Accepted Manuscript

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PII: S0032-3861(19)30202-2

DOI: https://doi.org/10.1016/j.polymer.2019.02.062

Reference: JPOL 21301

To appear in: *Polymer*

Received Date: 17 October 2018

Revised Date: 23 February 2019

Accepted Date: 27 February 2019

Please cite this article as: Shi K, Song N, Zou Y, Zhu S, Tan H, Tian Y, Zhang B, Yao H, Guan S, Porphyrin-based porous polyimides: Synthesis, porous structure, carbon dioxide adsorption, *Polymer* (2019), doi: https://doi.org/10.1016/j.polymer.2019.02.062.

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Porphyrin-based porous polyimides: Synthesis, porous structure,

carbon dioxide adsorption

Kaixiang Shi^a, Ningning Song^a, Yongcun Zou^c, Shiyang Zhu^a, Haiwei Tan^a, Ye Tian^a, Bo Zhang^a, Hongyan Yao^{b,**} and Shaowei Guan^{a,*}

^a Key Laboratory of High Performance Plastics (Jilin University), Ministry of Education, National & Local Joint Engineering Laboratory for Synthesis Technology of High Performance Polymer, Jilin University, Qianjin Street 2699, Changchun, 130012, People's Republic of China.

^b Department of Materials Science and Engineering, National University of Singapore, Singapore 117574, Singapore.

^c State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China.

* Corresponding author. ** Corresponding author. E-mail address:guansw@jlu.edu.cn, mseyaoh@nus.edu.sg.

Abstract: A novel dianhydride 3,3⁻-bis(3,4-dicarboxyphenoxy)-4,4⁻-diphenylethynyl biphenyl dianhydride (BPEBPDA) and a new tetramine monomer 5,10,15,20-tetra[4-[(3-aminophenyl)ethynyl]phenyl]porphyrin (TAPEPP) were successfully synthesized. Porphyrin-based polyimides (PPBPIs) were synthesized from BPEBPDA and porphyrin-based building blocks (TAPP and TAPEPP) via polymerization reactions. The porphyrin-based porous polyimide networks (PPBPI-CRs) were obtained from PPBPIs through thermal crosslinking reactions. The PPBPI-CRs exhibited BET surface areas (682 m² g⁻¹ and 693 m² g⁻¹) and CO₂ uptakes (2.0 mmol g⁻¹ and 1.67 mmol g⁻¹ at 273 K and 1 bar) as well as the separation factors of CO₂/N₂ (37.63, 28.97) and CO₂/CH₄ (7.51, 5.61). Meanwhile, PPBPI-CRs showed an enhanced CO₂ isosteric enthalpies of adsorption (25.1 kJ mol⁻¹ and 30.1 kJ mol⁻¹) than other porous polymers.

Keywords

Porphyrin-based porous polyimides; Crosslinking reaction; Carbon dioxide adsorption

1. Introduction

Porous organic polymers (POPs) are a class family of functional polymers with large surface areas, desirable pore sizes and outstanding properties. POPs have attracted a lot of attentions due to their diverse potential applications in gas storage and separation [1], heterogeneous catalysis [2,3], dye adsorption [4] and sensor [5], etc. Over the past decades, various POPs including polymers of intrinsic microporosity (PIMs) [6], covalent organic frameworks (COFs) [7,8], conjugated micro- and mesoporous polymers (CMPs) [9], hyper crosslinked polymers (HCPs) [10] and porous aromatic frameworks (PAFs) [11,12] have been developed.

Normally, POPs are constructed from rigid compounds via various reactions [13,14].

Among the POPs, porous polyimides (PPIs) are a kind of high performance polymers featuring with large specific surface areas, high small gas molecules adsorption capacities, excellently thermal and chemical stabilities [15,16]. Porphyrin and its derivatives with two-dimensional (2D) and large π systems offer well-defined planar and rigid building blocks. Rigid porphyrin-based building blocks are a kind of ideal candidates for constructing porous organic frameworks. Porphyrin-based porous polymers can exhibit large BET surface areas, high CO₂ capture capacities and excellent catalytic performances [15,17,18]. Taking advantage of the combination of imide linkages and porphyrin-based groups can endow aromatic polymers with porous structures and introduce more nitrogen atoms which is beneficial to carbon dioxide adsorption.

