Fine tailoring the steric configuration of initial building blocks to construct ultramicroporous polycarbazole networks with high CO₂ uptake and selectivity of CO₂ over N₂

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ARTICLE INFO

Article history:

Received 11 December 2014

Received in revised form

19 May 2015

Accepted 10 June 2015

Available online 14 June 2015

Keywords:

Conjugated microporous polymers

Polycarbazole

Steric configuration

ABSTRACT

Three carbazole based building blocks with similar propeller-like steric configuration are designed and synthesized. The polycarbazole networks P-4, 4'-biscarbazolyl-phenyl (P-BCz), P-tetracarbazolyl-p-difluorobenzene (P-TCz) and P-hexacarbazolyl-phenyl (P-HCz) are obtained with high surface areas and uniform ultramicropores. The aggregation morphologies of networks vary from regular spherical particles, ribbon-like structure to large lamellar structure as the number of carbazole increased around the benzene ring. The networks P-TCz, with four carbazole decorating on the benzene ring, have the largest surface area and highest gas uptake ability among the three networks. However, the CO₂ and CH₄ isosteric enthalpies increased linearly with increasing the number of carbazole. The networks P-HCz with six carbazole show the excellent CO₂/N₂ separative capacity (107 at 273 K, and 127 at 298 K), which is among the highest reported about CO₂ separation using organic pore networks. Fine designing and tailoring the topological structure of monomer can control the adsorption properties and optimize the gas uptake performance.

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1. Introduction

The sharply rising level of atmospheric CO₂ resulting from anthropogenic emissions is one of the greatest environmental concerns facing our civilization today [1]. The concentration of CO₂ in the atmosphere is as high as 392 ppm compared to its preindustrial level of ca. 280 ppm. To stabilize atmospheric CO₂ levels and prevent climatic situation worsening, it is imperative to develop viable CO₂ capture and sequestration (CCS) technologies. The way of CO₂ capture in physical process and utilizing clean energy source [2] such as hydrogen [3] are of interest to meet the energy and environmental demands. Physical adsorption of CO₂ relying on microporous organic polymers (MOPs) is potential candidate for CO₂ capture due to the large specific surface area, narrow pore size distribution and high chemical and thermal

stability of MOPs, which will provide a less energy penalty and cost associated with state-of-the-art gas uptake application.

Conjugated microporous polymers (CMPs) as a sub-family of MOPs can be prepared by versatile synthetic methods with an amorphous three-dimensional framework [4]. The unique feature of CMPs is that they combine the stiff pore skeleton and extended conjugated π -electron system in one bulk material which has been proved to be invaluable tools in the fields of gas storage [5], catalysis [6], and advanced applications in organic electronics and luminescent sensors [7]. In the past few years, significant research efforts have been focused on the development of novel CMPs for gas storage. The new CMPs such as polyfluorene microporous polymers had Brunauer–Emmett–Teller (BET) areas from 450 to 1043 m² g^{−1} and the highest CO₂ uptake reached to 12 wt% at 1.0 bar, 273 K [8]. Nishikyo-ku reported the tetrasubstituted [2.2] Paracyclophane CMPs with BET areas from 840 to 956 m² g^{−1} [9]. Ying Mu reported the MCTFs with the BET from 640 to 1510 m² g^{−1} showing excellent CO₂ uptake capacity up to 13.9 wt % at 273 K and 1 bar. Recently Jiang reported the bifunctionalized conjugated microporous polymers for high CO₂ capture [10] and

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Cooper reported through post-synthetic modification to promote the conjugated microporous polymers for CO₂ storage [11].

