Imide-linked microporous organic framework polymers for CO_2 adsorption

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A B S T R A C T

Microporous organic polymers containing CO_2-philic functionality gained much attention for their efficient CO_2 adsorption capability. Based on the combination of purely organic rigid and contorted macromolecular structures with low skeletal density, a series of imide-linked organic framework polymers with intrinsic microporosity (PIM-OFPs), have been synthesized using cost-effective protocol. Porosity analysis indicates that PIM-OFPs exhibit high BET surface areas ranging from 826 to 1381 $m^2 g^{-1}$ with uniform pore size distribution as verified by HK and NLDFT analyses. The CO_2 adsorption studies show a notable uptake capacity up to 4.91 (21.60 wt.%) and 3.19 $mmolg^{-1}$ (14.04 wt.%) at 273 and 295 K/1 bar respectively, combined with high isosteric heats of adsorption (28.52—30.56 kJ mol^{-1}). At higher pressure (35 bar), these polymers also show a high CO_2 uptake ability of 65.95 (295 K) and 42.84 wt. % (323 K). The impressive CO_2 adsorption capacity can be attributed to the significance of the microporosity and the imide functionalities within the framework structure. Moreover, their high physicochemical stability and good CO_2/N_2 selectivities, PIM-OFPs considered as a potential candidate for application in CO_2 scrubbing technology.

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1. Introduction

Carbon dioxide is thought to be one of the contributing factors in the rise of global warming [1]. Consequently the discovery for an efficient and economically valuable gas capturing system is highly in demand. Therefore there have been various recent developments in creating new, efficient and adaptable gas capturing materials [2]. Microporous organic based materials received great research efforts in the field of environmental related applications such as gas storage and separations due to their permanent porosity, low density (i.e. composed of light weight elements) and remarkable physicochemical stability [3]. Other fascinating features such as the great flexibility in surface chemical composition and structural architecture modifications by introducing a wide range of functionalities into their framework structure are also characterized by such materials. Therefore many linking moieties (e.g. triazine (CTF) [4], tetrazole [5], imidazole [6], phosphazene [7], imide [8,9], amine [10], carbazole [11], azo-bridged [12], have been used to build up

pore-functionalized organic frameworks that have high specific BET surface area and large storage gas capacity with applicable selectivity. For example, decorating the accessible pore wall of the organic frameworks by nitrogen containing functionality (nitrogen sites) has found a great impact on their gas uptake ability and selectivity. Accordingly, the excellent loading capacity of CO_2 with high selectivity over N_2 can be attributed the enhanced interaction of CO_2 with the framework through dipole—quadrupole interaction and/or hydrogen bonding [13]. The narrow pore size distribution which is characterized by these material, must be also considered in facilitating the multiwall interactions and consequently increase the upload capacity. Here it is worth to note that the CO_2 as greenhouse gas should be removed safely to reduce the global warming effect of CO_2. For that reason, developing a porous organic material with a competitive CO_2 absorption capacity under ambient conditions represent an alternative process to replace the expensive and existing chemical absorption method using ethanolamine solutions [14]. Based on the above aforementioned findings, many strategies have been adapted to synthesize microporous organic material with abundant nitrogen containing moieties content as a recently arising parameter to increase the CO_2 uptake capacity [15]. However, other functionalities such as sulfonic acid, lithium

sufonate, were also introduced and exhibit promising CO_2 adsorption capacities along with high CO_2/N_2 selectivity [16]. Therefore, many organic building blocks, characterized by irregularities, rigidity and functionalities as key properties to maximize the CO_2 uptake capacity, were covalently introduced in preparing microporous organic frameworks with desired properties for CO_2 storage and separation applications [17]. Seeking to obtain polymeric materials with outstanding properties in terms of chemical nature and porous properties as a perquisite for a gas storage and separation applications represents an on-going target by the researchers. This leads to design and construct different microporous organic based materials by exploiting the facile synthetic protocols as well as the diversification of primary building block organic components. Thus, five monomers containing different rigid aryl spacers have been prepared and incorporated into the PIM-based frameworks by using the efficient dioxane-forming reaction with the spirobiscatechol. The gas-adsorption properties of the resulting organic framework polymers have been evaluated to propose the related porous properties to the monomer architecture featuring imide moieties within the scaffold network polymers. The CO_2 storage capacities, isosteric heat of adsorption and the selectivity of CO_2 over N_2 gas were also evaluated.

