

Synthesis of Organic Photodimeric Cage Molecules Based on Cycloaddition *via* Metal-Ligand Directed Assembly

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Materials and Methods.

Single-crystal X-ray diffraction data were collected on a Bruker SMART-APEX CCD diffractometer using MoK α radiation ($\lambda = 0.71073$ Å).

XRPD data were recorded on a Rigaku RU15 diffractometer at 30kV, 15mA for CuK α ($\lambda = 1.5418$ Å), with a scan speed of 1°/min and a step size of 0.05° in 2 θ at room temperature.

Photodimerization reactions were carried out in a Rayonet RPR-600 Photochemical Reactor.

Preparation for **1**: 3,5-H₂PDC (13.4 mg, 0.08 mmol), Co(NO₃)₂·6H₂O (46.6 mg, 0.16 mmol), EtOH (1 mL), DMF (1 mL), Py (0.05 mL) were added to a 20 mL scintillation vial, and the solution was heated at a constant rate 1.5°C/min to 85°C for 12 h, then cooled at a constant rate 1°C/min to room temperature. Fuchsia block crystals were collected and air-dried, and were insoluble in H₂O and common organic solvents.

Preparation for **2**: H₂CDO·H₂O (8.1 mg, 0.04 mmol), Cu(NO₃)₂·2.5H₂O (9.3 mg, 0.04 mmol), DMF (1 mL), EtOH (1 mL), Py (0.1 mL) were added to a 20 mL scintillation vial, and the solution was heated at a constant rate 1.5°C/min to 85°C for 12 h, then cooled at a constant rate 1°C/min to room temperature. Light blue plate crystals

were collected and air-dried (15 mg, 90% yield), and were insoluble in H₂O and common organic solvents.

Preparation for **3**: Method 1: Crystals of **2** in a 20 mL scintillation vial were washed with DMF (1 mL) and EtOH (1 mL) three times, and the final solution with crystals placed in a photochemical reactor for 1 day (until crystals turn from light blue to light green). Light green plate crystals were collected and air-dried, and were insoluble in H₂O and common organic solvents.

Method 2: Crystals of **2** in a 20 mL scintillation vial were washed with DMF (1 mL) and EtOH (1 mL) three times and dried. The crystals were distributed in a thin layer on a recrystallization dish and placed in a photochemical reactor for 1 day (until crystals turn from light blue to light green). Light green plate crystals were collected, and were insoluble in H₂O and common organic solvents.

Preparation for **4**: Crystals of **3** in a 20 mL scintillation vial were washed with DMF (1 mL) and EtOH (1 mL) three times and dried. The crystals were then washed with H₂O three times and dried, followed by the addition of HNO₃ (1.0 mL 6N in 1.0 mL H₂O). The solution was heated at a constant rate 1.5°C/min to 85°C for 12 h, then cooled at a constant rate 1°C/min to room temperature, followed by successive heating at a constant rate 1.5°C/min to 105°C for 23 h and cooling at a constant rate 1°C/min to room temperature. Blue rod crystals were collected from the side wall of the vial.

Preparation for **5**: Crystals of **3** in a 20 mL scintillation vial were washed with DMF (1 mL) and EtOH (1 mL) three times and dried. The crystals were then washed with H₂O three times and dried, followed by the addition of NaOH (1.0 mL 8M in H₂O). The blue/green precipitate was filtered and concentrated HNO₃ added to ~pH 2.0, and

placed at 4°C for three days. Colorless plate crystals were collected from the vial and air dried (8 mg, 34% total yield based on $\text{H}_2\text{CDO}\cdot\text{H}_2\text{O}$).

