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BODIPY-Containing Porous Organic Polymers for Gas Adsorption

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Abstract

A series of BODIPY-containing microporous organic polymers was synthesized via Sonogashira-Hagihara cross-coupling reaction from a BODIPY derivative with triple polymerisable groups and a range of aryl-alkyne monomers. All of the polymers show high isosteric heats of CO_2 adsorption (23.3~27.3 kJ mol⁻¹) because the incorporation of heteroatoms (N, B, F) from BODIPY unit into the polymer skeleton enhanced the binding affinity between the pore wall and CO₂ molecules. The aryl-alkyne monomer has a large influence on the surface area and CO₂ adsorption performance of the resulting polymers. The polymer BDPCMP-3 shows a high Brunauer-Emmett-Teller specific surface area of up to 725 $m^2 g^{-1}$, while BDPCMP-2 with low surface area of 582 m² g⁻¹ shows a high CO₂ uptake ability of 2.25 mmol g⁻¹ at 1.13 bar/273 K with a CO₂/N₂ adsorption selectivity of 32.3.

Keywords: microporous organic polymers, BODIPY, gas adsorption, isosteric heats

1. Introduction

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Microporous organic polymers (MOPs), owing to their special features such as high specific surface area, excellent physicochemical and thermal stability, tunable pore properties, low skeleton density and synthetic diversity, show broad potential in applications such as gas storage and separation,^{1, 2} chemical sensors,³ light harvesting and light emitting devices,^{4, 5} heterogeneous catalysis,⁶ photocatalysis,^{7, 8} and electric energy conversion and storage.⁹ Over the past decade, a range of MOPs including polymers of intrinsic microporosity (PIMs),¹⁰ covalent organic frameworks (COFs),¹¹ conjugated microporous polymers (CMPs),^{12–14} porous polymer networks (PPNs),¹⁵ porous aromatic frameworks (PAFs),¹⁶ covalent triazine-based frameworks (CTFs),¹⁷ and hypercrosslinked porous polymers (HCPs)¹⁸ have been developed by using various polymerization methods, building blocks and synthetic strategies.

Increasing CO_2 emission from the rapid consumption of fossil fuels has led to the global climate change and some environmental issues. Therefore, developing efficient CO_2 capture and separation technologies or CO_2 capture materials would be a potential short-time strategy to solve these issues. The leading CO_2 capture technology of amine-based wet scrubbing technology suffers from the considerable energy penalty for CO_2 release and the regeneration of amine solution.¹⁹ MOPs, as a new class of CO_2 capture materials, have attracted much attentions recently because they adsorb CO_2 molecules through relatively weak van der Waals force, which makes the regeneration of the materials energy efficient. Recent studies demonstrated that the introduction of heteroatoms and polar functional groups into the skeleton of MOPs could enhance the binding affinity between the adsorbent and CO_2 molecules through the strong dipole-quadrupole interaction, which leads to a significant increase in the CO_2 capture capacity. For instance, the nitrogen-doped porous polymer framework of

PPF-1 exhibited a CO₂ uptake of 6.1 mmol g^{-1} at 273 K/1.0 bar,²⁰ the azg-linked every structe Online Displayer of 6.1 mmol g^{-1} at 273 K/1.0 bar,²⁰ the azg-linked every structure on the structure of the structur nanoporous polymer of ALP-1 showed a remarkable CO₂ uptake of up to 5.36 mmol g^{-1} at 273 K/1.0 bar with a CO₂/N₂ adsorption selectivity of 35 at 273 K,²¹ the nanoporous covalent organic polymer of TB-COP-1 with tröger's base functionality exhibited a CO₂ capture capacity of 5.19 mmol g^{-1} with a CO₂/N₂ adsorption selectivity of 79.2 at 273 K²², the porous covalent triazine polymer network of PCTP-1 exhibited a high CO₂ uptake capacity of up to 4.92 mmol g^{-1} at 273 K/1.0 bar,²³ the microporous polycarbazole of CPOP-1 showed a CO₂ capture capacity of 4.82 mmol g^{-1} with a CO₂/N₂ adsorption selectivity of 25 at 273 K,¹ the covalent triazine-based framework of CTF-TPC showed a high surface area of 1668 $m^2 g^{-1}$ and could adsorb CO₂ up to 4.25 mmol g^{-1} with a CO₂/N₂ adsorption selectivity of 20 at 273 K.²⁴ These results demonstrated that such MOPs with polar functional groups or heteroatoms have great potential to increase the CO₂ capture capacity or CO₂/N₂ adsorption selectivity. BODIPY is an efficient chromophore that has been studied widely for light-emitting,^{25, 26} chemical sensing²⁷ and solar cell.²⁸ Recent studies have revealed that BODIPY could be an efficient building block for making functional porous polymers. For example, Liras et al.²⁹ reported the synthesis of luminescent BODIPY-based porous polymer of CMPBDP, which showed efficient heterogeneous photocatalytic activity for the oxidation reaction of thioanisole to methylphenyl sulfoxide. Zhuang et al.³⁰ synthesized a novel nanocarbon (carbon nanosphere, carbon nanotube, and grapheme) by heating treatment of the BODIPY-based porous polymer precursors.

