Selective gas adsorption in a magnesium-based metal–organic framework†

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Received (in Cambridge, UK) 26th May 2009, Accepted 6th July 2009

A doubly interpenetrated magnesium-based porous metal–organic framework exhibits thermal stability up to 500 °C and selective gas sorption properties for H2 and O2 gases over N2, and CO2 gas over CH4.

Porous metal–organic frameworks (MOFs) have attracted great attention because of their potential applications in gas separation,1–9 gas storage,10,11 ion exchange,12 and fabrication of nanoparticles.13 In particular, MOFs that selectively absorb O2 over N2, and H2 over N2 are very important because they have potential to be applied in the separation of these gases from air and the H2 enrichment from the N2–H2 exhaust in ammonia synthesis, respectively. Despite their importance, MOFs that show selective gas adsorption behaviour are not so common.1–9,15–17 Although most of the porous MOFs reported so far are constructed from transition metal ions and organic building blocks, MOFs can be constructed from light main group metals such as Mg2+.14 The ionic radius of Mg2+ (74 pm) is similar to those of transition metals such as Zn2+ (74 pm) and Cu2+ (73 pm), but the molar mass of Mg is much smaller than those of transition metals.14 Therefore, Mg-based MOFs can provide a reduced framework density. Although Mg-based porous MOFs have been reported previously, they are still quite rare.5,15,16 They commonly show low porosity and low hydrogen uptake capacities, except [Mg4(dhtp)] (dhtp = 2,5-dihydroxyterephthalate) reported by Matzger and co-workers.15 Here, we report a doubly interpenetrated magnesium-based MOF, [Mg(TCPBDA)(H2O)2]-6DMF-6H2O (1), where TCPBDA2− is N,N,N′,N′'-tetrakis(4-carboxyphenyl)-biphenyl-4,4'-diamine. The desolvated solid of 1, [Mg(TCPBDA)] (SNU-25), which was prepared by heating 1 at 210 °C under vacuum for 4 h, exhibits thermal stability up to 500 °C, and selective gas sorption properties for H2 and O2 gases over N2 at 77 K, as well as for CO2 gas over CH4 at 195, 273, and 298 K.

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Yellow plate-shaped crystals of [Mg(TCPBDA)(H2O)2]-6DMF-6H2O (1) were prepared by heating Mg(NO3)2·6H2O and H4TCPBDA in DMF–EtOH–H2O (4 : 1 v/v) at 110 °C for 24 h. 1 was formed independently of the stoichiometry of Mg₂TCPBDA, contrary to common MOFs whose framework structures greatly depend on the stoichiometry. 1 was insoluble in common organic solvents such as DMF, EtOH, chloroform, acetone, 1,4-dioxane, and diethyl ether. The TCPBDA units in 1 exist as positively charged radicals, as evidenced by the X-ray crystal structure, elemental analysis data, and the EPR spectrum that shows a strong isotropic peak at g = 2.004 (see ESI†). It has been reported that a triarylamine can be easily oxidized to a cationic radical.17

The X-ray crystal structure of 1 is shown in Fig. 1. In 1, Mg2+ ions show an octahedral coordination geometry by binding four TCPBDA2− ligands at the equatorial positions and two water molecules at the axial positions. The average Mg–O TCPBDA bond distance is 2.102(4) Å and the Mg–O H2O bond distance is 2.113(5) Å. The nitrogen atoms of TCPBDA2− exhibit sp2 hybridization, showing unusually short N–C distances (av. 1.420(5) Å) and C–N–C bond angles of av. 120.0(0)°. The phenyl rings around the nitrogen atom in TCPBDA2− are tilted towards each other, with dihedral angles of av. 69.56(13)°. The dihedral angle between two central phenyl rings is 12.09(20)°. The coordinated aqua ligands form hydrogen bonds with free carbonyl oxygens (O100···O2 distance, 2.59(1) Å; O100···O3 distance, 2.86(1) Å) of TCPBDA2− to form six-membered rings (Fig 1a). Every square-shaped Mg2+ building unit is linked with four trapezoidal TCPBDA2− ions and every TCPBDA2− unit is linked to four Mg2+ units to give rise to a 3D network. Framework 1 is doubly interpenetrated, and the two phenyl rings of a TCPBDA2− unit are involved in face-to-face π-π interactions with those of the adjacent interpenetrated net.

