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Cryst. Growth Des., **Just Accepted Manuscript** • DOI: 10.1021/acs.cgd.5b01307 • Publication Date (Web): 04 Jan 2016

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Supramolecular Isomers of Metal-Organic Frameworks Derived from a Partially Flexible Ligand with Distinct Binding Motifs

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ABSTRACT: Three novel metal-organic frameworks (MOFs) were isolated upon reacting a heterofunctional ligand 4-(pyrimidin-5-yl)benzoic acid (4,5-pmbc) with mixed valence Cu(I,II) under solvothermal conditions. X-ray crystal structural analysis reveals that the first compound is a layered structure composed of one type of inorganic building block, dinuclear paddlewheel [$Cu_2(O_2C–)_4$], which are linked through 4,5-pmbc ligands. The two other supramolecular isomers are composed of the same Cu(II) dinuclear paddlewheel and a dinuclear Cu_2I_2 cluster, which are linked via the 4,5-pmbc linkers to yield two different 3-periodic frameworks with underlying topologies related to **lvt** and **nbo**. The observed structural diversity in these structures is due to the distinct coordination modes of the two coordinating moieties (the carboxylate group on the phenyl ring and the N-donor atoms from the pyrimidine moiety).

Introduction

Metal-organic frameworks (MOFs) are a thriving class of functional solid-state materials that have attracted considerable attention due to their modular nature[1] and accessible pore system for potential use in various key applications, such as catalysis,[2] luminescence,[3] gas storage and separation.[4]

In this particular burgeoning class of periodic solids, there has been noticeable efforts and progress toward designing periodic functional structures with desired geometrical attributes and chemical properties for targeted applications.[5] This route has become reasonably feasible with the implementation of the molecular building block (MBB) approach, where organic and inorganic MBBs with given geometry and directionality (e.g., triangles, squares, etc.) are targeted and pre-selected prior the assembly process.[6] Markedly, The assembly of preprogrammed MBBs allows the formation of discrete supramolecules of variable geometries, as evidenced by the myriad of metallo-supramolecular polygons, cages and polyhedra.[7] Perceptively, targeting structures based on the assembly of metallamacrocycles, especially supramolecular hexagons, is of particular interest due to the plausible prospective to mimic biological systems.[8-9]

Nitrogen containing heterocycles have been employed in supramolecular chemistry to target and assemble diverse structures ranging from molecular rings, layered structures to 3-D metal organic frameworks. In particular, pyrimidine based ligands were used successively to construct discrete polygons as well as extended frameworks.[10] It is worth mentioning that the deliberate synthesis of a particular MOF with a precise and intricate topology starting from simple MBBs is often challenging. Potentially, this could be attributed to the lack of control over the coordination modes of the metal ions and/or the flexibility of the ligand[11].

Our primary objective was to isolate an extended MOF enclosing hexagonal supramolecular building units. Noticeably, the combination of the two requisite building blocks for the formation of a hexagon, namely a bent ligand (120° angle) with a linear bridging component, was reported by Stang.[12] Similarly, discrete metallo-supramolecular hexagons based on pyrimidines (e.g. pyrimidine, 2-hydroxypyrimidine, 2,4-dihydroxypyrimidine, 2-aminopyrimdines) have been reported by Navarro *et al.*[13]

Inspired by the aforementioned discrete assemblies, we opted to use an in-house synthesized pyrimidine-based ligand (H_2-4,5-pmbc: 4-(pyrimidyl-5-yl)benzoic acid) and explore its potential in directing the assembly of extended frameworks based on hexagonal supramolecular building units. The 4,5-pmbc is a multifunctional ligand encompassing one carboxylate group and two aromatic N-donors centers, offering several coordination modes as depicted in Scheme 1.