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In this work, a series of BODIPY-functionalized microporous organic polymers was synthesized via Sonogashira-Hagihara cross-coupling reaction from a BODIPY derivative with triple polymerisable groups and a range of aryl-alkyne monomers. We expect that the high crosslinked polymer structure formed from the monomers with $\frac{1}{2}$ with $\frac{1}{2}$ and $\frac{1}{2}$ high connective sites can substantially increase the surface area of the resulting BODIPY-containing polymers. On the other hand, BODIPY contains a large number of heteroatoms (B, N, F), which could enhance the binding affinity between the polymer and CO₂ molecules due to the existence of the C=O polar bonds, and thus we hypothesized that the introduction of BODIPY segments into the porous polymer skeleton could lead to the increase of CO₂ capture capacity.

2. Experimental section

2.1 Chemicals

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2,4-Dimethyl-1*H*-pyrrole, 4-iodobenzoic acid, SOCl₂, 1,4-diethynylbenzene (DEB), 1,3,5-triethynylbenzene (TEB) and potassium carbonate were purchased from TCI. Pyrene, tetraphenylthylene and trimethylsilylacetylene (TMSA) were purchased from Across. Tetrakis(triphenylphosphine)palladium(0), *N*,*N*-dimethylformamide and triethylamine were purchased from J&K Scientific Ltd. All chemicals were used as received without further purification. 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (TEPE) and 1,3,6,8-tetraethynylpyrene (TEPY) were synthesized by the literature.^{31, 32} 1,3,5,7-Tetramethyl-2,6-diiodo-8-(4-iodophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*S*-in dacene (TI-BDP) was prepared according to the literature.³³

2.2 Synthesis of BODIPY-containing microporous organic polymers

All of the polymer networks were synthesized by palladium(0)-catalyzed Sonogashira–Hagihara cross-coupling reaction of the aryl-alkyne monomers of DEB, TEB, TEPE or TEPY with the BODIPY derivative of TI-BDP. The general synthetic route for the porous polymer networks was shown in Scheme 1. All reactions were carried out at a fixed reaction temperature and reaction time (100 C/48 h).

BDPCMP-1: TI-BDP (350 mg, 0.5 mmol), 1,4-diethynylbenzene (DEB) (94.5 mg,

0.75 mmol) tetrakis(triphenylphosphine)palladium(0) (15 mg), copper(I) iodide $10^{0.06N,0010128}$ mg) were dissolved in a mixture of DMF (5.0 mL) and Et₃N (5.0 mL). The mixture was degassed under freeze-pump-thaw, purged with N₂ and stirred at 100 °C for 48 h. The mixture was then cooled down to room temperature and the precipitated polymer network was filtered and washed with water, methanol, chloroform and acetone, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was dried under vacuum for 24 h at 70 °C and obtained as a dark red powder (232 mg, yield: 91%). Elemental combustion analysis (%) Calcd for (C₃₄H₂₂BF₂N₂)_n: C 80.47, H 4.34, N 5.52; found: C 75.63, H 4.06, N 4.86. The deviation of the elemental analysis from the theoretical value could be attributed to the unreacted end groups, and trapped gases and water from air in the porous polymers due to their high microporosities.³⁴

BDPCMP-2: TI-BDP (350 mg, 0.5 mmol), 1,3,5-triethynylbenzene (TEB) (76 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg) and copper(I) iodide (10 mg) were dissolved in DMF (5.0 mL) and Et₃N (5.0 mL). The mixture was degassed under freeze–pump–thaw, purged with N₂ and stirred at 100 °C for 48 h. The mixture was then cooled down to room temperature and the precipitated polymer network was filtered and washed with water, methanol, chloroform and acetone, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was dried under vacuum for 24 h at 70 °C and obtained as a red powder (206 mg, yield: 88%). Elemental combustion analysis (%) Calcd for (C₃₁H₂₂BF₂N₂)_n: C 78.98, H 4.67, N 5.94; found: C 74.37, H 4.14, N 5.38.

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BDPCMP-3: TI-BDP (350 mg, 0.5 mmol), 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (TEPE) (160 mg, 0.375 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg) and copper(I) iodide (10 mg) were dissolved in DMF (5.0 mL) and Et_3N (5.0 mL). The mixture was degassed under freeze-pump-thaw, purged with N2 and stirred at 100 °C for 48 h. The mixture was then cooled down to room temperature and the precipitated polymer network was filtered and washed with water, methanol, chloroform and acetone, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was dried under vacuum for 24 h at 70 °C and obtained as a black powder (232 mg, yield: 91%). Elemental combustion analysis (%) Calcd for (C_{44.5}H₃₁BF₂N₂)_n: C 83.18, H 4.83, N 4.36; found: C 76.73, H 4.27, N 3.94.

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BDPCMP-4: TI-BDP (350 mg, 0.5 mmol), 1,3,6,8-tetraethynylpyrene (TEPY) (110 mg, 0.375 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg) and copper(I) iodide (10 mg) were dissolved in DMF (5.0 mL) and Et₃N (5.0 mL). The mixture was degassed under freeze-pump-thaw, purged with N₂ and stirred at 100 °C for 48 h. The mixture was then cooled down to room temperature and the precipitated polymer network was filtered and washed with water, methanol, chloroform and acetone, respectively. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was obtained as a black powder (232 mg, yield: 91%). Elemental combustion analysis (%) Calcd for $(C_{37}H_{23,5}BF_2N_2)_n$: C 81.54, H 4.32, N 5.14; found: C 75.74, H 3.97, N 4.63.



