Supporting Information for

Cu(I)-MOF: naked-eye colorimetric sensor for humidity and formaldehyde in single-crystal-to-single-crystal fashion

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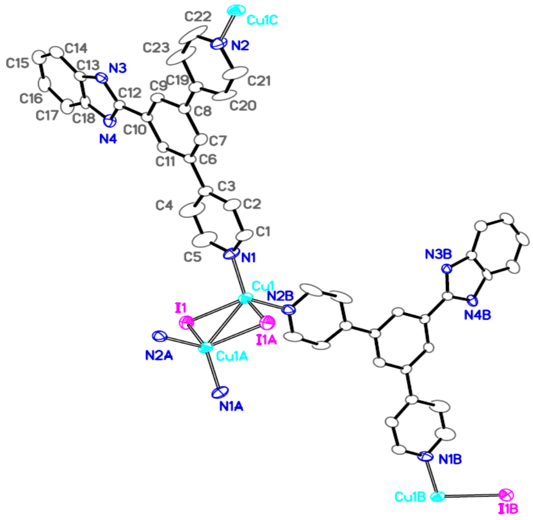
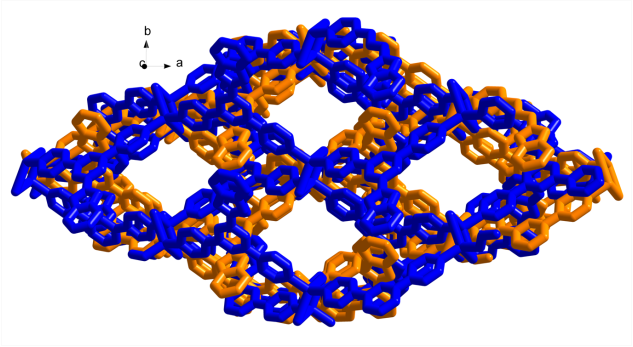




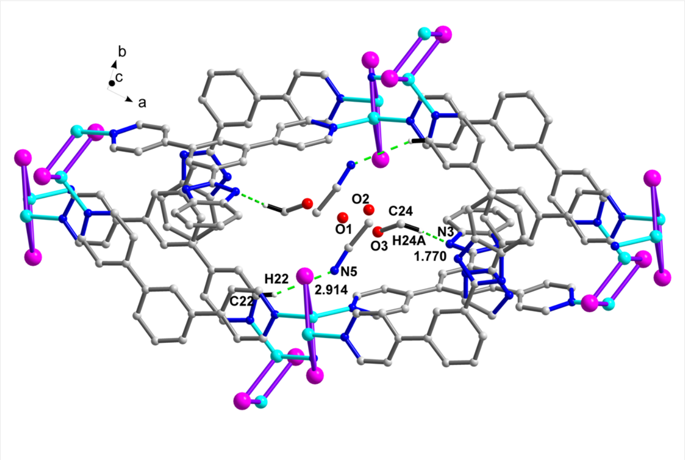


Fig. S1 Top left: ORTEP figure of **1** (displacement ellipsoids drawn at the 30 % probability level, the H atoms, solvent, and uncoordinated nitrate not shown for clarity). Top right: Two sets of 2D networks interlock together to generate the square-like channels along the crystallographic *c* axis. The different nets are shown in blue and orange, respectively. Bottom: Encapsulated solvent molecules are hydrogen-bonded to the framework.

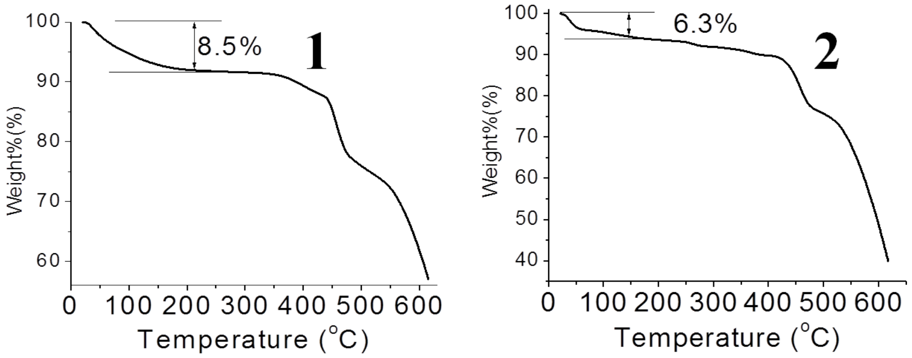


Fig. S2 TGA traces of **1** and **2**. The observed solvent mass loss is 8.5% (calculated 8.3%) for **1**. The observed solvent mass loss for **2** is 6.3% (calculated 6.3%).

