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
First published as an Advance Article on the web 5th August 2009
DOI: 10.1039/b910228k

A doubly interpenetrated magnesium-based porous metal–organic framework exhibits thermal stability up to 500 °C and selective gas sorption properties for H_2 and O_2 gases over N_2, and CO_2 gas over CH_4.

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 O_2 over N_2, and H_2 over N_2 are very important because they have potential to be applied in the separation of these gases from air and the H_2 enrichment from the N_2–H_2 exhaust in ammonia synthesis, respectively. Despite their importance, MOFs that show selective gas adsorption behaviour are not so common.[1–7,9] 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 Mg^{2+}.[12e] The ionic radius of Mg^{2+} (72 pm) is similar to those of transition metals such as Zn^{2+} (74 pm) and Cu^{2+} (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 [Mg_2(dhtp)] (dhtp = 2,5-dihydroxyterephthalate) reported by Matzger and co-workers.[15]

Here, we report a doubly interpenetrated magnesium-based MOF, [Mg(TCPBDA)(H_2O)$_2$]·6DMF·6H_2O (**1**), where $TCPBDA^{2-}$ 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 H_2 and O_2 gases over N_2 at 77 K, as well as for CO_2 gas over CH_4 at 195, 273, and 298 K.

Yellow plate-shaped crystals of [Mg(TCPBDA)(H_2O)$_2$]·6DMF·6H_2O (**1**) were prepared by heating $Mg(NO_3)_2$·6H_2O and H_4TCPBDA in DMF–EtOH–H_2O (4 : 1 : 1 v/v) at 110 °C for 24 h. **1** was formed independently of the stoichiometry of Mg : TCPBDA, 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**, Mg^{2+} ions show an octahedral coordination geometry by binding four $TCPBDA^{2-}$ 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 $TCPBDA^{2-}$ exhibit sp^2 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 $TCPBDA^{2-}$ 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 $TCPBDA^{2-}$ to form six-membered rings (Fig 1a). Every square-shaped Mg^{2+} building unit is linked with four trapezoidal $TCPBDA^{2-}$ ions and every $TCPBDA^{2-}$ unit is linked to four Mg^{2+} units to give rise to a 3D network. Framework **1** is doubly interpenetrated, and the two phenyl rings of a $TCPBDA^{2-}$ unit are involved in face-to-face π–π interactions with those of the adjacent interpenetrated net

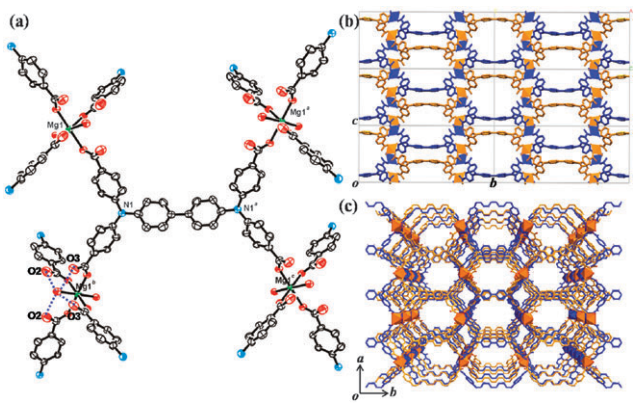

Fig. 1 The X-ray crystal structure of **1**. (a) An ORTEP drawing of **1**. Hydrogen bonding interactions are indicated as dotted lines. Views of the doubly interpenetrated network seen on (b) the *bc* plane and (c) the *ab* plane.

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† Electronic supplementary information (ESI) available: Experimental details, EPR spectrum, X-ray structures of **1**, PXRD patterns, TGA/DSC traces, N_2 sorption isotherms at 77 K and 195 K, CO_2 and CH_4 sorption isotherms at 195 K, 273 K and 298 K, H_2 sorption isotherms at 77 K and 87 K, a plot of isosteric heats of H_2, CO_2, and CH_4 adsorption, tables of crystallographic data and bond distances and angles. CCDC 739772. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b910228k

(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 $TCPBDA^{2-}$ 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 H_2O guests as well as two coordinated aqua ligands (calcd. 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–H_2O (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 $2\theta = 6.7°$ 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 N_2, H_2, O_2, CO_2, and CH_4 gases (Fig. 2). **SNU-25** slightly adsorbs N_2 gas, 13.40 $cm^3\ g^{-1}$ at 77 K and 1 atm. However, it adsorbs significant amounts of CO_2 and CH_4 gases at 195 K, 273 K, and 298 K, as well as H_2 and O_2 gases at 77 K and 87 K. The present selective gas sorption properties over N_2 gas must be attributed to a molecular sieving effect, considering the kinetic diameters of the gases (H_2, 2.89 Å; CO_2, 3.3 Å; O_2, 3.46 Å; N_2, 3.64 Å; CH_4, 3.82 Å).[20] The better sorption capacity for CH_4 than N_2, despite the larger kinetic diameter of CH_4, may be related to the stronger interaction of CH_4 than N_2 with the open Mg sites.[21]

SNU-25 adsorbs CO_2 gas up to 26.3 wt% (134.05 $cm^3\ g^{-1}$ at STP, 5.99 mmol g^{-1}) at 195 K and 1 atm, 9.1 wt% (46.38 $cm^3\ g^{-1}$ at STP, 2.07 mmol g^{-1}) at 273 K and 1 atm, and 6.5 wt% (33.43 $cm^3\ g^{-1}$ at STP, 1.49 mmol g^{-1}) at 298 K and 1 atm. The DR (Dubinin–Radushkevich) surface area