Fig. 1 The X-ray crystal structure of 1. (a) An ORTEP drawing of 1. Hydrogen bonding interactions are indicated as dotted lines. Views of the doubly interpenetrated network seen on (b) the bc plane and (c) the ab plane.
(shortest C–C distance: 3.80(1) Å) (see ESI†). Framework 1 generates 3D channels that extend parallel to the crystallographic a, b, and c axes. Seen on the ab plane, there exist two kinds of channels, honeycomb- and rhombic-channels, whose window sizes are 3.5 Å × 8.6 Å and 1.3 Å × 2.4 Å, respectively. On the bc plane, channels with an effective aperture size of 6.0 Å × 7.8 Å are generated. The framework has two kinds of inner pores, the size of small pores is 6.8 Å and that of large pores is 11.6 Å as estimated by Material Studio software, version 4.1 (see ESI†). The channels are hydrophilic because the free carbonyl oxygen atoms of the TCPBDA ligands as well as the coordinated water molecules point toward the channels. The free void volume of 1 is 61.5% (62.7%) with (without) coordinated water molecules, as estimated by PLATON.18 Thermogravimetric analysis (TGA) of 1 indicates a 46.8 wt% weight loss at 25–250 °C, corresponding to the loss of six DMF and six H2O guests as well as two coordinated aqua ligands (calcld. 45.9%) per formula unit, and the framework is thermally stable up to 500 °C (see ESI†).

When 1 was heated at 210 °C under vacuum for 4 h, the coordinated water molecules as well as the guest solvent molecules were removed to result in the desolvated solid [Mg(TCPBDA)] (SNU-25), which contains open metal sites as clearly evidenced by the TGA data that show no weight loss up to 500 °C (see ESI†). The PXRD patterns of 1 and SNU-25, and the simulated pattern derived from the X-ray single crystal data of 1 are compared (see ESI†). The PXRD pattern of 1 is almost coincident with the simulated pattern, indicating that the bulk sample is the same as the single crystal. The PXRD pattern of SNU-25 is not exactly the same as that of the simulated one, but it shows peaks that match the positions for (020), (220) and (112) calculated from the X-ray single crystal data, indicating that some kind of change occurs on desolvation with the major framework structure maintained.

When SNU-25 is re-exposed to the vapor of DMF–H2O (28 : 7 v/v) at 38 °C for 3 days, the peak (112) disappears with the peaks corresponding to (020) and (220) remaining. It should be noted that SNU-25 adsorbs moisture on exposure to air, and its PXRD pattern shows a new peak at 2θ = 6.7° with the other peaks being retained (see ESI†), indicating a partial conversion to another phase.19

To see the porosity of SNU-25, the gas sorption isotherms were measured for N2, H2, O2, CO2, and CH4 gases (Fig. 2). SNU-25 slightly adsorbs N2 gas, 13.40 cm3 g−1 at 77 K and 1 atm. However, it adsorbs significant amounts of CO2 and CH4 gases at 195 K, 273 K, and 298 K, as well as H2 and O2 gases at 77 K and 87 K. The present selective gas sorption properties over N2 gas must be attributed to a molecular sieving effect, considering the kinetic diameters of the gases (H2: 2.89 Å; CO2: 3.3 Å; O2: 3.46 Å; N2: 3.64 Å; CH4: 3.82 Å).20 The better sorption capacity for CH4 than N2, despite the larger kinetic diameter of CH4 may be related to the stronger interaction of CH4 than N2 with the open Mg sites.21

SNU-25 adsorbs CO2 gas up to 26.3 wt% (134.05 cm3 g−1 at STP, 5.99 mmol g−1) at 195 K and 1 atm, 9.1 wt% (46.38 cm3 g−1 at STP, 2.07 mmol g−1) at 273 K and 1 atm, and 6.5 wt% (33.43 cm3 g−1 at STP, 1.49 mmol g−1) at 298 K and 1 atm. The DR (Dubinin–Radushkevich) surface area estimated from the CO2 sorption data at 195 K by using the data in the range of P/P0 = 0.008–0.04 is 795 m2 g−1, which is higher than the surface areas (150–418 m2 g−1) of the Mg-based MOFs reported so far,3 except that (1495 m2 g−1) of [Mg3(dlt)]15 The DR pore volume is 0.368 cm3 g−1. Compared to the CO2 adsorption data, SNU-25 adsorbs much less CH4 gas, up to 4.87 wt% (68.09 cm3 g−1 at STP, 3.04 mmol g−1) at 195 K and 1 atm, 1.07 wt% (15.09 cm3 g−1 at STP, 0.67 mmol g−1) at 273 K and 1 atm, and 0.73 wt% (10.22 cm3 g−1 at STP, 0.45 mmol g−1) at 298 K and 1 atm. The higher uptake capacity for CO2 gas over CH4 in SNU-25 may be associated with the quadrupole moment of CO2 (−1.34 × 10−39 Cm2) which induces efficient interaction with the framework.3,8 The boiling point difference between the two gases, 195 K vs. 109 K, may also contribute to the adsorption selectivity.22