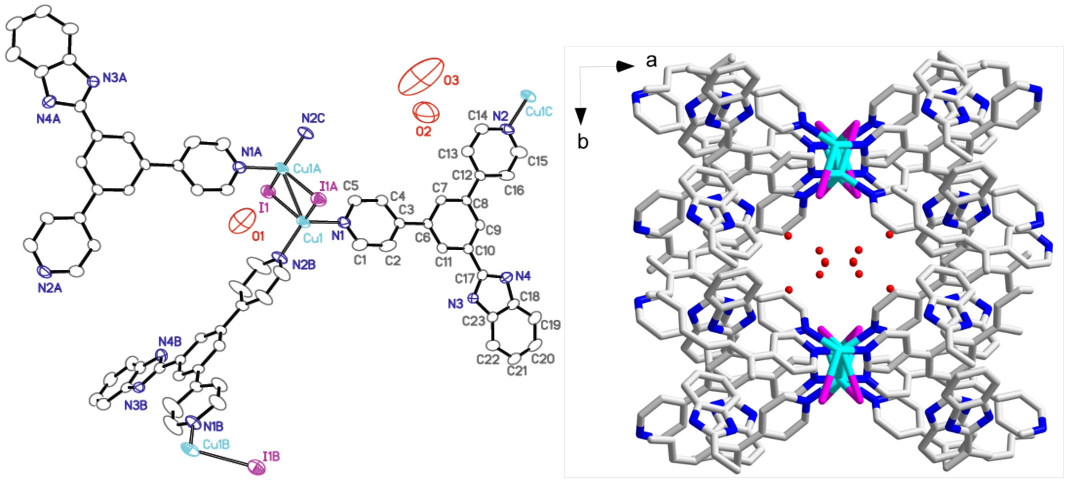


Fig. S3 ORTEP figure of **2** (displacement ellipsoids drawn at the 30 % probability level, the H atoms, solvent, and uncoordinated nitrate not shown for clarity). Right: Encapsulated water molecules are suspended in the framework and no significant host-guest interactions have been found.

