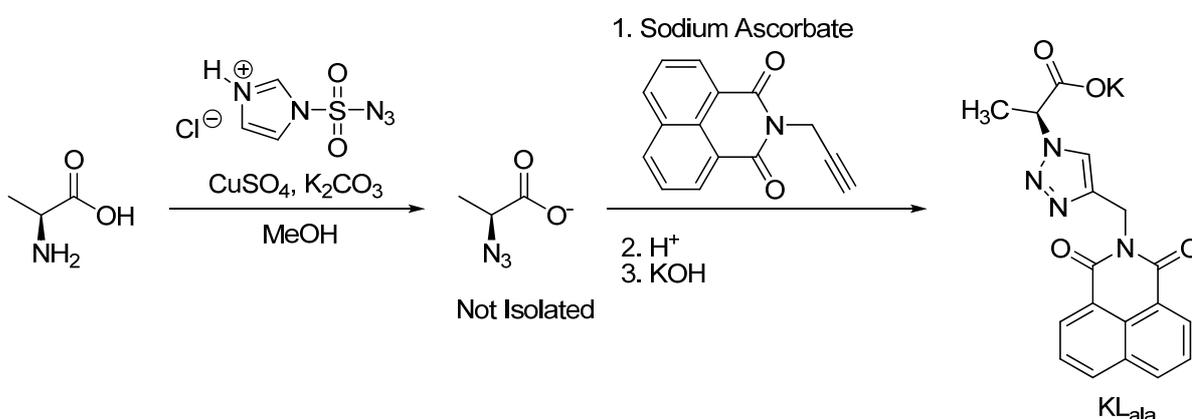


Supplementary Information for Homochiral, Helical Metal Organic Framework Structures Organized by Strong, Non-Covalent π - π Stacking Interactions

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Synthesis of Ligands HL_{ala} and KL_{ala}



Potassium (*S*)-2-(4-((1,8-naphthalamido)methyl)-1H-1,2,3-triazolyl)propanoate (KL_{ala})

Imidazole-1-sulfonyl azide hydrochloride¹ (5.00 g, 24 mmol), K_2CO_3 (1.78 g, 20 mmol), and L-alanine (1.78 g, 20 mmol) were stirred together in 100 ml of dry methanol. $CuSO_4$ (200 mg, 0.80 mmol) was added, and the mixture was stirred for 24 hours. A solution of sodium ascorbate (1.59 g, 8.0 mmol) dissolved into 80 ml of water was added, followed by *N*-propargyl-naphthalimide (4.23 g, 18 mmol) and 100 ml acetone. This suspension was stirred for a further 24 hours, then concentrated to a volume of approximately 80 ml via rotary evaporation. The residue was diluted with water until turning clear, and then acidified by the careful dropwise addition of 3 M HCl. The product, (*S*)-2-(4-((1,8-naphthalamido)methyl)-1H-1,2,3-triazolyl)propanoic acid (HL_{ala}), was isolated by suction filtration, washed well with water, and dried overnight in vacuo to yield 5.89 g of an insoluble white solid. A powdered sample of this HL_{ala} (3.50 g, 10 mmol) was stirred for one hour with a stoichiometric amount of 1 M methanolic KOH (10 ml, 10 mmol). Additional methanol was then added to dissolve the ligand (total volume ca. 275 ml), the solution filtered through a short plug of celite to remove traces of insoluble impurities, and the solvent removed by rotary evaporation to yield 3.35 g (86%) of a white solid. $[\alpha]_D^{20} +3.77^\circ$ (c 1.0 M, MeOH). 1H NMR (CD_3OD) δ 1.73 (d, $J = 7.3$ Hz, 3H, CH_3), 5.14 (q, $J = 7.3$ Hz, 1H, CH), 5.43 (s, 2H, CH_2), 7.76 (t, $J = 8.2$ Hz, 2H, *nphth*), 8.00 (s, 1H, *triazole*), 8.29 (d, $J = 8.5$ Hz, 2H, *nphth*), 8.52 (d, $J = 4.1$ Hz, 2H, *nphth*). ES/MS for $\{C_{18}H_{13}N_4O_4\}^-$: Calcd 349.0937, Obsd 349.0944. Anal. Calcd for $C_{18}H_{13}N_4O_4K$: C, 55.66; H, 3.37; N, 14.42. Found: C, 55.50; H, 3.22; N, 14.39.

