A biporous coordination framework with high H_2 storage density†

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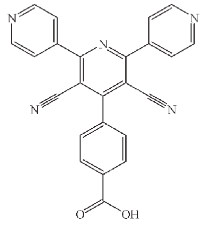
A biporous three dimensional (3,6)-connected coordination framework is reported which exhibits excellent H_2 adsorption at low pressures ($\leqslant$1 bar) with high H_2 adsorption density.

Rapid progress has been made in recent years in the design and construction of coordination frameworks with extended architectures.[1] A significant focus of research has been the development of porous coordination frameworks showing size- and shape-selective adsorption properties with potential applications in catalysis, ion-exchange, gas storage, and separation processes.[2] Among the numerous studies devoted to such materials, metal carboxylate units have been found to be especially effective in generating families of porous materials.[3,4] We envisaged that the pore walls of coordination frameworks, which typically comprise organic ligands, can be designed to incorporate additional functional groups[5] that might protrude into the framework pores, thereby offering the potential to tune the adsorption properties through both size and chemical selectivity.[6] One area of intense current interest is the development of coordination frameworks as materials for gas storage[7] and in particular for H_2 capture.[8]

In this study we present the use of a newly designed polytopic ligand, 3,5-dicyano-4-(4-carboxyphenyl)-2,2′:6′4″-terpyridine (Hdccptp), in the synthesis of a three-dimensional (3,6)-connected coordination framework, $[\mathrm{Cu(dccptp)(NO_3)}]\cdot0.5(1,4\text{-dioxane})\cdot0.5\mathrm{MeOH}$ **1**, which contains two distinct channels that adsorb different guest molecules from the mixture of two solvents used in the synthesis. Compound **1** also exhibits strong H_2 absorption capacity, particularly in terms of the adsorbed H_2 density.


Hdccptp

Hdccptp was synthesized from β-amino-β-(pyrid-4-yl)acrylonitrile, prepared by a modification of Yamagushi's method,[9] and 4-carboxybenzaldehyde in acetic acid. Green crystals of **1** were harvested from the reaction of Hdccptp with $\mathrm{Cu(NO_3)_2\cdot2.5H_2O}$ in a mixture of MeOH and 1,4-dioxane at 100 °C. The composition of **1** was confirmed by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy and TGA investigations, and the phase purity of the bulk sample was confirmed by powder XRD. In the IR spectrum, a strong band centred at around 2350 $\mathrm{cm^{-1}}$, characteristic of the stretching vibration of non-coordinated cyano groups, confirms the presence of the cyano groups within the dccptp ligands.

