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## COMMUNICATION

## Non-interpenetrated IRMOF-8: synthesis, activation, and gas sorption†‡

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The synthesis and successful activation of IRMOF-8 ( $\text{Zn}_4\text{O}(\text{ndc})_3$ , ndc = naphthalene-2,6-dicarboxylate) is presented. Room temperature synthesis effectively suppresses interpenetration. Although conventional activation under reduced pressure leads to structural collapse, activation by flowing supercritical  $\text{CO}_2$  yields a guest-free material with a BET surface area of  $4461 \text{ m}^2 \text{ g}^{-1}$ .

Despite surface areas exceeding  $5000 \text{ m}^2 \text{ g}^{-1}$  in microporous coordination polymers (MCPs),<sup>1</sup> many difficulties still exist in achieving sorption properties commensurate with theoretical expectations. Reasons cited for experimental surface areas falling short of values computed from ideal, guest-free crystallographic models include incomplete guest removal,<sup>2</sup> structural amorphitization<sup>3</sup> or transformation<sup>4</sup> upon guest removal, and interpenetration.<sup>5</sup> With the tremendous growth of the field, the need to understand and overcome these obstacles has become imperative. Our group<sup>6</sup> and others<sup>5,7</sup> have begun to analyze non-ideal behavior in MCPs in detail. In this work, we focus on IRMOF-8 ( $\text{Zn}_4\text{O}(\text{ndc})_3$ , ndc = naphthalene-2,6-dicarboxylate),<sup>8</sup> one of the earliest examples of a material which, though expected to have an outstanding surface area based on its guest-free crystal structure, has yet to exhibit predicted gas sorption properties.

IRMOF-8 has a cubic structure constructed from the linkage of basic zinc acetate clusters and ndc ligands (Fig. 1a). Soon after the initial report, it was scrutinized as a  $\text{H}_2$  storage material.<sup>9</sup> However, the maximum excess  $\text{H}_2$  uptake in this material is exceeded by the topologically identical materials IRMOF-1 and IRMOF-20,<sup>10</sup> a result at odds with that expected from their shorter linker lengths.<sup>11</sup> Researchers have proposed a number of reasons for the curious sorption behavior of IRMOF-8 including extra-framework zinc species,<sup>9b</sup> incomplete activation,<sup>9c</sup> and interpenetration.<sup>9d,12</sup> Indeed, a number of interpenetrated phases of  $\text{Zn}_4\text{O}/\text{ndc}$ -based systems have been discovered,<sup>13</sup> the syntheses of which are similar to that of IRMOF-8, lending credence to the possibility that typical

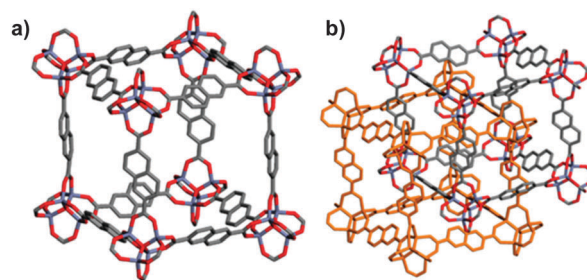


Fig. 1 Structures of (a) IRMOF-8 and (b) interpenetrated IRMOF-8 analogue. Blue = Zn, red = O, grey = C. Hydrogen atoms omitted for clarity.

solvothermally synthesized IRMOF-8 contains at least a significant amount of an interpenetrated phase. In this work, we report fully activated, non-interpenetrated IRMOF-8 and examine its sorption properties.

Initially, we synthesized IRMOF-8 using common solvothermal routes (hereafter denoted IRMOF-8-HT).<sup>8,9c</sup> After activation by solvent exchange with  $\text{CH}_2\text{Cl}_2$  and subsequent evacuation under reduced pressure ( $\sim 10^{-2}$  Torr), a BET surface area of  $1671 \text{ m}^2 \text{ g}^{-1}$  was obtained (Fig. 2a). Materials synthesized in dimethylformamide (DMF) or diethylformamide (DEF), as well as those activated using supercritical  $\text{CO}_2$ , exhibited similar surface areas. Thermogravimetric analysis (TGA) (Fig. S1, ESI†) of the activated samples revealed minimal mass loss, suggesting thorough removal of solvent on evacuation (though not discounting occluded non-volatile guests<sup>5,14</sup>). X-ray diffraction of the material before and after evacuation (Fig. S2, ESI†) indicates that bulk crystallinity is maintained; however, reflections in addition to those expected for phase-pure IRMOF-8 are observed (Fig. S3, ESI†). Previous reports<sup>9d,12</sup> have suggested framework interpenetration as the primary cause for low surface area arising from these synthetic procedures. Indeed, comparison with a hypothetical ndc-based framework derived from the structure of IRMOF-9<sup>12a</sup> (Fig. 1b) shows only modest agreement with our experimental data. Although comparison with recently reported interpenetrated  $\text{Zn}/\text{ndc}$ -based systems<sup>13</sup> did not yield better agreement, it stands to reason that the low surface area of IRMOF-8-HT is due, at least in part, to the presence of one or more interpenetrated phases.