In general, PPIs including crystalline and amorphous porous polymers [19,20], are constructed from rigid aromatic compounds via traditional polymerization reactions. Unlike rigid and robust porous polyimides, most hyperbranched polyimides (HBPIs) prepared via traditional polycondensation reactions have flexible skeletons, which causes the dense stacking and collapsing of the pore structures, thus these HBPIs do not have microporous structures. Crosslinked structures can be introduced to fix the three-dimensional networks and induce the formation of pore structures in the hyperbranched polyimides [21,22]. As reported, the crosslinking density in the networks had a significant effect on the pore sizes and BET surface areas of resultant polycyanurate networks [23]. It is a potential way to tune the porosity parameters of crosslinked hyperbranched polyimides by adjusting the crosslinking densities of groups. For the purpose, two tetramine alkynyl monomers 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP), 5,10,15,20-tetra[4-[(3-aminophenyl)ethynyl]phenyl]porphyrin (TAPEPP) and a novel dianhydride monomer 3,3'-bis(3,4-dicarboxyphenoxy)-4,4'-diphenylethynyl biphenyl dianhydride (BPEBPDA) were designed and successfully synthesized. TAPEPP and BPEBPDA contained crosslinkable alkynyl groups, but TAPP did not have C=C. In the present work, in order to study the effect of crosslinking density on the porosity parameters of PPBPI-CRs, firstly, two porphyrin-based hyperbranched polyimides with different crosslinkable alkynyl densities were synthesized using these monomers, subsequently, the porphyrin-based crosslinked polyimides (PPBPI-CRs) were prepared via crosslinking reactions. Their porosity parameters and carbon dioxide uptakes as well as the separations of CO₂/N₂ and CO₂/CH₄ were fully investigated.

2. Result and discussion

2.1. Synthesis and characterization of polymers

A novel dianhydride (BPEBPDA) containing two crosslinkable pendant alkynyl groups and a tetramine with alkynyl functional groups and porphyrin unit were synthesized. designed and As illustrated in Scheme 1. 3,3'-bis(3,4-dicarboxyphenoxy)-4,4'-diphenylethynyl biphenyl dianhydride (BPEBPDA) was obtained via a five-step chemical reaction. Firstly,

3,3'-dihydroxy-4,4'-diaminobiphenyl was reacted with sodium nitrite in the presence of hydrobromic acid via Sander Maier reaction to give 4,4 -dibromobiphenyl-3,3 -diol (I). Subsequently, 3,3'-bis(3,4-dicyanophenoxy)-4,4'-dibromo biphenyl (II) was obtained from I and 4-nitrophthalonitrile via nucleophilic substitution reaction. 3.3'-Bis(3.4-dicyanophenoxy)-4.4'-diphenylethynyl biphenyl (III) was synthesized from II and phenylacetylene via Sonogashira coupling reaction using PdCl₂(PPh₃)₂ and CuI as catalysts. 3,3'-Bis(3,4-dicyanophenoxy)-4,4'-diphenylethynyl biphenyl was hydrolyzed in the presence of potassium hydroxide solution to give the carboxylic monomer (IV). The final target product 3,3'-bis(3,4-dicarboxyphenoxy)-4,4'-diphenylethynyl biphenyl dianhydride (V) was obtained from IV via dehydration reaction in a mixture solution of acetic acid and acetic anhydride. 5,10,15,20-Tetra(4-aminophenyl) porphyrin (TAPP) was prepared literature the according to the (in ESI^{*}). 5,10,15,20-Tetra[4-[(3-aminophenyl)ethynyl]phenyl]porphyrin (TAPEPP) was a novel polyamine containing porphyrin building block and crosslinkable alkynyl groups. TAPEPP (Scheme 2) was synthesized via a two-step reaction. 5,10,15,20-Tetra(4-bromophenyl) porphyrin (H_2TPPBr_4) was produced by Alder-Longo reaction, and the final product was collected via Sonogashira Hagiwara coupling reaction. The resultant dianhydride and porphyrin-based monomers were characterized by FTIR, ¹H NMR, ¹³C NMR (Fig. S1, S2, S4, S5, S6, S7 in the ESI*).