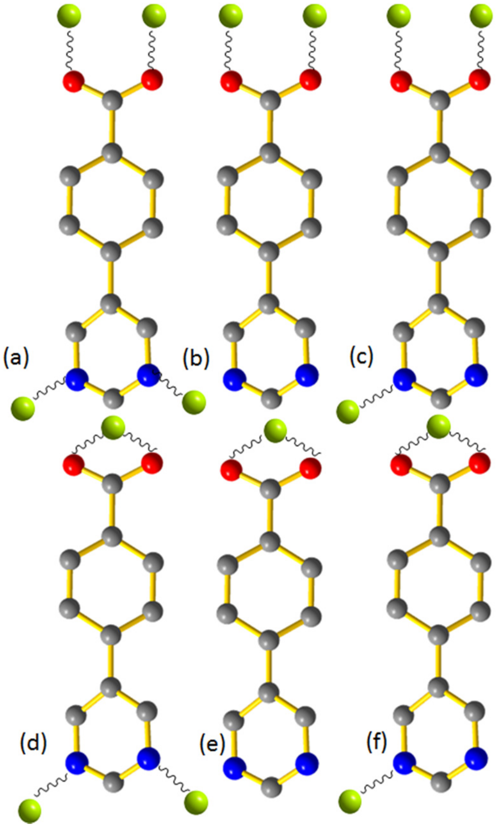
These binding modes include bis-monodentate and bidentate coordination modes for the carboxylate moiety; whereas, the pyrimidyl nitrogen coordinates in a monodentate mode. Scheme 1 (a-c) shows the likely modes of coordination when reacting this ligand with a Cu(II) metal source prompting the formation of a Cu(II) paddlewheel (bis-monodentate coordination) at the carboxylate functionality. Scheme 1 (d-f) depicts the relatively less plausible bidentate coordination mode for the Cu(II) centers.

Scheme 1 (b and e) depict the case when the nitrogen donor groups on the pyrimidine remain uncoordinated leading preferentially to the formation of discrete 0-periodic molecular coordination compounds.

In Scheme 1 (c and f), a 120° angle enclosed by the carboxylate group and the coordinated nitrogen atom in the pyrimidine ring is similar to that observed in isophthalic acid. In this regard, the isophthalate acts as a two connected bent linker bridging the [$Cu_2(O_2C–)_4$] paddlewheel MBBs to either sustain squares or triangles to form a square grid lattice or a Kagomé layer[14] respectively. Finally, in Scheme 1 (a and d) the second nitrogen on the pyrimidine ring can bridge the clusters and thus potentially promote the formation of a 3-periodic structure based on linked hexagonal polygons.

The combination of MBBs with multidentate ligands has proved to be an efficient pathway for targeting 2-D and 3-D MOFs, including supramolecular isomers. One of the most employed and targeted inorganic MBB is the well-known dinuclear paddle-wheel type cluster [$M_2(O_2C–)_4$]. This MBB can be easily targeted through the use of carboxylate based ligands and divalent transition metals (Cu, Zn, etc.) under mild solvothermal reaction conditions[15]. Examples include edge-transitive layers (square grid or Kagomé) synthesized from dicarboxylate based ligands. Inclusion of bifunctional N-donor based ligands (e.g. 4,4′-bipyridine) in the synthesis allows linking these layers *via* a "pillaring strategy" by connecting the axial (apical) position of the paddlewheel clusters.[16]

The use of Cu(I) complexes is particularly attractive because of their promising optical properties and the readily occurrence of various MBBs derived from copper halides (CuX).[17] CuX reacts readily with nitrogen-donor ligands as a result of the soft-soft bonding preference generating diverse geometries with various [Cu_nI_n] structural motifs.[18] These motifs range from Cu_2I_2 rhomboid square dimers,[19] triangular Cu_3I_3 clusters, cubane-like or chair like [Cu_4I_4] tetramers,[20] hexagonal Cu_6I_6 clusters[21], ladder-like or ribbon like [Cu_2I_2]$_n$ chains,[22] zigzag[23] [CuI]$_n$ or [Cu_3I_4]$_n$ chains[24] and [CuI]$_n$ layers.[25] Among the various clusters acting as connecting nodes, dimeric and tetrameric units are the most observed clusters.[26]



Scheme 1. (a-f) Noted coordination modes of 4,5-pmbc. **1** is composed of (a) and (c), **2** and **3** of (a) and (b) types of coordination modes. Color code (C = grey, O = red, N = blue; lime balls representing the metal ion)

Our envisioned strategy to construct 3-periodic MOFs encompassing hexagonal supramolecular building units using the heterofunctional ligand H_2-4,5-pmbc in combination with Cu(I) and Cu(II), under various solvothermal reaction conditions, had permitted the formation of a layered structure **1** and two supramolecular isomers **2** and **3** with **lvt** and **nbo** underlying topologies, respectively.