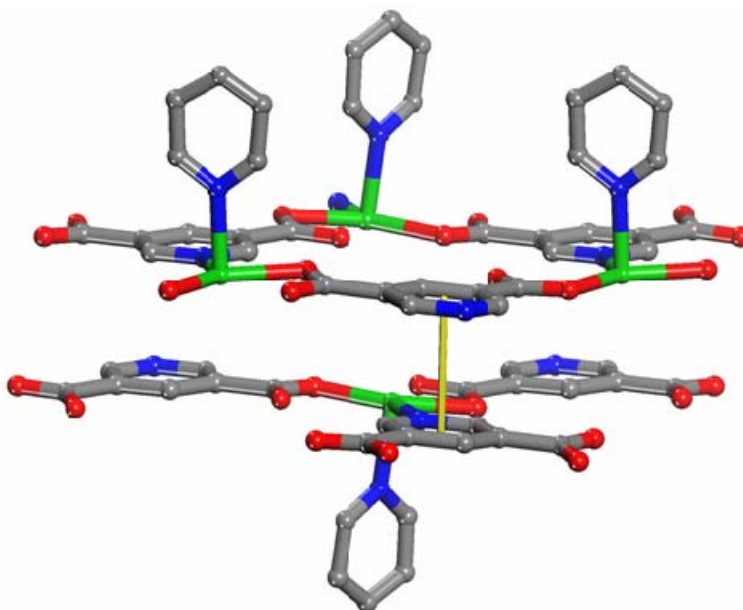


Figure S1. Analysis of the single-crystal structure of our Co-(3,5-PDC) MOF, **1**, shows alternating 2D honeycomb or (6,3) layers. The organic linkers are positioned in an anti conformation along the x axis with centroid...centroid distances of 7.47 Å and 3.55 Å, respectively. The latter distance (yellow) is within the appropriate range, in addition to the proper positioning of organic linkers, for [2+2] photodimerization. Water molecules and hydrogen atoms have been omitted for clarity; cobalt = green, carbon = gray; nitrogen = blue; oxygen = red.

