

# A nanotubular metal–organic framework with permanent porosity: structure analysis and gas sorption studies†

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A nanotubular metal–organic framework, PCN-19, was constructed based on a  $\mu_3$ -oxo-trinickel basic carboxylate secondary building unit (SBU) and the 9,10-anthracenedicarboxylate ligand; its permanent porosity was confirmed by  $N_2$  adsorption isotherms, and its  $H_2$  storage performances were evaluated under both low and high pressures at 77 K.

Extensive research interests have in recent years been attracted to the construction and exploration of porous metal–organic frameworks (MOFs)<sup>1</sup> for applications in hydrogen storage,<sup>2</sup> methane storage,<sup>3</sup> gas separation,<sup>4</sup> and carbon dioxide capture.<sup>5</sup> As a subfamily of porous MOFs, nanotubular MOFs have recently been of escalating interest.<sup>6</sup> Despite the increasing number of MOFs with tubular structures documented, gas sorption properties of those nanotubular MOFs, to our surprise, have not yet been reported.<sup>6</sup> This can be primarily ascribed to the loss of framework integrity after the removal of guest molecules in the channels, most often resulting from the simple connectivity of single metal ions and organic linkers in the structure.<sup>6</sup> To build nanotubular MOFs with enhanced robustness, one can turn to the utilization of metal clusters as secondary building units (SBUs),<sup>7</sup> which have been widely employed for the construction of rigid porous MOFs with high surface areas.<sup>8</sup> In this contribution, we report a nanotubular MOF, PCN-19 (PCN represents porous coordination network), which was built on a  $\mu_3$ -oxo-trinickel basic carboxylate SBU (Fig. 1(a)) and the 9,10-anthracenedicarboxylate ligand (adc, Fig. 1(b)).<sup>9</sup> Desolvated PCN-19 can maintain its permanent porosity as evidenced from  $N_2$  adsorption isotherms, and exhibits substantial  $H_2$  uptake at 77 K.

Under solvothermal conditions, the reaction between  $Ni(NO_3)_2 \cdot 6H_2O$  and  $H_2adc$  in dimethylacetamide (DMA) afforded light yellow green crystals of PCN-19, which has a formula of  $Ni_3O(H_2O)_3(adC)_3 \cdot 2(C_4H_{10}NO^+)$  based on

crystallography and elemental analysis. Single crystal X-ray crystallographic analysis‡ revealed that PCN-19 crystallizes in the trigonal space group  $P\bar{3}1c$ . It adopts a trimeric  $\mu_3$ -oxo-centered basic carboxylate cluster  $[Ni_3O(O_2CR)_6(H_2O)_3]^{2-}$  (Fig. 1(a)) as its SBU with a Ni– $\mu_3$ -O distance of 1.975 Å and adjacent Ni–Ni distance of 3.421 Å. In a SBU, the three Ni atoms and the  $\mu_3$ -O atom are on the same plane. Each pair of adjacent Ni centers are bridged by two carboxylate groups from two different adc ligands, and the coordination geometry of each Ni center is octahedral when the terminal aqua ligand is considered (Ni–O distance: 2.074 Å). This type of trinuclear basic carboxylate cluster,  $[M_3O(O_2CR)_6(L)_3]$ , where M represents trivalent metal ions ( $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ),<sup>10</sup> has been previously employed as an SBU for the construction of MOFs. However, trimeric basic carboxylate clusters with divalent metal ions are not common in MOFs.<sup>11</sup>

Each trinickel SBU connects six adc ligands, and each adc ligand binds two trinickel SBUs to enclose hexagonal nanotubes with anthracene rings serving as the corrugated walls (Fig. 2(a) and (b)). These hexagonal tubes extend infinitely along the *ab* plane with adjacent channels sharing the corrugated walls consisting of anthracene rings (Fig. 2(d)). The aqua ligands of the trinickel SBUs all point toward the center of the 1D nanochannels (Fig. S1, ESI†), and can be liberated when heated under vacuum (Fig. 2(c)) leading to a channel size of 1.41 nm along the diagonal. Calculated using PLATON,<sup>12</sup> PCN-19 has a solvent accessible volume of 47.2% (50.6% after removal of the aqua ligands).