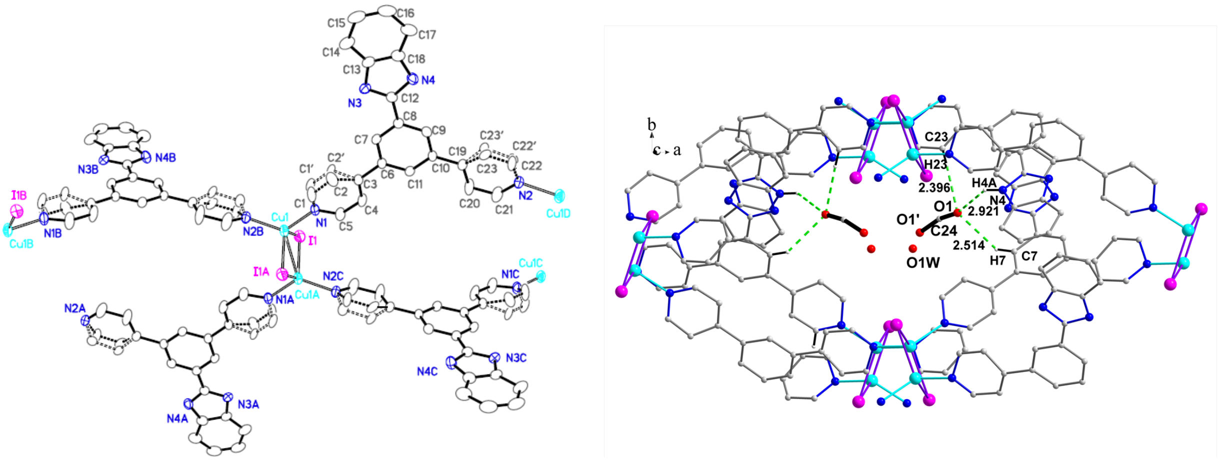


Fig. S4 Left: ORTEP figure of **3** (displacement ellipsoids drawn at the 30 % probability level, the H atoms, solvent, and uncoordinated nitrate not shown for clarity). Right: Encapsulated organic solvent molecules are hydrogen-bonded to the framework.

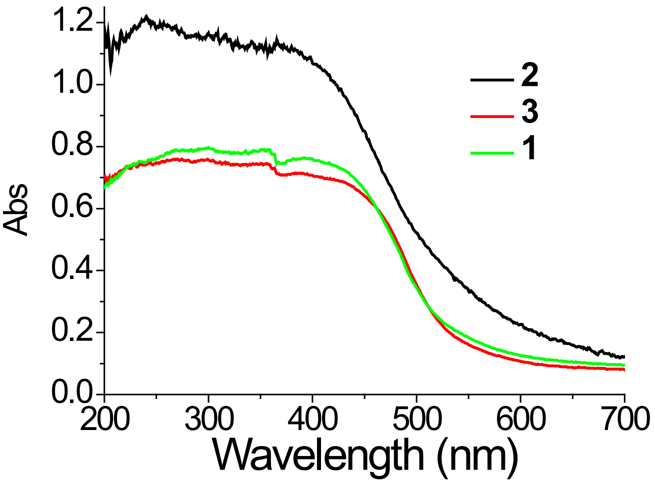


Fig. S5 Solid-state UV-vis spectra of **1-3**.

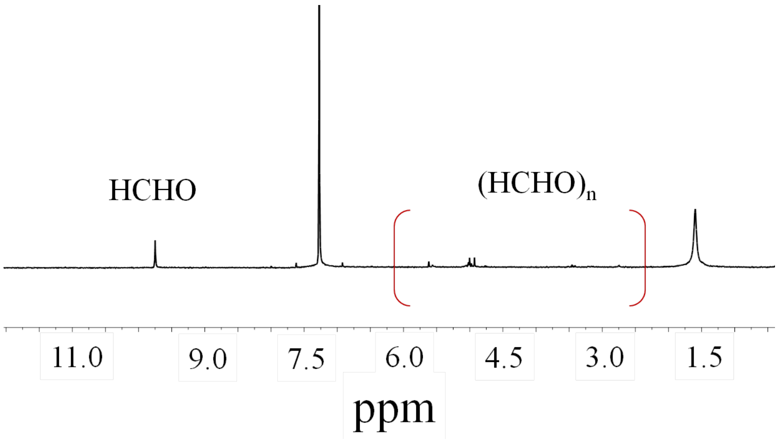


Fig. S6 ^{1}H NMR spectrum of commercial formaldehyde in CDCl$_3$.

