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Tetraphenyladamantane-based microporous polyimide for adsorption of carbon dioxide, hydrogen, organic and water vapors[†]

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Tetraphenyladamantane-based microporous polyimide was synthesized. It can uptake 14.6 wt% CO_2 at 273 K and 1 bar, 99.2 wt% benzene and 59.7 wt% cyclohexane at 298 K and 0.9 bar, exhibiting potential applications in gas storage and recovery of organic pollutants.

Adamantane is a cycloaliphatic hydrocarbon with diamond-like cage structure. It is attractive because its bulky molecular volume, rigidity and highly symmetrical tetrahedral shape render it an ideal building block for the construction of metal-organic frameworks (MOFs) and microporous organic polymers. Adamantane contains six secondary carbons and four tertiary carbons. Relatively, the four hydrogens attached to the tertiary carbons are chemically more active, and can be easily halogenated,¹ carboxylated² and nitrated.³ Moreover, after arylation, the four phenyls surrounding the adamantane core are convenient for further functionalization. In these aspects, Yaghi et al. synthesized 1,3,5,7-adamantane tetracarboxylic acid² and 1,3,5,7tetrakis(4-carboxylatophenyl)adamantane⁴ and used them for MOFs. Antonietti reported a covalent triazine-based framework obtained from 1,3,5,7-tetrakis(4-cyanophenyl)adamantane.⁵ Cooper et al. synthesized a conjugated microporous polymer from 1,3,5,7tetrakis(4-bromophenyl)adamantane⁶ via Yamamoto coupling reaction. Zhou et al. prepared a microporous polymer by homocoupling reaction of 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane.⁷

In the past years, some microporous polyimides have been developed, including linear polyimides with intrinsic microporosity and hyper-cross-linked microporous polyimide networks synthesized *via* polycondensation from various dianhydrides with tetrakis-(4-aminophenyl)methane, tris(4-aminophenyl)amine and 1,3,5-tris(4-aminophenyl)benzene.⁸ Up to now, however, microporous polyimides constructed from the tetraphenyladamantane unit have not appeared in the literature. In fact, different from other microporous polyimide network is unique since, besides the possible microporous structure

and large surface area, it simultaneously contains heterocyclic, cycloaliphatic and aromatic components. The abundant nitrogen and oxygen atoms in the imide ring may give rise to high carbon dioxide (CO_2) adsorption owing to the dipole–quadrupole interactions between the pore surface and the CO_2 molecule,⁹ while the large amount of phenyls and aliphatic rings can enhance affinity for both aromatic and aliphatic vapors, which are desirable as adsorbents for removal of organic pollutants in the environmental protection field.

The syntheses of the tetraamine monomer 1,3,5,7-tetrakis-(4-aminophenyl)adamantane (TAPA) and the polyimide network (PI-ADPM) are depicted in Scheme 1. The raw compound tetraphenyladamantane (TPA) was obtained from 1-bromoadamantane and benzene in the presence of $AlCl_3$.¹⁰ Then, with reference to the procedure¹¹ with some modifications, the nitration of TPA and subsequent reduction by Pd/C gave 1,3,5,7-tetrakis(4-aminophenyl)adamantane (TAPA) in good yield. The polyimide network was prepared through one-pot polycondensation in *m*-cresol from TAPA and pyromellitic dianhydride (PMDA), using isoquinoline as a catalyst.



Scheme 1 Synthesis route of the polyimide network.

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Fig. 1 (a) Nitrogen adsorption–desorption isotherm of the polyimide network at 77 K, and (b) pore size distribution obtained by the NLDFT method.

The resultant brown solid is insoluble in any common organic solvents, indicative of the hyper-cross-linked structure. In the FTIR spectrum (Fig. S1, ESI[†]), the bands at 1776 cm⁻¹ and 1720 cm⁻¹ are attributed to the asymmetric and symmetric vibrations of the imide ring, respectively. The absorption at 1375 cm⁻¹ is due to the characteristic vibration of the C–N–C linkage. As shown in the ¹³C solid NMR spectrum (Fig. S2, ESI[†]), the resonance at around 40.9 ppm belongs to the carbons of adamantane, while that at 166.0 ppm is ascribed to the carbonyl carbon of the imide ring. The signal at 151.2 ppm is attributed to the carbons appear at 126–139 ppm.

The microporosity of PI-ADPM was examined by the physical sorption of nitrogen at 77 K (Fig. 1). The steep rise in nitrogen uptake at the low relative pressure indicates its microporous structure as evidenced by the pore size distribution derived from nonlinear density functional theory (NLDFT), which displays two microporous peaks at 1.06 nm and 1.34 nm, and one ultramicroporous peak at 0.68 nm. From the sorption isotherm, the calculated BET and Langmuir surface areas are 868 m² g⁻¹ and 1154 m² g⁻¹, respectively. Its total pore volume calculated at $P/P_0 = 0.99$ and micropore volume derived from the *t*-plot method are 0.372 cm³ g⁻¹ and 0.319 cm³ g⁻¹, respectively.