In addition to CO₂ storage, selectivity capacity is another crucial parameter for CO₂ capture materials. As we know, the flue gas contains about 70% N₂ (post-combustion CO₂ capture), usually the high CO₂ over N₂ selectivity can help to concentrate the CO₂ together. As to the natural gas, the existence of CO₂ in it can reduce the energy density, so the effective selectivity of CO₂ over CH₄ is essential in practical application. Efficient CO₂ adsorption/separation depends on the high surface area, narrow pore structure, and different chemical functionality of the material. The building blocks of CMPs show great influence on the above three parameters, thus, to design or select the specific configuration of initial building block is the key issue for gathering CO₂. Based on the above consideration, we have designed and synthesized three novel ultra-micropores polycarbazole CMPs for gas storage and separation [12]. The carbazole based three initial building blocks 4, 4'-biscarbazolyl-phenyl (BCz), tetracarbazolyl-p-difluorobenzene (TCz) and hexacarbazolyl-phenyl (HCz) have the similar propeller-like 3-dimensional (3D) steric configuration, and the polycarbazole networks have been straightforward synthesized by FeCl₃ oxidative coupling polymerization. The gas adsorption results show that the performance of the polycarbazole networks have close relationship with the molecular structures.

2. Experimental section

2.1. Materials and synthesis

1,4-Dibromobenzene, 2,2'-bipyridine, 1,10-phenanthroline, sodium hydride (NaH), hexafluorobenzene were obtained from Aldrich. K₂CO₃ and CuI were purchased from J&K. All the solvents were obtained from Acros Chemical Co., unless otherwise specified they were used as received. Anhydrous chloroform was distilled over sodium/benzophenone and calcium hydride under N₂ prior to use. BCz, TCz and HCz were synthesized according to the literature methods [13]. The details of synthesis were shown below.

2.1.1. 4,4'-biscarbazolyl-phenyl (BCz)

A mixture of 1, 4-dibromobenzene (2.82 g, 12 mmol), carbazole (5.00 g, 30 mmol), K₂CO₃ (9.95 g, 72 mmol), CuI (5.71 g, 30 mmol), 2, 2'-bipyridine (0.005 g), 1, 10-phenanthroline (0.005 g) were dissolved in 1, 2-dichlorobenzene (10 mL) under argon protection and shielded from light with tin foil, the mixture then was stirred at 180 °C for 24 h. After the solution cooled to room temperature, the mixture was diluted by CH₂Cl₂ and filtered to remove CuI. The filtrate was removed by rotary evaporation, and the residue was purified by column chromatography (petroleum ether/dichloromethane, 3:1) to give white solid BCz (2.48 g, 51%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.20–8.18 (d, 4H), 7.82 (s, 4H), 7.58–7.56 (d, 4H), 7.49–7.47 (t, 4H), 7.35–7.33 (t, 4H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 140.76, 135.68, 128.38, 126.13, 123.57, 120.46, 120.28, 109.75.

2.1.2. Tetracarbazolyl-p-difluorobenzene (TCz)

Carbazole (1 g, 6 mmol) in 10 mL of dry dimethyl formamide (DMF) was added 60% NaH (7 mmol) under argon at room temperature and shielded from light with tin foil, the mixture then was stirred for 30 min and hexafluorobenzene (0.27 mg, 1.5 mmol) dissolved in 10 mL DMF was slowly added. The mixture was stirred at 60 °C for 2 h and then cooled to room temperature. The reaction was quenched by water and then the mixture extracted with CH₂Cl₂. The organic extract was washed with water and dried over MgSO₄. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (petroleum

ether/dichloromethane, 3:1) to give white solid (0.9 g, 75%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.80–7.77 (d, 8H), 7.26–7.24 (d, 8H), 7.13–7.09 (t, 16H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 138.96, 125.67, 124.78, 124.68, 124.01, 120.88, 120.09, 109.91. MS, *m/z*: calcd. for C₅₄H₃₂F₂N₄ 774.86; found [M+H]⁺ 775.2.

2.1.3. Hexacarbazolyl-phenyl (HCz)

Carbazole (1 g, 6 mmol) in 10 mL of dry DMF was added 60% NaH (48 mmol) under argon at room temperature and shielded from light with tin foil, the mixture then was stirred for 30 min and hexafluorobenzene (0.18 g, 1 mmol) dissolved in 10 mL DMF was slowly added. The mixture was stirred at 80 °C for 12 h and then cooled to room temperature. The reaction was quenched by water and the precipitate was collected to give white solid HCz (0.6 g, 56%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.34–7.33 (d, 12H), 7.23–7.21 (d, 12H), 6.77–6.75 (t, 12H), 6.68–6.61 (t, 12H). MS, *m/z*: calcd. for C₇₈H₄₈N₆ 1068.26; found [M+H]⁺ 1069.40.

