Terminal co-ligand directed synthesis of a neutral, non-interpenetrated (10,3)-*a* metal–organic framework

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A neutral, non-interpenetrated porous metal–organic framework (MOF) having (10,3)-*a* topology, Cu(3,5-PDC)(DMF)(py), (DMF = *N,N′*-dimethylformamide, py = pyridine), has been constructed *via* the assembly of the achiral tri-connected building blocks 3,5-pyridinedicarboxylate (3,5-PDC) and $CuN(CO_2)_2$, synthesized *in situ*. Similarly, a 2D structure having (6,3) topology has been generated, each by means of terminal co-ligand directed synthesis.

Metal–organic frameworks have myriad potential applications, including gas storage,[1] catalysis, and separations.[2] Through top-down design, previously enumerated networks[3] are dismantled into their specific primary building units or nodes. For any given simple node, there exist predominant structures,[4] commonly classified as default structures, and these prevalent topologies are set as logical targets for the would-be designer. Suitable inorganic and organic molecular building blocks (MBBs) are rationally predesigned and chosen to contain the required geometrical information and directional binding functionalities to facilitate the molecular assembly of frameworks having predetermined topologies. This approach has formerly permitted the bottom-up construction, *via* metal–ligand directed synthesis, of metal–organic assemblies having common topologies.[5]

Of special interest is the rational design and synthesis of chiral networks, which offer great potential in nonlinear optics,[6] asymmetric catalysis, and chiral separation.[2] Therefore, a logical target for synthesis would be a default structure that possesses chirality. The (10,3)-*a*[7] network meets these requirements since it is mutually chiral and regarded as the default 3-D structure for the assembly of tri-connected building blocks.

Chiral MOFs having (10,3)-*a* topology can be targeted and constructed in one of two manners: (a) organic or inorganic bridging of tri-connected inorganic or organic MBBs; or (b) direct assembly of tri-connected inorganic and organic MBBs. These two approaches have previously permitted the synthesis of predominantly charged and/or *n*-fold interpenetrated chiral (10,3)-*a* networks.[7] Therefore, the element of design would be necessary to attain a neutral and non-interpenetrating (10,3)-*a* network. Recently, we have shown that the design of metal–organic assemblies can be achieved through the utilization of a multifunctional ligand and a heterocoordinated metal, and here we have elected a similar route.[8]

As such, the multifunctional ligand 3,5-pyridinedicarboxylic acid (3,5-H_2PDC) is of particular interest for obtaining a neutral (10,3)-*a* network. Specifically, this ligand possesses two potential carboxylic acid coordinating sites, which can each be deprotonated, resulting in a divalent anion, and a third, neutral aromatic nitrogen coordinating site. Overall, 3,5-PDC will then act as a tri-connected node that eliminates the need for charge balance by guest molecules when properly coordinated to divalent metal cations.[9] Given the proper three-connected heterocoordination about the metal center, 3,5-PDC offers great potential for obtaining the desired neutral tri-connected (10,3)-*a* network.

Herein, we report the assembly of 3,5-PDC and Cu(II) into the desired chiral MOF having (10,3)-*a* topology, Cu(3,5-PDC)(DMF)(py), **1**†. To our knowledge, **1** is a rare example of a (10,3)-*a* network that is neither charged nor interpenetrated.[7] As expected, the framework exists as a uniform network comprised of tri-connected Cu(II) centers coordinated to and bridged by three crystallographically independent homologous tri-connected 3,5-PDC ligands, $CuN(CO_2)_2$.

Each copper center of **1** is coordinated to two oxygens and one nitrogen, respectively, of three crystallographically independent 3,5-PDC ligands. The square pyramidal (MN_2O_3) coordination geometry of copper is completed by the nitrogen of a terminal pyridine ligand and the oxygen of a terminal DMF to give a "T"-shaped tri-connected secondary building unit (SBU), as shown in Fig. 1a, which becomes trigonal in the resulting topology (Fig. 1d). The coordinated py and DMF orient to the interior of the channels, running along the *x*- and *z*-axes, each predominantly filling the void space in the channels running along the *z*-axis and thus preventing self-interpenetration.

