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A highly stable MOF with rod SBU and tetracarboxylate linker: unusual topology and CO₂ adsorption behaviour at ambient condition†

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A Mn-based rod metal-organic framework (MOF), ROD-6, with new lrk net is synthesized. It represents an unusual type of MOF topology containing both 1-periodic secondary building unit (rod SBU) and polytopic linker (here 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene), and also exhibits high stability (up to 500 °C) and unusual CO_2 uptake behaviour and selectivity despite the lack of strong interacting site, demonstrated by the low and increasing heat of adsorption.

The state of the art in metal-organic frameworks (MOFs)[1] research embraces the rapid development from both structural and functional aspects. From the structural viewpoint, recently an increasing number of MOFs are being made with more complicated topologies compared with those reported earlier.[2] Two main categories of MOFs that are of current intense interest: one type contains infinite 1-periodic metal secondary building units (rod SBUs),[3a] relative to those with finite SBUs,[2b] notably including MOF-74,[3b,c] MIL-53,[3d] NOTT-300,[3e] $Fe_2(BDP)_3$,[3f] and MCF-34,[3g] among several others;[2a] the other type, which has been recently reviewed,[2c] is the one with polytopic linkers, demonstrated systematically by the NU,[4a] PCN,[4b] NOTT,[4c] USF,[4d] and UTSA[4e] series, etc.

From the functional viewpoint, MOFs have been widely utilized for applications in many fields,[1] most significantly for gas adsorption for alternative fuels and separations for clean air.[5] Among these, the selective adsorption of CO_2 over N_2 in MOFs has gained considerable attention because of their advantage in the post-combustion process of carbon capture and storage (CCS).[5b,c,f] Aiming at enhancing CO_2/N_2 selectivity, researchers have developed several strategies[5c,6] by taking advantage of the higher polarizability and quadrupole moment of CO_2 compared with N_2, which leads to higher affinity of the interior surface of MOFs for CO_2. These surface functionalization methods, including exposed metal sites and subsequent amine-grafting,[6a,b] and strongly polarizing organic functional sites (notably nitrogen donor groups),[6c-f] would generate strong host-CO_2 interactions with high zero-coverage adsorption enthalpy (normally ranging from -30 to -100 kJ/mol; note

the liquefaction enthalpy of CO_2 is -17.5 kJ/mol).[5c] However, the use of a material that binds CO_2 too strongly would increase the energy cost for regeneration. Recently, an alternative strategy for kinetic CO_2/N_2 separation has been reported,[6g,h] featuring favourable, moderate CO_2 adsorption enthalpy and excellent CO_2/N_2 selectivity. Moreover, for practical application the CO_2/N_2 separation performance is better to be evaluated under ambient conditions (i.e. 1 atm, room temperature, CO_2 partial pressure 0.15 bar),[6i] and the thermal and chemical stability of MOFs must be taken into consideration, especially given that most carboxylate MOFs are susceptible to hydrolysis. A few important carboxylate MOFs, including MIL-53[7a] with rod SBUs and UiO-66[7b] with robust Zr_6 cluster units, have been shown to be water-stable.
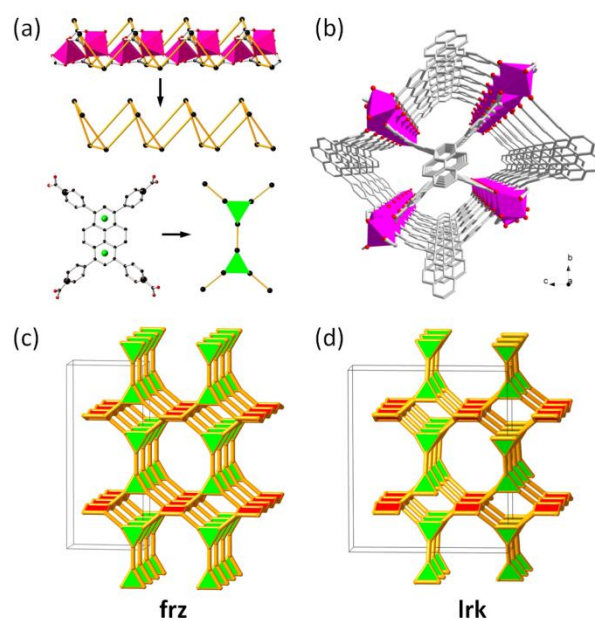

Fig. 1 Structure of ROD-6. (a) Deconstruction of the Mn-based rod SBU into a zigzag ladder and the tetracarboxylate into two linked triangles. (b) The overall framework of ROD-6. The underlying net **frz** of ROD-7 (c) and **lrk** of ROD-6 (d).