Scheme 1 Synthesis route to BPEBPDA.



Scheme 3 Synthesis routes to the porphyrin-based porous polyimide networks.

A series of porphyrin-based hyperbranched polyimides (PPBPI-1 and PPBPI-2) were prepared from BPEBPDA and two types of tetramine monomers (TAPP and

TAPEPP) via polymerization reactions (Scheme 3). Subsequently, the crosslinked hyperbranched polyimides (PPBPI-1-CR and PPBPI-2-CR) were obtained from crosslinking reactions.

For PPBPIs, the significant stretching bands in the FT-IR spectra (Fig. S3 in the ESI*) at 3310 cm⁻¹ were attributed to the porphyrin rings, demonstrating the successful incorporation of porphyrin units within polymer skeletons. The strong absorption bands at 1776 cm⁻¹ and 1722 cm⁻¹ were assigned to the carbonyl asymmetrical and symmetrical stretching, indicative of the formation of polyimides and the consumption of tetramines and dianhydride. The characteristic absorption bands existed in the FT-IR spectra at 2212 cm⁻¹ were on account of the presence of alkynyl groups. Meanwhile, compared with PPBPI-1, there was a more intense band around 2212 cm⁻¹ in the spectrum of PPBPI-2, it was ascribed to more alkynyl groups existing in both dianhydride and TAPEPP monomers. For PPBPI-CRs, the characteristic bands at 2212 cm⁻¹ disappeared, indicating that PPBPI-CRs had undergone crosslinking reactions. The disappearance of absorption bands at 3310 cm⁻¹ could be due to the fracture of N-H bonds of porphyrin structures accompanying with the crosslinking reactions.







Fig. 2 FE-SEM images of PPBPI-1 (2a), PPBPI-2 (2b), PPBPI-1-CR (2c),

PPBPI-2-CR (2d). Scale bar: 500 nm.

The ¹³C CP-MAS NMR spectra of PPBPIs and PPBPI-CRs were illustrated in Fig. 1. The resonance bands at 164 ppm were assigned to the carbonyl carbons, the aromatic carbons and the carbons of porphyrin rings located at the overlapping resonance bands from 110 to 155 ppm. The signal bands at 96, 90 and 84 ppm were attributed to the carbons of alkynyl groups for PPBPIs [24,25]. The absence of resonance bands of alkynyl carbons in PPBPI-CRs suggested that PPBPI-CRs had undergone crosslinking reactions. As shown in Table S1, the elemental analysis data was in accordance with the theoretical values.

DSC analysis was used to study the crosslinking behaviors of the alkynyl groups in the PPBPIs (Fig. S8 in the ESI^{*}). The disappearance of exothermic peaks which were attributed to the alkynyl groups indicated that the crosslinking reactions of PPBPI-CRs were complete.

The PPBPI-CRs had outstanding chemical and thermal stabilities. They were not dissolved in common organic solvents such as N,N-dimethyl formamide, 1-methyl-2-pyrrolidinone, acetone, tetrahydrofuran and chloroform due to the crosslinked structures [26]. Besides, PPBPI-CRs were also stable in acidic and alkaline solutions. TGA analysis (Fig. S9 in the ESI*) was conducted under a nitrogen atmosphere to evaluate the thermal stabilities of all the polymers. As illustrated in the TGA analyses curves, PPBPI-CRs had high 5% thermal decomposition temperatures above 500 °C and high residues of more than 60% at 800 °C. The slight loss at around 200 °C might be originated from the gas or solvents absorbed in the PPBPI-CRs skeletons [27].