The single-crystal diffraction analysis of **1** reveals a three-dimensional (3,6)-connected coordination framework constructed from binuclear $\{\mathrm{Cu_2}\}$ building-blocks and $\mathrm{dccptp^-}$ ligands.‡ Significantly, each $\mathrm{dccptp^-}$ ligand binds to Cu(II) *via* one carboxylate and the two outer pyridyl donors, leaving two nitrile groups and the inner pyridyl amine unbound. Within the binuclear $\{\mathrm{Cu_2}\}$ units each Cu(II) cation adopts a slightly distorted square-pyramidal coordination geometry, with the basal positions occupied by one $\mathrm{NO_3^-}$ oxygen, and by one carboxylate oxygen and two pyridyl nitrogens from three separate $\mathrm{dccptp^-}$ ligands, with another carboxylate oxygen from a fourth $\mathrm{dccptp^-}$ ligand bound at the axial site. Carboxylate bridging leads to the formation of a binuclear $\{\mathrm{Cu_2}\}$ building-block, which is significantly different to the well-known paddlewheel $[\mathrm{M_2(O_2CR)_4}]$[3a–d] clusters. In **1**, only two carboxylate groups bridge the metal centres rather than the four observed in paddlewheel clusters, and this results in a much longer intra-dimer Cu···Cu distance [4.268(2) Å] than in conventional paddlewheel species (*ca.* 2.65 Å[3c,d,8e]). The binuclear $\{\mathrm{Cu_2}\}$ unit serves as a six-connected octahedral unit and the bridging $\mathrm{dccptp^-}$ ligands acting as three-connected nodes resulting in an infinite 3D (3,6)-connected porous coordination framework (Fig. 1a) of $(4^2\cdot6)_2(4^4\cdot6^2\cdot8^7\cdot10^2)$ topology (Fig. 1b). The same topology is observed in $\{[\mathrm{Cd(5\text{-}(4\text{-}pyridyl)\text{-}1,3,4\text{-}oxadiazole\text{-}2\text{-}thiolate)_2]\cdot CHCl_3}\}_n$ reported by Xu and co-workers.[10] Three-dimensional frameworks with mixed connectivities and unbound donors such as that reported here remain relatively rare[8f,11] although (3,6)-connected topologies have been observed in rutile [Schläfli symbol $(4\cdot6^2)_2(4^2\cdot6^{10}\cdot8^3)$],[12a,b,c] pyrite $(6^3)_2(6^{12}\cdot8^3)$,[12d,e] and anatase $(4^2\cdot6)_2(4^4\cdot6^2\cdot8^8\cdot10)$[12f] materials. Interestingly, two distinct channels (A and B) exist within the coordination framework of **1** (Fig. 1c). Both the cyano groups from $\mathrm{dccptp^-}$ ligands and coordinated $\mathrm{NO_3^-}$ anions protrude into the rhombic channel A. Channel B is surrounded both by the aromatic faces of phenyl groups and coordinated pyridyl rings of $\mathrm{dccptp^-}$ ligands, with the uncoordinated central pyridyl nitrogen atoms located at the corner of the channel. The approximate dimensions of the channels are 4.7 × 5.4 Å (channel A) and 4.6 × 7.8 Å (channel B) with the two acting as different hosts; channel A is filled with molecules of MeOH sandwiched between the free cyano groups of $\mathrm{dccptp^-}$, and channel B contains only 1,4-dioxane molecules. Thus, **1** acts as a biporous host separating the solvents used in the synthesis. An

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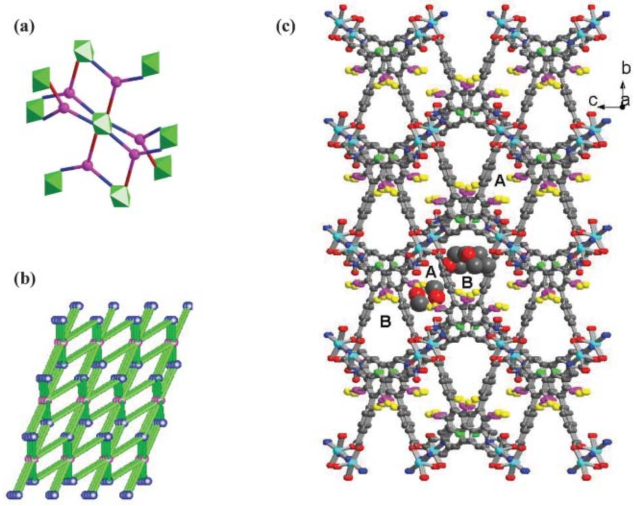

Fig. 1 (a) Schematic representation of the interconnectivity of the 3- and 6-connecting nodes; (b) schematic representation of the $(4^26)_2(4^46^28^710^2)$ topological net of **1** (viewed close to the [010] direction; purple balls representing six-connected $\{Cu_2\}$ nodes, and blue balls ones represent the 3-connected central pyridyl nodes; (c) View of the (3,6)-connected biporous framework of **1** viewed close to [100] direction. The two types of channel (A and B) are identified, with their respective MeOH and 1,4-dioxane guests (space-filling mode) illustrated in selected pores only for clarity. Colours for functional groups: nitrile C, purple; nitrile N, yellow; uncoordinated pyridyl N, green; Cu, cyan; N, blue; C, grey; and O, red. All hydrogen atoms omitted for clarity.

