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## Synthesis of 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane and its microporous polycyanurate network for adsorption of organic vapors, hydrogen and carbon dioxide<sup>†</sup>

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This report presents the synthesis of a tetraphenyladamantanebased microporous polycyanurate network with a BET surface area of 843 m<sup>2</sup> g<sup>-1</sup> and a pore size of 7.8 Å. It uptakes 98.0 wt% benzene (298 K,  $P/P_0 = 0.9$ ), 1.49 wt% H<sub>2</sub> (77 K/1 bar) and 12.8 wt% CO<sub>2</sub> (273 K/1 bar) with CO<sub>2</sub>/N<sub>2</sub> selectivity of up to 112.

Microporous organic polymers (MOPs) with large surface areas and excellent physicochemical stability are a newly developed class of functional polymer materials, having shown promising potential in  $H_2$  storage,  $CO_2$  capture, recovery of organic vapors, heterogeneous catalysis and low-k materials, *etc.*<sup>1</sup> The synthesis of MOPs requires an elaborate selection of building blocks,<sup>2</sup> which should be sufficiently rigid to open up the polymer segments to form pores. Moreover, MOPs usually have hypercross-linked structures<sup>1–3</sup> to retain their permanent microporous characteristics in harsh environments such as high temperature, high humidity and varied pressure.

Cyanate resins refer to the compounds containing two or more cyanate groups (–NCO) per molecule. Upon heating, the –NCO groups are cyclotrimerized to form a hyper-cross-linked polycyanurate network with triazine-ring net nodes linked with ether linkages.<sup>4</sup> Abundant heteroatoms in the network are quite appealing for MOPs because the nitrogen- and oxygen-rich microporous polymers generally possess high CO<sub>2</sub> adsorption capabilities due to enhanced dipole–quadrupole interaction between the polymer skeleton and CO<sub>2</sub> molecules.<sup>1c,5</sup> Moreover, in contrast to other triazine-based microporous polymers such as CTFs<sup>6</sup> that are prepared by the cyclotrimerization of aromatic nitriles in molten ZnCl<sub>2</sub> at very high temperatures of over 400 °C, the crosslinking reactions of cyanate resins can be readily conducted at a significantly lower temperature without the utilization of corrosive ZnCl<sub>2</sub> medium or tedious evacuating and tube-sealing operations.<sup>7</sup> In this paper, we present the first report of the design and synthesis of a tetraphenyladamantane-based cyanate resin monomer, 1,3,5,7-tetrakis(4-cyanatophenyl)adamantane (TCAD). After cyclotrimerization in diphenylsulfone, a three-dimensional crosslinked network is obtained, in which there are two kinds of net nodes, *i.e.*, a tetraphenyladamantane node and a triazine-ring node. The incorporation of rigid and bulky tetraphenyladamantanes ensures the generation of pores, while the triazine-ring nodes further subdivide the void into smaller pores, resulting in micropores and even ultramicropores (pore size smaller than 7 Å). It has been reported that an ultramicroporous structure is advantageous for the adsorption of small gas molecules, such as H<sub>2</sub> and CO<sub>2</sub>, because of a trapping effect.<sup>1d,8</sup>

The synthetic routes of cyanate monomer **TCAD** and its polycyanurate network are outlined in Scheme 1. The bromination of TPAD catalyzed by iron powder in a chloroform solution of bromine gives **TBAD**. The reaction of **TBAD** with sodium methoxide



Scheme 1 Synthetic routes of cyanate monomer TCAD and its polycyanurate network (PCN-AD).

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and cuprous bromide yields **TMAD**. Subsequently, **THAD** is obtained through a demethylation reaction of **TMAD** by boron tribromide, which is then converted to the target product **TCAD** by the reaction of **THPA** with cyanogen bromide using triethylamine to absorb the generated acid. Finally, the polycyclotrimerization of **TCAD** in diphenylsulfone using nonylphenol as a catalyst leads to the tetraphenyladamantane-based polycyanurate network (**PCN-AD**).