Powder X-ray diffraction of PPBPIs and PPBPI-CRs (Fig. S10 in the ESI*) were studied and exhibited amorphous nature characteristic of polymers [28,29]. The surface morphologies of PPBPIs and PPBPI-CRs were measured by field-emission scanning electron microscopy (Fig. 2, and Fig. S13 in the ESI*). As shown in Fig. 2, the samples showed rough surfaces and irregular morphologies, which were consisted of tight agglomerates of tiny nanoparticles. Meanwhile, transmittance electron microscopy (in Fig. S11, S12, in the ESI*) was studied to confirm the porous structures of PPBPI-CRs. The images revealed that the micropore channels existed within the PPBPI-CRs networks [30].

2.2. The BET surface areas and pore size distribution of PPBPI-CRs

Brunauer-Emmett-Teller (BET) surface areas of PPBPI-CRs were investigated by physical sorption of nitrogen in the liquid nitrogen irrigation at 77 K. The sorption isotherms revealed porosity parameters of crosslinked polymer networks and elucidated the characteristic of permanent micropores. As illustrated in Fig. 3, the sorption isotherms belonged to the characteristic type I sorption curves according to IUPAC classifications. The isotherms displayed a steep rise at a very low relative pressure (P/P₀ < 0.01), indicating that abundance of micropores existed in the PPBPI-CRs skeletons [31]. And the distinct capillary hysteresis loops of sorption isotherms exhibited the presence of mesopores in the pore channels and the swelling effect between PPBPI-CRs skeletons and nitrogen [32].

The BET surface areas of PPBPI-1-CR and PPBPI-2-CR were calculated to be 682 m² g^{-1} and 693 m² g^{-1} , respectively. Simultaneously, the total pore volumes of PPBPI-CRs revealed 0.429 cm³ g⁻¹ and 0.457 cm³ g⁻¹, respectively. It was reported that porous structures of HBPI-CRs was mainly influenced by the crosslinked structures rather than by the topological structures of polyamines [21]. TAPP and TAPEPP were both porphyrin-based tetramine monomers offering rigid building blocks, but the numbers of their alkynyl functional groups were different. In contrast to TAPP, TAPEPP had four crosslinkable alkynyl groups linked with extended benzene rings through the C=C triple bonds. Therefore, PPBPI-2 had a higher crosslinking density of alkynyl group than that of PPBPI-1, but the BET surface areas and the total pore volumes of PPBPI-1-CR and PPBPI-2-CR were close to each other, which perhaps because steric hindrance restricted the chain segment movement of crosslinkable alkynyl groups within polymer skeletons [13]. Meanwhile, in Fig. 3, this clearly showed that PPBPI-2-CR had more mesopores, which could account for the higher total pore volume of PPBPI-2-CR than that of PPBPI-1-CR. However, PPBPI-1-CR possessed more micropores, thus it had larger micropore surface area and higher micropore volume than PPBPI-2-CR.



Fig. 3 (a) Adsorption (filled) and desorption (empty) isotherms of N_2 at 77 K for

PPBPI-CRs, (b) pore size distribution by DFT method.

Pore size distribution (PSD) was collected from nitrogen sorption isotherms at 77 K by original Density Functional theory (DFT). The pore size distribution of PPBPI-1-CR and PPBPI-2-CR were shown in Fig. 3, they had similar pore size distribution including mesopores and ultramicropores. The pore diameters of PPBPI-CRs (in Table 1) were around at 0.6 nm and 1.2 nm. The pores with bigger sizes might come from the possible crosslinked structures formed during the crosslinking reactions (Scheme. S1 in the ESI*) [33-36]. The pores with smaller sizes could be derived from the hyperbranched polyimide skeletons [37]. The total pore volumes of PPBPI-CRs were mainly ascribed to the micropores and mesopores existing in the PPBPI-CRs networks, which was beneficial for carbon dioxide adsorption.

Table 1 Specific surface area, pore volume, and pore size distribution in PPBPI-CRs networks.