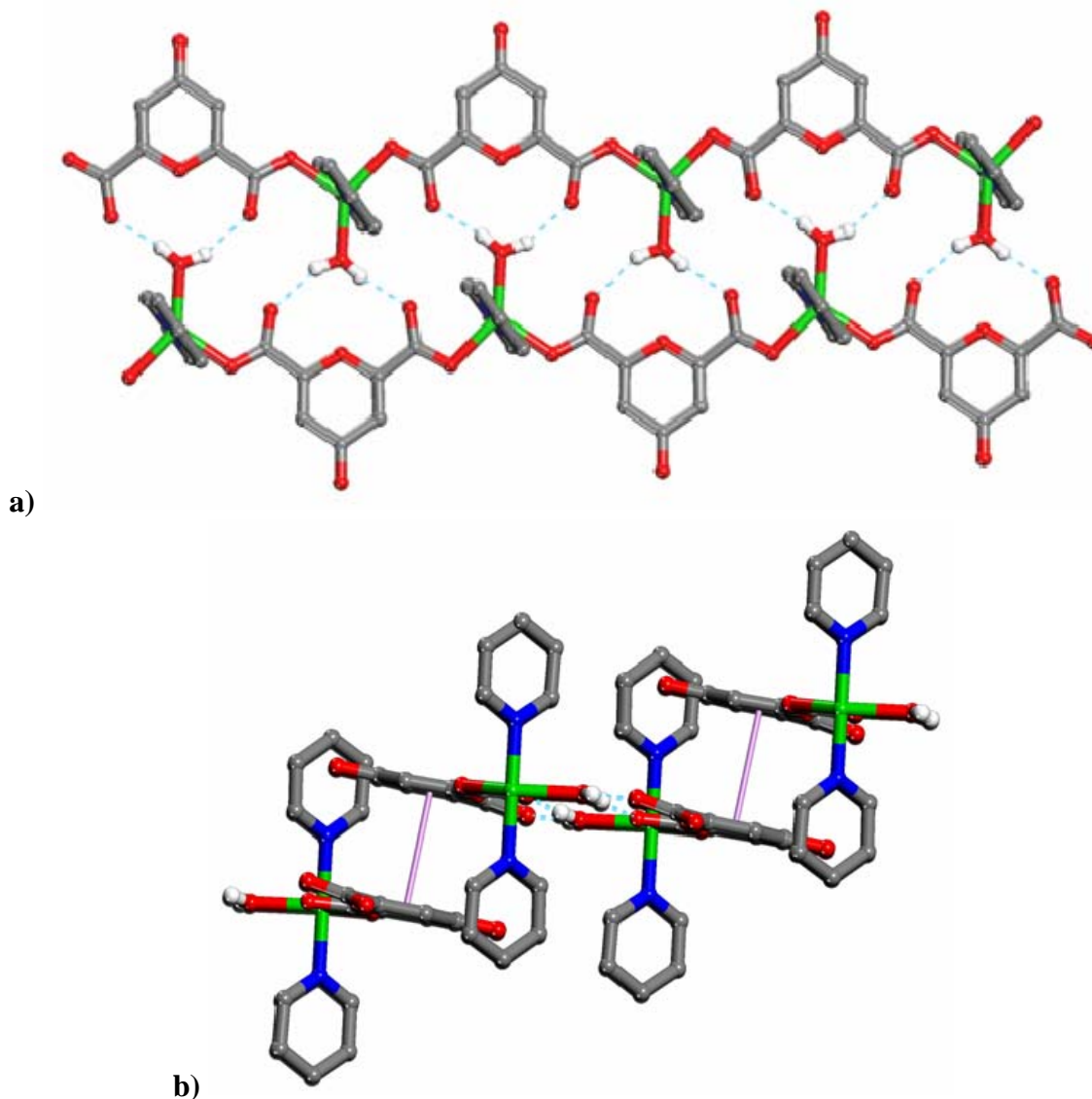


Figure S2. Single-crystal structure of **2**: a) the metal-organic chains of **2** hydrogen bond to neighboring chains through the coordinated water molecules, resulting in metal-organic ladders, and b) are separated by axial terminal pyridine molecules and held in close proximity by CDO...CDO interactions (centroid...centroid distance represented in fuschia). Excepting water molecules, hydrogen atoms have been omitted for clarity; copper = green, carbon = gray; nitrogen = blue; oxygen = red.