2.1.4. Network of P-4,4'-bis(carbazol-9-yl)-phenyl (P-BCz)

The solution of monomer BCz (200 mg, 0.49 mmol) dissolved in 30 mL of anhydrous chloroform was dropwise transferred to a suspension of ferric chloride (476 mg, 2.94 mmol) in 20 mL of anhydrous chloroform. The solution mixture was stirred for 24 h at room temperature under nitrogen protection, and then 100 mL of methanol was added to the above reaction mixture. The resulting precipitate was collected by filtration and washed with methanol, H₂O₂ and concentrated hydrochloric acid solution. After extracted in a Soxhlet extractor with methanol for 24 h, and then with tetrahydrofuran (THF) for another 24 h extraction, the desired polymer was collected (brownish powder, 90% in yield) and dried in vacuum oven at 80 °C overnight. Calcd. C₃₀H₂₀N₂: C, 88.21%; N, 6.86%; H, 4.93%; Found: C, 86.06%; N, 6.58%; H, 4.27%.

2.1.5. Network of P-tetracarbazolyl-p-difluorobenzene (P-BCz)

The same procedure with P-BCz network gave brownish powder, yielding 99%. Calcd. C₅₄H₃₂F₂N₄: C, 83.70%; N, 7.23%; H, 4.16%; Found: C, 70.85%; N, 4.11%; H, 3.46%.

2.1.6. Network of P-hexacarbazolyl-phenyl (P-HCz)

The same procedure with P-BCz network gave brownish powder, yielding 94%. Calcd. C₇₈H₄₈N₆: C, 87.62%; N, 7.86%; H, 4.52%; Found: C, 84.45%; N, 5.90%; H, 4.24%.

2.1.7. Instrumentations

¹H and ¹³C NMR spectra were recorded on a Bruker AV 600M spectrometer with tetramethylsilane (TMS) as the internal reference. FT-IR spectra were collected in attenuated total reflection (ATR) mode on a Thermo Nicolet 6700 FT-IR spectrometer. Scanning electron microscopy (SEM) was recorded using a Hitachi S-4800 with acceleration voltage 3 kV, and samples were coated with a thin layer of Au before investigation. Thermogravimetric analysis (TGA) was carried out using a SDT Q600 V20.9 Build with a temperature ramp of 10 °C min⁻¹ from 20 °C to 800 °C. X-ray diffraction (XRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 2θ = 5° up to 60° with 2° step increment. For gas adsorption test, the two networks were degassed at 120 °C for 800 min under vacuum before analysis. BET surface areas and pore size distributions of P-BCz, P-TCz and P-HCz were measured by nitrogen adsorption-desorption at 77 K. H₂ isotherms were measured at 77 K, up to 1.1 bar. CO₂ and N₂ isotherms were measured at 273 K and 298 K up to 1.1 bar. All the gas adsorption isotherms were tested on a Quantachrome Instruments Autosorb-iQ-MP-VP volumetric adsorption analyzer with the same degassing procedure.

3. Results and discussion

Three conjugated ultramicropores polycarbazole networks P-BCz, P-TCz and P-HCz were straightforward synthesized by FeCl_3 oxidative coupling polymerization shown in Scheme 1. Two carbazole linked monomer BCz was prepared by copper catalytic Ullmann reaction with the core of benzene ring to form the double impeller like geometrical configuration. Four and six carbazole linked monomer TCz and HCz were prepared by base catalysis (NaH) to obtain four and six impeller like initial units. The rigid fused ring of carbazole is beneficial for formation of polymers with permanent porosity stability, and the *N*-containing structure can increase CO_2 -framework interactions by means of the dipole–quadrupole interactions. The CO_2 -philic functional groups, also is in favour of CO_2 selectivity. In addition, the well-known highly reactive oxidation coupling in the 3, 6-site of carbazole promoted the polymerization process smoothly under mild conditions and gave high yield.