We have been interested in MOFs with rod SBUs.[2a,8] Our recent reports of rod MOFs (names given here) included Fe-based (ROD-2, **yzh**; ROD-3, **wnf**; ROD-4, **oab**)[8a] and Zn-based (ROD-5, **sra**)[8b] ones, all with rod SBUs linked by ditopic linkers (the 3-letter codes in bold are RCSR symbols for identifying nets[9]). In this work, a tetratopic linker with a pyrene core,[10] 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H$_4$TBAPy), is used to construct a new rod MOF, [Mn$_2$(TBAPy)(H$_2$O)$_2$]·DMF·H$_2$O (ROD-6, see ESI† for experimental details). The structure of ROD-6 is closely related to a reported In-based MOF,[10a] but the CO$_2$ adsorption ability was not evaluated in detail. For comparison the In-based MOF is also synthesized and referred to as ROD-7 here.

As shown in Fig. 1a and 1b, the 3-periodic framework of ROD-6 contains 1-periodic rod SBUs linked by the tetratopic linker, with nanoscale one dimensional channels viewed along **a** direction (porous void volume 40.2 %, see ESI† for crystal structure description). There are two main differences between the structures of ROD-6 and ROD-7. i) In ROD-6, one of the Mn^{II} ion is coordinated to two H$_2$O besides the carboxyl-O, while due to the extra valency of In^{III} there must be hydroxyl instead, giving the formula of [In$_2$(TBAPy)(OH)$_2$]·guests[10a] for ROD-7. ii) All the pyrene cores in ROD-7 are parallel (pyrene-pyrene distance 7.12 Å), while those in ROD-6 are arranged within two sets of intersecting planes (dihedral angle 88.3 °), giving a much closer contact (4.32 Å) between the pyrene cores. By applying a proposed deconstruction method,[2a] the 1-periodic rod SBU can be viewed as a zigzag ladder, and the tetratopic linker with two branch points is simplified into two linked triangles (Fig. 1a).[2c] In this way, the topology of ROD-6 and ROD-7 are shown to be **lrk** (Fig. 1d) and **frz** (Fig. 1c), respectively (see ESI† for detailed topological analysis). They are all new nets (assigned by RCSR) of the unusual kind containing both rod SBU and polytopic linker aforementioned. Note the directions of the linked triangles clearly depict the different pyrene arrangements.

Thermogravimetric analysis reveals the activated sample of ROD-6 is stable up to almost 500 °C (Fig. S6 in ESI†). This thermal stability is comparable with that of the iconic UiO-66[7b] and MIL-53,[7a] exceeding the usual decomposing temperature range of 350−400 °C for most MOFs. The exceptional stability of UiO-66 was attributed to the highly robust Zr$_6$ SBU.[7b] Recently, NU-1000 based on the Zr$_6$ SBU and TBAPy linker exhibited similar stability.[10c,d] The high stability of MIL-53 may be due to the high valency of the metal ions and the connectivity of the rod SBUs,[5c,7a] but ROD-7 based on In^{III} with a zigzag-ladder SBU similar to that of ROD-6 is only stable up to 380 °C.[10a] We speculate the shorter pyrene-pyrene contacts in ROD-6 may also contribute to its better thermal stability. The crystalline sample of ROD-6 is also resistant to hydrolysis at room temperature. After suspended in water, hydrochloric acid solution (pH = 2) or sodium hydroxide solution (pH = 11) at room temperature for 12 h, the samples can retain crystallinity, indicating the framework does not collapse due to hydrolysis (Fig. S7 in ESI†).

The CO$_2$ capture ability and CO$_2$/N$_2$ selectivity of ROD-6 are evaluated (Fig. 2) and then compared with those of ROD-7[10a] and NU-1000[10d] based on the same linker. The type-I sorption isotherm for N$_2$ at 77 K (Fig. S9 in ESI†) reveals the moderate surface area for ROD-6, significantly lower than those of ROD-7 and mesoporous NU-1000 (Table 1). At 195 K, the CO$_2$ uptake (29.46 wt%, 1 atm) of ROD-6 is also much lower than that of ROD-7 (Fig. S10 in ESI†), which is directly related to their difference in surface area.
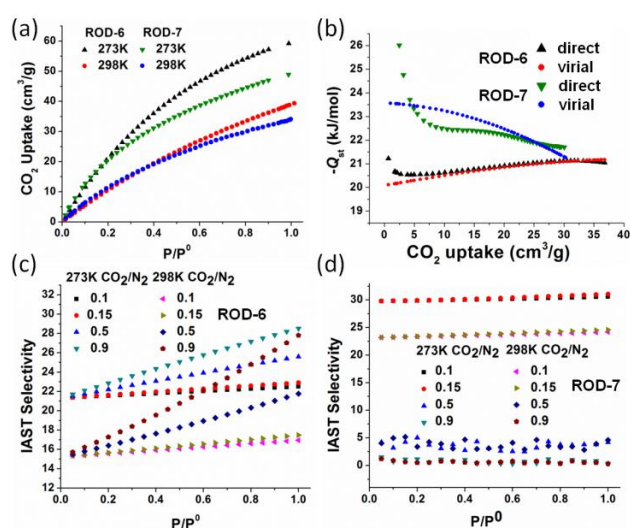

Fig. 2 Gas adsorption property of ROD-6 and ROD-7 under ambient conditions, showing CO$_2$ uptake isotherms (a), isosteric adsorption enthalpy calculated from direct and virial methods (b), and IAST predicted CO$_2$/N$_2$ selectivity at various gas mixture ratios calculated from SSL fitting for ROD-6 (c) and DSL for ROD-7 (d).