The chemical structures of TCAD and its polymerized product were confirmed by various methods. For TCAD, IR absorption of -O- $C \equiv N$  appears at 2238 and 2270 cm<sup>-1</sup> (Fig. 1). The bands at 2938 and 2836 cm<sup>-1</sup> are attributed to the stretching vibrations of the CH<sub>2</sub> and CH groups in the adamantane moiety. All the resonance peaks in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for TCAD (Fig. S1 and S2, ESI<sup>†</sup>) can be assigned to the corresponding protons or carbons. After polymerization, absorptions belonging to  $-O-C \equiv N$  disappear completely. Instead, PCN-AD displays characteristic bands of the triazine ring at 1559 and 1361 cm<sup>-1,7,9</sup> Furthermore, the solidstate <sup>13</sup>C CP/MAS NMR spectrum (Fig. S3, ESI<sup>+</sup>) shows a signal at 174 ppm, attributed to the carbons of the triazine ring. The two phenyl carbons adjacent to adamantane and the ether group appear at 150 and 154 ppm, respectively. A strong signal at 39 ppm is because of the aliphatic carbon atoms of adamantane,<sup>8a</sup> while the unsubstituted phenyl carbon signals are located at 126 and 116 ppm. The calculated chemical compositions for the networks are consistent with the measured values by elemental analysis.

The resultant **PCN-AD** is amorphous, as revealed by the XRD pattern (Fig. S4, ESI<sup>†</sup>). Thermogravimetric analysis exhibits decompositions at around 450 and 540 °C (Fig. S5, ESI<sup>†</sup>) due to the cleavages of the triazine ring and aromatic skeleton, respectively.<sup>7,9</sup> The FE-SEM image of **PCN-AD** displays the typical morphology of MOPs composed of agglomerates of tiny particles (Fig. S6a, ESI<sup>†</sup>).<sup>7,10</sup> The HR-TEM observation shows that **PCN-AD** has uniform pore channels (Fig. S6b, ESI<sup>†</sup>).

The sorption isotherm of  $N_2$  at 77 K for **PCN-AD** shows a rapid uptake at very low relative pressure (Fig. 2), which is indicative of substantially microporous material. The major pore appears at around 7.8 Å (NLDFT), which is close to the ultramicroporous



**Fig. 2** Nitrogen adsorption/desorption isotherms for the polycyanurate network at 77 K (the inset shows the pore size distribution obtained by the NLDFT method).

0.4

Relative pressure, P/P

0.6

0.8

1.0

0.2

0.0

region. Similar to other MOPs, the sample exhibits hysteresis with the desorption curve lying above the adsorption curve because of the swelling effect in liquid nitrogen.<sup>11</sup> The BET surface area of **PCE-6** is 843 m<sup>2</sup> g<sup>-1</sup> and the total pore volume determined from the nitrogen isotherm at  $P/P_0 = 0.9$  is 0.62 cm<sup>3</sup> g<sup>-1</sup>.

The sorption isotherms of  $H_2$  and  $CO_2$  at different temperatures are presented in Fig. 3. The uptakes for both  $H_2$  and  $CO_2$  show an obvious drop with an increase in temperature, indicating that adsorption is physical in nature. The  $H_2$  uptake of 1.49 wt% at 77 K/1 bar is considerably higher than that of other microporous cyanate resins (**CEs**) (0.45–1.11 wt%),<sup>7</sup> and is comparable to most MOPs reported in the literature, even though some of them possess larger surface areas. The high  $H_2$  uptake of **PCN-AD** probably arises from its uniform and small pore size. The isosteric enthalpies of adsorption from  $H_2$  isotherms display a decreasing trend with adsorption capacity (Fig. 4), implying that  $H_2$  is preferentially adsorbed on the pore surface rather than aggregated with the  $H_2$ molecules itself.



Fig. 1 FTIR spectra of cyanate monomer TCAD and its polycyanurate network PCN-AD.



Fig. 3 Adsorption (filled) and desorption (empty) isotherms of  $CO_2$  and  $H_2$  for the polycyanurate network.



Fig. 4 Variations of isosteric enthalpies with the adsorbed amounts of  $H_2$  and  $CO_2$  for the polycyanurate network.