2. Materials and methods

All the chemicals were of reagent grade purity and used without further purification. The dry solvent Dimethylformamide (DMF) with water content less than 0.005% was purchased from Aldrich Co. The finely grounded anhydrous potassium carbonate was used after further drying at 200 °C. ^{1}H-NMR spectrum of monomers were recorded on a Bruker DPX 400 MHz spectrometer using CDCl$_3$ and DMSO-D6 as the solvents. Solid state ^{13}C-NMR measurement was carried out on a Bruker Avance II 600 MHz spectrometer equipped with a cross polarization magic angle spinning (CP/MAS) probe and a fully automated pneumatic unit for sample spinning. FT-IR spectra were recorded on a JASCO FT/IR-6300. Elemental analyses were carried out using Elementar Vario Micro Cube. Mass analyses were done on a Thermo DFS Mass spectrometer. Melting points were measured with a Griffin melting point apparatus. Thermogravimetric analysis (TGA) was performed with a TA instrument at a heating rate of 10 °C/min under nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) of sample was measured by a Siemens D5000 diffractometer. Microscopic techniques employed are Scanning Electron Microscopy (SEM: JEOL Model 6300) and High Resolution Transmission Electron Microscopy (HRTEM: JEOL Model JEM- 3010). Nitrogen and CO_2 adsorption measurements and were performed on a Micromeritics ASAP 2020 sorptometer. The high pressure CO_2 adsorption capacity was investigated (35 bar, 295 and 323 K) using a high pressure volumetric analyzer (Micromeritics HPVA-100).

2.1. Synthesis of monomer (1a)

Tetrafluorophthalic anhydride was added to a stirred solution of 4,4′-methylenedianiline in glacial acetic acid and refluxed for 12 h. After cooling, the precipitated product was filtered and washed with petroleum ether to give a light yellow solid. Yield 78%; mp > 300 °C; ^{1}H NMR (DMSO-d6, 400 MHz, δ ppm): 4.11 (s, 2H), 7.37−7.39 (d, 4H), 7.45−7.47 (d, 4H); IR (KBr) ν/cm^{-1}: 3044, 2925, 1781, 1725, 1509, 1409, 1375, 1313, 1090, 944, 755. CHN Calc. (%) for C$_{29}$H$_{10}$F$_8$N$_2$O$_4$ (602.40) C, 57.82; H, 1.67; N, 4.65. Found: C, 57.56; H, 1.82; N, 4.78; MS (EI): m/z (%) 602 (M$^+$, 100%).

The other octafluoro monomers (1b, 1c, 1d & 1e) with different imide-linked spacers were synthesized and characterised according to the above mentioned procedure [See ESI † Figs S1(a-e) and S2 (a-e)].

2.2. 1b

Yield 76%; mp > 300 °C; ^{1}H NMR (DMSO-d6, 400 MHz, δ ppm): 8.2 (d), 7.8 (d), 7.75 (t). IR (KBr) ν/cm^{-1}: 3077, 2971, 1789, 1725, 1733, 1509, 1409, 1313, 1090, 944, 751. CHN Calc. (%) for C$_{26}$H$_6$F$_8$N$_2$O$_4$ (562.34) C, 55.53; H, 1.08; N, 4.98. Found: C, 55.60; H, 1.15; N, 5.16; MS (EI): m/z (%) 562 (M$^+$, 100%).

