

# Highly Selective CO<sub>2</sub>-Capturing Polymeric Organic Network Structures

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The combustion of hydrocarbon fuels to satisfy the current energy requirements increases the emission of gases that contribute to global-warming<sup>[1]</sup> and thus to climate change, such as carbon dioxide (CO<sub>2</sub>). Porous structures including COFs (covalent organic frameworks),<sup>[2]</sup> PIMs (polymers of intrinsic microporosities),<sup>[3]</sup> HCPs (hyper-cross-linked polymers),<sup>[4]</sup> CMPs (conjugated microporous polymers),<sup>[1c,5]</sup> and CTFs (covalent triazine-based frameworks)<sup>[6]</sup> have been considered to be very successful in capturing CO<sub>2</sub> with high capacities. Meanwhile, there is still the great challenge of realizing highly selective CO<sub>2</sub>-capturing materials for practical use in ambient conditions, which could allow many practical applications and help to significantly slow the greenhouse effect.

Herein, we report new highly selective CO<sub>2</sub>-capturing polymeric organic networks (PONs) synthesized using (methanetetrayltetra-4,1-phenylene)tetrakisboronic acid and three kinds of halogen-substituted struts that include heterocyclic groups. The structures and morphology of the networks are studied by solid-state NMR, Fourier-transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). PON-1 has only phenyl group, while PON-2 and -3 contain pyridyl and thiophenyl groups, respectively. While all the PONs have moderate surface areas, they are very attractive for use in capturing a large amount of CO<sub>2</sub> under ambient conditions. Moreover, it was found that PONs offer high selective adsorption for CO<sub>2</sub> over CH<sub>4</sub> and H<sub>2</sub> under ambient conditions.

(Methanetetrayltetra-4,1-phenylene)tetrakisboronic acid<sup>[8]</sup> has been used as a tetrahedral building unit to assemble into highly porous three-dimensional network structures. It also has the potential to react with various dihalogenated struts, and there are many useful coupling reactions between boronic acids and halogen atoms on diverse aromatic and heterocyclic compounds.<sup>[7]</sup> For the efficient synthesis of porous structures, we selected representative conditions of the coupling reaction using (methanetetrayltetra-4,1-phenylene)tetrakisboronic acid and 1,4-dibromobenzene to give a tetrahedral structure (Supporting Information, Table S1). The reactions were carried out at 90 °C in the presence of water for 5 days to give sufficient

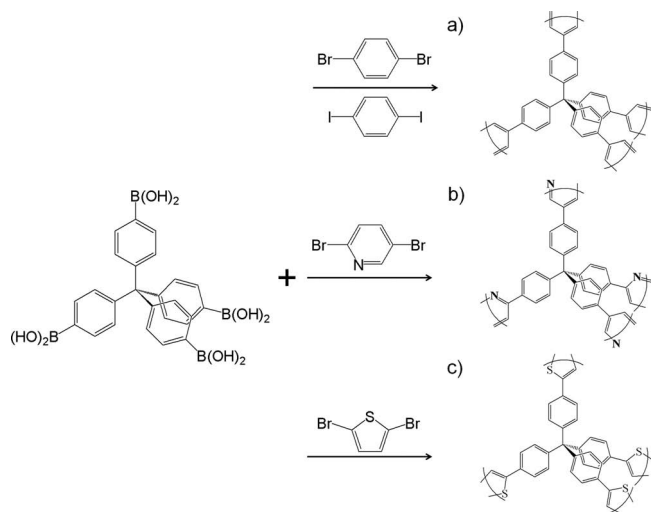
reaction times. Except under conditions using toluene and 1,2-dimethoxyethane (DME), we found that insoluble polymers were produced. Next, the polymers recovered after filtration were washed with CH<sub>2</sub>Cl<sub>2</sub>, HCl solution, MeOH, and acetone and dried for 3 days at 150 °C in a vacuum. Despite the excess washing, some polymer networks exhibited yields in excess of 100%. This observation implies that the condensation rate is lower than expected, thus some reactants remain and contribute to the sample mass.<sup>[5e,5f]</sup> The Brunauer-Emmett-Teller (BET) method was used to determine the surface areas using desorption branches over 0.05–0.25 P/P<sub>0</sub> of Ar isotherm at 87 K.<sup>[2d]</sup> The reaction without water was found not to result in the relevant polymerization. In addition, we found that a combination of relevant base and solvent chemicals was more important for the polymerization than the catalyst itself. N,N-Dimethylformamide (DMF) and 1,4-dioxane are appropriate for Na<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub>, respectively, for this purpose. The TGA results indicate that all the synthesized structures were very stable without solvents in the structures (Supporting Information, Figure S1), although their elemental compositions varied with reaction conditions (Supporting Information, Table S1). Compared to the networks formed using DMF, the products formed with 1,4-dioxane showed low contents of carbon, but high yields. These results imply that reactions with 1,4-dioxane as solvent have a relatively lower condensation rate than that with DMF. Furthermore, as the product of entry 7 using Pd(OAc)<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, and a mixture of DMF and H<sub>2</sub>O was unveiled to give a good surface area of 763 m<sup>2</sup> g<sup>-1</sup> (Langmuir surface 1087 m<sup>2</sup> g<sup>-1</sup>), we conducted additional experiments with this reaction condition over different reaction times (Supporting Information, Table S2). As a result, we found that a reaction time of 24 h is sufficient for polymerization, and this resulted in a highly porous polymeric organic network designated as PON-1, with a surface area of 999 m<sup>2</sup> g<sup>-1</sup> (Langmuir surface 1438 m<sup>2</sup> g<sup>-1</sup>). Also, we synthesized tetrahedral structures with 1,4-diiodobenzene, 2,5-dibromopyridine, and 2,5-dibromothiophene, as demonstrated in **Figure 1**. These resulted in dark gray, yellow, and brown polymers, respectively, which were insoluble in organic solvents and acid condition (Supporting Information, Table S3).