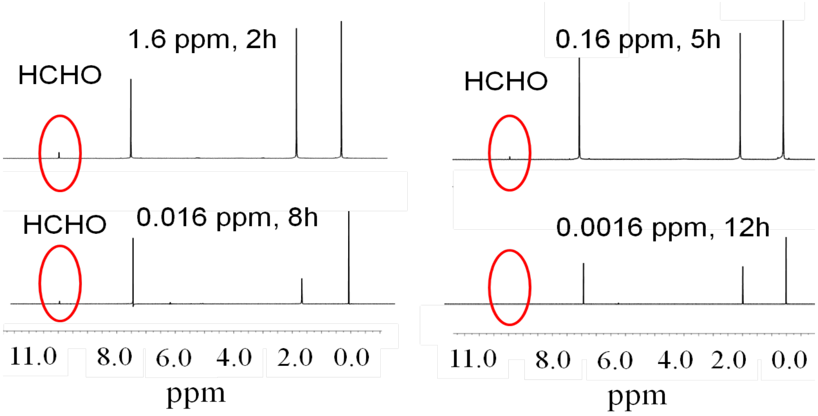
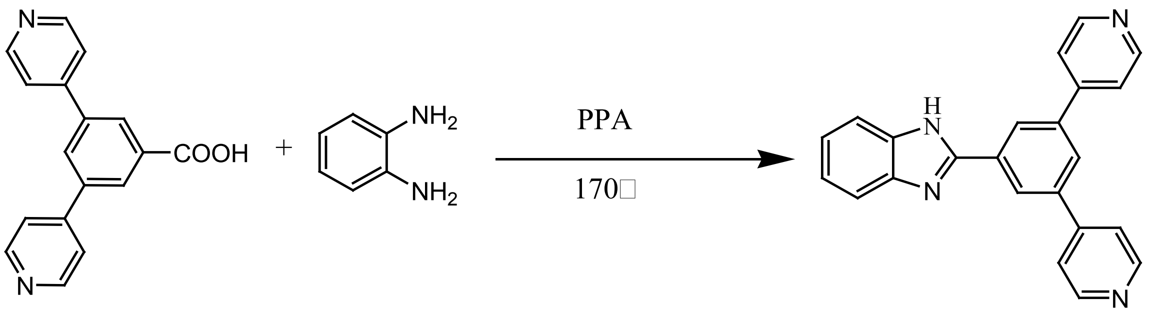


Fig. S7 ^{1}H NMR spectra on the CDCl$_3$ extracts obtained from the bulk crystal samples of **2** in formaldehyde vapour at different vapor concentrations. In 1.6, 0.16 and 0.016 ppm formaldehyde vapor atmospheres, the small single peaks at ~9.8 ppm corresponding to the HCHO protons were found. In contrast, no HCHO signal was detected in 0.016 ppm formaldehyde vapor, which is consistent with the observed color change.

Experimental Section. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10°C/min. XPS spectra were obtained from THI5300 (PE) and ^{1}H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS.

Synthesis of L.



A mixture of 3, 5-bis(4-pyridyl)benzoic acid (2.76 g, 10 mmol), 1,2-diaminobenzene (1.08 g, 10 mmol) and PPA (30 g) was heated to 170°C for 6 h. The obtained sample was purified by column to generate light yellow crystalline solids 2.6 g (Yield, 75 %). ^{1}H NMR (300 MHz, DMSO, 25 °C TMS): δ = 13.16 (s, 1H, -C_3N_2H), 8.75 (d, 4H, -C_5H_4N), 8.66 (s, 2H, -C_6H_3), 8.30 (s, 1H, -C_6H_3), 7.97 (d, 4H, -C_5H_4N), 7.74 (d, 1H, -C_6H_4), 7.62 (d, 1H, -C_6H_4) , 7.25 (m, 2H, -C_6H_4). IR (KBr pellet cm^{-1}): 3430.97 (s), 3124.27 (m), 2359.97 (w), 1594.65 (s), 1430.93 (w), 1460.86 (m), 1420.87 (m), 1401.20 (m), 1332.30 (s), 1274.20 (w), 1225.78 (w), 1108.11 (w), 1069.46 (m), 1001.17 (w), 963.52 (w), 814.58 (m), 767.68 (m), 742.15 (s), 648.73 (w), 615.66 (m), 435.86 (w). Elemental analysis calcd (%): C 79.31, H 4.60, N 16.09; found: C 79.28, H 4.65, N 16.07.

Synthesis of 1. A solution of CuI (15 mg, 0.079 mmol) in CH_3CN (7 mL) was layered onto a solution of **L** (10 mg, 0.029 mmol) in CH_2Cl_2/CH_3OH (6 mL). The solutions were left for about two days at room temperature, and yellow rod-like crystals (6.9 mg) were obtained. Yield, 41%. IR (KBr pellet, cm^{-1}): 3418.60 (s), 3269.76 (s), 1637.74 (m), 1605.86 (s), 1551.66 (w), 1526.27 (w), 1503.56 (w), 1461.96 (m), 1421.55 (m), 1402.92 (m), 1384.82 (m), 1331.14 (m), 1278.20 (w), 1225.33 (w), 1144.27 (w), 1070.15 (w), 1005.36 (w), 975.53 (w), 889.69 (w), 821.41 (s), 767.98 (m), 750.53 (m), 660.96 (m), 626.94 (m), 589.77 (m), 500.46 (w), 437.19 (w).