Scheme 1. Synthetic route to the BODIPY-based microporous organic polymers and the notional polymer structures.

2.3 Characterization

The FT-IR spectra were measured in transmission mode on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. The thermal properties of the polymer networks were evaluated using thermogravimetric analysis (TGA) with a 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 the control of 10 °C min⁻¹. Powder X-ray diffraction measurement was carried out on an X-ray Diffractometer (D/Max-3c). Elemental analysis was performed on a EURO EA3000 Elemental Analyzer. The morphologies of the polymer networks were obtained using a field emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan). Surface areas and pore size distributions 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 (P/P_o) range from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the N₂ adsorption branch of the isotherms using non-local density functional theory (NL-DFT). The samples were degassed at 120 °C for 12 h under vacuum (10⁻⁵ bar) before analysis. The gas sorption isotherms were measured on an ASAP 2420-4 as well.

3. Results and discussion

All of the polymer networks are insoluble in common organic solvents because of their highly crosslinked structures, and they are also chemically stable. The resulting polymer networks exhibit high thermal stability in nitrogen atmosphere, as revealed by TGA (*Fig. S1*). It was found that BDPCMP-3 has the best thermal stability among the four polymers, which could be possibly attributed to the high crosslinking degree and molecular weight of BDPCMP-3 because of more polymerizable functional groups of TEPE than DEB and TEB, and smaller steric hindrance of TEPE than TEPY due to the C-C bond rotation in TEPE. The FT-IR spectra of the polymer networks (Fig. 1) are consistent with the expected network structure showing the alkyne of $-C\equiv C$ - band at 2190 cm⁻¹, the stretching vibration band of C-N-C at 1636 cm⁻¹, and the characteristic vibration of C=C bond at ~1530

cm⁻¹. The -CH₃ stretching vibration from the BODIPY segment was also obsegged are watche order around 2925 cm⁻¹ for the polymers. The C-I bands of the monomer of TI-BDP at \sim 743 cm⁻¹ and \sim 520 cm⁻¹ were disappeared, and a new vibration peak around 833 cm⁻¹ was observed for the polymers, indicating that the polymerization reaction was almost complete. Powder X-ray diffraction measurements indicated that the polymer networks are amorphous in nature without showing any clear diffraction peaks (*Fig. S2*). The broad peak indicated the formation of an amorphous random polymer network. The different 2θ values and different sharpness of the broad peaks could be derived from the different molecular size of the four aryl-alkyne monomers and the imparity of the short-range length. Scanning electron microscopy (SEM) images revealed that the resulting polymer networks show very similar morphology with relatively uniform solid nanoparticles (Fig. 2).



Fig. 1 FT-IR spectra of the BDPCMPs



Fig. 2. Scanning electron microscopy images of the BDPCMPs with a scale bar of 5.0 µm.



Fig. 3. (a) Nitrogen adsorption (filled symbols) / desorption (empty symbols) isotherms for the polymer networks collected at 77.3 K; (b) Pore size distribution curves calculated by NL-DFT.

The porous properties of the polymer networks were investigated by nitrogen adsorption analyses at 77.3 K. As shown in Fig. 3a, all of the polymer networks gave rise to Type I nitrogen gas sorption isotherms with a steep nitrogen gas uptake at low relative pressure ($P/P_0 < 0.001$) according to IUPAC classification,³⁵ indicating the

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abundant micropores in the polymer networks. A steep rise in the nitrogen adsorption address isotherms was also observed at high relative pressures ($P/P_0 > 0.9$), indicating the presence of some mesopores and/or macropores in the polymers that are probably due to inter-particle porosity or void.³⁶ Hysteresis was observed upon desorption branch of the isotherm for the polymer networks, which is consistent with elastic deformations or swelling as a result of gas sorption.³⁷ Fig. 3b shows the pore size distribution (PSD) curves for the polymer networks as calculated using nonlocal density functional theory (NL-DFT). All of the polymer networks exhibit abundant microporous structure with the main pore size around 1.0 nm, and BDPCMP-4 shows the smallest micropore pore size around 0.91 nm among the four polymers. The apparent Brunauer-Emmet-Teller (BET) specific surface area varies between 482 m² g⁻¹ for BDPCMP-1 and 725 m² g⁻¹ for BDPCMP-3 (Table 1), indicating that the aryl-alkyne monomers with different number of polymerisable groups and different geometries have a large influence on the surface area of the polymer networks. The high surface area of 725 m² g⁻¹ for BDPCMP-3 could be attributed to the high degree of crosslinking because of the four polymerisable groups of 1,1,2,2-tetrakis(4-ethynylphenyl)ethene and the relative flexible backbone of the polymer. The surface area is much higher than that of reported BODIPY-based microporous organic polymers, such as the CMPBDP (299 $m^2 g^{-1}$ ²⁹ and the dimensionality controlled CMPs with BODIPY segment (593-622 $m^2 g^{-1}$).³⁰ All of the polymer networks show high microporous surface area ratio over 74% and microporous volume ratio over 55%, and BDPCMP-2 shows the highest microporous surface area ratio of 87.28% and microporous volume ratio of 75.00% among the four polymers (Table 1), again suggesting that the pores of the polymer networks are dominated by microporous, which is in agreement with the character of the nitrogen sorption isotherms.