More detailed analysis of the structures of the polymers were confirmed by FT-IR spectra (Fig. 1). One can observe with the number of carbazole increasing the absorption peaks turned broad, indicating the higher degree of crosslinking was obtained as the polymerization branches increasing from four to eight and even twelve. The signals at 744, 1224, 1469 and 1608 cm^{-1} are assigned to characteristic bands of carbazole. The structures of polycarbazole were examined by solid state magic angle spinning ^{13}C CP/MAS NMR spectra and the corresponding assignments of the resonances are shown in Fig. S1. The *N*-substituted phenyl carbon has been confirmed by the characteristic resonance with a corresponding peak at around 145 ppm, and the overlapping signals from 121 to 137 ppm belong to the other aromatic sp^2 carbons in backbone. To investigate the thermal stabilities of the polycarbazole networks, thermogravimetric analysis (TGA) measurements under nitrogen

atmospheres were conducted in the range from $25\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ (Fig. S2). The networks exhibit excellent heat resistance with decomposition temperatures ($T_{\text{d}50}$) up to ca. $583\text{ }^\circ\text{C}$ for P-TCz and $560\text{ }^\circ\text{C}$ for P-HCz at 50 wt% weight loss, indicative of good thermal stability. The small weight loss observed at the initial stage is due to the residual solvents inside the micropore. Scanning electron microscopy images (Fig. 2) show that P-BCz, P-TCz and P-HCz have the different aggregation morphologies. It is interesting that P-BCz is regular spherical particles, P-TCz is ribbon-like networks and P-HCz is large lamellar structure, which means that the steric configurations of monomers have significant effect on the morphologies of the target networks. To further investigate the morphologies, the powder X ray diffraction (P-XRD) was used and the results show that the three polycarbazole networks are amorphous aggregation and there is no any crystalline phase (Fig. S3).

3.1. N_2 gas sorption analysis

The porosity properties of three polycarbazole were measured by adsorption analysis using nitrogen as the probe molecule at 77 K shown in Fig. 3a. The isotherms demonstrate steep rise in nitrogen uptake at the relative pressure (P/P_0) less than 0.01, indicating significant microporosity in the obtained networks. According to the IUPAC classification, the three polycarbazole networks exhibited a combination of type I and II nitrogen sorption isotherms [14]. When the Brunauer–Emmett–Teller (BET) model is adopted to calculate the apparent surface area, the values of P-BCz, P-TCz and P-HCz networks are 640 , 1109 and $790\text{ m}^2\text{ g}^{-1}$, respectively. It is interesting that under the same polymerization process, as the number of carbazole decorating on the benzene ring increased, the BET surface area of the polycarbazole increased firstly and then decreased. This is probably because the existence of carbazole molecules not only changed the geometrical configuration of the

Scheme 1. Synthetic routes towards the networks of P-BCz, P-TCz and P-HCz.

Fig. 1. FT-IR spectra for P-BCz, P-TCz and P-HCz networks were collected in attenuated total reflection (ATR) mode.

Fig. 2. Field-emission scanning electron microscopy images (x 50.0 K).

monomer, but also the solubility during the polymerization process. As a result, less extended networks were obtained. The BET surface area of P-TCz networks is comparable to other reported conjugated polymers, such as CMP series is $512\text{--}1018\text{ m}^2\text{g}^{-1}$ [15], HCMP series is $827\text{--}842\text{ m}^2\text{g}^{-1}$ [16], pyrene is $505\text{ m}^2\text{g}^{-1}$ [17], porphyrin is $1270\text{ m}^2\text{g}^{-1}$ [18], spiro-fluorene is $450\text{--}1000\text{ m}^2\text{g}^{-1}$ [19]. The porosity structural parameters of the three polycarbazole networks are shown in Table 1. To get an accurate comparison of the number of carbazole influencing on the pore size distribution (PSD), the quenched solid density functional theory (QSDFT) was employed and the result are shown in Fig. 3b. The obtained polycarbazole networks exhibited narrow pore distribution and the domain pore width centered at 0.52 nm and 0.54 nm which located in the ultramicropore range. P-HCz shows the apparent mesoporous characteristic at 4.1 nm . It is consistent with the analysis of N_2 adsorption isotherms at relative high pressure range ($P/P_0 > 0.8$, Fig. 3a). The pore size distribution gives a strong evidence that the domain pore of the networks is highly depending on the degree of crosslinking inside the bulk. The N_2 adsorption results

demonstrated there are trade-off among the monomer steric configuration, solubility and the BET surface areas. Under the same polymerization process, slightly structural change of the building block will have significant effect on the BET surface areas, but little effect on the pore size distribution. It shows that fine tailoring the twist angle between the carbazole and benzene ring core could regulate the target networks with different porosity parameters.