Experimental Section

Preparations: All materials and solvents were used as received from Aldrich Chemical Co. and Fischer Scientific, respectively, without further purifications.

Single-crystal X-ray diffraction data was collected using Bruker X8 PROSPECTOR APEX2 CCD diffractometer (Cu Kα λ = 1.54178 Å. Crystallographic data and structural refinements of **1**, **2** and **3** are summarized in Table S1. Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical X'Pert PRO MPD X-ray diffractometer at 45 kV, 40 mA for Cu Kα (λ = 1.5418 Å). PXRD measurements were performed on DMF washed samples for **1**, **2** and **3**, as shown in Figures S4, S5 and S6. High resolution dynamic thermal gravimetric analysis (TGA) were performed under a continuous N_2 flow and recorded on a TA Instrument Hi-Res TGAQ500 thermal gravimetric analyzer. TGA experiments were performed on a DMF washed samples for **1**, **2** and **3** under N_2 and at a heating rate of 5°C min^{-1}, as shown in Figures S1, S2 and S3.

Synthesis of 4-(pyrimidin-5-yl)benzoic acid (H_2-4,5-pmbc). This compound was prepared according to our previously reported procedure.[6] In a Schlenk tube under argon atmosphere, a mixture of 5-bromopyrimidine (8 mmol, 1.272 g), 4-ethoxycarbonylphenylboronic acid (9 mmol, 1.746 g), [1,1′-bis(diphenylphosphino) ferrocene] dichloropalladium(II) (0.2 mmol, 0.146 g), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.4 mmol, 0.168 g), finely grinded $K_3(PO_4)$ (14 mmol, 3 g), and 18-crown-6 ether (3.7 mmol, 1 g) in a mixture of degassed THF (20 mL) and EtOH (5 mL) was prepared and reacted at 85°C for 24 h. The reaction mixture was then filtered through celite. The residue was subjected to column chromatography (10% to 40% EtOAc in hexane) to yield colorless needles (1.7 g, 7.45 mmol, 93% yield). Hydrolysis of the ester was accomplished by stirring the solid with 10 equivalents of NaOH in a mixture of THF/EtOH/water 1:1:1 kept at 60°C for 24h, followed by acidification using 1N HCl, extraction in EtOAc, drying over Na_2SO_4 and stand for crystallization (white solid, 80% yield). NMR data match those reported earlier.[27] ^{13}C NMR (DMSO-d6, 150MHz): δ = 155.0, 154.9, 132.4, 132.1, 130.0, 129.8, 127.2, 127.0. 1H NMR (DMSO-d6, 600MHz): δ = 9.20 (s, 1H), 9.19 (s, 1H), 8.06 (d, J = 8.4, 2H), 7.91 (d, J = 7.8, 2H) ppm.

Synthesis of [$Cu_2(C_{11}H_7N_2O_2)_4$]·$(CH_3CN)_2$ (1)

$Cu(NO_3)_2\cdot 2.5H_2O$ (5.8 mg, 0.025 mmol) and H_2-4,5-pmbc (10 mg, 0.05 mmol) were added to a 3 mL solution of N,N′-dimethylformamide (DMF) and 1 mL acetonitrile (CH_3CN) in a 20 mL scintillation vial, heated at 85°C for 48 h, and cooled to room temperature. The as-synthesized blue rod-like crystals are insoluble in water and common organic solvents.

Synthesis of [$(Cu_2I_2)Cu_2(C_{11}H_7N_2O_2)_4$]·$(DMF)_{7.4}$ $(H_2O)_{4.6}$ (2)

CuI (4.76 mg, 0.025 mmol) and H_2-4,5-pmbc (10 mg, 0.05 mmol) were added to a 3 mL solution of DMF and 1 mL of CH_3CN in a 20 mL scintillation vial, heated to 85°C for 48 h, and cooled to room temperature. The as-synthesized green hexagon-like crystals are insoluble in water and common organic solvents.