The overall structure of PCN-19 is three dimensional, and topologically possesses a semiregular, non-uniform ( $4^9.6^6$ )-Archimedean (*acs*) net (Fig. 3) with the vertex symbol of 4.4.4.4.4.4(2).4(2).6(4).6(4).6(4).6(4).6(4).6(4), which is very rare in MOFs.<sup>10</sup>

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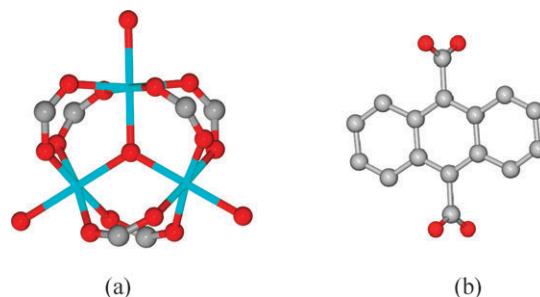
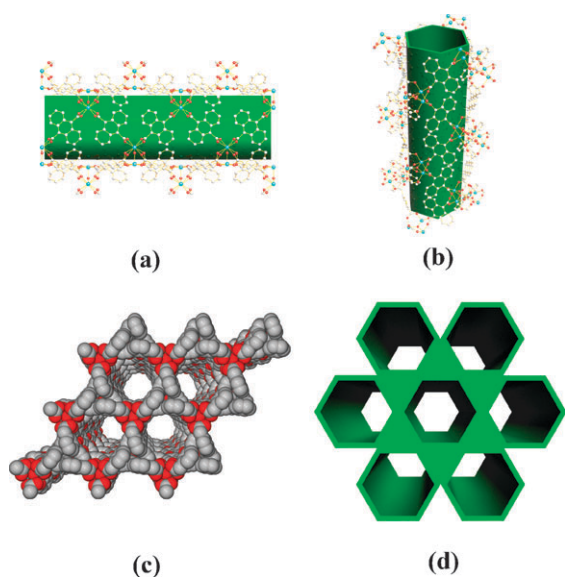
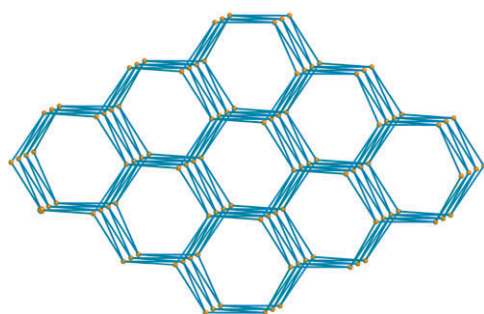


Fig. 1 (a) The  $\mu_3$ -oxo-trinickel basic-carboxylate SBU; (b) the adc ligand (carbon, grey; oxygen, red; nickel, turquoise).

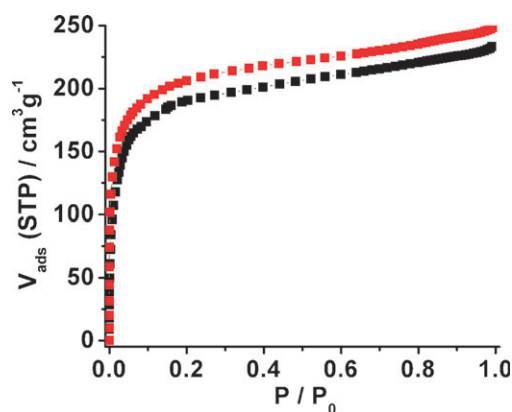


**Fig. 2** (a) Nanotube enclosed by adc ligands and trinickel SBUs, viewed from the crystallographic *a* or *b* direction; (b) a hexagonal tube; (c) 1D nanochannels with terminal aqua ligands of trinickel SBUs removed; (d) hexagonal nanotubes perpendicular to the *ab* plane.



**Fig. 3**  $(4^9,6^6)$ -*acs* topological net.

The intriguing nanotubular structure of PCN-19 prompted us to test its permanent porosity. A freshly prepared sample of PCN-19 was soaked in methanol for three days to remove free DMA guest molecules in the nanochannels, and then pumped under a dynamic vacuum at 50 °C overnight to activate the