2.3. 1c

Yield 70%; mp > 300 °C; ^{1}H NMR (DMSO-d6, 400 MHz, δ ppm) 2.08 (s, 12H); IR (KBr), ν/cm-1: 1792, 1730, 1511, 1499, 945. CHN Calc. (%) for C$_{26}$H$_{12}$F$_8$N$_2$O$_4$ (568.38): C, 54.94; H, 2.13; N, 4.93. Found: C, 54.92; H, 2.17; N, 5.16; MS (EI): m/z (%) 568 (M$^+$, 60).

2.4. 1d

Yield 75%; mp > 300 °C; ^{1}H NMR (DMSO-d6, 400 MHz, δ ppm): 7.61 (s, 4H), 2.20 (s, 12H); IR (KBr) ν/cm^{-1}: 2971, 2926, 1777, 1728, 1509, 1405, 1363, 1181, 1098, 948, 792. CHN Calc. (%) for C$_{32}$H$_{16}$F$_8$N$_2$O$_4$ (644.48) C, 59.64; H, 2.50; N, 4.35. Found: C, 59.56; H, 2.52; N, 4.57; MS (EI): m/z (%) 642 (M$^+$, 100%).

2.5. 1e

Yield 80%; mp > 300 °C; ^{1}H NMR (DMSO-d6, 400 MHz, δ ppm): 7.64 (d 4H) 7.59 (d, 4H); IR (KBr) ν/cm^{-1}: 3106, 3045, 1784, 1728, 1719, 1604, 1517, 1366, 1251, 1205, 1176, 1133, 1089, 971, 940, 901, 839, 768, 739. CHN Calc. (%) for C$_{31}$H$_8$F$_{14}$N$_2$O$_4$ (738.40) C, 50.43; H, 1.09; N, 3.79. Found: C, 50.26; H, 1.18; N, 3.65; MS (EI): m/z (%) 738 (M$^+$, 20%).

3. Synthesis of PIM-OFP-1

A mixture of monomer 1a (0.753 g, 1.25 mmol) and spirobiscatechol (0.851 g, 2.5 mmol) in dry DMF (100 ml) and finely ground anhydrous K$_2$CO$_3$ (2.1 g) was heated at 100 °C for 24 h. After cooling, the reaction mixture was poured into deionised water and the solid product collected by filtration and washed with methanol. The purification was done by refluxing the crude product with deionised water, THF, methanol and acetone respectively. The obtained yellow fluorescent powder was dried under vacuum 100 °C for 24 h (Yield 80%), mp > 300 °C; ^{13}C CP/MAS NMR (150 MHz) δ ppm 167.78, 149.23, 147.42, 145.86, 143.8, 142.41, 132.42, 130.59, 128.42, 125.40, 118.11, 117.92, 117.68, 115.35, 112.67, 58.36, d 40.5, 29.5; IR (KBr) ν/cm^{-1}: 3423, 2925, 2954, 1771, 1720, 1461, 1318, 1081, 986, 876, 787, 754. CHN Calc. (%) for C$_{71}$H$_{50}$N$_2$O$_{12}$ (1122) C, 75.93; H, 4.49; N, 2.49. Found: C, 70.89; H, 4.98; N, 2.57.

The other framework polymers were synthesized by using the same procedure adopted for PIM-OFP-1 (Scheme 1).

3.1. PIM-OFP-2

Yield 72%; mp > 300 °C; ^{13}C CP/MAS NMR (150 MHz) δ 151.27, 149.70, 143.77, 130.12, 114.72, 61.06, 56.66, 46.49, 33.04; IR (KBr) ν/cm^{-1}: 3425, 2931, 2955, 1773, 1723, 1723, 1461, 1318, 1211, 1091, 984, 876, 782, 756. CHN Calc. (%) for C$_{68}$H$_{52}$N$_2$O$_{12}$ (1082) C, 75.41; H, 4.25; N, 2.49. Found: C, 72.49; H, 4.31; N, 2.37.

3.2. PIM-OFP-3

Yield 81%; mp > 300 °C; ^{13}C CP/MAS NMR (150 MHz) δ 165.29,