Preparation of Metal Complexes

Cu(L_{ala})₂(4,4'-bipy)(H₂O)₂•4.25 H₂O (1)

Three solutions were prepared – A 5 mM aqueous solution of copper(II) acetate (solution **A**), a mixture of 1:1 MeOH:H₂O (solution **B**), and a methanolic solution 10 mM in both KL_{ala} and 4,4'-bipyridine (solution **C**).

5 ml of **A** was added to a 16 mm test tube, and 2 ml of **B** carefully added to form a “buffer” layer. 5 ml of **C** was layered onto this, and the tube was tightly capped and left in a quiet location. Large green hexagonal rods of **1** suitable for X-ray diffraction grew over a period of 5-10 days. Anal. Calcd for C₄₆H_{46.5}N₁₀O_{14.25}Cu: C, 60.16; H, 3.73; N, 15.25. Found: C, 59.76; H, 3.59; N, 15.08.

Analytical figures for **2** were measured on the above analytical sample of **1** by drying the sample to constant weight. Both the interstitial and coordinated waters were lost, as confirmed by TGA (9.76% weight loss observed, 9.70% calculated for 6.25 H₂O, see Figure S6). Anal Calcd for C₄₆H₃₄N₁₀O₈Cu: C, 53.59; H, 4.55; N, 13.59. Found: C, 53.61; H, 4.35; N, 13.66.

Crystals with absorbed D₂O (**3**) were prepared by placing a vial with a pierced septum cap containing a sample of crystalline **1** inside a larger vial, and holding the sample under vacuum for 10 hours. D₂O from a freshly opened ampoule was introduced into the space between the two vials, and the vials backfilled with dry nitrogen. The crystals changed color from dark blue to light green, and were allowed to stand overnight. Anal. Calcd for C₄₆H₃₈D_{8.5}N₁₀O_{14.25}Cu: C, 53.15; H, 5.33; N, 13.47. Found: C, 53.41; H, 5.08; N, 13.58.

X-Ray Structure Determinations

X-ray diffraction intensity data for both compounds were measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$).² The raw area detector data frames were processed with SAINT+.² The reported unit cell parameters were determined by least-squares refinement of a large number of reflections taken from each data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXTL.³

Cu(L_{ala})₂(4,4'-bipy)(H₂O)₂•4.25 H₂O (1)

The compound crystallizes in the hexagonal crystal system. The enantiomorphous space groups P6₁ / P6₅ and P6₁22 / P6₅22 were indicated by the pattern of systematic absences in the intensity data. The space group P6₁22 was eventually confirmed by trial solutions and refinements, and with the ADDSYM program in PLATON.⁴ The absolute structure (Flack) parameter in P6₁22 after the final refinement cycles was 0.016(17). For comparison, the Flack parameter in P6₅22 after refinement was 0.979(0.026). The asymmetric unit consists of (formally half of) one copper atom located on the C₂ rotational axis parallel to the [100] directions, one C₁₈H₁₃N₄O₄ ligand, half of a 4,4'-bipyridine ligand located on the same C₂ axis as the copper atom, a

coordinated water molecule and region of interstitial water molecules. Three interstitial water molecule sites were located: O1S, O2S, and O3S. O1S and O2S refined as fully occupied; O3S is located on the C_2 axis along the [1-20] directions, and refined to near $\frac{1}{4}$ -occupancy. Its occupation factor was fixed at that value. The displacement parameters for the interstitial atoms are inflated relative to those of the copper and ligand atoms. This likely indicates some minor positional disorder of these species. O3S could not be refined freely due to strong correlation between its occupancy and displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters except O3S (isotropic). Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. Reasonable positions for the water hydrogens bonded to O5, O1S and O2S could be located in difference maps. After location, their coordinates were adjusted to give $d(\text{O-H}) = 0.84 \text{ \AA}$ and they were treated as riding on their parent oxygen atoms with $U(\text{iso}, \text{H}) = 1.5 U(\text{eq}, \text{O})$. No hydrogen atoms were located or calculated for O3S.