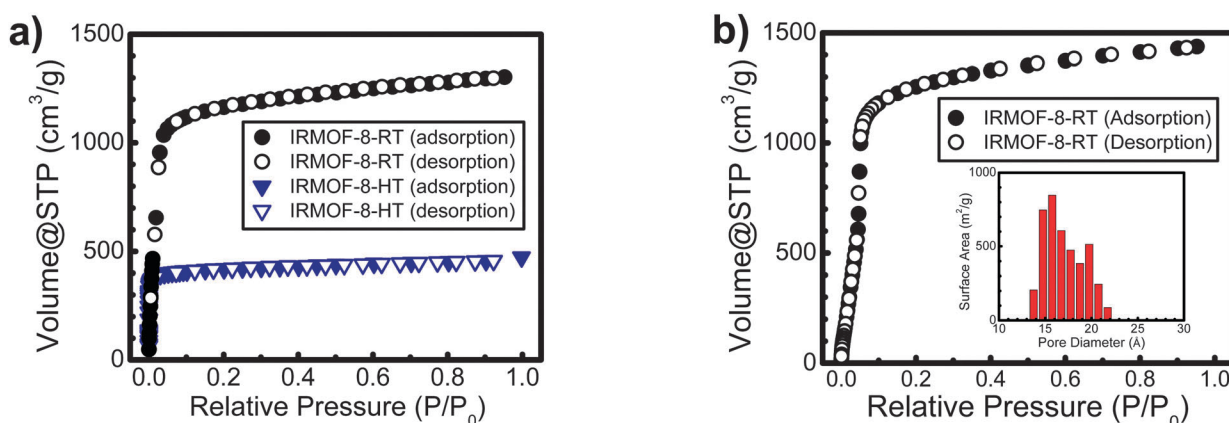
Incubation of ndc and  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  at room temperature in DEF<sup>15</sup> for one week afforded colorless  $\sim 100$  micron truncated cubic crystals of high optical quality (hereafter denoted IRMOF-8-RT, Fig. 3a). Data from powder X-ray diffraction (PXRD) showed excellent agreement with that

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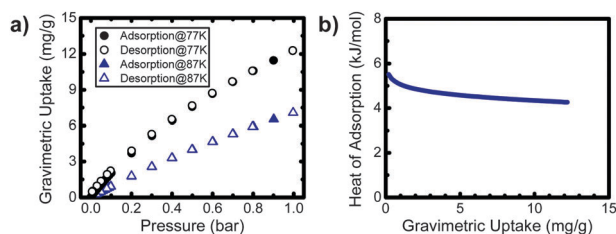
‡ Electronic supplementary information (ESI) available: Experimental and analytical procedures and materials characterization. See DOI: 10.1039/c2cc34689c



**Fig. 2** (a) N<sub>2</sub> sorption isotherms of IRMOF-8-HT (blue triangles) and IRMOF-8-RT (black circles). (b) Ar sorption isotherm of IRMOF-8-RT. Inset: Pore size distribution from NLDFT fit.

simulated from the original crystal structure (Fig. 3b).<sup>8</sup> However, upon solvent exchange with CH<sub>2</sub>Cl<sub>2</sub> and subsequent evacuation, a relatively low BET surface area of 773 m<sup>2</sup> g<sup>-1</sup> was obtained. PXRD data of the evacuated material are consistent with partial structural collapse, accounting for a surface area significantly lower than the calculated geometric accessible surface area<sup>16</sup> of 4350 m<sup>2</sup> g<sup>-1</sup>. Activation using supercritical CO<sub>2</sub> applied in a flow apparatus<sup>18</sup> yielded a BET surface area of 4461 m<sup>2</sup> g<sup>-1</sup>, an unusually high value for a material with cubic symmetry. Characterization of IRMOF-8-RT by Ar sorption and subsequent NLDFT fitting (Fig. 2b) yielded a surface area-weighted average pore size of 17.1 Å, closely matching the crystal structure pore size of 17.5 Å.<sup>19</sup> In contrast, IRMOF-8-HT Ar sorption data yielded a lower surface area-weighted average pore size of 11.0 Å, consistent with an interpenetrated material.