Synthesis of 2. Bright yellow crystals of compound **1** were exposed to air for 3-4 h to generate red-brown crystals of **2** quantitatively. IR (KBr pellet, cm^{-1}): 3415.64 (s), 3271.42 (s), 1637.54 (m), 1605.72 (s), 1557.33 (w), 1524.59 (w), 1504.35 (w), 1461.49 (m), 1421.15 (m), 1402.59 (m), 1384.97 (m), 1330.63 (m), 1277.90 (w), 1224.92 (w), 1144.87 (w), 1069.57 (w), 1005.13 (w), 888.30 (w), 821.07 (s), 768.02 (m), 750.50 (m), 660.70 (m), 626.76 (m), 589.94 (m), 500.85 (w), 436.40 (w).

Synthesis of 3. A small vial (25 mL) with the red-brown crystals of **2** was sealed in a larger vial (250 mL) with 16% formalin solution (20 mL) for 24 h, the red-brown crystals of **2** changed to the yellow crystals of **3** quantitatively. IR (KBr pellet, cm^{-1}): 3418.48 (s), 3242.18 (s), 1645.23 (m), 1605.26 (s), 1551.46 (w), 1525.32 (w), 1503.15 (w), 1461.91 (m), 1421.31 (m), 1402.79 (m), 1384.74 (m), 1330.62 (m), 1278.17 (w), 1225.53 (w), 1112.39 (w), 1070.71 (w), 1018.25 (w), 900.76 (w), 821.64 (s), 768.22 (m), 751.61 (m), 660.46 (m), 626.84 (m), 501.41 (w), 437.01 (w).

Sensing for humidity. Humidity-controlled solutions (250 mL) of 96% H_2SO_4, saturated $MgCl_2$, saturated K_2CO_3, saturated $Mg(NO_3)_2$ and saturated NaCl were put in closed glass chambers of 1L, which respectively provide different constant RH (30°C): about 5, 33, 43, 57, and 75.8% after 24 h.[1] The solid state luminescent spectra of **1** in different RH atmospheres were performed after humidity sensor was placed in the chamber.

Sensing for formaldehyde. Formaldehyde aqueous solution (16%, Formaldehyde Ampules, Methanol-Free) was obtained from Thermo Fisher Scientific Company ($\rho = 1.000$ g/cm^3). The 16, 1.6, 0.16 and 0.016 ppm vapor atmospheres were prepared by heating (~75°C) the 16, 1.6, 0.16 and 0.016% of formaldehyde solutions in a sealed vial (1000 mL), respectively. The formaldehyde vapor concentrations were obtained according to the following equation:

$$C = \frac{\omega \rho V}{V_0}$$

C: formaldehyde concentration (ppm), ω: mass fraction of formaldehyde solution, ρ: density of formaldehyde solution (g/cm^3), *V*: volume of formaldehyde solution (μL), V_0: system volume (L).

Table S1. Formaldehyde concentrations preparation

Mass fraction of formaldehyde solution	Volume of formaldehyde solution (μL)	Vial volume (mL)	Concentration of formaldehyde (ppm)
16%	10 μL	1000 mL	1.6 ppm
1.6%	10 μL	1000 mL	0.16 ppm
0.16%	10 μL	1000 mL	0.016 ppm
0.016%	10 μL	1000 mL	0.0016 ppm

Reversible guest-exchange: Compound **3** (**3'**) can also be directly obtained by immersing **1** in formaldehyde solution (16%), but took a longer time (24h). Compound **2** (**2'**) can be obtained by exposing **3** in air for 4h. Compound **1** (**1'**) can be regenerated by immersing **2** in CH_3CN/MeOH mixed-solvent system. The corresponding CIF files of **1'**, **2'** and **3'** are provided.