$\text{Cu}(\text{L}_{\text{ala}})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2$ (2**)**

The space group was again determined to be $P6_122$ following the same procedure as for compound **1**. The final absolute structure (Flack) parameter refined to 0.04(2). The asymmetric unit of **2** is identical to **1** except for the absence of interstitial water molecules. Careful examination of the Fourier difference map in the interstices between the $\text{Cu}(\text{L}_{\text{ala}})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2$ chains showed no electron density above the normal background level. The largest residual electron density peaks (ca. $0.37 \text{ e}^-/\text{\AA}^3$) are near the copper atom. The largest electron density concentration in the interstices is $0.20 \text{ e}^-/\text{\AA}^3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. Reasonable positions for the water hydrogens bonded to O5 were located in difference maps. Their coordinates were adjusted to give $d(\text{O-H}) = 0.84 \text{ \AA}$ and they were subsequently treated as riding on O5 with $U(\text{iso}, \text{H}) = 1.5 U(\text{eq}, \text{O})$.

References

- (1) Goddard-Borger, E. D.; Stick, R. V. *Organic Letters* **2007**, *9*, 3797-3800.
- (2) SMART Version 5.625, SAINT+ Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2001.
- (3) SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.
- (4) MISSYM (ADDSYM) Algorithm - (a) LePage, Y. J. *Appl. Crystallogr.* 1987, *20*, 264-269. (b) Spek, A. L. *J. Appl. Crystallogr.*, 1988, *21*, 578-579. (c) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.

Table S1. Tabulated data for hydrogen-bonding in **1** and **2**.

	Donor	Hydrogen	Acceptor	Type	H...A	D...A	D-H...A
Compound 1	O5	H5A	O4	Intramolecular	1.86	2.68	165°
	O5	H5B	O1	Intrasheet	1.94	2.78	177°
	O1S	H1SB	O2S	Intrachain	1.94	2.78	176°
	O2S	H2SB	O3S	Intrachain	2.43	3.25	165°
	O1S	H1SA	O2	Chain-Npht	2.06	2.89	169°
	O2S	H2SA	O3	Chain-Acid	2.24	2.99	150°
Compound 2	O5	H5A	O4	Intramolecular	1.92	2.71	158°
	O5	H5B	O4	Intrasheet	2.04	2.81	153°

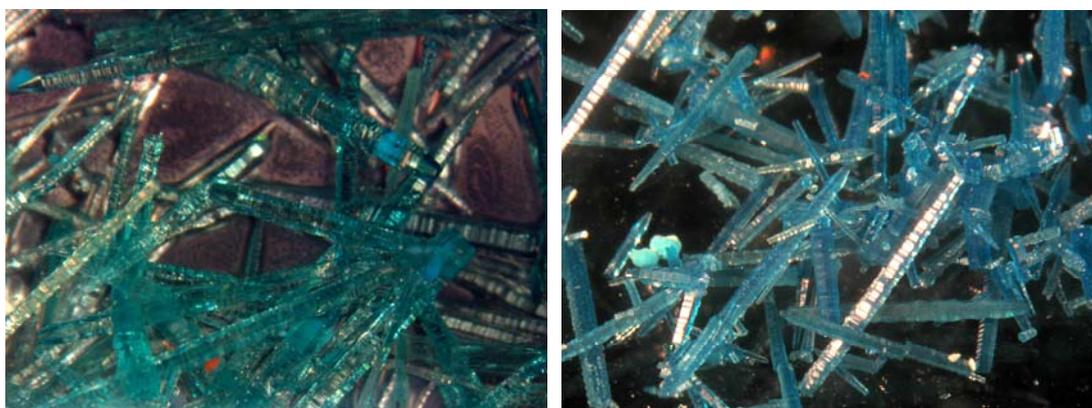


Figure S2. Crystals of $\text{Cu}(\text{L}_{\text{ala}})_2(\text{bipy})(\text{H}_2\text{O})_2$ hydrated (left) and dehydrated (right).

