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Novel mode of 2-fold interpenetration observed in a primitive cubic network of formula $[\text{Ni}(\text{1,2-bis(4-pyridyl)acetylene})_2(\text{Cr}_2\text{O}_7)]_n$

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 Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A primitive cubic (pcu) network of formula $[\text{Ni}(\text{1,2-bis(4-pyridyl)acetylene})_2(\text{Cr}_2\text{O}_7)]_n$, **DICRO-2-Ni-i**, has been synthesised and found to exhibit a novel type of inclined 2-fold interpenetration and an isosteric heat of adsorption (Q_{st}) of 30.5 kJ/mol towards CO_2 at zero loading. Q_{st} is relatively high in the broad context but less than that observed in related hybrid ultramicroporous materials, a feature that can be understood after studying pore structure and molecular simulations of CO_2 adsorption.

Our understanding of how molecular structure influences crystal packing, crystal structure and, therefore, physicochemical properties has progressed steadily over the past two decades. Now, crystal engineering¹ offers a number of rational design strategies for the creation of new families of crystalline materials with desired functional properties. Metal-Organic Materials (MOMs),² also known as coordination polymers or metal-organic frameworks,³ represent a broad class of materials particularly suited to the principles of crystal engineering as their modular nature lends itself to systematic study of properties of relevance to applications as diverse as gas separation and storage,⁴ catalysis,⁵ small-molecule separation⁶ and chemical sensing⁷. An important subclass of MOMs is emerging, which combines two features that can enhance sorbent-sorbate interactions: the presence of inorganic anions that offer strong electrostatics when compared with organic linker ligands; ultramicropores (<0.7 nm) that offer a good fit for important sorbates such as CO_2 and CH_4 . This subclass, which could be termed *Hybrid Ultramicroporous Materials*, or HUMs, have recently been found to exhibit benchmark selectivity for small polar gases such as CO_2 over competing less polar gases like N_2 .⁸

Two families of HUMs or "HUM platforms" have been developed by our group. The first platform is derived from parent materials comprised from square lattice (sql) nets constructed from transition metals and dipyrindyl ligands⁹

pillared with hexafluorometallate anions (*i.e.* SiF_6^{2-} , TiF_6^{2-} , etc.)¹⁰ to generate pcu structures with pores ranging from <0.4 nm to >1.3 nm.⁸ The second platform is also based upon sql nets built from transition metals and dipyrindyl ligands, but the inorganic pillar is chromate, molybdate or tungstate (CrO_4^{2-} , MoO_4^{2-} or WO_4^{2-}). These oxyanions serve as angular pillars and afford structures that adopt a novel topology, **mno**.^{8a, 8b} Aiming to expand the scope of HUMs, we analysed the Cambridge Structural Database (CSD),¹¹ which revealed a potential platform based upon dichromate pillars: pcu networks derived from $[\text{M}^{\text{II}}(\text{4,4'-bipyridine})_2(\text{Cr}_2\text{O}_7)]_n$ (where $\text{M} = \text{Fe}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+}).¹² To adopt a consistent nomenclature, we have named this platform of materials **DICRO-X-M**, where **DICRO** = dichromate anion, **X** = ligand, numbered by order of publication and **M** = transition metal. In the case of interpenetration -i is appended. Using this nomenclature, the previously published structures belong to the subset **DICRO-1-M-i**.

We report herein the second subset of this platform, $[\text{Ni}(\text{1,2-bis(4-pyridyl)acetylene})_2(\text{Cr}_2\text{O}_7)]_n$ **DICRO-2-Ni-i** (Fig. 1), a 2-fold interpenetrated structure that represents the first example of a pcu network in which the frameworks are orientated in an inclined arrangement, resulting in a 1D channel running through the structure. **DICRO-2-Ni-i** was characterised by single-crystal and powder X-ray diffraction, thermogravimetric analysis, FT-IR spectroscopy and gas