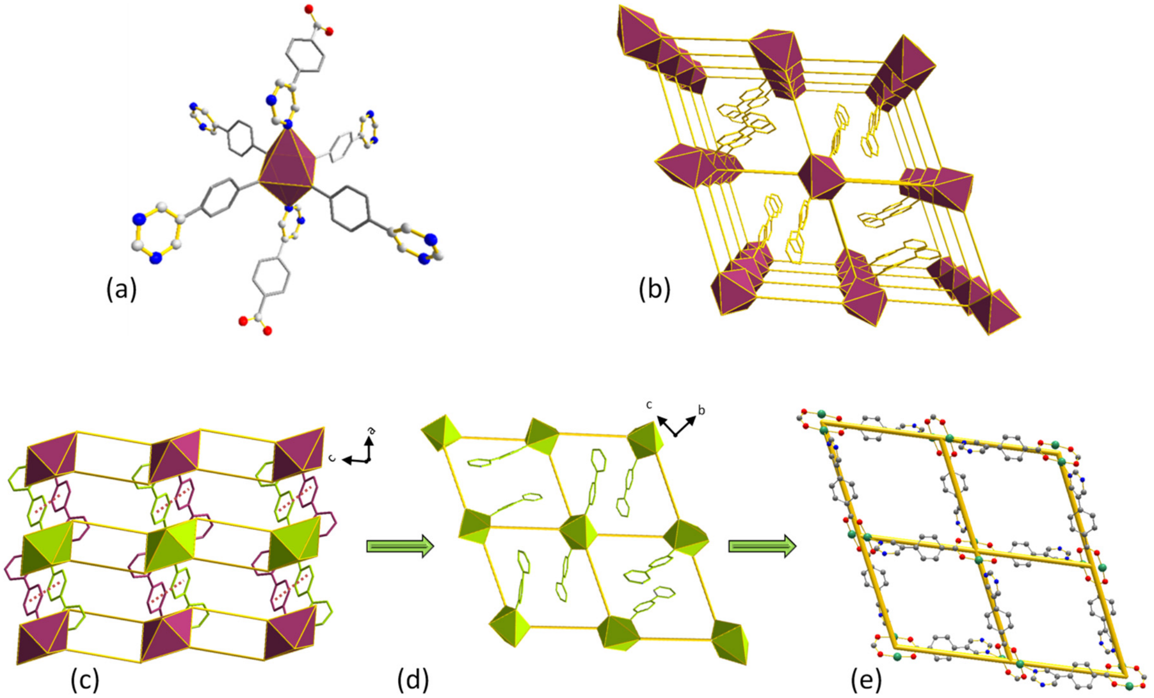


Figure 1. Crystal Structure of **1**: (a) octahedral coordination environment around the paddlewheel; (b) polyhedral representation of **1** revealing the intercalation of terminal ligands into the channels; (c) the 2-D layers locked through π-π interactions (illustrated by the dotted lines); (d) highlights one layer; (e) schematic representation of **sql** topology. Color code (C = grey, O = red, N = blue).

Synthesis of $[(Cu_2I_2)Cu_2(C_{11}H_7N_2O_2)_4]\cdot(NMP)_{6.4}\ (H_2O)_{2.4}$ (3)

CuI (3 mg, 0.016 mmol), $Cu(NO_3)_2\cdot3H_2O$ (4 mg, 0.016 mmol) and H_2-4,5-pmbc (6.4 mg, 0.032 mmol) were added to a 2 mL solution of N-methyl-2-pyrrolidone (NMP), 2 mL CH_3CN and 1 mL EtOH in a 20 mL scintillation vial, heated to 85°C for 24 h and cooled to room temperature. The as-synthesized green crystals are insoluble in water and common organic solvents.