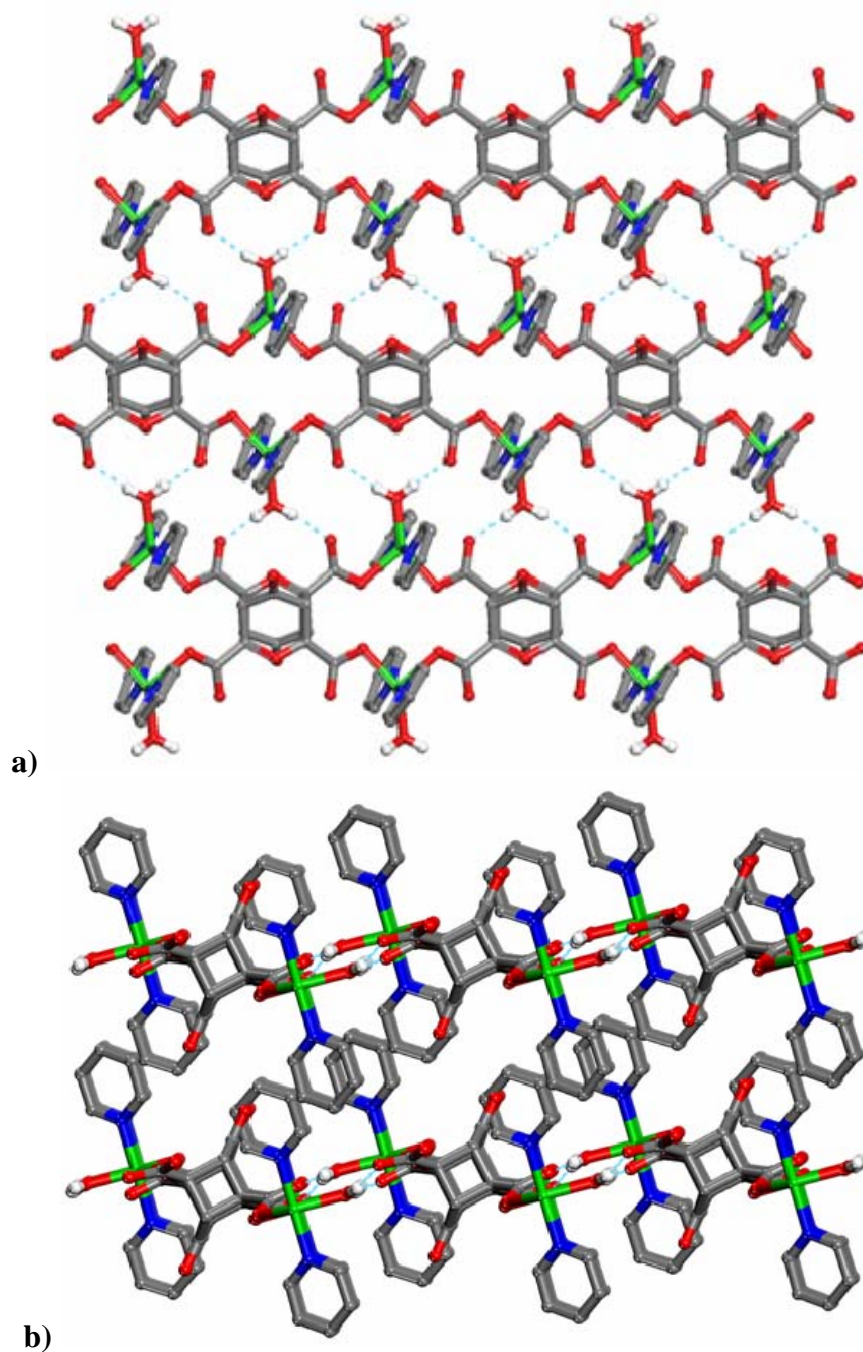


Figure S3. Single-crystal structure of **3**: a) [2+2] photodimerized CDO ligands, EE1 (Eubank-Eddaoudi-1), in **3** result in metal-organic ladders that hydrogen bond to neighboring ladders to form 2D layers, and b) these layers are separated by the axial terminal pyridine molecules. Excepting water molecules, hydrogen atoms have been omitted for clarity; copper = green, carbon = gray; nitrogen = blue; oxygen = red.