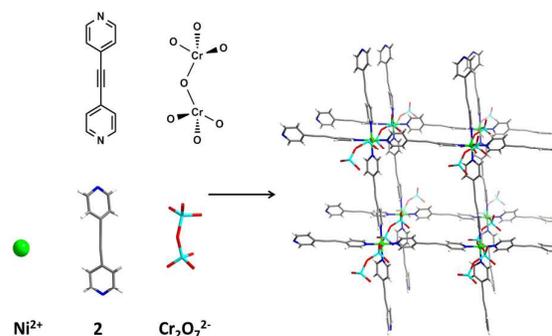


Figure 1. **DICRO-2-Ni-i** is formed by self-assembly of octahedral Ni^{2+} centres (green), organic linkers (**2**) (grey C and dark blue N) and dichromate anions that serve the role of pillars (light blue Cr and red O).

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† Electronic Supplementary Information (ESI) available: Complete synthetic protocol, compound characterisation and crystallographic details. See DOI: 10.1039/x0xx00000x

sorption measurements (CO_2 and N_2). In addition, molecular simulations of CO_2 adsorption were conducted in order to enable interpretation of the experimental gas sorption measurements.

DICRO-2-Ni-i was synthesised at room temperature (see Electronic Supplementary Information, ESI[†]) by layering an aqueous solution of $\text{NiCl}_2/\text{K}_2\text{Cr}_2\text{O}_7$ over an acetonitrile solution of ligand **2** (see Fig. 1). The crystal structure of the resulting product was determined by single-crystal X-ray diffraction (ESI[†]) from data collected at 100 K and found to crystallise in the orthorhombic space group *I*222. Powder X-ray diffraction experiments (ESI[†]) indicate that the bulk material obtained from slow-diffusion layering consisted of a single phase and that this phase matches the pattern calculated from the structure determined from single-crystal X-ray diffraction. Thermal stability measurements (ESI[†]) reveal that **DICRO-2-Ni-i** is stable up to ca. 200 °C, after which point it undergoes significant weight loss attributable to decomposition (Fig. S2).

In **DICRO-2-Ni-i**, each Ni^{2+} cation adopts octahedral coordination geometry: four nitrogen atoms from four different dipyriddy linker ligands (**2** in Fig. 1) form the equatorial plane with an average Ni-N bond distance of 2.049(16) Å; ligand **2** exhibits a torsion angle of 53.3° between pyridyl groups. The octahedral coordination geometry is completed with two oxygen atoms from two different dichromate anions ($\text{Cr}_2\text{O}_7^{2-}$) that bind at the axial positions of the Ni^{2+} cations with Ni-O bond distances of 2.018(13) Å. These distances correspond closely with the value observed in the parent compound **DICRO-1-Ni-i**.^{12c} Each Cr atom adopts tetrahedral geometry with O-Cr-O bond angles ranging from 106.3(13) - 114.78(11)°; while the Cr-O-Cr angle is 141.6(2)°. The Ni-O-Cr angles are acute at 166.8(8)°, as seen in chromate pillared *mmo* nets. The four organic linker ligands, which generate the equatorial plane, bridge to adjacent Ni^{2+} cations, resulting in a 2D (4,4) square lattice (*sql*). Two oxygen atoms from each $\text{Cr}_2\text{O}_7^{2-}$ anion are coordinated to two Ni^{2+} cations from different *sql* layers, thereby pillaring the *sql* layers and generating the observed *pcu* network.

While self-assembly of judiciously chosen “nodes” and “linkers” can afford MOMs with predictable network topologies, control over the presence, mode and level of interpenetration remains a challenge.¹³ This is exemplified by interpenetrated 2D square lattices (*sql*) and pillared square grids, which exhibit *primitive cubic* topology (*pcu*) and are also susceptible to interpenetration. Interpenetrated nets are of topical interest because interpenetration can profoundly affect bulk properties such as luminescence⁷ and gas sorption.¹⁴ When referring to interpenetration, the topology nomenclature it has been suggested that it should be modified with a *-c* extension to signify catenation.¹⁵ However, this designation does not address the mode of interpenetration. The novel mode of interpenetration is therefore analysed using Hopf ring network analysis, which can differentiate between modes of interpenetration. Interpenetrated *pcu* then becomes *pcu-c*. While beyond the scope of this article, investigations into controlling interpenetration have been explored elsewhere.¹⁶

