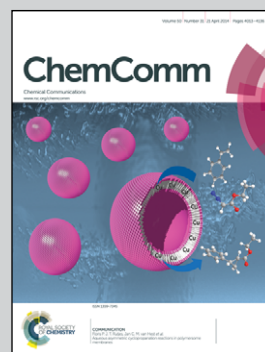


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A highly stable MOF with a rod SBU and a tetracarboxylate linker: unusual topology and CO₂ adsorption behaviour under ambient conditions

Metal-organic frameworks (MOFs) are usually made of finite secondary building units (SBUs) and ditopic linkers, giving numerous pleasing topologies. The reported ROD-6 is of an unusual kind that contains both an infinite 1-periodic SBU and a polytopic linker, with notably high stability and selective adsorption of carbon dioxide over nitrogen.

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A highly stable MOF with a rod SBU and a tetracarboxylate linker: unusual topology and CO₂ adsorption behaviour under ambient conditions†

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A Mn-based rod metal–organic framework (MOF), ROD-6, with a new 1-periodic secondary building unit (rod SBU) and a polytopic linker (here 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene), and also exhibits high stability (up to 485 °C) and unusual CO₂ uptake behaviour and selectivity despite the lack of strong interacting sites, 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 have been made with more complicated topologies compared with those reported earlier.² There are 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} Fe₂(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 separation for clean air.⁵ Among these, the selective adsorption of CO₂ over N₂ 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 the CO₂/N₂ selectivity, researchers have developed several strategies^{5c,6} by taking advantage of the higher polarizability and quadrupole moment of CO₂ compared with N₂, which leads to higher affinity of

the interior surface of MOFs for CO₂. 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–CO₂ interactions with a high zero-coverage adsorption enthalpy (normally ranging from –30 to –100 kJ mol^{–1}; note the liquefaction enthalpy of CO₂ is –17.5 kJ mol^{–1}).^{5c} However, the use of a material that binds CO₂ too strongly would increase the energy cost for regeneration. Recently, an alternative strategy for kinetic CO₂/N₂ separation has been reported,^{6g,h} featuring favourable, moderate CO₂ adsorption enthalpy and excellent CO₂/N₂ selectivity. Moreover, for practical application the CO₂/N₂ separation performance is better to be evaluated under ambient conditions (*i.e.* 1 atm, room temperature, CO₂ 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 Zr₆ cluster units, have been shown to be water-stable.

We have been interested in MOFs with rod SBUs.^{2a,8} Our recent reports on 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 nets⁹). In this work, a tetratopic linker with a pyrene core,¹⁰ 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H₄TBAPy), is used to construct a new rod MOF, [Mn₂(TBAPy)(H₂O)₂]-DMF·H₂O (ROD-6, see ESI† for experimental details). The structure of ROD-6 is closely related to a reported In-based MOF,^{10a} but the CO₂ 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 b, the 3-periodic framework of ROD-6 contains 1-periodic rod SBUs linked by the tetratopic linker, with nanoscale one dimensional channels viewed along the *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 H₂O besides the carboxyl-O, while due to the extra valency of In^{III} there must be hydroxyl instead, giving the formula of [In₂(TBAPy)(OH)₂]₂ guests^{10a} for ROD-7. (ii) All the pyrene cores in ROD-7 are parallel

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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/c3cc49684h

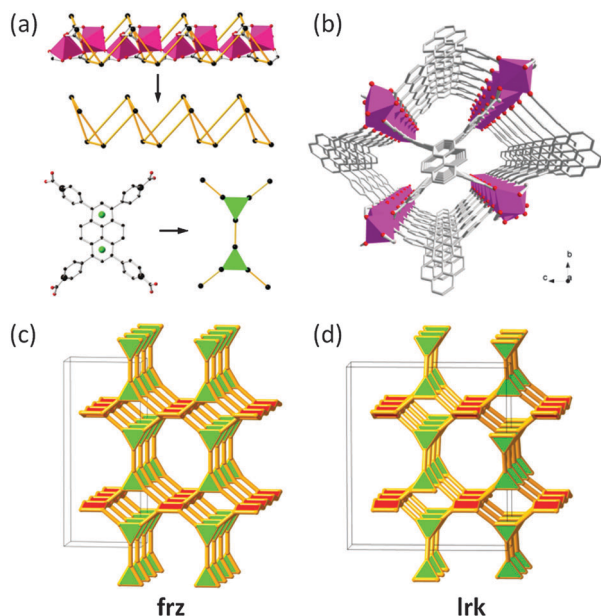


Fig. 1 Structure of ROD-6. (a) Deconstruction of the Mn-based rod SBU into a zigzag ladder and the tetracarboxylate into two linked triangles. (b) The overall framework of ROD-6. The underlying net **frz** of ROD-7 (c) and **lrk** of ROD-6 (d).

(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 tetra-topic 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 is 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 SBUs and polytopic linkers aforementioned. Note the directions of the linked triangles clearly depict the different pyrene arrangements.