3.2. Hydrogen storage

Hydrogen, owing to their zero emission and high calorific value of combustion, is a good candidate as the new pollution-free fuel which has gained great interests nowadays. The bottleneck problems of its application are the storage and transportation resulting from its nature of lightweight and fast diffusion speed. Polycarbazole P-BCz, P-TCz and P-HCz with high BET surface area, ultramicropores and electron-rich system are good candidates for gas sorption and storage. The U. S. Department of Energy has set storage targets of $4.5\text{ wt\%}$ per 28 g L^{-1} (2010) and $5.5\text{ wt\%}$ per

Fig. 3. (a) N_2 adsorption–desorption isotherms of the P-BCz, P-TCz and P-HCz networks were measured at 77 K . (b) Pore size distributions were calculated by application of quenched solid density functional theory (QSDFT).

Table 1
Porosity structural parameters of networks P-BCz, P-TCz and P-HCz networks.

Networks [units]	S_{BET} [m ² g ^{−1}] ^a	S_{lang} [m ² g ^{−1}]	V_{mic} [cm ³ g ^{−1}] ^b	V_{Tot} [cm ³ g ^{−1}] ^c	Domain pore size [nm]	CO ₂ /CH ₄		CO ₂ /N ₂	
						273 K	298 K	273 K	298 K
P-BCz	640	740	0.25	0.85	0.52, 1.00	2.5	2.6	18.2	9.4
P-TCz	1109	1275	0.43	1.31	0.54, 1.00	6.6	5.0	35.8	36.5
P-HCz	790	938	0.30	1.20	0.54, 1.10	5.6	7.7	106.5	127

^a BET surface area calculated based on nitrogen adsorption–branch isotherm using the relative pressure range $P/P_0 = 0.05–0.15$.

^b Microporous volume was calculated at $P/P_0 = 0.10$.

^c Total pore volume was calculated at $P/P_0 = 0.99$.

40 g L^{−1} (2015) for hydrogen fuel cell vehicles [20]. The H₂ sorption isotherm of P-BCz, P-TCz and P-HCz networks was measured at 77 K up to 1.1 bar (Fig. 4), which showed 1.14 wt%, 1.65 wt% and 1.25 wt%, respectively. The H₂ uptake ability was linearly related to the BET surface areas and total porous volume (Table 1). The H₂ adsorption isotherms showed that no saturation will be achieved in this condition, which means more storage capacity can be expected at high pressure condition. In the low pressure range, polycarbazole skeleton exhibits favorable interaction with the H₂ molecules, suggesting the importance of ultramicropore structure and electron-rich system for gas adsorption which is the unique nature of conjugated polymers compared with other porous organic polymers. The H₂ uptake of P-TCz network is among the highest reported CMPs, such as PAF-1 (1.5 wt%) [21], CMP-2 (0.91 wt%) [15], polyanilines (0.85 wt%) [22], and PPN-3 (1.58 wt%) [23].

3.3. Carbon dioxide and methane

To compare the effect of the initial building blocks of P-BCz, P-TCz and P-HCz on gas adsorption, CO₂ adsorption isotherms were collected at 273 K and 298 K up to 1.1 bar and the results are shown in Fig. 5a. The emission of CO₂ due to the combustion of fossil fuels is one of the major sources for the accumulation of CO₂ in the atmosphere. In most industries, aqueous amine-ammonia solution is used to separate large scale CO₂ relying on the chemical adsorption. The downside of this process is that it has severe corrosion problem and high energy consumption. While the CO₂ capture and storage relying on physical adsorption in MOPs is a promising method to deal with the problem of excessive CO₂ emission, because of the physicochemical stability and lower regeneration energy penalty of the MOPs [24]. The CO₂ sorption