The CO₂ sorption isotherm of PI-ADPM was measured at 273 K and 298 K (Fig. 2), which shows a 14.6 wt% CO₂ uptake at 273 K and 1 bar. This value is higher than those of many porous organic polymers under the same conditions like COF-5 (5.9 wt%, 1670 m² g⁻¹),¹² COF-103 (7.6 wt%, 3530 m² g⁻¹),¹² and BLP-1H (7.4 wt%, 1360 m² g⁻¹)¹³ even though they have larger surface area.

The isosteric enthalpies of adsorption (Q_{st}) were calculated from the CO₂ isotherms at different temperatures.¹⁴ As shown in Fig. 3, the Q_{st} values display an apparently decreasing trend with the adsorbed amount of CO₂, implying that the gas–material interaction is stronger than the gas–gas interaction. The virial plots of CO₂ for the polyimide have good linear relationships at both temperatures (Fig. 4), from which the first virial coefficients can be calculated. Subsequently, Henry's law constant (K_{H}) is obtained using the equation $K_{H} = \exp(A_0)$, whereas the limiting enthalpy of adsorption (Q_0), *i.e.*, Q_{st} at zero surface CO₂ coverage, is derived from the plot



Fig. 2 Adsorption isotherms of CO₂ and H₂ of the polyimide network.



Fig. 3 Variations of isosteric enthalpies with the adsorbed amount of H_2 and CO_2 .



Fig. 4 Virial plots of CO₂ and H₂ for the polyimide network.

slope of $\ln K_{\rm H}$ vs. 1/*T*. As a measure of the interaction between the pore wall and the CO₂ molecule, the Q_0 value of CO₂ is 34.4 kJ mol⁻¹ (Table S1, ESI[†]), which is higher than those for other porous materials such as ZTF-1 (25.4 kJ mol⁻¹)¹⁵ and BILP-1 (26.5 kJ mol⁻¹).¹⁶ This is due to the enhanced affinity for the CO₂ molecule because of



Fig. 5 Organic and water vapor adsorption isotherms at 298 K of the polyimide network, P_0 is the saturated vapor pressure of those vapors.

the abundant nitrogen and oxygen atoms in the polyimide network as well as the molecular sieving effects of the micropores and ultramicropores.^{9,17}

At 77 K and 1 bar, PI-ADPM exhibits 1.27 wt% hydrogen (H₂) uptake. It can be seen that, in the measured pressure range, the H₂ uptake has not reached saturation, implying that larger storage can be expected at higher pressure. The high adsorption capacity may have arisen from the ultramicropores in the polyimide network.¹⁸ The $Q_{\rm st}$ values calculated according to the H₂ isotherms recorded at 77 K and 87 K display a rapid decrease with the adsorbed amount, indicative of the favourable interaction between the network and H₂. Table S1 (ESI[†]) shows that the Q_0 value is 6.76 kJ mol⁻¹, similar to those of other porous polymers and microporous polyimides.⁸c,¹²

The adsorption isotherms of benzene, *n*-hexane, cyclohexane and water vapors measured at 298 K are illustrated in Fig. 5. It is interesting to observe that the presence of cycloaliphatic structure results in PI-ADPM possessing significantly higher uptakes of aliphatic vapors than the wholly aromatic porous polymers. For example, the adsorbed amounts of hexane and cyclohexane for PI-ADPM are as high as 49.8 wt% and 59.7 wt%, respectively, whereas the values for microporous polybenzimidazoles19 and porous aromatic frameworks (PAF-2)²⁰ are only 1 to 8 wt%. Most recently, a porphyrin-based porous polymer also exhibited exceptional uptake capacity of saturated hydrocarbons.²¹ On the other hand, PI-ADPM exhibits an uptake of 99.2 wt% benzene vapor, surpassing the previously reported polymers with a similar BET surface area such as CE-1 (960 m² g⁻¹, 58.5 wt%),²² PAF-2 $(891 \text{ m}^2 \text{ g}^{-1}, 13.8 \text{ wt}\%)$ and PAF-11 $(891 \text{ m}^2 \text{ g}^{-1}, 87.4 \text{ wt}\%)$.²³ This may be attributed to the strong π - π interaction between the benzene molecule and the phenyl groups as well as the more opened pore channels caused by the bulky tetraphenyladamantane nodes. In contrast, the isotherm for water vapor exhibits type V sorption, indicative of the hydrophobic nature of the PI-ADPM network. As a consequence, its uptake of water vapor is 28.45 wt%, lower than that of the organic vapors.

In conclusion, we have successfully synthesized a microporous polyimide network based on the tetraphenyladamantane unit. The sample uptakes 14.6 wt% CO_2 at 273 K and 1 bar and 1.27 wt% H_2 at 77 K and 1 bar. Different from previous porous

polymers, the tetraphenyladamantane simultaneously possesses aromatic and aliphatic characteristics, which endow it with remarkably high uptakes of both aromatic and alkyl hydrocarbon vapors, exhibiting promising applications in environmental protection as adsorbents to adsorb organic pollutants.

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