Samples	S_{BET}^{a}	$S_{Langmuir}^{\ \ b}$	S _{micro} ^c V _{total} ^d	V _{micro} ^e	PSD^{f}	
	$m^2 g^{-1}$	$m^2 g^{-1}$	$m^2 g^{-1} cm^3 g^{-1}$	$cm^3 g^{-1}$	nm	
PPBPI-1-CR	682	930	332 0.429	0.155	0.59,1.27	
PPBPI-2-CR	693	1050	275 0.457	0.147	0.54,1.26	

^{a, b} The Brunauer-Emmett-Teller and Langmuir surface areas of samples were calculated from the sorption isotherms of nitrogen.

^c The micropore surface areas were collected basing on t-plot method.

^d Total pore volume derived from N₂ isotherms at $P/P_0 = 0.99$.

^e Micropore volume determined from t-plot method.

^f Pore size distribution (PSD) was based on original density functional theory.

2.3. Carbon dioxide adsorption and selectivity of $\mathrm{CO}_2/\mathrm{N}_2$ and $\mathrm{CO}_2/\mathrm{CH}_4$ of PPBPI-CRs

CO₂ sorption isotherms (Fig. 4) were collected at 273 K and 295 K to calculate CO₂ uptakes (in Table 2) and CO₂ isosteric heats of adsorption (Q_{st}). The CO₂ uptakes of PPBPI-1-CR and PPBPI-2-CR were 2.0 mmol g⁻¹ and 1.67 mmol g⁻¹ at 273K and 1 bar, respectively. The previous reports had revealed that N and O functionalities, high micropore volumes and small micropore sizes facilitated the small gas molecules adsorption capacities [23,38]. The CO₂ uptakes of PPBPI-CRs could be attributed to two reasons: first, there were N and O functionalities existing in the crosslinked polymer skeletons; second, PPBPI-CRs had abundant micropores and considerable micropore volumes. Compared with PPBPI-2-CR, the CO₂ uptake of PPBPI-1-CR was higher. The higher CO₂ adsorption value of PPBPI-1-CR was probably due to the larger micropore volume/total pore volume = 0.361) than those of

PPBPI-2-CR (0.147 cm⁻¹ g⁻¹, 0.322). Moreover, the CO₂ uptake of PPBPI-1-CR was comparable to or exceeded those of many other porous organic polymers with high specific surface areas, such as PAF-1 (2.07 mmol g⁻¹, 5640 m² g⁻¹) [39], COF-5 (1.34 mmol g⁻¹, 1670 m² g⁻¹) [40], CMP-1 (2.05 mmol g⁻¹, 837 m² g⁻¹) [41].

 CO_2 isosteric enthalpies of adsorption (Q_{st}) (Fig. 5) were calculated at two different temperatures by Clausius-Clapeyron equation to evaluate the interaction forces between the crosslinked polymers and CO₂ molecules. As illustrated in Table S2 (in the ESI*), Q_0 , K_H , and A_0 were calculated by using $LnP=Q_{st}/RT+C$ and $d[LnK_H]/dT = Q_0/RT^2$, the K_H and A_0 values of PPBPI-1-CR exceeded those of PPBPI-2-CR, respectively. Q_0 is the enthalpy of adsorption and the indication of binding affinity at zero coverage. The Q_{st} isotherms revealed that PPBPI-2-CR had a much higher Q_0 (30.1 kJ mol⁻¹) than those of PPBPI-1-CR (25.1 kJ mol⁻¹) and other porous organic polymers such as PAFs (15.6-27.8 kJ mol⁻¹) [39], STPIs (28-36 kJ mol⁻¹) [42], and CMP-1 (26.8 kJ mol⁻¹) [41]. PPBPI-2-CR had higher Q_0 than PPBBPI-1-CR, which meant PPBPI-2-CR had stronger binding affinity between its crosslinked polymer skeleton and CO₂. The higher Q_0 of PPBPI-2-CR compared to PPBPI-1-CR might be attributed to the porosities, network structures and complexities of pore channels in the skeletons [43]. And the enhanced binding affinity was probably attributed to the interaction of dipolar and quadrupolar between CO₂ guest molecules and porous networks [44]. Besides, the virial plots of CO₂ adsorption for PPBPI-CRs at 273 and 295 K (Fig. 6) revealed good linear relationships. The pore sizes calculated from CO₂ sorption isotherms at 273 K were centered at around 0.6 nm, indicative of the presence of ultramicropores within the crosslinked polymer networks.

