	0.98	1.99	1.16	57
Network–7	0.95	1.92	1.12	119

^a Data collected by volumetric H₂ sorption method at 77.3 K and 1.0 bar;

^b Data collected at 273 K and 1.0 bar; ^c Data collected at 298 K and 1.0 bar;

^d Calculated from ideal adsorbed solution theory by using the CO₂ and N₂ adsorption isotherms collected at 273 K.

The difference in pore properties (micropore volume & micropore surface area) of the networks suggested that these materials may have good selectivity for CO₂/N₂. The carbon dioxide and nitrogen adsorption isotherms were therefore measured at 273 K for the copolymer networks (Fig. S5–S11). The selectivities of the networks were calculated using experimental single-component gas sorption isotherms and the simplified Ideal Adsorbed Solution Theory (IAST)³⁸ model at an equilibrium partial pressure of 0.85 bar (N₂) and 0.15 bar (CO₂) in the bulk phase.³⁹ This composition closely matches that of

relevance for CCS. The network–1 with 100% TPE showed a moderate CO₂/N₂ selectivity of 33:1, while a high selectivity of 119:1 was obtained for the network–7 with 100% TPD (Table 2), although this network shows the lowest surface area and the absolute CO₂ uptake capacity. The relatively high CO₂/N₂ selectivity of network–7 could be due to the favorable interactions between the polarizable CO₂ molecules and the accessible open polar hydroxyl groups through hydrogen bonding and/or dipole–quadrupole interactions since network–7 possesses the highest hydroxyl group density, which is not applicable to non-polar N₂ molecules.⁴⁰ This is also evidenced by the isosteric heat of CO₂ adsorption (Q_{st}), network–7 shows the highest Q_{st} of 28.2 kJ mol⁻¹, while the network–1 with 100% TPE shows the lowest Q_{st} of 23.3 kJ mol⁻¹ among the resulting networks (Fig. S4). However, as the low surface area and pore volume, network–7 just captured a few of CO₂ molecules (1.92 mmol g⁻¹). All of the values of the Q_{st} (24.2–26.2 kJ mol⁻¹) at zero coverage for the copolymer networks (2–6) lie in between those of homocoupled polymer network–1 and network–7, although they don't show a simple increase order with increase the ratio of TPD as expected (Fig. S4), which is similar to the CMP copolymer networks, where the isosteric heat of sorption for H₂ of the CMP copolymer networks was found not to fall into a simple rational order.²⁹ This suggests that variability at the molecular level may be dominating in the copolymer networks.²⁹ The CO₂/N₂ selectivity of 119 for network–7 lies towards the upper end when compared to other HCPs, such as the pyrrole-based HCPs (117)³³ and aniline-based HCPs (49),²⁶ but is still lower than that of some other type POPs with the selectivity higher than 100 (Table 3). Ideally, high uptake and selectivity are both required for practical applications. As such, the high CO₂ uptake capacity and the high adsorption selectivity for CO₂ over N₂ by these polymer networks make them promising candidates for applications in post-combustion CO₂ capture and sequestration technology.

Table 3 Comparison of CO₂/N₂ selectivity of network-7 and some of other promising POPs for CO₂ capture

POPs	CO ₂ uptake [mmol g ⁻¹]	CO ₂ /N ₂ Selectivity	Reference
Network–7	1.92 ^a	119 ^a	This work
Pyrrole-HCP	2.71 ^a	117 ^a	33
Azo-COP-2	2.55 ^a	110 ^a	41
Azo-COP-2	0.71 ^b	288 ^b	42
FCTF-1-600	5.53 ^a	152 ^c	43
POP-2	0.95 ^d	155 ^d	28
PPN-6-CH2DETA	4.30 ^e	442 ^e	27

^a Data collected at 273 K and 1.0 bar; ^b Data collected at 323 K and 1.0 bar;

^c Data obtained by breakthrough experiment of gas mixture absorption at 298 K and 1.0 bar. ^d Data collected at 298 K and 1.0 bar; ^e Data collected at 295 K and 1.0 bar.

Conclusion

In summary, a series of hypercrosslinked microporous organic

copolymer networks was synthesized via Friedel-Crafts alkylation of tetraphenylethylene and/or 1,1,2,2-tetraphenylethane-1,2-diol using a formaldehyde dimethyl acetal crosslinker promoted by anhydrous FeCl₃. These copolymer networks are stable in various solvents. The copolymer networks from statistical co-polymerization demonstrated that the ratios of micropore surface area and the micropore volume for the resulting polymer networks could be controlled by adjusting the content of TPD segments. The homocoupled network-1 with 100% TPE shows high BET specific surface area up to 1980 m² g⁻¹ with a high CO₂ uptake ability of 3.63 mmol g⁻¹ (1.0 bar / 273 K), while the homocoupled network-7 with 100% TPD shows the highest CO₂/N₂ adsorption selectivity of 119 among the networks. Given the high surface area, the outstanding CO₂ sorption performances, and the inexpensive reagents and catalyst employed, these polymer networks are promising candidates for potential applications in post-combustion CO₂ capture and sequestration technology.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Synthesis of the polymer networks in detail, FT-IR, TGA, PXRD, isosteric heat of CO₂ adsorption and the gas adsorption. See DOI: 10.1039/b000000x/

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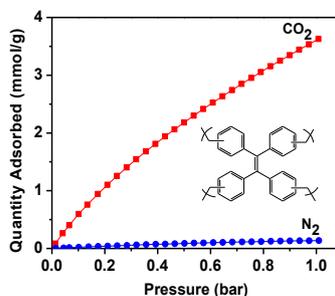
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A series of hypercrosslinked microporous organic copolymer networks was synthesized via Friedel-Crafts alkylation of tetraphenylethylene (TPE) and/or 1,1,2,2-tetraphenylethane-1,2-diol (TPD) promoted by anhydrous FeCl₃.



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