SNU-25 adsorbs H2 gas up to 1.08 wt% (121.24 cm3 g−1 at STP, 5.41 mmol g−1) at 77 K and 1 atm, and 0.83 wt% (93.61 cm3 g−1 at STP, 4.18 mmol g−1) at 87 K and 1 atm. These values are much higher than the first magnesium-based MOF, [Mg3(NDC)] (0.46 wt%);22 but lower than those of other transition metal based MOFs such as SNU-5 (2.87 wt%);15 and CU-K-1 (1.6 wt%);23 under the same temperature and pressure. The zero coverage isotherm of H2 adsorption in SNU-25 is 6.58 kmol m−2 (see ESI†). This is lower than those of [Mg3(NDC)] (9.5 kmol m−2) and other transition metal MOFs (6.1–15.1 kmol m−2),3,10,11 which contain open metal sites. It is probable that free carboxylate oxygen atoms around the Mg ion might fill the vacant Mg coordination sites by ligand rotations on desolvation, as shown by the changes in the PXRD patterns.

Interestingly, SNU-25 adsors a high amount of O2 gas, up to 33.3 wt% (233.3 cm3 g−1 at STP, 10.41 mmol g−1) at 77 K and 0.19 atm, and 33.4 wt% (234.3 cm3 g−1 at STP, 10.45 mmol g−1) at 87 K and 0.69 atm. These O2 capacities are very high compared to other MOFs, although lower than that (618 cm3 g−1, 950 mg m−2 at 77 K and 0.19 atm) of the best O2 adsorption material Co(BDP).22 Interestingly, the density of O2 adsorbed in SNU-25 at 77 K and 0.19 atm, as estimated by using the pore volume (0.368 cm3 g−1) obtained from the CO2 isotherm, is 1244 kg m−3, which is comparable to the density (1140 kg m−3) of liquid O2. It is also the highest value among the data for the MOFs reported so far. For
example, the densities of adsorbed O$_2$ at 0.19 atm in the previously reported FMOF-1$^{23}$ and SNU-15$^3$ were 592 kg m$^{-3}$ and 998 kg m$^{-3}$, respectively. MOFs showing selective gas sorption behaviors for H$_2$ over N$_2$ or for O$_2$ over N$_2$ are not so common,$^{1,3}$ but they are very important for gas separation processes. It has been reported that carbon membrane$^{24}$ and carbon/ZSM-5 nanocomposite membrane$^{25}$ show selectivities for O$_2$–N$_2$ gas pairs by control of pore size with the shape of carbon membrane and the tuning of the large pore size of ZSM-5 by carbon matrix, respectively.

In conclusion, we have prepared a doubly interpenetrated Mg-based porous MOF, [Mg(TCPBDA)(H$_2$O)$_2$] 6DMF·6H$_2$O (I), which generates 3D channels. The desolvated solid SNU-25 exhibits high thermal stability up to 500 °C, and selective gas sorption properties for H$_2$ and O$_2$ gases over N$_2$. The O$_2$ adsorption density in previously reported FMOF-123 and SNU-153 were 592 kg m$^{-3}$ and ammonia synthesis. 26

Notes and references

† Crystal data for I: MgC$_{6}$H$_{12}$N$_{2}$O$_{10}$, Mr = 720.97, orthorhombic, space group Imma, a = 25.1600(20), b = 36.592(18), c = 15.727(2) Å, V = 144.79(14) Å$^3$, Z = 8, T = 298(2) K, $\rho_{calc}$ = 0.662 g cm$^{-3}$, $F_{000}$ = 2992, Mo K\alpha radiation, $\lambda$ = 0.71073 Å, $\theta_{max}$ = 25.25, 31 218 reflections collected, 6243 unique ($R_{int}$ = 0.1586). Final GOF = 0.879, $R_1$ = 0.1109, w$R_2$ = 0.2728, R indices based on 6243 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 244 parameters, 0 restraints. Electron densities of the disordered guest molecules were flattened by using the ‘SQUEEZE’ option of PLATON.$^{25}$ CCDC 739772 contains the supplementary crystallographic data.$^{†}$