Single-Crystal Structure Determination. Suitable single crystal of **1** was selected and mounted in air onto thin glass fibers. X-ray intensity data of **1** were measured at 123(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data for **1-3** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[2] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[2] The crystal showed no evidence of crystal decay during data collection. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique. Crystal data, data collection parameters, and refinement statistics for **1-3** are listed in Tables S2-4. Relevant interatomic bond distances and bond angles for **1-3** are given in Tables S5-7. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 963997-963999. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S2. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	$C_{24.50}H_{20}CuIN_{4.50}O_{1.25}$	
Formula weight	587.89	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 26.268(5) Å	alpha = 90°
	b = 10.6462(18) Å	beta = 111.641(3)°
	c = 18.295(3) Å	gamma = 90°
Volume	4755.6(14) $Å^3$	
Z, Calculated density	8, 1.642 Mg/m^3	
Absorption coefficient	2.243 mm^{-1}	
F(000)	2324	
Crystal size	0.20 x 0.10 x 0.03 mm	
Theta range for data collection	1.67 to 25.50 deg.	
Limiting indices	-31<=h<=24, -11<=k<=12, -21<=l<=22	
Reflections collected / unique	12191 / 4399 [R(int) = 0.0616]	
Completeness to theta = 25.50	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. Transmission	0.9358 and 0.6626	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4399 / 22 / 322	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0623, wR2 = 0.1346	
R indices (all data)	R1 = 0.1031, wR2 = 0.1510	
Largest diff. peak and hole	1.124 and -0.657 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement for **2**.

Identification code	**2**
Empirical formula	$C_{23}H_{20}CuIN_4O_2$
Formula weight	574.87
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 26.195(7) Å alpha = 90°
	b = 10.604(3) Å beta = 112.035(3)°
	c = 18.493(5) Å gamma = 90°
Volume	4762(2) Å^3
Z, Calculated density	8, 1.604 Mg/m^3
Absorption coefficient	2.240 mm^{-1}
F(000)	2272
Crystal size	0.40 x 0.15 x 0.06 mm
Theta range for data collection	1.68 to 25.50°
Limiting indices	-30<=h<=31, -12<=k<=5, -22<=l<=22
Reflections collected / unique	11874 / 4415 [R(int) = 0.0343]
Completeness to theta = 25.50	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8773 and 0.4678
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4415 / 12 / 289
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1648
R indices (all data)	R1 = 0.0917, wR2 = 0.1863
Largest diff. peak and hole	1.288 and -0.405 e.A^{-3}

Table S4. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	$C_{48}H_{38}Cu_2I_2N_8O_3$	
Formula weight	1155.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 26.407(13) Å	alpha = 90°
	b = 10.549(5) Å	beta = 111.635(7)°
	c = 18.435(9) Å	gamma = 90°
Volume	4773(4) $Å^3$	
Z, Calculated density	4, 1.608 Mg/m^3	
Absorption coefficient	2.233 mm^{-1}	
F(000)	2280	
Crystal size	0.24 x 0.12 x 0.05 mm	
Theta range for data collection	1.66 to 25.50°	
Limiting indices	-31<=h<=13, -12<=k<=12, -21<=l<=22	
Reflections collected / unique	12229 / 4425 [R(int) = 0.0451]	
Completeness to theta = 25.50	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8965 and 0.6163	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4425 / 3 / 318	
Goodness-of-fit on F^2	0.951	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1266	
R indices (all data)	R1 = 0.0910, wR2 = 0.1389	
Largest diff. peak and hole	0.798 and -0.452 e.$Å^{-3}$	

Table S5. Interatomic Distances (Å) and Bond Angles (°) with esds () for **1**.