isotherms show no hysteresis and the process are reversible in all case. At 273 K and 1.1 bar, the CO₂ uptake capacity of P-BCz, P-TCz and P-HCz can be up to 9.27, 16.02 and 9.41 wt%. As to 298 K and 1.1 bar, the CO₂ uptake capacity are 5.14, 8.68 and 4.40 wt%, respectively. The isosteric enthalpies (Q_{st}) of P-BCz, P-TCz and P-HCz networks are calculated to be 38.10, 44.12 and 37.90 kJ mol^{−1} at zero loading based on Clausius–Clapeyron equation (Fig. 5b). The Q_{st} of the three networks are higher than most of the CMPs reported, such as PPN-6-SO₃H (30.4 kJ mol^{−1}) [25], BILP-10 (38.2 kJ mol^{−1}) [26], PECONF-4 (34 kJ mol^{−1}) [27], and acid-functionalized CMP-1-COOH (32.6 kJ mol^{−1}) [28]. The high Q_{st} may be ascribed to the ultramicropores and nitrogen-containing surface of polycarbazole networks. The dipole–quadrupole interaction between CO₂ and the wall of ultramicropores, and the Lewis acid–base interaction between CO₂ and polycarbazole are the main forces for the high Q_{st} [29–31]. It is interesting when the loading more than 0.25 mmol g^{−1}, all the Q_{st} almost remains stable and keeps the order $Q_{\text{st}}\text{-P-HCz} > Q_{\text{st}}\text{-P-TCz} > Q_{\text{st}}\text{-P-BCz}$ with regard to the number of carbazole decorating on the benzene ring.

Natural gas has the potential to replace petroleum as the world's primary fuel for transportation. Methane is the main composition of nature gas which is available in large quantities and environmentally preferable than other hydrocarbons. Physical adsorption of methane onto a support at low pressure in principle can provide a safe and economical approach for energy densities storage comparable to compressed gas. The volumetric storage target for methane set by the U.S. Department of Energy is 180 v/v at 35 bar and 298 K. The methane isotherms of the networks are shown in Fig. 6a. The CH₄ uptake values of P-BCz, P-TCz and P-HCz networks are 1.46, 2.00 and 1.34 wt% at 273 K, 1.1 bar, at 298 K and 1.1 bar are 0.81, 0.83 and 0.26 wt%, respectively. As the loading increasing, the variation trend of Q_{st} was $Q_{\text{st}}\text{-P-HCz} > Q_{\text{st}}\text{-P-TCz} > Q_{\text{st}}\text{-P-BCz}$ and almost consistent with that of CO₂ (Fig. 6b).

3.4. Selectivity of CO₂/CH₄ and CO₂/N₂

In order to deeply understand the relationship of structure and performance, the gas selectivity of the three polycarbazole networks was further investigated. Apart from the adsorption capacity, the ability of selective adsorption of CO₂ from other gases like CH₄ (natural gas) and N₂ (flue gas) is vitally important. The CO₂/CH₄ and CO₂/N₂ selectivity was estimated using the ratios of the Henry law constants calculated from the initial slopes of the pure component isotherms at low pressure range shown in Fig. 7 and the data are summarized in Table 1. One can observe that as the number of carbazole decorating on the benzene ring increasing, both selectivity of CO₂/CH₄ and CO₂/N₂ increased ($S\text{-P-HCz} > S\text{-P-TCz} > S\text{-P-BCz}$). P-HCz shows the highest separate ability than P-BCz and P-TCz in this system. At 273 K and 298 K, the selectivity of CO₂/N₂ can be up to more than 100, which is

Fig. 4. H₂ adsorption isotherms of P-BCz, P-TCz and P-HCz networks at 77 K.

Fig. 5. (a) CO₂ adsorption isotherms of P-BCz, P-TCz and P-HCz networks at 273 K and 298 K. (b) The variation of CO₂ isosteric enthalpies with the CO₂ adsorbed amount.

Fig. 6. (a) CH₄ adsorption isotherms of P-BCz, P-TCz and P-HCz networks at 273 K and 298 K. (b) CH₄ isosteric enthalpies variation with the adsorbed amount.

comparable to the highest reported pore materials, such as APOP-1-F (43.4 at 273 K) [32], BILP-2 (71 at 298 K) [27] and O-TTPP (50.7, 273K) [12a].