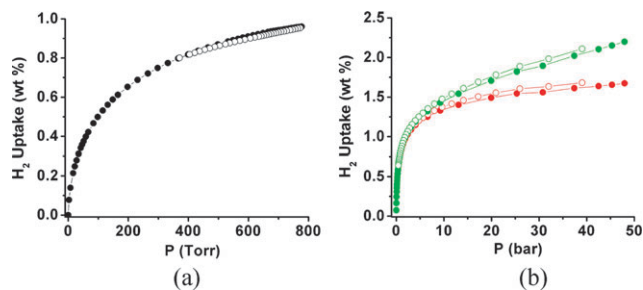


**Fig. 4**  $N_2$  adsorption isotherms of PCN-19 at 77 K: black, activated at 50 °C; red, activated at 150 °C.

sample. An  $N_2$  adsorption isotherm at 77 K (Fig. 4, black) reveals that PCN-19 exhibits type-I sorption behaviour, as expected for microporous materials. Derived from the  $N_2$  adsorption data, PCN-19 activated at 50 °C has a BET surface area of  $669 \text{ m}^2 \text{ g}^{-1}$  (Langmuir surface area,  $776 \text{ m}^2 \text{ g}^{-1}$ ) and a total pore volume of  $0.36 \text{ cm}^3 \text{ g}^{-1}$ . To remove the aqua ligands from the trinickel SBUs, we elevated the activation temperature to 150 °C. As indicated in Fig. 4 (red), PCN-19 still maintains its permanent porosity even after the liberation of the aqua ligands of the trinickel SBUs. The slightly higher surface area (BET,  $723 \text{ m}^2 \text{ g}^{-1}$ ; Langmuir,  $823 \text{ m}^2 \text{ g}^{-1}$ ) and larger total pore volume ( $0.38 \text{ cm}^3 \text{ g}^{-1}$ ) of PCN-19 activated at 150 °C compared to those of PCN-19 activated at 50 °C can be attributed to the space occupied by the aqua ligands of the trinickel SBUs, in good agreement with the differing solvent accessible volumes as calculated above.

To evaluate the hydrogen storage performance of this nanotubular MOF, hydrogen sorption isotherms of PCN-19 activated at 150 °C were measured under both low and high pressures at 77 K.<sup>13,14</sup> As shown in Fig. 5(a), PCN-19 can adsorb 0.95 wt% (excess) without any hysteresis at 77 K, 760 Torr. With the pressure increased to 48 bar, the excess gravimetric hydrogen uptake of PCN-19 can reach 1.67 wt% at 77 K, while the absolute gravimetric hydrogen adsorption capacity can achieve 2.20 wt% (Fig. 5(b)). Calculated from the crystal density of the PCN-19 with aqua ligands of the trinickel SBUs removed ( $0.954 \text{ g cm}^{-3}$ ), PCN-19 has an excess volumetric hydrogen storage capacity of  $15.93 \text{ g L}^{-1}$  and a corresponding absolute volumetric value of  $20.99 \text{ g L}^{-1}$ . These values are relatively lower than those of other reported three-dimensional MOFs,<sup>2</sup> which can be ascribed to the much lower surface area of PCN-19 compared to those reported MOFs. However, the hydrogen uptake capacities of PCN-19 are comparable with those of some carbon nanotubes,<sup>15</sup> and it represents, to the best of our knowledge, the first instance of hydrogen sorption in nanotubular MOFs.

In summary, a nanotubular metal–organic framework, PCN-19 with a rare *acs* topology was constructed based on the robust  $\mu_3$ -oxo-trinickel basic carboxylate SBU and the 9,10-anthracenedicarboxylate ligand.  $N_2$  adsorption isotherm data at 77 K confirmed its permanent porosity even after removal of the aqua ligands of the trinickel SBUs. Hydrogen sorption studies under both low and high pressures demonstrated impressive hydrogen uptake capacities of PCN-19



**Fig. 5** Hydrogen sorption isotherms of PCN-19 at 77 K: (a) low pressure (excess); (b) high pressure; (solid symbols, adsorption; open symbols, desorption; red symbols, excess; green symbols, total).

at 77 K, indicating the promise of nanotubular MOFs as potential candidates for hydrogen storage application.

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## Notes and references

† X-Ray crystal data for PCN-19:  $C_{48}H_{24}O_{16}Ni_3$ ,  $M_r = 1032.74$ , trigonal,  $P\bar{3}1c$ ,  $a = 15.5510(3)$ ,  $b = 15.5510(3)$ ,  $c = 16.3640(5)$  Å,  $V = 3427.18(14)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 90$  K,  $D_c = 1.007$  g cm<sup>-3</sup>,  $R_1 (I > 2\sigma(I)) = 0.0563$ ,  $wR2 = 0.1361$ , GOF = 0.902 [10151 reflections collected, 2631 unique ( $R_{int} = 0.0963$ )].

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