Results and Discussions

Crystals of **1** were isolated by reacting H_2-4,5-pmbc in DMF with Cu(II) under mild conditions. Single-crystal X-ray diffraction (SCXRD) analysis revealed a layered structure that crystallized in a monoclinic space group $P2_1/c$. The layered structure is constructed from dinuclear copper paddlewheel $[Cu_2(O_2C–)_4]$ MBBs, where the equatorial plane contains four carboxylate groups from four independent 4,5-pmbc ligands, and the two apical positions are occupied by nitrogen atoms from the pyrimidyl moieties of two separate ligands (Figure 1).Two free ligands with *trans*-carboxylate groups located in the equatorial plane intercalate into the voids of the square grids of adjacent layers filling the empty space (Figure 1a and 1b). Head-to-tail π-π interactions are observed between pyrimidine and phenyl groups with a mean centroid-centroid distance of 3.789(3) Å between adjacent layers.

Topological analysis using TOPOS[28] corroborates the exclusion of the terminal ligands, regarded as no points of extension, as they are not contributing to the overall resultant network connectivity and net underlying topology. Hence the structure can be reduced to a 4-connected net where the 4-c nodes $[Cu_2(O_2C–)_2(N–)_2]$ are linked *via* a bifunctional bent linker to form a 2-periodic MOF structure with a 4,4-connected **sql** topology (Figure 1e).

As stated earlier, the ability of the two N-donor groups in the pyrimidine ring to concurrently participate in a metal coordination bonding offers potential to augment the connectivity of the 4,5-pmbc ligand and subsequently promote the prospective formation of a 3-periodic MOF structure. The 4,5-pmbc can be regarded as a partially flexible ligand, where the carboxylate group and the pyrimidine ring can twist and bend, as shown in Figure 2, which could lead to the formation of supramolecular isomers through conformational diversities. In order to target and isolate these isomers, we slightly changed the reaction conditions; either by replacing Cu(II) with Cu(I), knowing that Cu(I) can be oxidized into Cu(II), as a mean to control the reaction rate which resulted in **2**, or by mixing both Cu(I) and Cu(II) resulting in **3**.

A solvothermal reaction between H_2-4,5-pmbc and CuI in DMF yielded **2** in pure phase, featuring the formation of two distinct clusters based on Cu(I) and Cu(II). The SCXRD analysis of **2** revealed the formation of a 3-periodic MOF that crystallized in a tetragonal space group $I4_1/a$.

The resultant structure encloses two distinct types of copper ions (Cu(I) and Cu(II)), one type of iodide anion and two crystallographically independent ligands. The overall structure reveals the formation of two distinct inorganic MBBs with the ligand acting as a bifunctional-multidentate linker. MBB-1 is based on a dinuclear cluster represented by copper iodide rhomboid dimeric units $[Cu_2I_2]$.

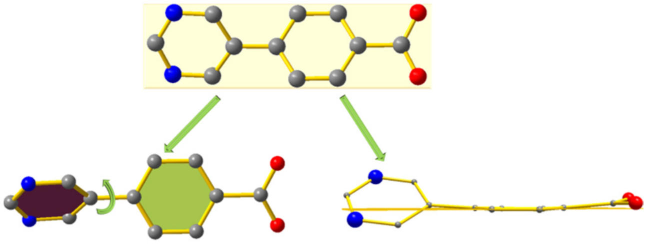


Figure 2. A schematic representation illustrating the twist around the pyrimidine ring, and the bending angle of the carboxylate group.