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Table 1. Summary of pore properties for the polymer networks						DOI: 10.1039/C6NJ01812B		
Polymer	$S_{ m BET}{}^{ m a}$	$S_{ m Micro}{}^{ m b}$	$V_{ m Micro}{}^{ m c}$	$V_{\mathrm{Total}}{}^{\mathrm{d}}$	$S_{ m Micro}/S_{ m BET}$	V _{Micro} / V _{Total}		
	$[m^2 g^{-1}]$	$[m^2 g^{-1}]$	$[cm^{3}g^{-1}]$	$[cm^3 g^{-1}]$	[%]	[%]		
BDPCMP-1	482	390	0.18	0.28	80.91	64.28		
BDPCMP-2	582	508	0.24	0.32	87.28	75.00		
BDPCMP-3	725	539	0.25	0.45	74.34	55.55		
BDPCMP-4	501	422	0.20	0.29	84.23	68.96		

Table 1. Summary of pore properties for the polymer networks

^a Surface area calculated from N₂ adsorption isotherm in the relative pressure (P/P_o) range from 0.05 to 0.20; ^b Microporous surface area calculated from the N₂ adsorption isotherm using *t-plot* method based on the Harkins Jura Equation. ^c The microporous volume derived from the *t-plot* method; ^d Total pore volume at $P/P_o = 0.90$.



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Fig. 4. (a) Volumetric H_2 sorption curves for the polymer networks at 77.3 K up to 1.13 bar; (b) CO₂ adsorption isotherms collected at 273 K (solid point) and 298 K (empty point) up to 1.13 bar; (c) Isosteric heats of adsorption for CO_2 calculated from the adsorption isotherms collected at 273 K and 298 K; (d) CH₄ adsorption isotherms collected at 273 K.

The microporous nature of the BODIPY-containing polymer networks inspired us to investigate their gas uptake capacity. Fig. 4a shows the hydrogen sorption curves

of the polymer networks measured at 77.3 K up to a pressure of 1.13 bar. BDPCMP1059/C6NJ01812B exhibits the largest hydrogen uptake capacity of 115 cm³ g⁻¹ (~1.02 wt%) among the four polymer networks, which is comparable to that of some other porous polymers at the same conditions, such as the nitrogen-rich CMP of DA-CMP1 (1.01 wt%, S_{BET} = $662 \text{ m}^2 \text{ g}^{-1}$),³⁸ the borazine-linked porous polymer of BLP-1 (0.68 wt%, S_{BET} = $503 \text{ m}^2 \text{ g}^{-1}$),³⁹ the isoindigo-based microporous organic polymer of TBMIDM (0.95 wt%, S_{BET} = $763 \text{ m}^2 \text{ g}^{-1}$),⁴⁰ the nitrogen-rich azo-bridged porphyrin conjugated microporous network of Azo-1 (0.86 wt%, S_{BET} = $571 \text{ m}^2 \text{ g}^{-1}$),⁴¹ and the phthalazinone-based covalent triazine framework of PHCTF-1b (0.66 wt%, S_{BET} = $955 \text{ m}^2 \text{ g}^{-1}$),⁴² although it is still lower than that of the carbazole-based CPOP-1 with the hydrogen uptake capacity of 2.80 wt% at 1.13 bar/77.3 K,¹ the copolymerized conjugated microporous polymer of CP-CMP5 (2.24 wt%, S_{BET} = $2241 \text{ m}^2 \text{ g}^{-1}$),⁴⁴

The CO₂ uptakes of the polymer networks were measured up to 1.13 bar at 273 K and 298 K, respectively. As shown in Fig. 4b, all of the polymers show high CO₂ uptake since the microporous nature of the polymers and the heteroatoms (B, N, F) from BODIPY unit enhanced the binding affinity between the polymer and CO₂ molecules. It is noteworthy that the CO₂ adsorption capacity of these polymers persistently increases with increasing the pressure, and has not reached saturation at 1.13 bar, indicating that higher CO₂ uptake ability can be achieved at higher pressures. The polymer networks of BDPCMP-2 shows the highest CO₂ uptake ability of 2.25 mmol g⁻¹ at 1.13 bar/273 K among the four polymers, which could be attributed to its higher micropore surface area ratio (87.28%) and micropore volume ratio (75.00%) as discussed above. In addition, the elemental analysis showed that the BDPCMP-2 has the highest nitrogen containing (5.38%) among the four polymers, which could be