Interpenetration is particularly relevant with respect to gas sorption because it can lead to the formation of ultramicropores which enhance sorption performance, and, when controlled, allows for comparison between interpenetrated and non-interpenetrated variants of the same compound (polymorphs). Enhanced sorption performance is particularly seen when the pore structure is such that pores are lined by highly electrostatic inorganic species. In such a situation, the small pore diameter means that the adsorbate is necessarily confined to a cavity that is only slightly larger than the kinetic diameter of the gas molecule itself. The adsorbate is thereby forced to interact with all walls of the cavity simultaneously as opposed to just a surface. When combined with the strong electrostatics of inorganic anions, new benchmarks for important parameters such as Q_{st} and selectivity can be achieved.⁸

A review of the literature reveals that all previous examples of 2-fold *pcu-c* networks exhibit interpenetration in which the linkers are parallel to one another, *i.e.* independent

networks are shifted in a parallel direction to one another through translation. Individual networks in **DICRO-2-Ni-i** interpenetrate in such a way that the organic dipyriddy linkers intersect one another at an angle of ca. 35° (see Fig. 2), suggesting translation and a rotation of the second framework in reference to the first. Hopf ring net analysis¹⁷ was used to classify the interpenetration of **DICRO-2-Ni-i** by topological type. In HRN analysis, each *strong ring* in an individual network is replaced with a single node located at that ring's barycentre. This node is then connected to every node

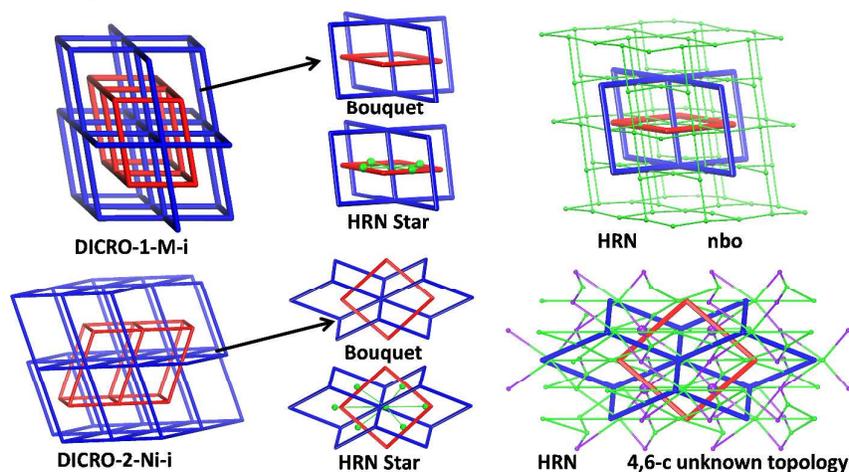


Figure 2. Comparison of interpenetration in **DICRO-1-M-i** (top row) and **DICRO-2-Ni-i** (bottom row): *Left* – scheme of interpenetration, *Centre* – bouquet and HRN star, *Right* – HRN topology.

that is constructed from rings originating from the second network that catenate the first ring (see Fig. 2). In this way, the number of rings from one network that catenate each ring in the second network, leads to the connectivity of the node derived from the catenated ring. Therefore, the HRN topology reveals information on both the number and modes of catenation between two interpenetrating frameworks.