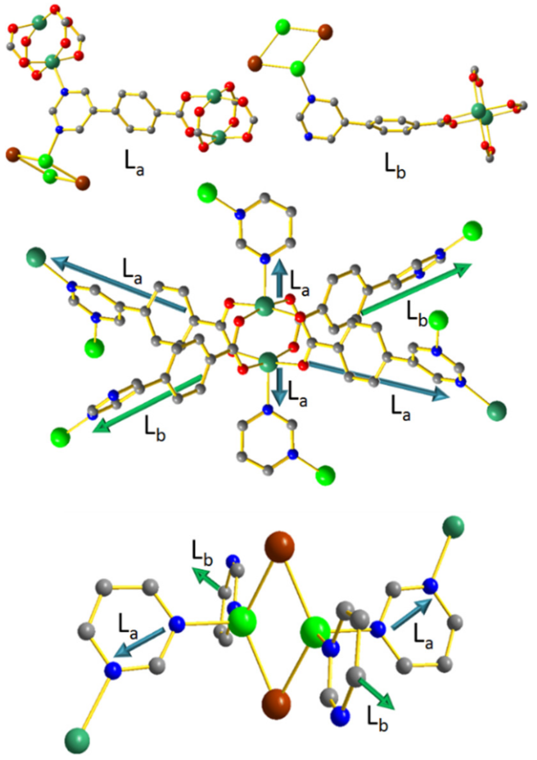


Figure 3. Coordination environments surrounding MBB-1 and MBB-2: 4-connected $[Cu_2I_2(N–)_4]$, MBB-1 (to the right). 6-connected paddlewheel $[Cu_2(O_2C–)_4(N–)_2]$, MBB-2 (to the left). Color code (Cu(I) = bright green, Cu(II) = sea green, I = brown).

Each Cu(I) has a tetrahedral coordination geometry with two coordination sites occupied by two nitrogen atoms from two separate ligands and the remaining sites coordinated to two iodide anions. The two Cu(I) centers are bridged *via* two iodide anions, balancing the charge, and affording a dinuclear cluster with Cu(I)···Cu(I) distance of 2.537(2) Å. MBB-2 is the conventional dinuclear cluster with two Cu(II) ions, $[Cu_2(O_2C–)_4(N–)_2]$ with Cu(II)···Cu(II) distance of 2.608(2) Å. It is to note that there is a significant twist between the phenyl ring and the pyrimidyl ring with dihedral angles of 37.5° (3) and 44.0° (3) for L_a and L_b respectively. Each Cu(II) displays a square pyramidal coordination geometry with four oxygen atoms from four distinct carboxylates and one N-donor from the pyrimidine moiety. The two crystallographic independent ligands show different coordination modes represented by L_a and L_b (Figure **3**). L_a acting as a tritopic linker, as shown in Figure **3**, where the two N-atoms from the pyrimidine moiety coordinate to two distinct MBBs and the carboxylate group being occluded into the paddlewheel. On the other hand, L_b with only one of its nitrogen atoms coordinating acts as a bridging linker. Two of the *trans*-L_b ligands coordinate through carboxylate groups in a bis-monodentate fashion and contribute to the formation of the dinuclear copper paddlewheel $[Cu_2(O_2C–)_4]$ MBB, while the associated pyrimidine moieties coordinate via only one nitrogen and promote the formation of the second inorganic MBB, $[Cu_2I_2(N–)_4]$.

As for the tritopic ligand, L_a, apart from the coordination modes observed in L_b, links both MBBs to a second MBB-1 through the coordination of the second N-atom on the pyrimidine ring to the apical position of the paddlewheel. Therefore, L_a spans through two 4-connected MBB-1, $[Cu_2I_2(N–)_4]$, and one 6-connected MBB-2, $[Cu_2(O_2C–)_4(N–)_2]$; whereas, L_b spans through one MBB-1 and one MBB-2. The resulting paddlewheel is surrounded by 4 L_a ligands and 2 L_b ligands to yield a 6-connected MBB, $[Cu_2(O_2C–)_4(N–)_2]$; whereas, two L_a and two L_b support the formation of the 4-connected MBB, $[Cu_2I_2(N–)_4]$ (Figure **3**). The 3-periodic structure in **2** is sustained by two dinuclear clusters MBB-1 and MBB-2 that are linked to each other *via* L_a and L_b to form square-like channels that run along c-axis with a pore diameter of 9 Å (Figure **3**).

In order to describe the underlying topology of **2** and **3**, it is noteworthy to briefly introduce secondary building units (SBUs) as the geometrical entity representing the points of extension of the molecular building blocks (MBBs). From the viewpoint of an underlying topology,[29] **2** can be simplified as follows. In **2**, when all coordination sites are considered as points of extension, the connecting nodes becomes as such: MBB-1 coordinating to 6 ligands, forming a 6-c node representing an octahedral building unit, as shown in Figure S7 (a) and (b). The rhomboid dimeric unit $[Cu_2I_2(N–)_4]$ can be viewed as a 4-c node (Figure S7 (c) and (d)). L_a represents a 3-c node, Figure S7 (e) and (f). Hence the overall topology of **2** is a new (3,4,6)-connected net with a transitivity of [3443], Figure S9.