Thermogravimetric analysis (TGA) indicates two major weight changes around 175 and 265 °C. The first loss of nearly 25% accounts for the liberation of coordinated guest molecules. The second major weight loss of *ca.* 45% primarily accounts for the framework decomposition. Elemental analysis and single crystal data support the absence of free guest molecules in **1**, confirming that the initial weight loss observed in the TGA is mainly due to the liberation of coordinated guest molecules. The fully evacuated framework retains its structural integrity as confirmed by the preservation of the majority of the X-ray powder diffraction (XRPD) peaks initially observed for the as-synthesized compound, **1**.

Two-dimensional structures can also be constructed from tri-connected nodes, and it is known that the (6,3) network is the default two-dimensional structure, existing in brick wall, herringbone, or, most commonly, honeycomb pattern.[10] Therefore, it is logical that such a structure could also be constructed from the assembly of 3,5-PDC and Cu(II), $CuNO_2$, as in **1**, by controlling the coordination functionality and thus geometry of the inorganic building units.

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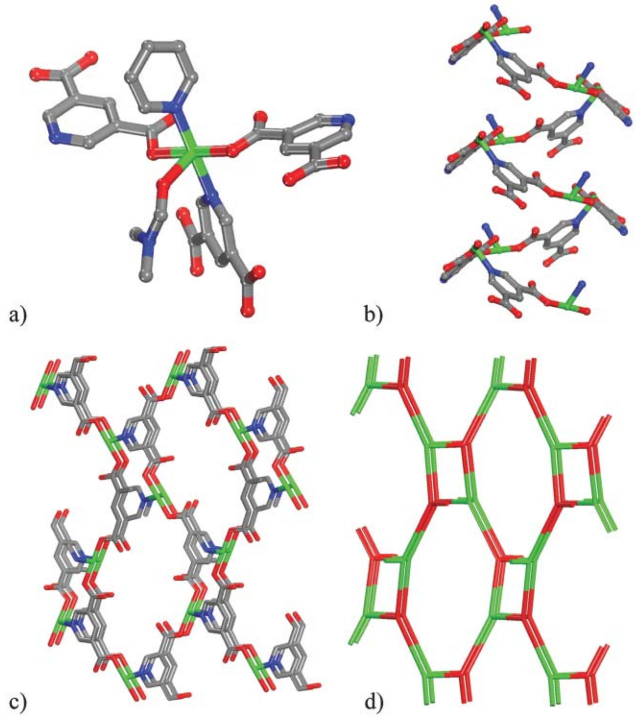

Fig. 1 (a) Cu(3,5-PDC)(DMF)(py) tri-connected SBU of **1**, (b) the side-on view of one of the spring-like pores looking down the *y*-axis (010 direction), (c) the chiral network of **1** Cu(3,5-PDC)(DMF)(py) looking down the *x*-axis (100 direction), and (d) the (10,3)-*a* topology. In each example (except d), carbon is gray, copper is green, nitrogen is blue, and oxygen is red. Hydrogen, py, and DMF have been omitted for clarity where necessary.

Herein, we report the synthesis of the default 2D network as a distorted honeycomb *via* the assembly of tri-connected nodes. Cu(3,5-PDC)(py)$_2$, **2**,† was obtained from relatively similar conditions and reagents as with **1**. Excess pyridine, a terminal co-ligand in **1**, directs variation of the copper coordination sphere *in situ*, allowing the metal centers in **2** to contain two pyridine ligands, MN_3O_2, (eliminating terminal DMF) and thus permits the assembly of the desired (6,3) network (Fig. 2).

Both pyridine molecules occupy the axial positions of the trigonal bipyramidal copper (MN_3O_2), placing them as interlamellar barriers between the undulating layers of Cu(3,5-PDC). These (6,3) layers stack in a staggered AB fashion, where each copper is situated between the hexagonal pores of neighboring layers.