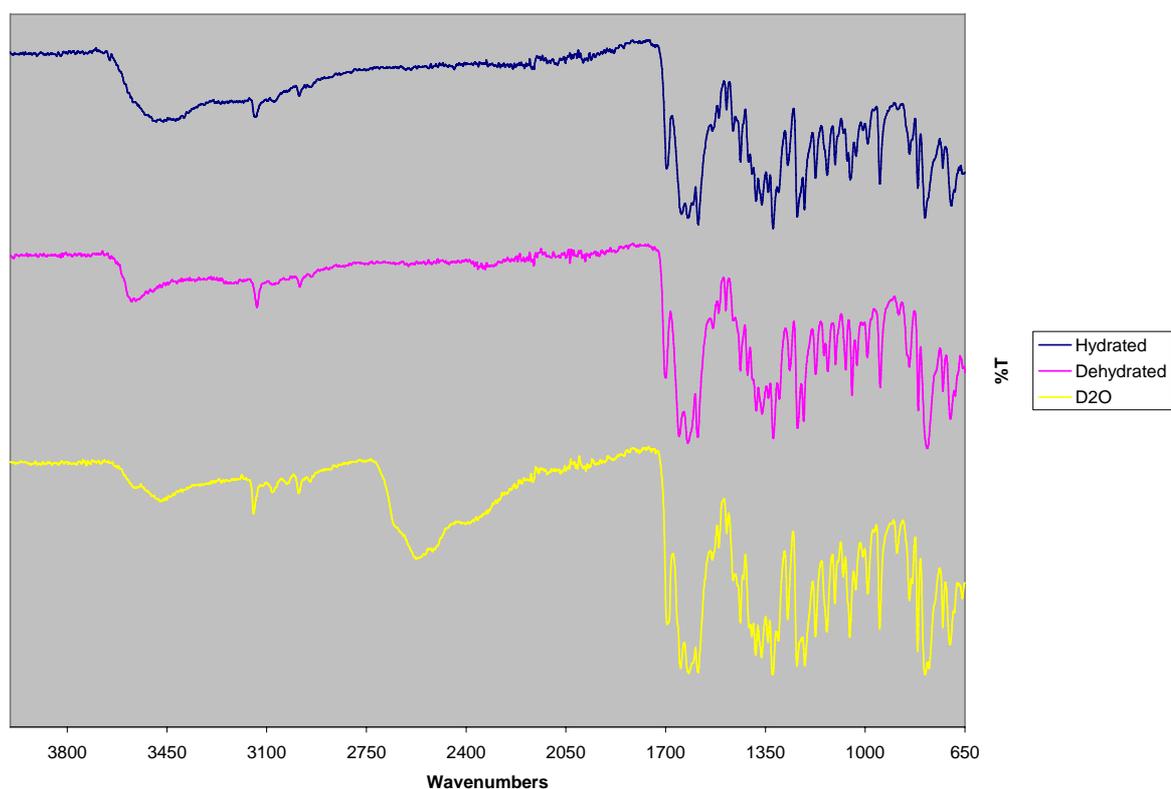


Figure S3. Infrared spectra of **1** (top, blue), **2** (center, magenta) and **3** (bottom, yellow).

Table S4. Selected parameters for Hydrated **1** and Dehydrated **2**.

Property	Hydrated (1)	Dehydrated (2)
Nphth Dipole Angle	65.7°	60.6°
Nphth Planar Tilt	6.2°	5.1°
Lateral Slippage (Å) ^{6a}	0.429 Å	0.433 Å
Intrachain H-Bond	1.938 Å, 177.2°	2.035 Å, 153.4°
Helix Pitch (c-axis)	62.45 Å	60.94 Å
Cu-O(3)	2.013(2) Å	1.981(3) Å
Cu-O(5)	2.339(2) Å	2.435(3) Å
Cu-N(5)	2.049(3) Å	2.029(5) Å
Cu-N(6)	2.034(3) Å	2.004(4) Å
O(3)-Cu-O(3a)	178.67(11)	179.19(17)°
O(3)-Cu-O(5)	92.82(8)°	95.15(12)°
O(3)-Cu-O(5a)	87.14(8)°	84.82(12)°
O(3)-Cu-N(5)	90.66(6)°	90.41(9)°
O(3)-Cu-N(6)	89.34(6)°	89.59(9)°
O(5)-Cu-O(5a)	177.13(11)°	175.46(17)°

O(5)-Cu-N(5)	91.44(5)°	92.27(9)°
O(5)-Cu(1)-N(6)	88.56(5)°	87.73(9)°
N(5)-Cu-N(6)	180°	180°