Cu(1)-N(1)	2.003(6)	Cu(1)-N(2)#1	2.022(7)
Cu(1)-I(1)#2	2.6777(12)	Cu(1)-I(1)	2.6994(12)
Cu(1)-Cu(1)#2	2.7390(19)	I(1)-Cu(1)#2	2.6777(12)
N(2)-Cu(1)#3	2.022(6)		
N(1)-Cu(1)-N(2)#1	121.8(3)	N(1)-Cu(1)-I(1)#2	106.41(19)
N(2)#1-Cu(1)-I(1)#2	102.4(2)	N(1)-Cu(1)-I(1)	104.7(2)
N(2)#1-Cu(1)-I(1)	103.82(19)	I(1)#2-Cu(1)-I(1)	118.76(4)
N(1)-Cu(1)-Cu(1)#2	121.8(2)	N(2)#1-Cu(1)-Cu(1)#2	116.40(18)
I(1)#2-Cu(1)-Cu(1)#2	59.77(4)	I(1)-Cu(1)-Cu(1)#2	58.99(4)
Cu(1)#2-I(1)-Cu(1)	61.24(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+5/2,z+1/2 #2 -x+2,-y+2,-z+1 #3 x-1/2,-y+5/2,z-1/2

Table S6. Interatomic Distances (Å) and Bond Angles (°) with esds () for **2**.

Cu(1)-N(1)	2.017(5)	Cu(1)-N(2)#1	2.021(5)
Cu(1)-I(1)#2	2.6973(12)	Cu(1)-I(1)	2.7177(14)
Cu(1)-Cu(1)#2	2.7601(19)	I(1)-Cu(1)#2	2.6973(12)
N(2)-Cu(1)#3	2.021(5)		
N(1)-Cu(1)-N(2)#1	121.6(2)	N(1)-Cu(1)-I(1)#2	100.85(18)
N(2)#1-Cu(1)-I(1)#2	106.80(17)	N(1)-Cu(1)-I(1)	105.33(17)
N(2)#1-Cu(1)-I(1)	104.6(2)	I(1)#2-Cu(1)-I(1)	118.71(4)
N(1)-Cu(1)-Cu(1)#2	116.38(16)	N(2)#1-Cu(1)-Cu(1)#2	122.02(19)
I(1)#2-Cu(1)-Cu(1)#2	59.72(4)	I(1)-Cu(1)-Cu(1)#2	58.99(4)
Cu(1)#2-I(1)-Cu(1)	61.29(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z-1/2 #2 -x,-y+1,-z+1 #3 x+1/2,-y+1/2,z+1/2

Table S7. Interatomic Distances (Å) and Bond Angles (°) with esds () for **3**.

Cu(1)-N(2)#1	2.024(5)	Cu(1)-N(1)	2.027(5)
Cu(1)-I(1)#2	2.6773(14)	Cu(1)-I(1)	2.6841(16)
Cu(1)-Cu(1)#2	2.756(2)	I(1)-Cu(1)#2	2.6773(14)
N(2)-Cu(1)#3	2.024(5)		
N(2)#1-Cu(1)-N(1)	123.1(2)	N(2)#1-Cu(1)-I(1)#2	106.06(18)
N(1)-Cu(1)-I(1)#2	102.71(17)	N(2)#1-Cu(1)-I(1)	104.66(18)
N(1)-Cu(1)-I(1)	103.20(17)	I(1)#2-Cu(1)-I(1)	118.13(4)
N(2)#1-Cu(1)-Cu(1)#2	121.01(18)	N(1)-Cu(1)-Cu(1)#2	115.86(16)
I(1)#2-Cu(1)-Cu(1)#2	59.19(5)	I(1)-Cu(1)-Cu(1)#2	58.94(4)
Cu(1)#2-I(1)-Cu(1)	61.87(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z-1/2 #2 -x,-y,-z+1 #3 x+1/2,-y+1/2,z+1/2

Reference

(1) (*a*) Z. Li, H. Zhang, W. Zheng, W. Wang, H. Huang, C. Wang, A. G. MacDiarmid, Y. Wei, *J. Am. Chem. Soc.*, 2008, **130**, 5036. (*b*) Q. Kuang, C. Lao, Z. L. Wang, Z. Xie, L. Zheng, *J. Am. Chem. Soc.*, 2007, **129**, 6070.

(2) Sheldrick, G. M. SHELXTL Version 5.12; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.