Table 1 Gas adsorption performances of ROD-6, ROD-7 and NU-1000

MOFs	S$_{BET}$ (m^2/g)[a]	CO$_2$ (wt %)[b]	−Q$_{st}$ (kJ/mol)[c]	Selectivity[d]
ROD-6	345	7.73	20 to 21	15 to 17
ROD-7	1189	6.70	26 to 22	23
NU-1000	2320	7.92	17	8

[a] Brunauer-Emmett-Teller (BET) surface area; [b] CO$_2$ uptake capacity at 1 atm/298 K (NU-1000 at 293 K); [c] isosteric heat of adsorption calculated from Clausius-Clapeyron equation; [d] CO$_2$/N$_2$ (10:90) selectivity at 0–1 atm/298 K (NU-1000 at 293 K) calculated from Ideal Adsorbed Solution Theory (IAST). Data collection and analysis of ROD-7 are performed here using reproduced samples;[10a] those of NU-1000 are taken from literature.[10d]

Interestingly, at ambient condition the CO$_2$ uptake capacity of ROD-6 surpasses that of ROD-7 (Fig. 2a), even approaching that of NU-1000 (Table 1). In order to understand this unusual CO$_2$ capture behaviour, the isosteric heat of adsorption is calculated from Clausius-Clapeyron equation (Fig. 2b). The low and slightly increasing Q_{st} values indicate the lack of strongly interacting site on the interior surface of ROD-6; in contrast, for ROD-7 there exist weak interaction sites, presumably the hydroxyl groups similar to the case of MIL-53,[3d] evidenced by the higher and decreasing Q_{st}. This is consistent with the observation that at low loading (P/P° < 0.2) the uptake for ROD-7 increases faster than that of ROD-6, but after that it is surpassed (Fig. 2a). Moreover, the adsorption isotherms for ROD-6 can be fit better to the single-site Langmuir (SSL) model; for ROD-7 dual-site Langmuir (DSL) model is more appropriate (see ESI† for detailed adsorption measurements and analysis). The additional site for ROD-7 can be the hydroxyl group, but this driving force between the polar sites and the quadrupole moment of CO$_2$ is too weak to play a crucial role on the uptake ability. In fact, the Zr$_6$ SBUs in NU-1000 also have exposed hydroxyl groups, but its mesopores further weaken this role, shown by the very low Q_{st} (Table 1) and SSL fitting.[10d] Despite its mesopores and high surface area, NU-1000 shows CO$_2$ capture ability similar to that of ROD-6 under ambient conditions. The responsible factor for the CO$_2$ capture behaviour of ROD-6 is still unclear, but its micropores, compared with the mesopores of NU-1000, would facilitate the CO$_2$ adsorption, indicated by the slightly increasing Q_{st}.

ROD-6 and ROD-7 show completely different scenarios for CO_2/N_2 selectivity (Fig. 2c and 2d; Table 1), predicted by Ideal Adsorbed Solution Theory (IAST). Most notable are i) the CO_2/N_2 selectivity for ROD-6 increases steadily upon loading, while those for ROD-7 and NU-1000 stay constant, and ii) the CO_2/N_2 selectivity for ROD-7 drops to almost ineffective when the $CO_2:N_2$ mixture ratio is larger than 0.5, whereas the reverse situation is true for ROD-6. The CO_2/N_2 selectivity increases considerably upon the increment of the CO_2 ratio in the gas mixture (Fig. 2c). NU-1000 exhibits moderate and constant CO_2/N_2 selectivity (ca. 8) under ambient conditions, which can be improved (to ca. 12) through functionalization.[10d] The CO_2 uptake and selectivity at ambient conditions are lower than excellent candidates such as MOF-74 (Table S7 in ESI†), but ROD-6 with high stability and interesting CO_2 adsorption process deserves to be further studied.

Taken together, this work reports a newly synthesized Mn-based MOF, ROD-6, containing rod SBU and tetratopic carboxylate linker. The topological analysis method for such unusual type is demonstrated by ROD-6 and ROD-7, a closely related In-based MOF. Moreover, ROD-6 exhibits exceptional thermal (up to 500 °C) and chemical stability, which is comparable to the highly robust Zr-based MOFs, UiO-66 and NU-1000. Albeit the surface area of ROD-6 is moderate, its ability to capture CO_2 under ambient conditions is comparable with that of the mesoporous NU-1000, by exhibiting an unusual sorption behaviour with low and increasing isosteric heat of adsorption and increasing CO_2/N_2 selectivity upon loading.

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† Electronic Supplementary Information (ESI) available: Experimental details, crystal structure description, topological analysis (.cgd file), additional characterization, gas adsorption measurements and analysis. CCDC 977204. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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