Thermogravimetric analysis reveals that the activated sample of ROD-6 is stable up to 485 °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 Zr₆ SBU.^{7b} Recently, NU-1000 based on the Zr₆ 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 that 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 being suspended in water, hydrochloric acid solution (pH = 2) or sodium hydroxide solution (pH = 11) at room temperature for 12 h, the samples can retain their crystallinity, indicating that the framework does not collapse due to hydrolysis (Fig. S7 in ESI†).

The CO₂ capture ability and CO₂/N₂ selectivity of ROD-6 are evaluated (Fig. 2) and then compared with those of ROD-7^{10a}

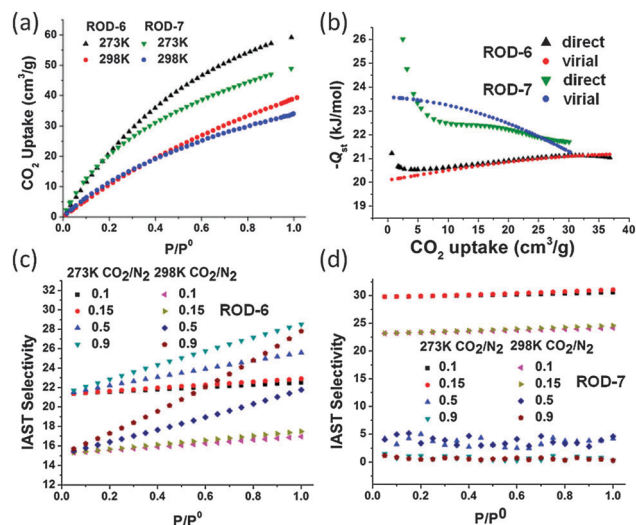


Fig. 2 Gas adsorption property of ROD-6 and ROD-7 under ambient conditions, showing CO₂ uptake isotherms (a), isosteric adsorption enthalpy calculated using direct and virial methods (b), and IAST predicted CO₂/N₂ selectivity at various gas mixture ratios calculated from SSL fitting for ROD-6 (c) and DSL for ROD-7 (d).

and NU-1000^{10d} based on the same linker. The type-I sorption isotherm for N₂ at 77 K (Fig. S9 in ESI†) reveals the moderate surface area for ROD-6, which is significantly lower than those of ROD-7 and mesoporous NU-1000 (Table 1). At 195 K, the CO₂ 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 the difference in their surface areas.

Interestingly, under ambient conditions the CO₂ 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 CO₂ capture behaviour, the isosteric heat of adsorption is calculated using the Clausius–Clapeyron equation (Fig. 2b). The low and slightly increasing Q_{st} values indicate the lack of strongly interacting sites 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 ($P/P^0 < 0.4$, 298 K) 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 the dual-site Langmuir (DSL) model is more appropriate (see ESI†

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

MOFs	S_{BET}^a (m ² g ⁻¹)	CO ₂ ^b (wt%)	$-Q_{st}^c$ (kJ mol ⁻¹)	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 CO₂ uptake capacity at 1 atm/298 K (NU-1000 at 293 K). ^c Isosteric heat of adsorption calculated using the Clausius–Clapeyron equation. ^d CO₂/N₂ (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 the literature.^{10d}

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 CO₂ is too weak to play a crucial role in the uptake ability. In fact, the Zr₆ 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 CO₂ capture ability similar to that of ROD-6 under ambient conditions. The responsible factor for the CO₂ capture behaviour of ROD-6 is still unclear, but its micropores, compared with the mesopores of NU-1000, would facilitate the CO₂ adsorption, indicated by the slightly increasing Q_{st}.

ROD-6 and ROD-7 show completely different scenarios for CO₂/N₂ selectivity (Fig. 2c and d; Table 1), predicted by Ideal Adsorbed Solution Theory (IAST). It should be noted that (i) the CO₂/N₂ selectivity for ROD-6 increases steadily upon loading, while those for ROD-7 and NU-1000 stay constant, and (ii) the CO₂/N₂ selectivity for ROD-7 becomes almost ineffective when the ratio of the CO₂:N₂ mixture is larger than 0.5, whereas the reverse situation is true for ROD-6. The CO₂/N₂ selectivity increases considerably upon the increment of the CO₂ ratio in the gas mixture (Fig. 2c). NU-1000 exhibits moderate and constant CO₂/N₂ selectivity (ca. 8) under ambient conditions, which can be improved (to ca. 12) through functionalization.^{10d} The CO₂ uptake and selectivity under ambient conditions are lower than that of excellent candidates such as MOF-74 (Table S7 in ESI[†]), but ROD-6 with high stability and interesting CO₂ adsorption deserves to be further studied.

Taken together, this work reports a newly synthesized Mn-based MOF, ROD-6, containing a rod SBU and a tetraprotic 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 485 °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 CO₂ 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 CO₂/N₂ selectivity upon loading.

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