**Figure 2** shows <sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) NMR spectra, where the peaks at ca. 64 ppm arise from the central C atoms of tetraphenylmethane and the peaks at ca. 145 ppm from core C atoms in the benzene ring. Also, the peaks at ca. 126 and 130 ppm indicate C atoms in the –CH units of the benzene ring. These results demonstrate that PONs were constructed from the starting materials. Meanwhile, the intensity of the signal at ca. 139 ppm arising from C atoms

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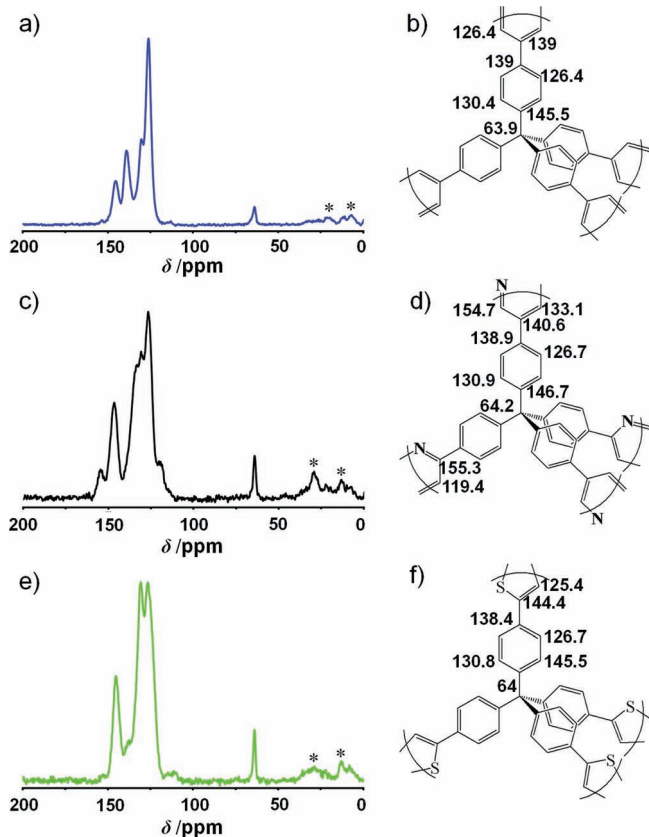


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**Figure 1.** Synthetic strategy for a) PON-1, b) PON-2, and c) PON-3.

bound to a phenyl ring was quite variable according to the kind of strut used. The weak peaks at 139 ppm peaks in the spectra of PON-2 and -3 show that the degrees of polymerization in these cases were relatively low. However, there are unique peaks arising from pyridine and thiophene in the spectra of PON-2