Tri-connected MBBs have been utilized to form (6,3) and (10,3)-*a* networks, and here we have demonstrated the novel design of both such networks. Chiral (10,3)-*a* frameworks have previously been assembled from tri-connected metal–organic building blocks, but most examples are interpenetrated and/or charged networks.[7] Here we have presented an example of the rational design and co-ligand directed synthesis of a 3D neutral, non-interpenetrated (10,3)-*a* framework and a 2D analogue. The chiral framework offers myriad opportunities for chiral catalysis and separation. As these frameworks are designed and deliberately created, new applications are emerging.‡

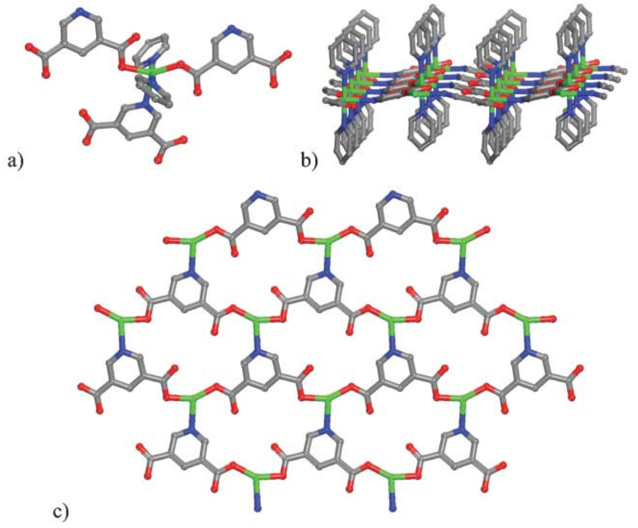

Fig. 2 (a) Cu(3,5-PDC)(py)$_2$ tri-connected SBU of **2**, (b) axial pyridines separate the honeycomb layers, and (c) one of the (6,3) network layers when viewed down the *x*-axis with carbon in gray, copper in green, nitrogen in blue, and oxygen in red (hydrogen and py have been omitted for clarity where necessary).

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Notes and references

† Synthesis of **1**: 3,5-pyridinedicarboxylic acid (0.04 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.04 mmol), 1.5 mL *N*,*N*′-dimethylformamide (DMF), 0.5 mL ethanol (EtOH), and 0.1 mL pyridine (py) . Solution heated at 85 °C for 12 h, then cooled to room temperature. Dark blue polyhedron crystals collected and air dried (74% yield). As-synthesized material is insoluble in water and common organic solvents. CHN elemental analysis (%) for **1**, $C_{15}H_{15}N_3O_5Cu$: Calcd. C, 47.30; H, 3.97; N, 11.04; Found C, 44.89; H, 3.925; N, 11.11. FT-IR (4000–600 cm^{-1}): 1642(s), 1500(w), 1435(w), 1410 (m), 1342(s), 1277(m), 1130(m), 1092(w), 1043(w), 825(m). Synthesis of **2**: 3,5-pyridinedicarboxylic acid (0.04 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.04 mmol), DMF (1.5 mL), EtOH (0.5 mL), and py (0.4 mL). Solution heated at 85 °C for 12 h, then cooled to room temperature. Light blue needle crystals collected and air dried (85% yield). As-synthesized material is insoluble in water and common organic solvents. FT-IR (4000–600 cm^{-1}): 1603(s), 1571(m), 1440(m), 1408(m), 1364(s), 1310(w), 1222(w), 1130(w), 836(w), 781(s).

‡ Crystal data for **1**, $C_{15}H_{15}N_3O_5Cu$: M = 380.84, orthorhombic, $P2_12_12_1$, a = 7.8199(7), b = 10.4971(10), c = 19.0810(18) Å, V = 1566.3(3) Å^3, Z = 4, Dc = 1.615 Mg m^{-3}, μ = 1.426 mm^{-1}, 10024 [(R(int) = 0.0559] reflections of which 3129 assumed as observed ($I > 2\sigma(I)$). Final $R1$ = 0.0437, $wR2$ = 0.1060 (for $I > 2\sigma(I)$). Absolute structure parameter 0.01(2). Crystal data for **2**, $C_{17}H_{13}N_3O_4Cu$: M = 386.84, monoclinic, $P2_1/n$, a = 10.0877(10), b = 11.5960(11), c = 14.6823(14) Å, V = 1713.9(3) Å^3, Z = 4, Dc = 1.499 Mg m^{-3}, μ = 1.300 mm^{-1}, 7242 [R(int) = 0.0416] unique reflections of which 2937 assumed as observed ($I > 2\sigma(I)$). $R1$ = 0.0480, $wR2$ = 0.1001 (for $I > 2\sigma(I)$). CCDC reference number for **1** is 255537–255538. See http://www.rsc.org/suppdata/cc/b4/b417013j for crystallographic data in CIF file or other electronic format.

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