A survey of all known 2-fold interpenetrated **pcu-c** networks (*ca.* 300) revealed that only two modes of interpenetration had previously been reported. In the vast majority of cases (98%), the mode of interpenetration is such that each ring of one network is entangled with four similar rings from the second network (Fig. 2). This generates a Hopf ring net (HRN) that is 4-c and adopts **nbo** topology. There have also been a handful of instances, involving bent ligands, which lead to 2-fold interpenetrated **pcu-c** systems in which the HRN adopts a 6-c net with **hxg** topology. **DICRO-2-Ni-i** represents the first example of a third pattern of interpenetration wherein rings from the two independent networks entangle to form a HRN that adopts a binodal 4,6-c network with previously unknown topology (Fig. 2). This new topology has point symbol $(4^2.6^3.8)_2(4^4.6^9.8^2)$.

In addition to the unique interpenetration mode, the key difference between **DICRO-1-M-i** and **DICRO-2-Ni-i** is that the latter incorporates a longer organic linker ($N\cdots N$ **1** = ~ 7 Å; **2** = ~ 9 Å) because ligand **2** incorporates an alkynyl group that extends length and conjugation. The novel mode of interpenetration between the two nets results in a 1D channel parallel with the *a*-axis with a pore diameter of *ca.* 3.6 Å. The permanent microporosity of **DICRO-2-Ni-i** was verified by N_2 sorption experiments performed at 77 K, where the *apparent* BET surface area was calculated to be 234 m²/g. Based on liquid filling of N_2 at the saturated state, the uptake of 63.4 cm³/g at $P/P_0 = 0.25$ corresponds to a pore volume of 0.091 cm³/g, which is close to 0.094 cm³/g calculated from single-crystal data. CO_2 sorption isotherms of **DICRO-2-Ni-i** at 273, 283 and 293 K were conducted and are presented in Fig. 3. CO_2 uptakes of 26.0, 23.4 and 19.9 cm³/g were measured at 1 bar and 273, 283 and 293 K, respectively. The N_2 uptake at 1 bar and 293 K was observed to be only 2.6 cm³/g. For a gas mixture at 1 bar comprised of 85% N_2 and 15% CO_2 , the selectivity predicted using *Ideal Adsorbed Solution Theory*¹⁸ for **DICRO-2-Ni-i**, based on the single-component CO_2 and N_2 sorption isotherms at 293 K, was calculated to be 41. **DICRO-2-Ni-i** should therefore exhibit selective adsorption for CO_2 over N_2 (Fig. S8) and with higher selectivity than compounds such as **HKUST-1** (20.1)¹⁹ and **SIFSIX-2-Cu** (13.7).^{8c}

In order to evaluate the strength of interaction between CO_2 and the framework, the CO_2 isotherms measured at 273, 283 and 293 K were fitted using the virial equation (Fig. S6), and the isosteric heats of adsorption (Q_{st}) were calculated using the Clausius–Clapeyron equation. The enthalpy at zero loading for **DICRO-2-Ni-i** is 30.5 kJ/mol (Fig. S7). This value is consistent with values observed in other classes of MOMs with **pcu** topology type incorporating hexafluorometallate as linear inorganic anions for pillars, **SIFSIX-2-Cu-i** (31.9 kJ/mol),^{8c} **TIFSIX-1-Cu** (26.5 kJ/mol)^{8d} and **SNIFSIX-1-Cu** (26.5 kJ/mol).^{8d}

However, the Q_{st} of **DICRO-2-Ni-i** is much smaller than that of **CROFOUR-1-Ni** (*ca.* 50 kJ/mol),^{8b} a HUM with **mno** topology, and **SIFSIX-3-Zn**.^{8e} The Q_{st} in **CROFOUR-1-Ni** was validated using molecular simulations, which indicate that electrostatics of the exposed oxygen atoms of the CrO_4^{2-} anion results in attraction towards CO_2 that is enhanced by induced polarisation. That **DICRO-2-Ni-i** exhibits weaker attraction for

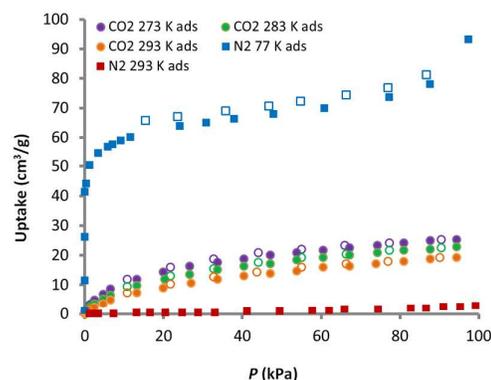


Figure 3. Single component gas adsorption (filled symbols) and desorption (empty symbols) isotherms for **DICRO-2-Ni-i**.