**Figure 2.** Solid-state  $^{13}\text{C}$  CP-MAS NMR spectra of a) PON-1, c) PON-2, and e) PON-3.  $^{13}\text{C}$  chemical shift assignments for b) PON-1, d) PON-2, and f) PON-3. Asterisks denote spinning sidebands.

and -3, and the elemental analysis corroborates the existence of heterocycles in the network structures (Supporting Information, Table S3). Elemental analysis of PON-1 demonstrates that the polymerization of benzene occurs more actively than for heterocyclic compounds. In addition, FT-IR measurements were obtained from pressed KBr pellets of the PONs (Supporting Information, Figure S2). The spectra unveil a significant decrease in presence of the boronic acid hydroxyl groups, which thus demonstrates formation of the phenyl–phenyl or phenyl–heterocyclic bonding. However, despite the significant decrease of the intensity of signals arising from the boronic acid, PON-3 still shows some absorption due to this. SEM shows that PON-1 has an aggregated nanoparticle morphology while PON-2 and -3 contain fused polymeric masses (Supporting Information, Figure S3). In addition, the TGA shows that the PONs possess high decomposition temperatures with the maximum weight loss occurring in excess of 450 °C (Supporting Information, Figure S4).

The porosity of the PONs was measured using Ar and  $\text{N}_2$  as adsorbate molecules (Supporting Information, Figure S5). **Table 1** shows the BET surface areas calculated with Ar and their corresponding Langmuir surface areas. PON-1 showed a type IV isotherm with H4 hysteresis and type IV isotherm with H2 hysteresis on the Ar and  $\text{N}_2$  isotherms, respectively. Although the hysteresis of PON-1 is different with the used gases, the type IV isotherms demonstrate clearly that PON-1 is composed of micropores and mesopores. The pore size distribution of PONs was obtained using nonlocal density functional theory (NL-DFT) from Ar isotherms with an Ar cylinder pore kernel at 87 K (Supporting Information, Figure S6). PON-1 contains micropores of ca. 5.5 Å and mesopores. A combination of micropores and mesopores was also confirmed by using the  $\text{N}_2$  isotherm at 77 K with the similar pore size distribution (Supporting Information, Figure S7). This measurement showed shoulders around the specific mesopore sizes, which indicates an irregular pore size distribution. The surface area of PON-1 made from 1,4-diiodobenzene was revealed to be higher than that of PON-1 from 1,4-dibromobenzene, which could be attributed to the reactivity of the strut molecule, 1,4-diiodobenzene. In general, a benzene molecule substituted with iodine atoms is more reactive than one substituted with bromine atoms, which thus gives a high degree of condensation.<sup>[7]</sup> Meanwhile, PON-2 and -3 showed type III isotherms with H3 hysteresis. The pyridine and thiophene used for PON-2 and -3 were less suitable for formation of porous structures compared to substituted benzene molecules, as demonstrated by their lower BET surface areas. This result is consistent with the weakness of the 139 ppm peak in the NMR data and with the FTIR data of PON-3. In particular, the strut of PON-3, 2,5-dibromothiophene is part of a pentagonal structure and the orientation of the two bromine atoms is not parallel, such that the molecule does not offer the proper cross-linking angle. We consider that this mismatch induces the coupling reaction in a random and sparse network structure which includes a residue of reactants like the boronic acid. As a result, this structure lost porosity. The total pore volumes calculated with Ar at  $P/P_0^{-1} = 0.99$  for PONs were 0.89  $\text{cm}^3 \text{g}^{-1}$  for PON-1, 0.71  $\text{cm}^3 \text{g}^{-1}$  for PON-2, and 0.18  $\text{cm}^3 \text{g}^{-1}$  for PON-3.