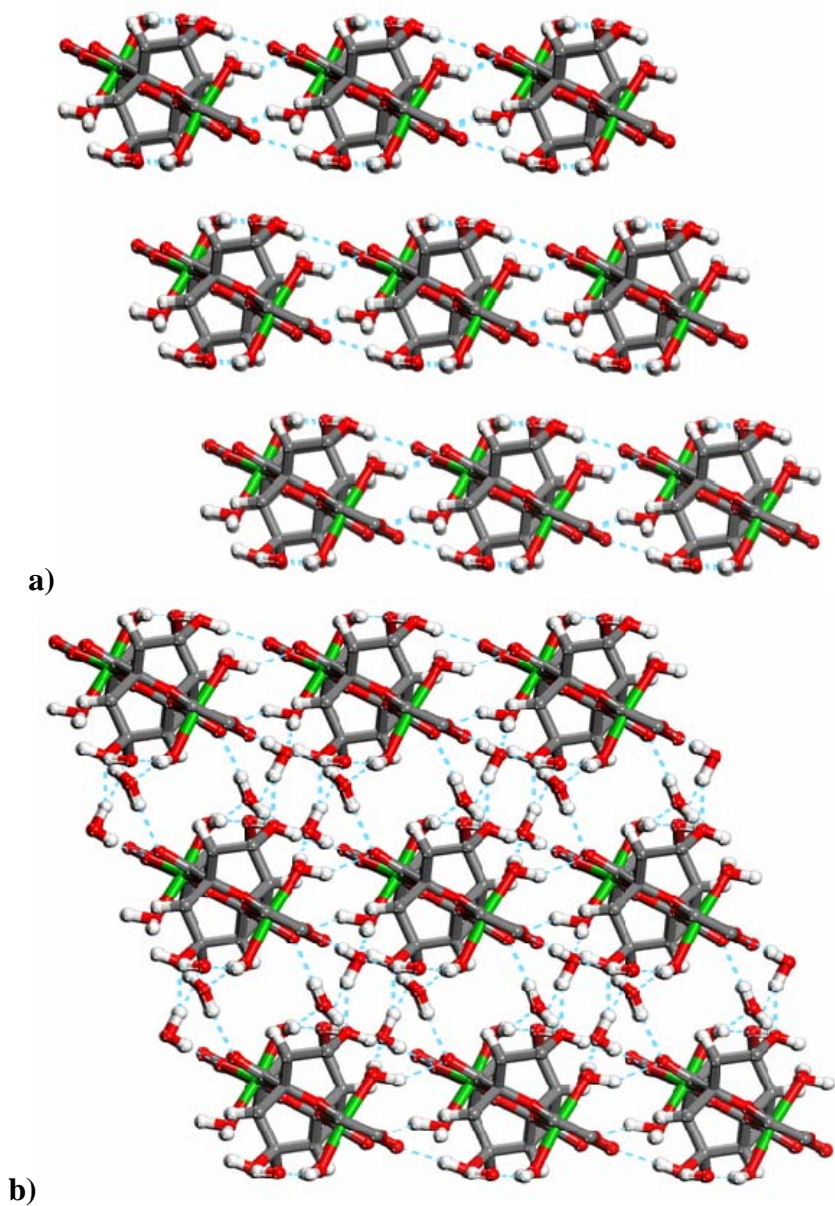


Figure S4. Single-crystal structure of **4**: a) the metal-organic ladders of **4** are hydrogen bonded through coordinated water molecules to form 2D layers, and b) these layers are hydrogen bonded to guest water molecules to form a 3D structure. Copper = green, carbon = gray; oxygen = red.

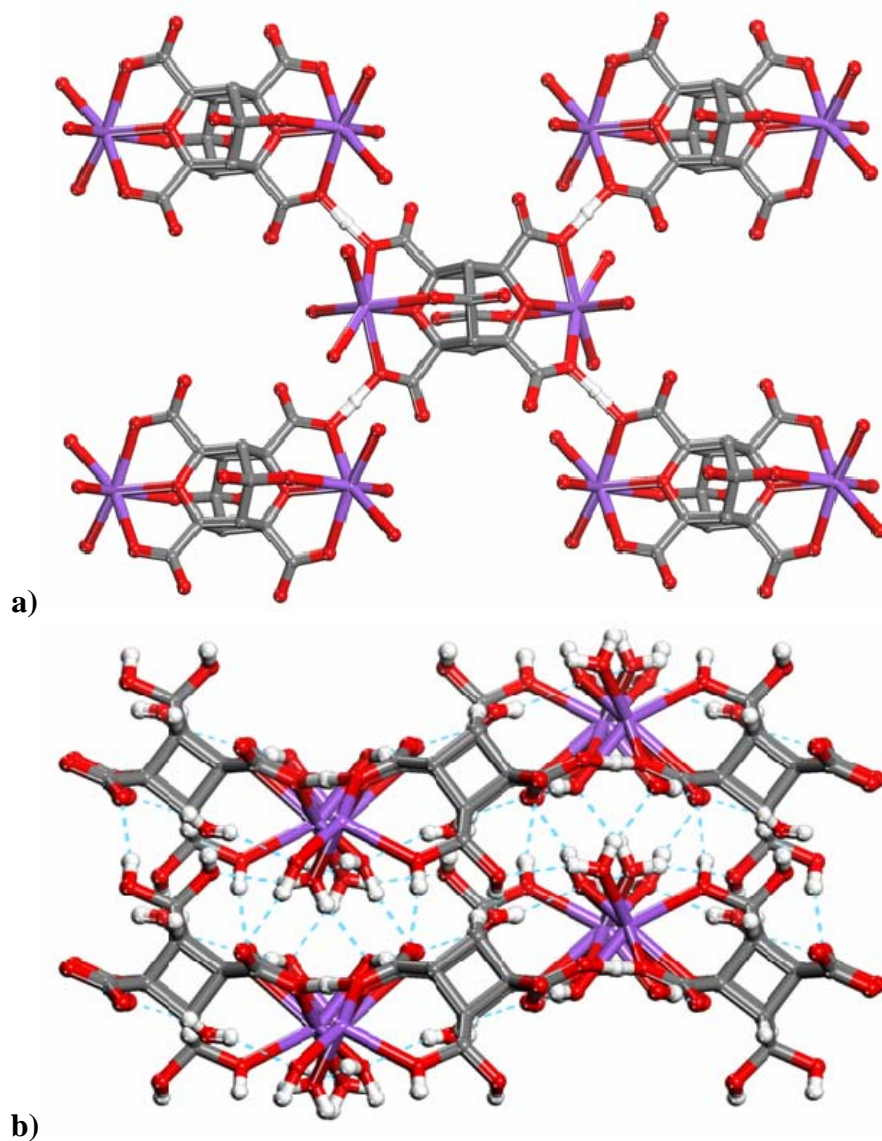


Figure S5. Single-crystal structure of **5**: a) multiple O-H...O HBs between ligands in **5** unite the individual EE2 (Eubank-Eddaoudi-2) molecules into layers having 4.4 square grid topology, indicating the potential use of EE2 as a 4-connected linker in MOFs, and b) the additional O-H...O HBs between ligands and water molecules result in a 3D organic framework. Sodium = violet, carbon = gray; oxygen = red.