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The CO₂ uptake capacity of 2.25 mmol g^{-1} for BDPCMP-2 is higher than that of many other reported CMPs produced from Sonogashira-Hagihara coupling reaction under the same conditions (Table 2), such as the amide-functionalized CMP of CMP-1-AMD1 (1.51 mmol g^{-1} , $S_{BET} = 316 \text{ m}^2 g^{-1}$),⁴⁶ the pyrene-based porous aromatic framework of PAF-20 (1.16 mmol g^{-1} , $S_{BET} = 702 \text{ m}^2 g^{-1}$),⁴⁷ and the hexabenzocoronene-based porous organic polymer of HBC-POP-1 (2.05 mmol g⁻¹, $S_{BET} = 668 \text{ m}^2 \text{ g}^{-1}$.⁴⁸ It is also much higher than that of some other type of porous materials with much higher BET surface area under the same conditions, such as PAF-1 (2.1 mmol g^{-1} , $S_{BET} = 5460 \text{ m}^2 \text{ g}^{-1}$),⁴⁹ COF-102 (1.56 mmol g^{-1} , $S_{BET} = 3620$ $m^2 g^{-1}$),⁵⁰ the tetraphenylmethane-based HCPs (1.66 mmol g^{-1} , $S_{BET} = 1679 m^2 g^{-1}$),⁵¹ and the spirobifluorene-based porous organic polymer of POP-1 (1.92 mmol g⁻¹, S_{BET} = 983 m² g⁻¹).⁵² It has been proved that the electron-rich porous polymers networks can yield strong dipole-quadrupole interaction with polarizable CO₂ molecules, and thus leading to a significant increase in the CO_2 capture capacity. Therefore, the high CO₂ uptake ability of these BODIPY-based polymer networks could be mainly attributed to the nature of the heteroatom-rich (N, B, F) porous polymers, which enhanced the interactions between the polymer networks and CO₂ molecules. However, due to the moderate surface area, the CO₂ uptake capacities of these BODIPY-based polymers are still low in comparison with those of the leading CO₂ adsorbents (Table 2), such as the imine-linked porous polymer network of PPF-1 (6.1 mmol g^{-1} , $S_{BET} = 1740 \text{ m}^2 \text{ g}^{-1}$,²⁰ the porous pyridine-functionalized polymer of P-PCz (5.57 mmol g^{-1} , $S_{BET} = 1647 \text{ m}^2 \text{ g}^{-1}$),⁵³ the fluorinated polycarbazole covalent triazine framework of FCTF-1-600 (5.5 mmol g^{-1} , $S_{BET} = 752 m^2 g^{-1}$),⁵⁴ and the porous covalent triazine polymer network of PCTP-1 (4.92 mmol g^{-1} , $S_{BET} = 1200 m^2$

 g^{-1}).²³ Therefore, one could expect to get high surface area porous polymers. With g^{-1} with g^{-1} enhanced gas adsorption ability by using some non-planar three-dimensional comonomers (such as tetraphenylmethane, tetraphenyl adamantine and triptycene) for polymerization with BODIPY since these three-dimensional building blocks are efficient to produce high surface area porous organic polymers.^{24, 55–58}

	$S_{ m BET}$	CO ₂ uptake ^a	Ref.	
Porous materials	$[m^2 g^{-1}]$	$[mmol g^{-1}]$		
BDPCMP-2	582	2.25	this work	
CMP-1-AMD1	316	1.51	46	
PAF-20	702	1.16	47	
HBC-POP-1	668	2.05	48	
PAF-1	5460	2.1	49	
COF-102	3620	1.56	50	
HCPs	1679	1.66	51	
POP-1	983	1.92	52	
PPF-1	1740	6.1	20	
P-PCz	1647	5.57	53	
FCTF-1-600	752	5.5	54	
PCTP-1	1200	4.92	23	

Table 2. Summary of the CO₂ uptake capacity of some reported porous materials

^a data obtained at 1.13 bar and 273 K.

The isosteric heat of adsorption (Q_{st}) of the polymers was calculated from the Clausius-Clapeyron equation using the CO₂ adsorption data collected at 273 K and 298 K. As shown in Fig. 4c, all of the polymer networks show high isosteric heats of CO₂ adsorption over 23 kJ mol⁻¹, indicating that the incorporation of BODIPY unit into the framework of the porous polymers enhanced the binding affinity between the porous polymer and CO₂ molecules. BDPCMP-4 shows a slight higher Q_{st} (27.3 kJ mol⁻¹) than the other three polymers at the zero-coverage, which could be attributed to the smaller micropore size of BDPCMP-4 as discussed above, and small pore sizes known to increase the heat of adsorption. All of the polymers show nearly constant Q_{st} over a wide range of CO₂ loading, which suggests that a significantly higher CO₂

micropore volumes of the adsorbent. The Q_{st} values of these polymer networks are comparable to those of many known porous polymers, such as the porous benzimidazole-linked polymers (26.7-28.8 kJ mol⁻¹),³⁴ the carbazole-based CMPs (27.1-30.8 kJ mol⁻¹),⁵⁹ and the tetraphenylethylene-based HCPs (23.3-28.2 kJ mol^{-1}),⁶⁰ although they are lower than those of some porous polymers with strong polar groups, such as PAF-26-COONa (35 kJ mol⁻¹),⁶¹ PPN-6-SO₃Li (35.7 kJ mol^{-1}),⁶² PPN-6-SO₃NH₄ (40 kJ mol⁻¹),⁶² and TBMID (33.5 kJ mol⁻¹).⁴⁰ The CH₄ uptake of the polymer networks was measured up to 1.13 bar at 273 K (Fig. 4d). BDPCMP-2 exhibits the largest methane uptake capacity of 0.70 mmol g^{-1} among the four polymer networks, which is comparable to that of some other reported porous polymers, such as PMETBC (0.65 mmol g^{-1} , $S_{BET} = 540 \text{ m}^2 \text{ g}^{-1}$), ⁵⁹ CP-CMP7 (0.74 mmol g^{-1} , $S_{BET} = 699 \text{ m}^2 \text{ g}^{-1}$),⁴³ InCz-HCP1 (0.84 mmol g^{-1} , $S_{BET} = 750 \text{ m}^2 \text{ g}^{-1}$),⁶³ and TBMID (0.75 mmol g^{-1} , $S_{BET} = 688 \text{ m}^2 \text{ g}^{-1}$),⁴⁰ although it is still low in comparison with that of the benzimidazole-linked polymer of BILP-2 (0.87 mmol g^{-1})³⁴ and the nanoporous azo-linked polymer of ALP-4 (0.89 mmol g^{-1}).²¹