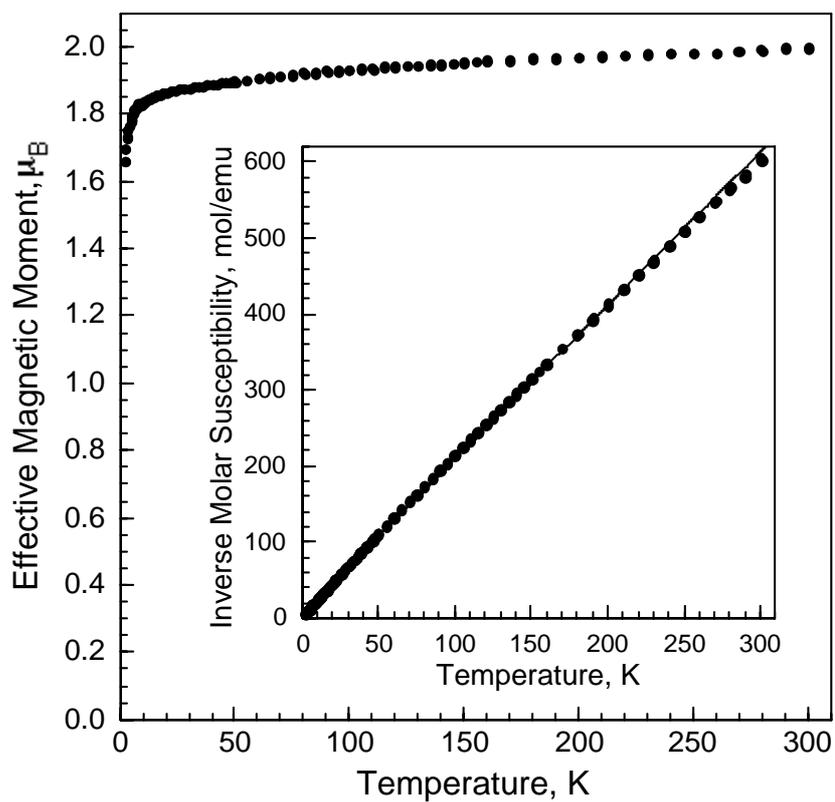


Figure S5. The temperature dependence of μ_{eff} observed for **1**. Inset: A Curie-Weiss law fit of $1/\chi_M$ obtained for **1**.

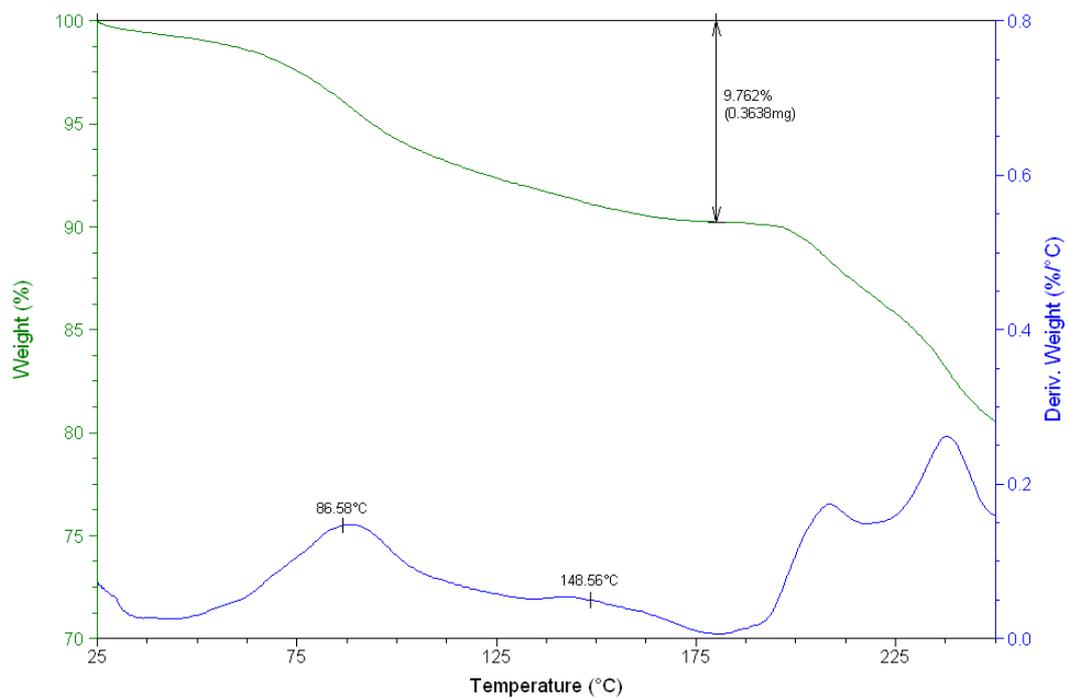


Figure S6. TGA curve for compound **1**.