The sorption isotherms of N_2 and CH_4 at 273 K were measured and compared with those of CO_2 to calculate the separation properties of PPBPI-CRs (Fig. 7 and Fig. S14). As reported, compared to N_2 and CH_4 , CO_2 had the stronger adsorption ability with polymer skeletons, leading to the high separation factors of CO_2/N_2 and CO_2/CH_4 [37,43]. For PPBPI-1-CR, the separation factors of CO_2/N_2 and CO_2/CH_4 from initial slopes of component sorption isotherms were 37.63 and 7.51, respectively, which were higher than those of PPBPI-2-CR (28.97 and 5.61). The higher CO_2/N_2 and CO_2/CH_4 selectivities of PPBPI-1-CR compared to PPBPI-2-CR were attributed to two reasons: first, PPBPI-1-CR possessed more micropores and higher micropore volume, causing the higher CO_2 uptake over N_2 and CH_4 because of the molecular sieving effect; second, the content of nitrogen atoms in PPBPI-1-CR was higher than that in PPBPI-2-CR, which was advantageous for the affinity of PPBPI-1-CR skeleton toward CO_2 [45].



Fig. 4 (a) CO_2 adsorption and desorption isotherms for PPBPI-CRs at 273 and 295 K, (b) pore size distribution for samples by density functional theory at 273



Fig. 5 Variation of CO₂ isosteric enthalpies of PPBPI-CRs with the adsorbed amount.



Fig. 6 Virial plots of CO₂ adsorption from PPBPI-CRs at 273 and 295 K.



Fig. 7 Adsorption isotherms of CO₂, N₂ and CH₄ gases at 273 K for PPBPI-CRs.

Table 2 CO_2 uptakes and pore size distribution from CO_2 sorption isotherms at 273 K, gas selectivities from CO_2 , N_2 and CH_4 sorption isotherms at 273 K.

Samples	CO ₂ uptake ^a	CO ₂ uptake ^b	Pore size ^c	Gas selectivity ^d	
	mmol g^{-1}	$mmol g^{-1}$	nm	CO_2/N_2	CO ₂ /CH ₄
PPBPI-1-CR	2.0	1.28	0.66	37.63	7.51
PPBPI-2-CR	1.67	1.05	0.68	28.97	5.61

^aCO₂ uptakes derived from CO₂ sorption isotherms at 1.0 bar and 273 K.

 b CO₂ uptakes determined at 1 bar and 295 K.

^c Pore size distribution was collected from CO₂ sorption isotherms at 273 K.

 d The CO₂/N₂ and CO₂/CH₄ selectivities were calculated from initial slopes of pure-component sorption isotherms.

3. Conclusions

Two porphyrin-based porous hyperbranched polyimides (PPBPI-1-CR and PPBPI-2-CR) were synthesized from a novel dianhydride (BPEBPDA) and two porphyrin building blocks (TAPP and TAPEPP) via polymerization and subsequent crosslinking reactions. PPBPI-CRs revealed specific surface areas (682 and 693 m² g⁻¹) and pore sizes (0.6 and 1.2 nm). Although PPBPI-CRs had different crosslinking densities of alkynyl groups, they exhibited similar BET surface areas due to steric hindrance. The PPBPI-CRs exhibited CO₂ uptakes (2.0 mmol g⁻¹ and 1.67 mmol g⁻¹) and CO₂ isosteric enthalpies (25.1 kJ mol⁻¹ and 30.1 kJ mol⁻¹) as well as the separation factors of CO₂/N₂ (37.63, 28.97) and CO₂/CH₄ (7.51, 5.61).

Acknowledgements

We thank the National Nature Science Foundation of China (Grant no. 51573067) for the financial support.