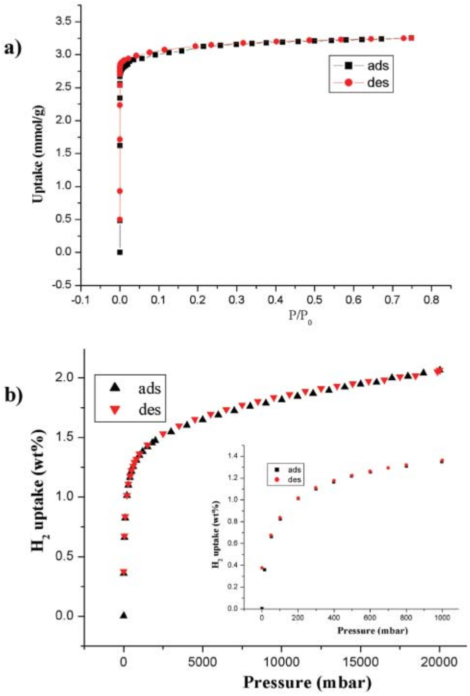

Fig. 2 (a) N_2 sorption isotherm and (b) H_2 sorption isotherm for **2** at 77 K with an enlargement of the low-pressure region of the H_2 isotherm (inset in b); ads = adsorption and des = desorption.

analysis of the host void of **1** reveals that 31.4% of the unit cell volume is occupied by the guest solvent species (Fig. 1a).[13]

Thermal gravimetric analysis (TGA) experiments on **1** confirm that the guest MeOH and 1,4-dioxane are both removed (total weight loss, 10.4%, calc. 10.2%) by 160 °C under a flow of N_2 at room pressure, significantly above the boiling point of 1,4-dioxane (101 °C). The guest-free framework is stable to further heating until two consecutive weight losses occur over the range 260–560 °C leading to decomposition. The desolvated form of **1**, hereinafter compound **2**, remains crystalline with a PXRD pattern very similar to the diffraction pattern simulated from the single-crystal diffraction data of **1** but with broadening of some diffraction peaks.

The desolvated framework **2** was generated by heating **1** at 125 °C for 20 h under high vacuum (10^{-8} mbar). The N_2 sorption isotherm at 77 K (Fig. 2a) reveals a reversible type-I sorption behaviour characteristic of a microporous material. The BET surface area is calculated to be 268 m^2 g^{-1}, and the given microporous volume is 0.113 cm^3 g^{-1}, confirming there are accessible micropores in **2**. These values are comparable to those for smaller-pore zeolites, but are significantly lower than the values reported for many MOFs with high surface areas.[2a,b,8] The pore size determined by applying the Dubinin–Astakhov (DA) equation[14] to the sorption data is 5.6 Å, with a narrow distribution, in good agreement with values calculated from single-crystal diffraction data for **1**.

A gravimetric H_2 sorption isotherm of **2** was recorded from 0–20 bar at 77 K. It also showed fully reversible type-I sorption behavior (Fig. 2b) indicative of the filling of the micropores only.[15] The capacity of **2** to adsorb H_2 increases from *ca.* 1.01 wt% at 0.2 bar to 1.91 wt% at 20 bar (Fig. 2b and Table S1†). It should be noted that there is a significant discrepancy between the measured pore volume (0.113 cm^3 g^{-1}) from the N_2 isotherm and the value calculated from the single-crystal X-ray structure (0.261 cm^3 g^{-1}) using PLATON.[13] This is possibly due to the N_2 molecules being unable to effectively enter small pores at 77 K, which can either be caused by some energy barrier or blocking of pores by strongly adsorbed N_2 molecules. The lack of biporous sorption behaviour in the N_2 isotherms also supports this observation. If either of these accounts for the low N_2 adsorption, the smaller dynamic diameter of H_2 may then allow more effective adsorption and diffusion into the pores of **2**. Therefore, the density of the maximum adsorbed H_2 (1.99 wt%, obtained from Langmuir plots of H_2 adsorption) was calculated with respect to $V_{\text{P-PLATON}}$ (0.261 cm^3 g^{-1}), giving a value of approximately 0.0762 g cm^{-3}, slightly higher than the density of liquid H_2 (0.0708 g cm^{-3}),[16] suggesting that H_2 is highly compressed within the pores of **2**. In addition, the rapid increase in H_2 uptake at low-pressures (Fig. 2b) is consistent with a strong interaction between H_2 molecules and the pore walls, possibly due to the presence of cyano groups within the pore walls. Using Dubinin–Radushkevich (DR) analysis,[14] the adsorption energy βE_0 and the isosteric heat of H_2 adsorption $q_{\text{st},\Phi=1/e}$ at the fraction filling of 1/*e* for **2** were found to be 5.21 and 6.12 kJ mol^{-1}, respectively. These are higher than values observed for active carbons[2c] (βE_0, ~3 kJ mol^{-1}; $q_{\text{st},\Phi=1/e}$, ~4 kJ mol^{-1}) and for reported microporous metal–organic frameworks such as $[Zn_2(L)]$ (L = 4,4′-bipyridine-2,6,2′,6′-tetracarboxylate) where βE_0 = 4.20 kJ mol^{-1}, $q_{\text{st},\Phi=1/e}$, 5.12 kJ mol^{-1}.[8c] These high values indicate that **2** has a relatively high affinity for H_2, and the amount of adsorbed H_2 can, therefore, rapidly approach its maximum capacity at low pressure (Fig. 2b).