CO_2 than the aforementioned HUMs could be attributed to structural orientation, electrostatic effects or both. In **DICRO-2-Ni-i**, the dichromate anions are orientated in such a way that they do not protrude into the channel thought to be the site of CO_2 binding according to molecular simulations. This is in contrast with **CROFOUR-1-Ni**, in which the binding sites for CO_2 are lined by oxygen atoms of chromate anions. A similar situation exists in other high performing HUMs such as **SIFSIX-3-Zn**^{8c} and **SIFSIX-3-Cu**,^{8e} whereby the cavities accessible to the CO_2 are lined with highly electrostatic inorganic anions.

Molecular simulations of CO_2 adsorption in **DICRO-2-Ni-i** have been performed and indicate that CO_2 molecules adsorb into the accessible 1D channel as viewed along the *a*-axis of the crystal structure (Fig. 4). The simulations reveal that the small pore size (3.6 Å diameter), a consequence of interpenetration, generates tight packing of CO_2 molecules within the channel. The simulations also reveal the absence of interactions between oxygen atoms of $Cr_2O_7^{2-}$ anions and guest CO_2 molecules, likely due to inaccessibility, which could

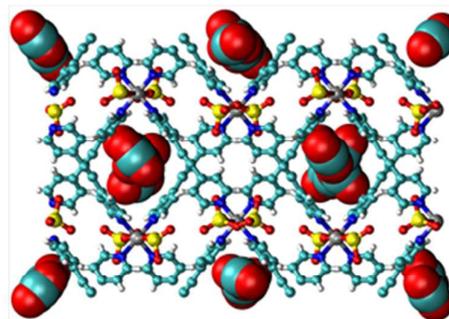


Figure 4. The *a*-axis view of the modelled $3 \times 2 \times 1$ system cell of **DICRO-2-Ni-i** at CO_2 saturation. Atom colours: C = cyan, H = white, N = blue, O = red, Cr =

explain the lower than expected Q_{st} value of 30 kJ/mol (~20 kJ/mol lower than **CROFOUR-1-Ni**).

In summary, a new 3D Hybrid Ultramicroporous Material (HUM), **DICRO-2-Ni-i**, has been constructed using dichromate anions as pillars to cross-link square lattices (sql) into a **pcu-c** network. This compound is the first example of 2-fold inclined interpenetration in **pcu-c** frameworks. This unique mode of interpenetration, complete with a new Hopf ring network topology, affords a distinct ultramicroporous 1D channel within the structure. Structural analysis, gas sorption experiments and molecular simulations indicate this channel is just large enough to adsorb molecules of CO₂. Additionally, molecular simulations suggest that CO₂ molecules are confined to the ultramicroporous channels and are effectively isolated from interacting with the strongly electrostatic dichromate anions. Isolation of the CO₂ molecules from the dichromate anions likely results in the somewhat lower than expected Q_{st} when compared with similar HUMs, which we attribute to very different pore chemistry. Future work will focus upon expanding the **DICRO-X-M** platform and further examples of **pcu-c** HUMs constructed using Cr₂O₇²⁻ in order to evaluate the effect of this anionic inorganic pillar upon gas sorption performance. The incorporation of a second metal centre (chromium) into these porous systems also offers the prospect of introducing a secondary function, including heterogenous catalysis or redox behaviour.

Notes and references

§ M.J.Z. acknowledges SFI (13/RP/B2549), and B.S. acknowledges the National Science Foundation (Award No. CHE-1152362). Computational resources were made available by XSEDE Grant No. TG-DMR090028. The use of the services provided by Research Computing at the University of South Florida is also acknowledged.

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