References

- [1] N.B. McKeown, P.M. Budd, Chem. Soc. Rev. 35(8) (2006) 675-683.
- [2] D.B. Shinde, S. Kandambeth, P. Pachfule, R.R. Kumar, R. Banerjee, Chem. Commun. 51(2) (2015) 310-313.
- [3] Y. Li, C. Liu, W. Yang, New J. Chem. 41(16) (2017) 8214-8221.
- [4] Y. Yuan, H. Huang, L. Chen, Y. Chen, Macromolecules 50(13) (2017) 4993-5003.
- [5] L. Zhao, M. Li, M. Liu, Y. Zhang, C. Wu, Y. Zhang, J. Hazard. Mater. 301 (2016) 233-241.
- [6] G. Cheng, B. Bonillo, R.S. Sprick, D.J. Adams, T. Hasell, A.I. Cooper, Adv. Funct. Mater. 24(33) (2014) 5219-5224.
- [7] R.W. Tilford, S.J.M. III, P.J. Pellechia, J.J. Lavigne, Adv. Mater. 20(14) (2008) 2741-2746.
- [8] J.W. Crowe, L.A. Baldwin, P.L. McGrier, J. Am. Chem. Soc. 138(32) (2016) 10120-10123.
- [9] J.-X. Jiang, A. Trewin, D.J. Adams, A.I. Cooper, Chem. Sci. 2(9) (2011) 1777-1781.
- [10] Y. Luo, B. Li, W. Wang, K. Wu, B. Tan, Adv. Mater. 24(42) (2012) 5703-5707.
- [11] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J.M. Simmons, S. Qiu, G. Zhu, Angew. Chem. Int. Ed. 48(50) (2009) 9457-9460.
- [12] Y. Yuan, Y. Yang, X. Ma, Q. Meng, L. Wang, S. Zhao, G. Zhu, Adv. Mater. 30(12) (2018) 1706507.
- [13] H. Yu, C. Shen, M. Tian, J. Qu, Z. Wang, Macromolecules 45(12) (2012) 5140-5150.
- [14] S. Meng, H. Ma, L. Jiang, H. Ren, G. Zhu, J. Mater. Chem. A 2(35) (2014) 14536-14541.
- [15] M.R. Liebl, J. Senker, Chem. Mater. 25(6) (2013) 970-980.
- [16] L. Jiang, Y. Tian, T. Sun, Y. Zhu, H. Ren, X. Zou, Y. Ma, K.R. Meihaus, J.R.

Long, G. Zhu, J. Am. Chem. Soc. 140(46) (2018) 15724-15730.