Compound **3** crystalizes in the hexagonal space group *R*-3. Crystals of **3** were obtained under similar reaction conditions to **2** upon the addition of a Cu(II) source. Similar MBBs are observed, MBB-1 containing a paddlewheel forming a 6-c node with an octahedral building unit as all the coordination sites of the dimeric clusters are occupied. In addition, a 4-c rhomboid dimer Cu_2I_2 cluster is also isolated, along with both modes of coordination of the 4,5-pmbc, L_a and L_b. Noticeably, the aromatic rings (phenyl and pyrimidyl) twisted out of plane with dihedral angles of 47.5° (1) and 46.1° (1) for L_a and L_b respectively. The topological analysis of **3** has been subjected to similar analysis followed for **2**. By accounting for all points of extension, a new (3,4,6)-c net was derived with a transitivity of [3432], Figure S11.

To better understand structures **2** and **3**, we opted to assess the intrinsic roles of each MBB in the associated structures. Close examination of the respective MBBs connectivity revealed that the rhomboid dimer $[Cu_2I_2(N–)_4]$ can be deliberately omitted in the topological analysis and still retain the 3-periodic overall structure. Resultantly, the connectivity of this structure can be simplified by means of the following attributes: L_a can be regarded as a 2-c node bridging two paddlewheels (Figure S8 (c) and (d) and L_b as a terminal ligand upon discounting the $[Cu_2I_2(N–)_4]$ (Figure 4, S8 (a)). Subsequently, the resultant connectivity of the paddlewheel differs from the common square SBU, $[Cu_2(O_2C–)_4]$, and can be regarded as a lozenge SBU, $[Cu_2(O_2C–)_2(N–)_2]$, when the points of extension are joined together, namely the two carboxylate C-atoms of L_a and the two pyrimidyl N-atoms (at the apical position) (Figure S8). Noticeably, the simplified structure can be viewed as a 3-periodic network based on 4-c nodes bridged *via* ditopic linker, resulting in a 4-connected net based on the **lvt** underlying topology, Figure S10.

Similarly, the topological analysis of structure **3** was subjected to identical connectivity simplification as applied to structure **2**. Noticeably, the exclusion of the rhomboid dimer didn't alter the 3-periodic nature of the structure. Consequently, the simplified structure of **3** can be regarded as a 3-periodic network based on a 4-c nodes SBU, , $[Cu_2(O_2C–)_2(N–)_2]$, bridged *via* ditopic L_a linker, resulting in a 4-connected net based on the **nbo** underlying topology, Figure S12.