In order to investigate the gas adsorption selectivity of the microporous polymer networks, CO₂, N₂, and CH₄ sorption properties were measured by volumetric methods at the same conditions. The selectivity of the polymer networks was first estimated using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at 273 K at the low pressure coverage less than 0.10 bar (*Fig. S3-6*). All of the polymers show very similar CO₂/CH₄ adsorption selectivity of around 5.1:1 at 273 K (Table 3), which is comparable to that of most other reported porous polymers, such as the phosphine oxide-based conjugated microporous polymer of TEPO-1 (12.6:1),⁶⁴ the nitrogen-rich

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conjugated microporous polymer of Azo-CMP2 (5.3:1)³⁶ and the isoindigo base dew Article Online microporous organic polymer of TBMID (9.7:1).⁴⁰ The calculated CO₂/N₂ adsorption selectivity for the polymers varies between 31.1:1 and 38.6:1 (Table 3). Though the CO_2/N_2 adsorption selectivities are moderate compared with those of some other reported MOPs with the CO_2/N_2 adsorption selectivity higher than 100, such as the tetraphenylethylene-based HCPs (119 for Network-7),⁶⁰ the porous covalent electron-rich organonitridic frameworks (109 for PECONF-1),⁶⁵ and the amine-based aromatic tri(4-ethynylphenyl) porous framework (251)for PAF-33-NH₂),⁶⁶ BDPCMP-2 shows higher CO₂ adsorption capacity than those adsorbents (Network-7: 1.92 mmol g⁻¹, PECONF-1: 1.86 mmol g⁻¹, and PAF-33-NH₂: 1.19 mmol g^{-1}) under the same conditions. Ideally, high uptake and selectivity are both required for practical applications. As such, the good CO₂ adsorption performance by these polymer networks make them potential candidates for applications in post-combustion CO_2 capture and sequestration technology. The gas adsorption selectivities were also predicted for $CO_2:N_2$ (15:85) and $CO_2:CH_4$ (5:95) mixtures by using ideal adsorbed solution theory (IAST) (Table 3), which is widely used to predict binary gas mixture adsorption selectivity in many porous materials.^{67–69} The calculated IAST selectivities are higher than the values obtained from Henry's constant ratios as observed for most reported porous organic polymers.^{70,} 71

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	Table 3. Summary of gas uptakes for the polymer networks						DOI: 10.1039/C6NJ01812E		
Polymer	H_2 uptake ^a	$^{\text{L}}$ CH ₄ uptake ^b	CO_2 uptake ^b	CO_2 uptake ^c	Henry Law Selectivity ^d		IAST Selectivity ^e		
	[wt%]	[inition g]	[iiiiioi g]	[inition g] -	CO_2/N_2	CO ₂ /CH ₄	CO ₂ /N ₂	CO ₂ /CH ₄	
BDPCMP-1	0.80	0.48	1.68	1.03	38.6	5.4	65.2	8.4	
BDPCMP-2	1.02	0.70	2.25	1.45	32.3	5.1	55.3	8.4	
BDPCMP-3	0.96	0.60	2.03	1.24	31.1	5.1	50.2	9.1	
BDPCMP-4	0.84	0.56	1.91	1.23	34.1	5.4	58.2	9.9	

Table 3. Summary of gas uptakes for the polymer networks

^a Data obtained at 77.3 K and 1.13 bar; ^b Data collected at 273 K and 1.13 bar; ^c Data collected at 298 K and 1.13 bar; ^d Selectivity was calculated by initial slope method at 273 K; ^e Selectivity was calculated by IAST method at the molar ratio of 15:85 for CO₂/N₂ and 5:95 for CO₂/CH₄ at 273 K.

4. Conclusion

In conclusion, BODIPY-functionalized microporous organic polymer networks have been synthesized via Sonogashira-Hagihara cross-coupling reaction. These polymer networks are stable in various solvents tested and thermally stable in nitrogen atmosphere. All of the polymers show high isosteric heats of CO₂ adsorption (23.3~27.3 kJ mol⁻¹) because the incorporation of electron-rich BODIPY unit into the skeleton of the porous polymers enhanced the binding affinity between the porous polymer and CO_2 molecules. The polymer BDPCMP-2 shows a high CO_2 uptake ability of 2.25 mmol g^{-1} and a CO₂/N₂ adsorption selectivity of 32.3. These results demonstrated that these BODIPY-containing microporous organic polymers are promising candidates for potential applications in post-combustion CO₂ capture and sequestration technology.

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Materials and Devices (2015-skllmd-04).