**Table 1.** Surface areas, pore volumes, and gas-sorption capacity of PONs.

Network	BET Surface Area [m <sup>2</sup> g <sup>-1</sup> ] <sup>a)</sup>	Langmuir Surface Area [m <sup>2</sup> g <sup>-1</sup> ] <sup>a)</sup>	Total Pore Volume [cm <sup>3</sup> g <sup>-1</sup> ] <sup>b)</sup>	BET Surface Area [m <sup>2</sup> g <sup>-1</sup> ] <sup>c)</sup>	Langmuir Surface Area [m <sup>2</sup> g <sup>-1</sup> ] <sup>c)</sup>	Total Pore Volume [cm <sup>3</sup> g <sup>-1</sup> ] <sup>d)</sup>	CO <sub>2</sub> Uptake [mg g <sup>-1</sup> ] <sup>e)</sup>
PON-1	1422	2054	0.89	1447	2067	1.0	976
PON-2	168	253	0.71	189	282	0.83	482
PON-3	51	333	0.18	44	168	0.09	525

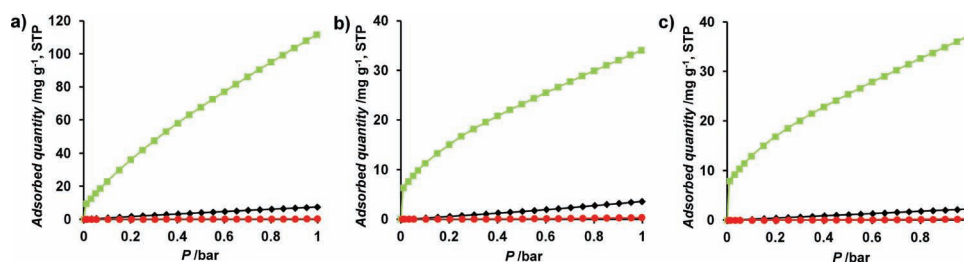
<sup>a)</sup>Calculated using desorption branches over 0.05–0.25 P P<sub>0</sub><sup>-1</sup> of Ar isotherm at 87 K; <sup>b)</sup>calculated from Ar adsorption at P P<sub>0</sub><sup>-1</sup> = 0.99; <sup>c)</sup>calculated using desorption branches over 0.05–0.25 P P<sub>0</sub><sup>-1</sup> of N<sub>2</sub> isotherm at 77 K; <sup>d)</sup>calculated from N<sub>2</sub> adsorption at P P<sub>0</sub><sup>-1</sup> = 0.99; <sup>e)</sup>CO<sub>2</sub> storage capacity at 195 K and 1 bar.

Despite the fact that PON-2 and 3 have a small number of pores, we ascertain that nitrogen and sulfur atoms present within the structures offer favorable interactions with CO<sub>2</sub> compared with those containing only carbon atoms. The reversible sorption data for CO<sub>2</sub> were determined through volumetric measurements at both 195 K and 298 K. The CO<sub>2</sub>-uptake abilities at 195 K were 976 mg g<sup>-1</sup> for PON-1, 482 mg g<sup>-1</sup> for PON-2, and 525 mg g<sup>-1</sup> for PON-3. Although the surface areas of PON-2 and -3 are approximately 8–32 times lower than that of PON-1, PON-2 and -3 exhibited higher CO<sub>2</sub>-uptake abilities. Interestingly, PON-3 exhibited a higher CO<sub>2</sub> uptake than PON-2. The result of a high CO<sub>2</sub>-uptake capacity without a high surface area is explained by the kinetic diameters of the adsorbate molecules.<sup>[5b,9]</sup> The kinetic diameter of CO<sub>2</sub> (3.3 Å) is smaller than that of N<sub>2</sub> (3.64 Å) and the small CO<sub>2</sub> molecules can access small pores, which are difficult to access for N<sub>2</sub> molecules. Since these amorphous network structures have a broad range in pore size distribution, are linked in a complex way, and swell during drying and gas sorption, this may affect their gas adsorption capacity.<sup>[5g]</sup> Also, there is a possibility that the presence of lone-pair electrons on the heteroatoms is important for selective CO<sub>2</sub> adsorption. Although the pyridyl and thiophenyl struts would not be suitable for formation of highly porous network structures due to their low activity as well as to the pentagonal structure of thiophene, lone-pair electrons appear to play a critical role in providing strong interaction sites through dipole-dipole interactions.<sup>[10]</sup> Meanwhile, the high CO<sub>2</sub>-uptake capacity of PON-1 might be attributed due to the high porosity caused by the coexistence of micropores and mesopores, as reported in our recent experimental finding that a pomegranate-like crystal which contains mesopores and micropores increases the CO<sub>2</sub>-uptake capacity.<sup>[11]</sup> Moreover, the PONs showed a very high