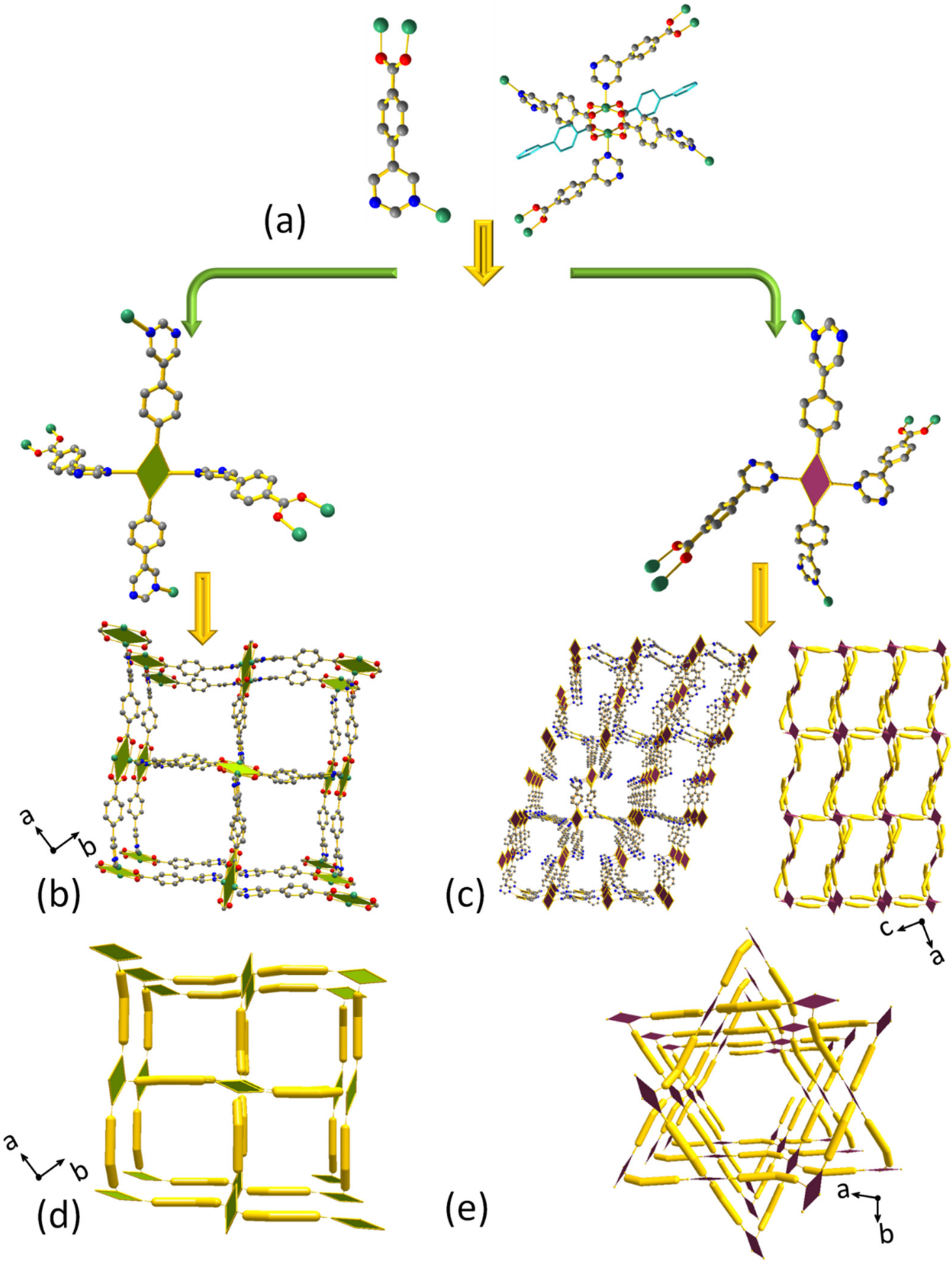


Figure 4. Topological analysis of **2** and **3**; (a) L_a bridging 4-c paddlewheel and L_b acting as terminal ligand (highlighted in turquoise); (b) and (c) molecular and schematic illustration of **2** and **3** as **lvt** and **nbo**, respectively; (d) and (e) View along the c-axis showing square and hexagonal channels of **2** and **3** respectively.

In summary, we here-in report the isolation of a layered structure **1** and supramolecular isomers **2** and **3** with network structural differences. We have shown that the concentration of Cu(II) in solution plays a role in the isolation of **3**, which could be driven by the kinetics of the reaction. In addition, the flexibility of 4,5-pmbc, allowing both the pyrimidyl group and the carboxylate group to twist and turn, provides additional degree of freedom in which the SBUs can be connected to form supramolecular isomers.

ASSOCIATED CONTENT

Supporting Information

PXRD, TGA, structure characterization and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the King Abdullah University of Science and Technology (KAUST)

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Supramolecular Isomers of Metal-Organic Frameworks Derived from a Partially Flexible Ligand with Distinct Binding Motifs

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In the present work, three novel MOFs were isolated upon reacting a heterofunctional ligand 4-(pyrimidin-5-yl)benzoic acid (4,5-pmbc) with mixed valence Cu(I,II) under solvothermal conditions. The two distinct coordinating moieties in the ligand (carboxylate group and the N-donor atoms) prompted the formation of two 3-periodic MOFs, supramolecular isomers, with underlying topologies related to **lvt** and **nbo**.