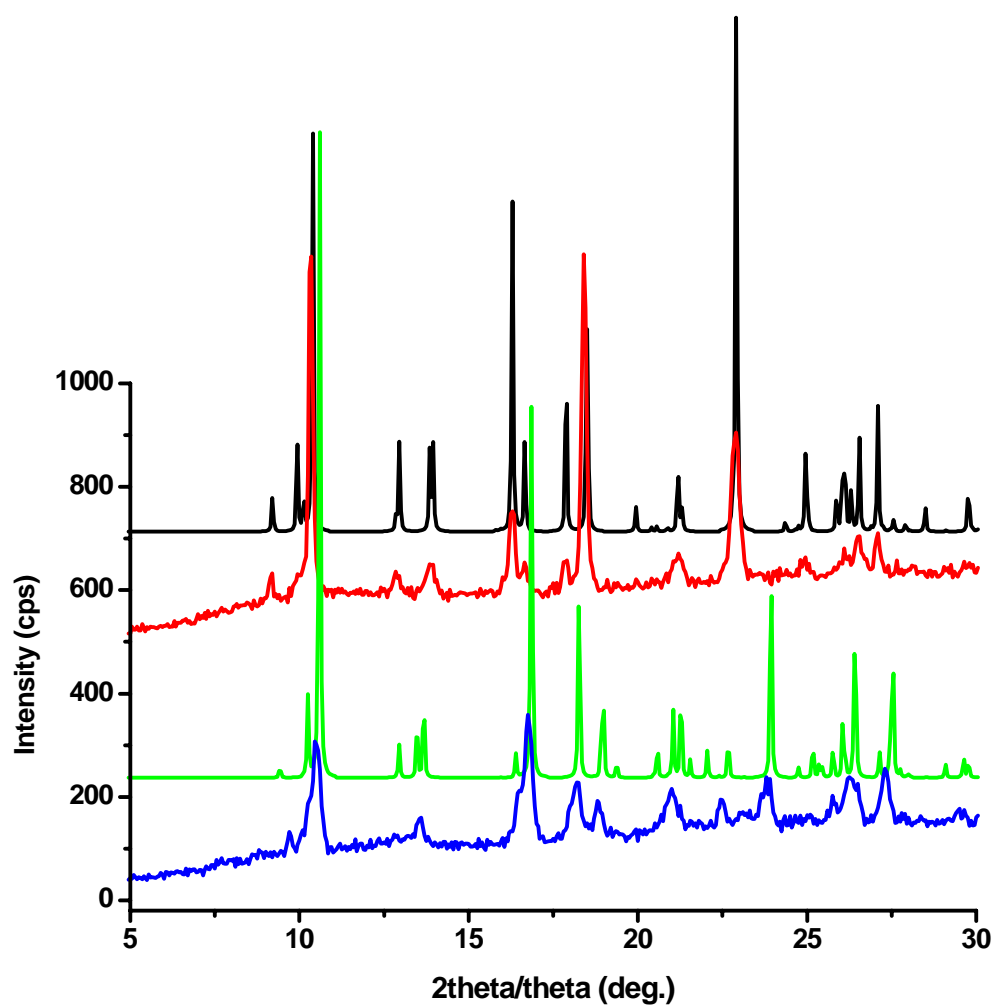


Figure S6. XRPD patterns for **2** (black = simulated, red = experimental), and **3** (green = simulated, blue = experimental).

Table S1. Crystal data and structure refinement for **1**, **2**, and **3**.