References

- 1 Q. Chen, M. Luo, P. Hammershoj, D. Zhou, Y. Han, B. W. Laursen, C. G. Yan and B. H. Han, J. *Am. Chem. Soc.*, 2012, **134**, 6084.
- 2 R. Dawson, E. Stöckel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, 4, 4239.
- 3 C. Gu, N. Huang, J. Gao, F. Xu, Y. H. Xu and D. L. Jiang, *Angew. Chem. Int. Ed.*, 2014, **53**, 4850.
- 4 L. Chen, Y. Honsho, S. Seki and D. L. Jiang, J. Am. Chem. Soc., 2010, 132, 6742.
- 5 Y. H. Xu, L. Chen, Z. Q. Guo, A. Nagai and D. L. Jiang, J. Am. Chem. Soc., 2011, 133, 17622.
- 6 X. D. Zhuang, F. Zhang, D. Q. Wu, N. Forler, H. W. Liang, M. Wagner, D. Gehrig, M. R. Hansen, F. Laquai and X. L. Feng, *Angew. Chem. Int. Ed.*, 2013, **52**, 9668.
- 7 R. S. Sprick, J.-X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2015, **137**, 3265.
- 8 V. S. Vyas and B. V. Lotsch, Nature, 2015, 521, 41.
- 9 F. Xu, X. Chen, Z. W. Tang, D. C. Wu, R. Fub and D. L. Jiang, *Chem. Commun.*, 2014, **50**, 4788.
- 10 P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.*, 2004, **40**, 230.
- 11 S. Y. Ding and W. Wang, Chem. Soc. Rev., 2013, 42, 548.
- 12 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 and A. I. Cooper, *Angew. Chem. Int. Ed.*, 2007, 46, 8574.
- 13 A. I. Cooper, Adv. Mater., 2009, 21, 1291.
- 14 J.-X. Jiang and A. I. Cooper, Top. Curr. Chem., 2010, 293, 1.
- 15 D. Yuan, W. Lu, D. Zhao and H. C. Zhou, Adv. Mater., 2011, 23, 3723.
- 16 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, Angew. Chem. Int. Ed., 2009, 48, 9457.
- 17 P. Kuhn, M. Antonietti and A. Thomas, Angew. Chem. Int. Ed., 2008, 47, 3450.

- 18 S. J. Xu, Y. L. Luo and B. Tan, Macromol. Rapid Commun., 2013, 34, 471.
- 19 F. X. Li and L. S. Fan, Energy Environ. Sci., 2008, 1, 248.
- 20 Y. L. Zhu, H. Long and W. Zhang, Chem. Mater., 2013, 25, 1630.
- 21 P. Arab, M. G. Rabbani, A. K. Sekizkardes, T. İslamoğlu and H. M. El-Kaderi, *Chem. Mater.*, 2014, 26, 1385.
- 22 J. Byun, S.-H. Je, H. A. Patel, A. Coskun and C. T. Yavuz, J. Mater. Chem. A, 2014, 2, 12507.
- 23 P. Puthiaraj, S.-S. Kim and W.-S. Ahn, Chem. Eng. J., 2016, 283,184.
- 24 S. Dey, A. Bhunia, D. Esquivelb and C. Janiak, J. Mater. Chem. A, 2016, 4, 6259.
- 25 Y. Ni and J. S. Wu, Org. Biomol. Chem., 2014, 12, 3774.
- 26 Z. Kostereli, T. Ozdemir, O. Buyukcakir and E. U. Akkaya, Org. Lett., 2014, 14, 3636.
- 27 L.-Y. Niu, Y.-S. Guan, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, J. Am. Chem. Soc., 2012, **134**, 18928.
- 28 Y. Ooyama, Y. Hagiwara, T. Mizumo, Y. Harima and J. Ohshita, New J. Chem., 2013, 37, 2479.
- 29 M. Liras, M. Iglesias and F. Sánchez, Macromolecules, 2016, 49, 1666.
- 30 X. D. Zhuang, D. Gehrig, N. Forler, H. W. Liang, M. Wagner, M. R. Hansen, F. Laquai, F. Zhang and X. L. Feng, *Adv. Mater.*, 2015, 27, 3789.
- 31 S. Bernhardt, M. Kastler, V. Enkelmann, M. Baumgarten and K. Müllen, *Chem. Eur. J.*, 2006, 12, 6117.
- 32 K. Yuan, P. G. Wang, T. Hu, L. Shi, R. Zeng, M. Forster, T. Pichler, Y. Chen and U. Scherf, *Chem. Mater.*, 2015, 27, 7403.
- 33 S. H. Lim1, C. Thivierge, P. N. Sliwinska, J. Y. Han, H. V. D. Bergh, G. Wagnières, K. Burgess and H. B. Lee, J. Med. Chem., 2010, 53, 2865.
- 34 M. G. Rabbani and H. M. El-Kaderi, Chem. Mater., 2012, 24, 1511.
- 35 K. Sing, D. Everett, R. Haul, L. Moscou, R. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.
- 36 J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. Jones, Y. Z. Khimyak and A. I. Cooper, J. Am. Chem. Soc., 2008, 130, 7710.
- 37 J. Weber, M. Antonietti and A. Thomas, Macromolecules, 2008, 41, 2880.