4. Conclusions

Three rigid carbazole based conjugated microporous networks P-BCz, P-TCz and P-HCz were designed and prepared by oxidative polymerization. Although the three initial building blocks have the similar propeller-like steric configuration, the obtained networks exhibit significant difference in aggregation morphologies. P-BCz is regular spherical particles, P-TCz is ribbon-like networks and P-HCz is large lamellar structure. The obtained three networks

show uniform pore distribution and remarkable ultramicropores centered around 0.54 nm. H₂, CO₂ and CH₄ isotherms showed the P-TCz with four carbazole has higher gas uptake ability than P-BCz and P-HCz. As the gas molecules loading increased, the isosteric enthalpies of the three networks are in line with the number of carbazole units decorating on the core of benzene ring in the building blocks. The selectivity of CO₂/N₂ for the three networks was increased with the number of carbazole increasing, and the P-HCz shows the selectivity more than 100, which is among the highest reported CMPs. The recognition of such an important structure–function relationship can certainly guide future work aimed at obtaining organic microporous networks with perfect gas uptake capability.

Fig. 7. Initial gas uptake slopes of the P-BCz, P-TCz and P-HCz networks for CO₂/CH₄ and CO₂/N₂ at (a) 273 K and (b) 298 K.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21274161, 51173199 and 51303197), the Ministry of Science and Technology of China (2014CB643501, 2010DFA52310).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2015.06.011>.