Given the consistency in N<sub>2</sub> and Ar sorption properties with theory, we elected to compare the hydrogen sorption properties of IRMOF-8-RT with previous reports on related materials.<sup>9a,c,20</sup> The H<sub>2</sub> uptake at cryogenic temperatures between 0 and 1 bar is given in Fig. 4a. The gravimetric uptake at 1 bar and 77 K is 12.3 mg g<sup>-1</sup> (1.23 wt%), lower than previously reported values ranging from 14.5–15.2 mg g<sup>-1</sup> under identical conditions; because the surface area of IRMOF-8-RT is dramatically greater than those of these other materials, the low uptake at 1 bar must be coupled with a lower isosteric heat of adsorption ( $Q_{st}$ ). The  $Q_{st}$  for IRMOF-8-RT was determined using a modified Clausius–Clapeyron equation<sup>21</sup> (Fig. 4b) by fitting the isotherms collected at 77 and 87 K to the Langmuir–Freundlich equation (Fig. S7, ESI†). Fits yielded

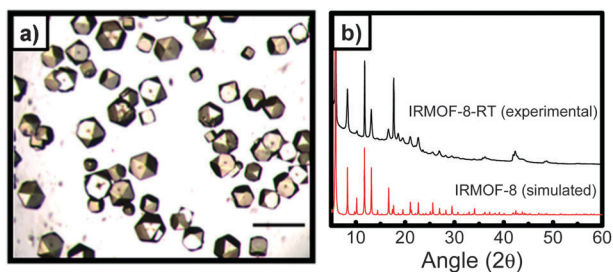


**Fig. 4** (a) H<sub>2</sub> sorption isotherms of IRMOF-8-RT at 77 and 87 K. (b) Isosteric heat of adsorption for H<sub>2</sub> uptake in IRMOF-8-RT.

values of 5.5 kJ mol<sup>-1</sup> and 4.6 kJ mol<sup>-1</sup> at low H<sub>2</sub> uptake and averaged over the examined pressure range, respectively (Fig. 4b). These values are significantly lower than that previously determined for IRMOF-8 (6.1 kJ mol<sup>-1</sup>),<sup>9c</sup> a discrepancy that can be explained by the less constricted pores of IRMOF-8-RT. In this context, it is worth noting that other non-interpenetrated Zn<sub>4</sub>O MCPs exhibit similarly low  $Q_{st}$  values: IRMOF-1, ~4–5 kJ mol<sup>-1</sup>,<sup>9c,22</sup> and UCMC-2, ~4.2 kJ mol<sup>-1</sup>.<sup>1b</sup>

The known isosteric heats of adsorption for all Zn<sub>4</sub>O-based MCPs (including IRMOF-8-RT) are well below the range needed for optimal H<sub>2</sub> sorption at room temperature.<sup>23</sup> However, at 77 K the optimal range for  $Q_{st}$  is significantly lower as well. Too high a  $Q_{st}$  at cryogenic temperatures is detrimental for sorbate release due to significant uptake below the lowest operating pressure (~1–1.5 bar) of the pressure swing cycle.<sup>23a</sup> In slit-pore carbons, a  $Q_{st}$  of ~6 kJ mol<sup>-1</sup> leads to an ideal operating temperature of 115 K. Theory predicts that for a  $Q_{st}$  of ~4 kJ mol<sup>-1</sup> for the same class of materials, an operating temperature of 77 K is ideal.<sup>23a</sup> Hence, for H<sub>2</sub> storage and delivery at 77 K, physisorbents such as IRMOF-8-RT are in fact better suited than lower surface area, higher affinity materials.

In summary, the gap between experimental and theoretical porosity in IRMOF-8 has been bridged. A high surface area in excess of 4400 m<sup>2</sup> g<sup>-1</sup> was obtained, and the pore size distribution and powder diffraction data are in excellent agreement with expectations based on crystallography. Cryogenic H<sub>2</sub> sorption data between 0 and 1 bar yields a modest heat of adsorption consistent with that obtained for other Zn<sub>4</sub>O-based MCPs, which may in fact be advantageous for deliverable hydrogen at cryogenic temperatures.



**Fig. 3** (a) Optical micrograph of crystals of IRMOF-8-RT immediately after synthesis. Scale bar = 500 μm. (b) Powder X-ray diffractogram of IRMOF-8-RT after supercritical CO<sub>2</sub> activation.

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## Notes and references

§ Many cubic networks are prone to interpenetration or collapse, although these obstacles have been overcome with node desymmetrization as in UCMC-8/UMCM-9<sup>18</sup> or adroit choice of net as in the (3,24)-connected *rht* net, as exemplified in MCPs by Zaworotko,<sup>24</sup> Lah,<sup>25</sup> and Zhou.<sup>1d</sup>

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