The virial plots of  $H_2$  and  $CO_2$  adsorptions of **PCN-AD** at different temperatures display good linear relationships (Fig. S7, ESI<sup>†</sup>). The intercepts are the first virial coefficients ( $A_0$ ), while Henry's constant ( $K_H$ ) is obtained by the equation  $K_H = \exp(A_0)$ , and the enthalpy of adsorption ( $Q_0$ ) at zero surface  $CO_2$  coverage is derived from the plot slope of  $\ln K_H$  vs. 1/*T*. Table S1 (ESI<sup>†</sup>) shows that the  $Q_0$  value of  $H_2$  for **PCN-AD** is 8.19 kJ mol<sup>-1</sup>. This value exceeds polyimides (**PIs**) (5.3–7.0 kJ mol<sup>-1</sup>),<sup>2</sup> COFs (6.0–7.0 kJ mol<sup>-1</sup>),<sup>12</sup> PAF-1 (4.6 kJ mol<sup>-1</sup>),<sup>13</sup> PPNs (5.5–7.6 kJ mol<sup>-1</sup>)<sup>1c,14</sup> and BILPs (7.8–8.3 kJ mol<sup>-1</sup>).<sup>15</sup>

**PCN-AD** can uptake 65.4 cm<sup>3</sup> g<sup>-1</sup> (12.8 wt%) CO<sub>2</sub> at 273 K/1 bar, which is the highest among the microporous cyanate resins,<sup>7</sup> and is superior to several triazine-based porous polymers such as PAF-16 (8.3 wt%).<sup>16</sup> The reason is that, in addition to the nitrogen-rich triazene rings, large numbers of oxygen atoms in **PCN-AD** also play a positive role in its CO<sub>2</sub> adsorption. This deduction is supported by the higher enthalpy of adsorption of **PCN-AD** (32.4 kJ mol<sup>-1</sup>) than that of PAF-16 (30.3 kJ mol<sup>-1</sup>).

On the other hand, the sorption curves at 273 K (Fig. S8, ESI<sup>†</sup>) show that the uptake of CO<sub>2</sub> is remarkably higher than that of N<sub>2</sub> and CH<sub>4</sub>. The CO<sub>2</sub>/N<sub>2</sub> selectivity of **PCN-AD** derived from the initial slope method is 112 (Fig. S9, ESI<sup>†</sup>), which is among the highest values for MOPs, including those of MPI-1 (102),<sup>10</sup> BILP-2 (113),<sup>15b</sup> and Py-1 (117).<sup>5a</sup> The CO<sub>2</sub>/CH<sub>4</sub> value of 11 is also comparable to other MOPs.

The adsorption isotherms of benzene, cyclohexane and water vapors are measured at 298 K and illustrated in Fig. 5. **PCN-AD** exhibits simultaneously high uptakes of benzene (98.0 wt%) and cyclohexane (57.4 wt%) at  $P/P_0 = 0.9$  because the tetraphenyladamantane moiety provides both cycloaliphatic and aromatic components in the network. In comparison with the organic vapors, the isotherm of water is a typical type III adsorption, displaying significantly lower adsorption capacity than those of the organic vapors, which is indicative of the hydrophobic nature of **PCN-AD**.

In summary, a new tetraphenyladamantane-based cyanate monomer and its microporous polycyanurate network have been



Fig. 5 Adsorption isotherms of organic and water vapors at 298 K for the polycyanurate network.

successfully synthesized, and the network has a large BET surface area of 843 m<sup>2</sup> g<sup>-1</sup> with a major pore size of 7.8 Å. The polymer uptakes 98.0 wt% benzene, 57.4 wt% cyclohexane (298 K,  $P/P_0 = 0.9$ ), 1.49 wt% H<sub>2</sub> (77 K/1.0 bar), and 12.8 wt% CO<sub>2</sub> (273 K/1.0 bar), and the selectivities of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/ CH<sub>4</sub> are as high as 112 and 11, respectively, which are the highest values among the reported microporous cyanate resins and superior to many other porous polymers, exhibiting potential applications in H<sub>2</sub> storage, CO<sub>2</sub> capture and recovery of toxic organic vapors.

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