References

- [1] (a) Y.S. Bae, R.Q. Snurr, *Angew. Chem. Int. Ed.* 50 (2011) 1586; (b) R. Dawson, A.I. Cooper, D.J. Adams, *Polym. Int.* 62 (2013) 345.
- [2] Z. Xiang, D. Cao, *J. Mater. Chem. A* 1 (2013) 2691.
- [3] F. Vilela, K. Zhang, M. Antonietti, *Energy Environ. Sci.* 5 (2012) 7819.
- [4] (a) A.I. Cooper, *Adv. Mater.* 21 (2009) 1291; R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams, A. I. Cooper, *Macromolecules*, 2010, 43, 8524; (b) J.X. Jiang, F. Su, A. Trewin, C.D. Wood, N.L. Campbell, H. Niu, C. Dickinson, A.Y. Ganin, M.J. Rosseinsky, Y.Z. Khimyak, A.I. Cooper, *Angew. Chem. Int. Ed.* 46 (2007) 8574.
- [5] Q. Chen, M. Luo, P. Hammershoj, D. Zhou, Y. Han, B.W. Laursen, C.G. Yan, B.H. Han, *J. Am. Chem. Soc.* 134 (2012) 6084.
- [6] (a) J.X. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y.Z. Khimyak, J. Xiao, S.J. Higgins, D.J. Adams, A.I. Cooper, *Angew. Chem. Int. Ed.* 50 (2011) 1072; (b) Y. Xie, T.T. Wang, X.H. Liu, K. Zou, W.Q. Deng, *Nat. Commun.* 4 (2013) 1960.
- [7] (a) C. Gu, Y. Chen, Z. Zhang, S. Xue, S. Sun, K. Zhang, C. Zhong, H. Zhang, Y. Pan, Y. Lv, Y. Yang, F. Li, S. Zhang, F. Huang, Y. Ma, *Adv. Mater.* 25 (2013) 3443; (b) Y. Xu, L. Chen, Z. Guo, A. Nagai, D. Jiang, *J. Am. Chem. Soc.* 133 (2011) 17622.
- [8] (a) J. Weber, M. Antonietti, A. Thomas, *Macromolecules* 41 (2008) 2880; (b) Q. Chen, J.X. Wang, Q. Wang, N. Bian, Z.H. Li, C.G. Yan, B.H. Han, *Macromolecules* 44 (2011) 7987; (c) J. Schmidt, J. Weber, J.D. Epping, M. Antonietti, A. Thomas, *Adv. Mater.* 21 (2009) 702.
- [9] Y. Morisaki, M. Gon, Y. Chujo, *J. Polym. Sci. Polym. Chem.* 51 (2013) 2311.
- [10] C. Zhang, X. Yang, Y. Zhao, X. Wang, M. Yu, J. Jiang, *Polymer* 61 (2015) 36.
- [11] T. Ratvijitvech, R. Dawson, A. Laybourn, Y.Z. Khimyak, D.J. Adams, A.I. Cooper, *Polymer* 55 (2014) 321.
- [12] (a) X. Chen, S. Qiao, Z. Du, Y. Zhou, R. Yang, *Macromol. Rapid Comm.* 34 (2013) 1181; (b) S. Qiao, Z. Du, W. Huang, R. Yang, *J. Solid State Chem.* 212 (2014) 69; (c) S. Qiao, Z. Du, R. Yang, *J. Mater. Chem. A* 2 (2014) 1877.
- [13] (a) S.V. Rosokha, I.S. Neretin, D. Sun, J.K. Kochi, *J. Am. Chem. Soc.* 128 (2006) 9394; (b) S. Huang, Q. Zhang, Y. Shiota, T. Nakagawa, K. Kuwabara, K. Yoshizawa, C. Adachi, *J. Chem. Theory Comput.* 9 (2013) 3872; (c) M. Takase, V. Enkelmann, D. Sebastiani, M. Baumgarten, K. Mullen, *Angew. Chem. Int. Ed.* 46 (2007) 5524; (d) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* 492 (2012) 234.
- [14] R. Babarao, S. Dai, D. Jiang, *Langmuir* 27 (2011) 3451.
- [15] J.X. Jiang, F. Su, A. Trewin, C.D. Wood, H. Niu, J.T. Jones, Y.Z. Khimyak, A.I. Cooper, *J. Am. Chem. Soc.* 130 (2008) 7710.
- [16] J.X. Jiang, F. Su, H. Niu, C.D. Wood, N.L. Campbell, Y.Z. Khimyak, A.I. Cooper, *Chem. Commun.* 4 (2008) 486.
- [17] G. Cheng, T. Hasell, A. Trewin, D.J. Adams, A.I. Cooper, *Angew. Chem. Int. Ed.* 51 (2012) 12727.
- [18] L. Chen, Y. Yang, D. Jiang, *J. Am. Chem. Soc.* 132 (2010) 9138.
- [19] J. Weber, A. Thomas, *J. Am. Chem. Soc.* 130 (2008) 6334.
- [20] DOE Targets for On Board Hydrogen Storage Systems for Light Duty Vehicles, available at: http://www1.eere.energy.gov/hydrogen_and_fuel_cells/storage/pdfs/targets_on_board_hydro_storage.pdf.
- [21] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J.M. Simmons, *Angew. Chem. Int. Ed.* 121 (2009) 9457.
- [22] J. Germain, F. Svec, J.M. Fréchet, *Chem. Mater.* 20 (2008) 7069.
- [23] W. Lu, D. Yuan, D. Zhao, C.I. Schilling, O. Plietzsch, T. Muller, S. Brase, J. Guenther, J. Blumel, R. Krishna, *Chem. Mater.* 22 (2010) 5964.
- [24] H. Furukawa, O.M. Yaghi, *J. Am. Chem. Soc.* 131 (2009) 8875.
- [25] W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna, H.C. Zhou, *J. Am. Chem. Soc.* 133 (2011) 18126.
- [26] P. Mohanty, L.D. Kull, K. Landskron, *Nat. Commun.* 2 (401) (2011) 55.
- [27] M.G. Rabbani, H.M. ElKaderi, *Chem. Mater.* 24 (2012) 1511.
- [28] R. Dawson, D.J. Adams, A.I. Cooper, *Chem. Sci.* 2 (2011) 1173.
- [29] G.D. Pirngruber, P. Raybaud, Y. Belmabkhout, J. Cejka, A. Zukal, *Phys. Chem. Chem. Phys.* 12 (2010) 13534.
- [30] J. Lennart, J.A. Swisher, B. Smit, *Langmuir* 29 (2013) 15936.
- [31] M. Nandi, H. Uyama, *Chem. Rec.* 6 (2014) 1134.
- [32] W.C. Song, X.K. Xu, Q. Chen, Z.Z. Zhuang, X.H. Bu, *Polym. Chem.* 4 (2013) 4690.