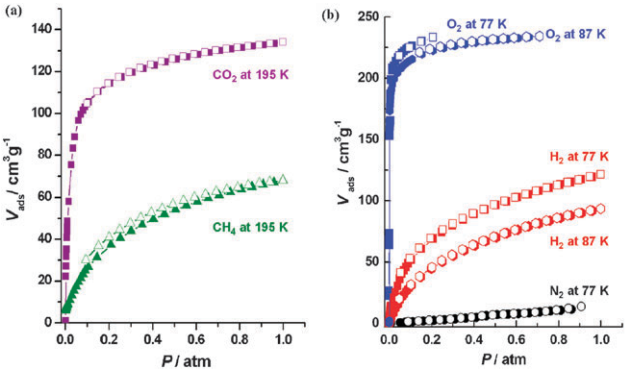

Fig. 2 Gas sorption isotherms of **SNU-25**. (a) CO_2 (■) and CH_4 (▲) at 195 K. (b) N_2 (black), H_2 (red), and O_2 (blue) at 77 K and 87 K. Filled shapes, adsorption; open shapes, desorption.

estimated from the CO_2 sorption data at 195 K by using the data in the range of $P/P_0 = 0.008$–0.04 is 795 $m^2\ g^{-1}$, which is higher than the surface areas (150–418 $m^2\ g^{-1}$) of the Mg-based MOFs reported so far,[5] except that (1495 $m^2\ g^{-1}$) of [Mg_2(dhtp)].[15] The DR pore volume is 0.368 $cm^3\ g^{-1}$. Compared to the CO_2 adsorption data, **SNU-25** adsorbs much less CH_4 gas, up to 4.87 wt% (68.09 $cm^3\ g^{-1}$ at STP, 3.04 mmol g^{-1}) at 195 K and 1 atm, 1.07 wt% (15.09 $cm^3\ g^{-1}$ at STP, 0.67 mmol g^{-1}) at 273 K and 1 atm, and 0.73 wt% (10.22 $cm^3\ g^{-1}$ at STP, 0.45 mmol g^{-1}) at 298 K and 1 atm. The higher uptake capacity for CO_2 gas over CH_4 in **SNU-25** may be associated with the quadrupole moment of CO_2 (-1.34×10^{-39} C m^2) 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.[2]

SNU-25 adsorbs H_2 gas up to 1.08 wt% (121.24 $cm^3\ g^{-1}$ at STP, 5.41 mmol g^{-1}) at 77 K and 1 atm, and 0.83 wt% (93.61 $cm^3\ g^{-1}$ at STP, 4.18 mmol g^{-1}) at 87 K and 1 atm. These values are much higher than the first magnesium-based MOF, [Mg_3(NDC)$_3$] (0.46 wt%),[5] but lower than those of other transition metal based MOFs such as SNU-5 (2.87 wt%)[11] and CUK-1 (1.6 wt%)[9] under the same temperature and pressure. The zero coverage isosteric heat of H_2 adsorption in **SNU-25** is 6.58 kJ mol^{-1} (see ESI†). This is lower than those of [Mg_3(NDC)$_3$] (9.5 kJ mol^{-1})[5] and other transition metal MOFs (6.1–15.1 kJ mol^{-1}),[3,10a,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** adsorbs a high amount of O_2 gas, up to 33.3 wt% (233.3 $cm^3\ g^{-1}$ at STP, 10.41 mmol g^{-1}) at 77 K and 0.19 atm, and 33.4 wt% (234.3 $cm^3\ g^{-1}$ at STP, 10.45 mmol g^{-1}) at 87 K and 0.69 atm. These O_2 capacities are very high compared to other MOFs, although lower than that (618 $cm^3\ g^{-1}$, 950 kg m^{-3} at 77 K and 0.19 atm) of the best O_2 adsorption material Co(BDP).[22] Interestingly, the density of O_2 adsorbed in **SNU-25** at 77 K and 0.19 atm, as estimated by using the pore volume (0.368 $cm^3\ g^{-1}$) obtained from the CO_2 isotherm, is 1244 kg m^{-3}, which is comparable to the density (1140 kg m^{-3}) of liquid O_2. 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,[1,3–7,9] although 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, $[Mg(TCPBDA)(H_2O)_2]\cdot 6DMF\cdot 6H_2O$ (**1**), 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 **SNU-25** is the highest among those of MOFs reported so far, which is even higher than the density of liquid O_2. **SNU-25** is a good candidate material for the gas separation processes of O_2 and N_2 from air and also in H_2 enrichment from N_2–H_2 exhaust mixtures resulting from ammonia synthesis.[26]

This work was supported by the Korea Research Foundation Grant (Basic Research Promotion Fund, KRF-2005-084-C00020), and by the SRC program through the Center for Intelligent Nano-Bio Materials (grant: R11-2005-008-00000-0), funded by the Korean Government.

Notes and references

‡ Crystal data for **1**: $MgC_{40}H_{28}N_2O_{10}$, Mr = 720.97, orthorhombic, space group *Imma*, a = 25.160(20), b = 36.592(18), c = 15.727(2) Å, V = 14 479(14) Å^3, Z = 8, T = 298(2) K, d_{calc} = 0.662 g cm^{-3}, F_{000} = 2992, Mo Kα radiation, λ = 0.71073 Å, θ_{max} = 25.25, 31 218 reflections collected, 6243 unique (R_{int} = 0.1586). Final GOF = 0.879, R_1 = 0.1109, wR_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.[27] CCDC 739772 contains the supplementary crystallographic data.†

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