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- 38 X. Y. Wang, Y. Zhao, L. L. Wei, C. Zhang and J.-X. Jiang, J. Mater. Chem. A, 2015, 3, 21185^{View Article Online} 39 T. E. Reich, K. T. Jackson, S. Li, P. Jena and H. M. El-Kaderi, J. Mater. Chem., 2011, 21, 10629.
- 40 Y. Zhao, X. Y. Wang, C. Zhang, F. Y. Xie, R. Kong and J.-X. Jiang, *RSC Adv.*, 2015, 5, 100322.
- 41 Y. Xu, Z. Li, F. Zhang, X. Zhuang, Z. Zeng and J. Wei, RSC Adv., 2016, 6, 30048.
- 42 K. Yuan, C. Liu, J. Han, G. Yu, J. Wang, H. Duan, Z. Wang and X. Jian, *RSC Adv.*, 2016, 6, 12009.
- 43 M. Yu, X. Wang, X. Yang, Y. Zhao and J.-X. Jiang, Polym. Chem., 2015, 6, 3217.
- 44 R. M. Kassab, K. T. Jackson, O. M. El-Kadri and H. M. El-Kaderi, *Res. Chem. Intermed.*, 2011, 37, 747.
- 45 T. Islamoglu, S. Behera, Z. Kahveci, T.-D. Tessema, P. Jena and H. M. El-Kaderi, ACS Appl. Mater. Interfaces, 2016, 8, 14648.
- 46 T. Ratvijitvech, R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Polymer*, 2014, **55**, 321.
- 47 Z. J. Yan, H. Ren, H. P. Ma, R. R. Yuan, Y. Yuan, X. Q. Zou, F. X. Sun and G. S. Zhu, *Microporous Mesoporous Mater.*, 2013, **173**, 92.
- 48 C. M. Thompson, F. Li and R. A. Smaldone, Chem. Commun., 2014, 50, 6171.
- 49 T. Ben, C. Y. Pei, D. L. Zhang, J. Xu, F. Deng, X. F. Jing and S. L. Qiu, *Energy Environ. Sci.*, 2011, 4, 3991.
- 50 H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 8875.
- 51 X. F. Jing, D. L. Zou, P. Cui, H. Ren and G. S. Zhu, J. Mater. Chem. A, 2013, 1, 13926.
- 52 Q.-Y. Ma, B.-X. Yang and J.-Q. Li, RSC Adv., 2015, 5, 64163.
- 53 T. Jin, Y. Xiong, X. Zhu, Z. Tian, D.-J. Tao, J. Hu, D.-E. Jiang, H. Wang, H. Liu and S. Dai, *Chem. Commun.*, 2016, **52**, 4454.
- 54 Y. F. Zhao, K. X. Yao, B. Y. Teng, T. Zhang and Y. Han, Energy Environ. Sci., 2013, 6, 3684.
- 55 D. Y. Chen, S. Gu, Y. Fu, Y. L. Zhu, C. Liu, G. H. Li, G. P. Yu and C. Y. Pan, *Polym. Chem.*, 2016, **7**, 3416.
- 56 Y. B. Wei, W. B. Chen, X. Y. Zhao, S. Y. Ding, S. Han and L. Chen, Polym. Chem., 2016, 7,

3983.

- 57 B. Zhang, G. Y. Li, J. Yan and Z. G. Wang, J. Phys. Chem. C, 2015, 119, 13080.
- 58 C. Zhang, P.-C. Zhu, L. Tan, J.-M. Liu, B. Tan, X.-L. Yang and H.-B. Xu, *Macromolecules*, 2015, **48**, 8509.
- 59 X. Y. Wang, Y. Zhao, L. L. Wei, C. Zhang, X. Yang, M. Yu and J.-X. Jiang, *Macromol. Chem. Phys.*, 2015, **216**, 504.
- 60 S. W. Yao, X. Yang, M. Yu, Y. H. Zhang and J.-X. Jiang, J. Mater. Chem. A, 2014, 2, 8054.
- 61 H. P. Ma, H. Ren, X. Q. Zou, S. Meng, F. X. Sun and G. S. Zhu, Polym. Chem., 2014, 5, 144.
- 62 W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna and H. C. Zhou, J. Am. Chem. Soc., 2011, 133, 18126.
- 63 D. Chang, M. Yu, C. Zhang, Y. Zhao, R. Kong, F. Y. Xie and J.-X. Jiang, *Microporous Mesoporous Mater.*, 2016, **228**, 231.
- 64 S. L. Qiao, W. Huang, Z. K. Du, X. H. Chen, F.-K. Shiehc and R. Q. Yang, New J. Chem., 2015, 39, 136.
- 65 P. Mohanty, L. D. Kull and K. Landskron, Nat. Commun., 2011, 2, 401(1-6).
- 66 W. G. Lu, W. M. Verdegaal, J. M. Yu, P. B. Balbuena, H.-K. Jeong and H. C. Zhou, *Energy Environ. Sci.*, 2013, 6, 3559.
- 67 S. Wu, S. Gu, A. Zhang, G. Yu, Z. Wang, J. Jian and C. Pan, J. Mater. Chem. A, 2015, 3, 878.
- 68 X. Zhang, J. Z. Lu and J. Zhang, Chem. Mater., 2014, 26, 4023.
- 69 G. Y. Li, B. Zhang and Z. G. Wang, Macromolecules, 2016, 49, 2575.
- 70 Y. Yuan, P. Cui, Y. Tian, X. Zou, Y. Zhou, F Sun and G. S. Zhu, Chem. Sci., 2016, 7, 3751.
- 71 T. Islamoglu, T. Kim, Z. Kahveci, O. M. El-Kadri and H. M. El-Kaderi, J. Phys. Chem. C, 2016, 120, 2592.

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BODIPY-containing microporous organic polymers were synthesized via Sonogashira-Hagihara coupling reaction from a BODIPY derivative and a range of aryl-alkyne monomers.



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BODIPY-Containing Porous Organic Polymers for Gas Adsorption