- [17] M.H. Kim, T. Song, U.R. Seo, J.E. Park, K. Cho, S.M. Lee, H.J. Kim, Y.-J. Ko, Y.K. Chung, S.U. Son, J. Mater. Chem. A 5(45) (2017) 23612-23619.
- [18] C.S. Diercks, S. Lin, N. Kornienko, E.A. Kapustin, E.M. Nichols, C. Zhu, Y. Zhao, C.J. Chang, O.M. Yaghi, J. Am. Chem. Soc. 140(3) (2018) 1116-1122.
- [19] Q. Fang, Z. Zhuang, S. Gu, R.B. Kaspar, J. Zheng, J. Wang, S. Qiu, Y. Yan, Nat. Commun. 5 (2014) 4503.
- [20] G. Li, B. Zhang, J. Yan, Z. Wang, J. Mater. Chem. A 4(29) (2016) 11453-11461.
- [21] H. Yao, N. Zhang, N. Song, K. Shen, P. Huo, S. Zhu, Y. Zhang, S. Guan, Polym. Chem. 8(8) (2017) 1298-1305.
- [22] H. Yao, N. Zhang, K. Shen, N. Song, K. Shi, S. Zhu, Y. Zhang, S. Guan, Polymer 115 (2017) 176-183.
- [23] C. Shen, J. Yan, G. Deng, B. Zhang, Z. Wang, Polym. Chem. 8(6) (2017) 1074-1083.
- [24] Y. Xie, T.T. Wang, X.H. Liu, K. Zou, W.Q. Deng, Nat. Commun. 4 (2013) 1960.
- [25] W. Chaikittisilp, A. Sugawara, A. Shimojima, T. Okubo, Chem. Eur. J. 16(20) (2010) 6006-6014.
- [26] Q. Chen, D.-P. Liu, J.-H. Zhu, B.-H. Han, Macromolecules 47(17) (2014) 5926-5931.
- [27] K.V. Rao, R. Haldar, C. Kulkarni, T.K. Maji, S.J. George, Chem. Mater. 24(6) (2012) 969-971.
- [28] Y. Liu, S. Wu, G. Wang, G. Yu, J. Guan, C. Pan, Z. Wang, J. Mater. Chem. A 2(21) (2014) 7795-7801.
- [29] S. Xiong, X. Fu, L. Xiang, G. Yu, J. Guan, Z. Wang, Y. Du, X. Xiong, C. Pan, Polym. Chem. 5(10) (2014) 3424-3431.
- [30] G. Guo, Q. Sun, N. Wang, R. Bai, J. Yu, Chem. Commun. 54(30) (2018) 3697-3700.
- [31] D. Chen, S. Gu, Y. Fu, Y. Zhu, C. Liu, G. Li, G. Yu, C. Pan, Polym. Chem. 7(20) (2016) 3416-3422.
- [32] D. Cui, C. Yao, Y. Xu, Chem. Commun. 53(83) (2017) 11422-11425.
- [33] Y. Liu, Z. Wang, H. Yang, L. Gao, G. Li, M. Ding, J. Polym. Sci. Part A: Polym. Chem. 46(12) (2008) 4227-4235.
- [34] X. Fang, D.F. Rogers, D.A. Scola, M.P. Stevens, J. Polym. Sci. Part A: Polym. Chem. 36 (1998) 461-470.
- [35] M.E. Wright, D.A. Schorzman, Macromolecules 32(25) (1999) 8693-8694.
- [36] M.E. Wright, D.A. Schorzman, Macromolecules 34(14) (2001) 4768-4773.
- [37] G. Li, Z. Wang, J. Phys. Chem. C 117(46) (2013) 24428-24437.
- [38] K.V. Rao, R. Haldar, T.K. Maji, S.J. George, Polymer 55(6) (2014) 1452-1458.
- [39] T. Ben, C. Pei, D. Zhang, J. Xu, F. Deng, X. Jing, S. Qiu, Energy Environ. Sci. 4(10) (2011) 3991-3999.
- [40] H. Furukawa, O.M. Yaghi, J. Am. Chem. Soc. 131(25) (2009) 8875-8883.
- [41] R. Dawson, A. Laybourn, Y.Z. Khimyak, D.J. Adams, A.I. Cooper, Macromolecules 43(20) (2010) 8524-8530.
- [42] C. Zhang, T.-L. Zhai, J.-J. Wang, Z. Wang, J.-M. Liu, B. Tan, X.-L. Yang, H.-B.

Xu, Polymer 55(16) (2014) 3642-3647.

- [43] G. Li, Z. Wang, Macromolecules 46(8) (2013) 3058-3066.
- [44] C. Shen, Z. Wang, J. Phys. Chem. C 118(31) (2014) 17585-17593.
- [45] J. Yan, B. Zhang, Z. Wang, ACS Appl. Mater. Interfaces 10(31) (2018) 26618-26627.

Highlights

- Two porphyrin-based porous polyimides (PPBPI-1-CR and PPBPI-2-CR) were synthesized via polymerization and post-crosslinking reactions.
- PPBPI-CRs revealed specific surface areas (682 and 693 m² g⁻¹) and CO₂ uptakes (2.0 and 1.67 mmol g⁻¹ at 273 K and 1 bar) as well as isosteric heats of adsorption (25.1 and 30.1 kJ/mol).
- Although PPBPI-CRs had different crosslinking densities of alkynyl groups, they exhibited similar BET surface areas due to steric hindrance.