CO<sub>2</sub>-uptake capacity at 298 K at 1 bar with values of 109 mg g<sup>-1</sup> for PON-1, 34 mg g<sup>-1</sup> for PON-2, and 37 mg g<sup>-1</sup> for PON-3. Although PON-1 has a lower surface area of about 1400 m<sup>2</sup> g<sup>-1</sup> than PAF-1 (5600 m<sup>2</sup> g<sup>-1</sup>) and MOF-177 (4500 m<sup>2</sup> g<sup>-1</sup>), it shows a higher CO<sub>2</sub>-uptake capacity at 298 K.<sup>[5g,12]</sup>

We also determined the CO<sub>2</sub>-capturing selectivity of our PONs from CH<sub>4</sub> and H<sub>2</sub> gases at 298 K and 1 bar (**Figure 3**). The selective separation of CO<sub>2</sub> is very important in that it could give a clean and durable energy supply by control of disastereous CO<sub>2</sub> molecules. The uptake capacity of CH<sub>4</sub> was 7.1 mg g<sup>-1</sup> for PON-1, 3.4 mg g<sup>-1</sup> for PON-2, and 2.2 mg g<sup>-1</sup> for PON-3 and the trend of the values corresponded to the surface areas. The values for H<sub>2</sub> were 0.2, 0.3, and 0.2 mg g<sup>-1</sup> for PON-1, -2, and -3, respectively. These values demonstrate that CH<sub>4</sub> and H<sub>2</sub> are hardly adsorbed onto the PONs, and give clear proof that the PONs, especially PON-1, have a very high selectivity for CO<sub>2</sub> under ambient conditions.

In summary, PONs were synthesized using (methane-tetra-yltetra-4,1-phenylene)tetrakisboronic acid and three kinds of halogen-substituted struts that included heterocyclic compounds. Our adsorption data demonstrate that the degree of polymerization for our PON structures is affected by the choice of struts and that the resulting PONs are very attractive to capture a large amount of CO<sub>2</sub> with high uptake. Moreover, it was found that PONs offer high selective adsorption for CO<sub>2</sub> over CH<sub>4</sub> and H<sub>2</sub> under ambient conditions. These high CO<sub>2</sub>-uptake capacity and separation by PONs may be attributed to the pore size distribution in polymeric network structures, the coexistence of mesopores and micropores for PON-1 and the dipole-dipole interaction between CO<sub>2</sub> and lone-pair electrons on the nitrogen and sulfur atoms for PON-2 and -3.



**Figure 3.** Selective CO<sub>2</sub>-capturing capability of a) PON-1, b) PON-2, and c) PON-3 at 298 K. CO<sub>2</sub>: green squares; CH<sub>4</sub>: black diamonds; H<sub>2</sub>: red circles.

## Experimental Section

**Synthesis of PON-1:** (Methanetetrayltetra-4,1-phenylene)tetrakisboronic acid (124 mg, 0.25 mmol) and 1,4-diodobenzene (165 mg, 0.5 mmol) were added to a mixture of sodium carbonate (212 mg, 2 mmol), and palladium(II) acetate (4.5 mg, 0.02 mmol) in DMF (10 mL) and distilled water (10 mL). The mixture was stirred at 90 °C for 24 h. After cooling to room temperature, the product was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL), 5 N HCl solution (3 × 50 mL), MeOH (3 × 50 mL), and acetone (3 × 50 mL), respectively. The product was dried in vacuo to give PON-1 as a dark gray powder (108.5 mg, 93% yield). Calcd for C<sub>37</sub>H<sub>24</sub>: C 94.87, H 5.13; found: C 89.58, H 5.37.

PON-2, and -3 were synthesized by same procedure used for PON-1 with struts of 2,5-dibromopyridine (119 mg, 0.5 mmol) for PON-2, and 2,5-dibromothiophene (121 mg, 0.5 mmol) for PON-3. The yields were 81% for PON-2, and 79% for PON-3. Calcd for C<sub>35</sub>H<sub>22</sub>N<sub>2</sub>: C 89.36, H 4.69, N 5.95; found: C 75.07, H 4.52, N 4.10 for PON-2; calcd for C<sub>33</sub>H<sub>20</sub>S<sub>2</sub>: C 82.5, H 4.17, S 13.33; found: C 70.1, H 4.04, S 9.22 for PON-3.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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