Although the maximum uptake of H_2 is relatively low in comparison to the highest capacity coordination framework materials reported to date (3.44–7.52 wt%),[8e,f,17] the performance of **2** at low pressures compares favourably with previous examples. The H_2 uptake of **2** at 1 bar (1.34 wt%) is comparable to microporous zeolites and aluminophosphates,[18] but lower than that of MOF-505 or [Cu_2(bptc)], which show high capacities of H_2 weight percentage uptake ($\sim$2.5 wt%) under similar conditions (77 K and 1 atm).[8e,17,19] Significantly, however, H_2 absorption by **2** at pressures $\leqslant$0.5 bar are appreciably higher than those of the best MOF materials, *e.g.* 1.01 wt% at 0.2 bar for **2** *vs.* 0.58 wt% at 0.2 bar for IRMOF-11, or 0.60 wt% at 0.5 bar for MOF-5.[16] At 1 bar, 67.3% of the H_2 storage capacity of **2** has been reached, also notably higher than the corresponding values for MOF-5 (24.4%), IRMOF-6 (24.5%) IRMOF-20 (19.4%), MOF-177 (13.2%) and IRMOF-11 (42.9%).[17] Moreover, the kinetic data for H_2 absorption of **2** indicate that equilibrium is achieved rapidly in less than two minutes for an isotherm pressure step (see ESI†). In addition, **2** shows a high volumetric H_2 uptake (23.9 g L^{-1}), comparable to some of the best MOFs (26.8–34.2 g L^{-1}),[17,19] but significantly lower than our recent report of the highest volumetric storage density of 43.6 g L^{-1} for [Cu_2(tptc)], a value very close to the 2010 DOE target of 45 g L^{-1}.[8e]

In summary, a three-dimensional (3,6)-connected biporous coordination framework has been synthesized using a designed polytopic ligand with nitrile appendages. The H_2 adsorption measurement at 77 K reveals that the desolvated framework, **2**, can absorb 1.01 wt% H_2 at 0.2 bar and reaches a value of 1.91 wt% at 20 bar. Although the maximum uptake of H_2 is modest, the H_2 adsorption density and the relative H_2 absorption at low pressure ($\leqslant$1 bar) is the highest reported thus far.

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Notes and references

‡ Crystal data for **1**: $C_{24}H_{12}CuN_6O_5 \cdot \frac{1}{2}(CH_3OH) \cdot \frac{1}{2}(C_4H_8O_2)$, M = 588.01, monoclinic, space group $C2/c$, a = 12.2342(11), b = 25.093(2), c = 19.6064(18) Å, β = 104.225(2)°, V = 5834.4(9) $Å^3$, Z = 8, T = 150(2) K, μ(Mo-Kα) = 0.799 mm^{-1}, 15 057 reflections measured, 5275 unique (R_{int} = 0.046) which were used in all calculations. Disorder of the cyano groups was modelled by allowing two alternative positions for each C or N atom: the final refined occupancies were 0.647(8) for C13 and N2 *versus* 0.353(8) for C13′ and N2′; and 0.545(7) for C14/N3 *versus* 0.455(7) for C14′ and N3′. Final R_1 = 0.0803, wR_2 = 0.235, maximum ΔF peak 1.15 e $Å^{-3}$. Solvent molecules were seriously disordered but were satisfactorily modelled. The SQUEEZE function within the PLATON suite of programs[13] was additionally used to confirm the solvent content within the unit cell as four dioxane and four methanol molecules per unit cell.

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