Compound	1	2	3
Empirical formula	CoC ₁₂ H ₁₀ N ₂ O ₅	CuC ₁₇ H ₁₄ N ₂ O ₇	CuC ₁₇ H ₄ N ₂ O ₇
Formula weight	321.15	421.84	411.76
Temperature	100(2)K	100(2)K	293(2)K
Wavelength	0.71073Å	0.71073Å	0.71073Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2(1)/c	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions	a=10.8654(14)Å b=9.8741(12)Å c=11.9102(14)Å α=90° β=91.465(2)° γ=90°	a=8.738(3)Å b=10.188(4)Å c=10.760(4)Å α=63.080(7)° β=83.713(8)° γ=76.770(7)°	a=8.586(2)Å b=9.954(3)Å c=10.576(3)Å α=62.738(4)° β=87.681(4)° γ=77.070(4)°
Volume	1277.4(3)Å ³	831.5(5)Å ³	781.1(3)Å ³
Z	4	2	2
Density (calculated)	1.670mg/m ³	1.685mg/m ³	1.751mg/m ³
Abs. coefficient	1.364mm ⁻¹	1.359mm ⁻¹	1.445mm ⁻¹
F(000)	652	430	410
θ range for data collect.	1.87 to 25.08°	2.29 to 26.50°	2.17 to 26.99°
Index ranges	-12≤h≤10 -11≤k≤10 -14≤l≤13	-10≤h≤10 -12≤k≤12 -12≤l≤13	-10≤h≤10 -12≤k≤12 -13≤l≤8
Reflections collect.	6606	4890	4661
Independent reflect.	2258[R(int)=0.0434]	3359[R(int)=0.0536]	3231[R(int)= 0.1838]
Complete. to θ max	99.6%	97.3%	94.8%
Abs. correction	SADABS	None	None
Refinement method	Full-matrix least-sq. on F ²	Full-matrix least-sq. on F ²	Full-matrix least-sq. on F ²
Data/restraints/param.	2258/0/218	3359/2/250	3231/22/250
Goodness-of-fit on F ²	1.065	0.939	1.002
Final R indices [I>2σ(I)]	R1 = 0.0418 wR2 = 0.1048	R1 = 0.0597 wR2 = 0.0913	R1 = 0.0543 wR2 = 0.0954
R indices (all data)	R1 = 0.0529 wR2 = 0.1104	R1 = 0.0999 wR2 = 0.1033	R1 = 0.1449 wR2 = 0.1383
Largest diff. peak/hole	0.673/-0.375 e.Å ⁻³	0.605/-0.646 e.Å ⁻³	1.475/-1.507e.Å ⁻³

Table S2. Crystal data and structure refinement for **4** and **5**.

Compound	4	5
Empirical formula	CuC ₇ H ₁₂ N ₂ O ₁₁	Na ₂ C ₁₄ H ₂₆ O ₂₂
Formula weight	363.73	592.33
Temperature	100(2)K	100(2)K
Wavelength	0.71073Å	0.71073Å
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 21/ <i>c</i>
Unit cell dimensions	a=7.729(3)Å b=8.805(3)Å c=9.393(3)Å α=62.493(6)° β=81.809(6)° γ=68.261(6)°	a=7.297(3)Å b=16.347(7)Å c=11.990(4)Å α=90° β=126.824(17)° γ=90°
Volume	526.3(3)Å ³	1144.9(8)Å ³
<i>Z</i>	2	2
Density (calculated)	2.295mg/m ³	1.718mg/m ³
Abs. coefficient	2.153mm ⁻¹	0.196mm ⁻¹
F(000)	370	616
θ range for data collect.	2.77 to 26.49°	2.46 to 25.49°
Index ranges	-9≤h≤9 -10≤k≤11 -11≤l≤7	-8≤h≤8 -19≤k≤19 -14≤l≤12
Reflections collect.	2947	5963
Independent reflect.	2094[R(int)=0.0945]	2106[R(int)= 0.1597]
Complete. to θ max	96.1%	99.0%
Abs. correction	None	None
Refinement method	Full-matrix least-sq. on F ²	Full-matrix least-sq. on F ²
Data/restraints/param.	2094/14/177	2106/0/203
Goodness-of-fit on F ²	1.000	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0524 wR2 = 0.1248	R1 = 0.0613 wR2 = 0.1615
R indices (all data)	R1 = 0.0861 wR2 = 0.1454	R1 = 0.0653 wR2 = 0.1645
Largest diff. peak/hole	1.414/-1.358e.A ⁻³	0.580/-0.536e.A ⁻³