Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

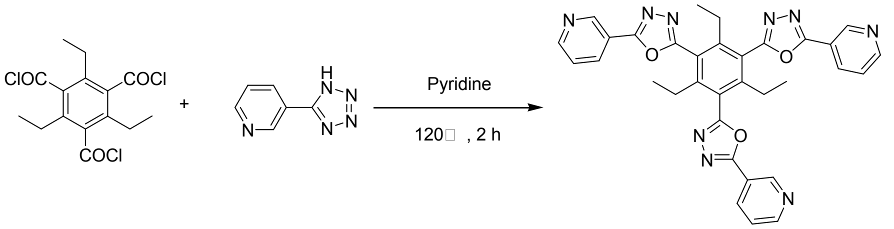
In situ self-assembled Cu_4I_4-MOF-based mixed matrix membrane for highly sensitive visual sensing of gaseous HCl

Chao-Wei Zhao, Jian-Ping Ma, Qi-Kui Liu, Xue-Ru Wang, Yi Liu, Jing Yang, Jia-Shi Yang and Yu-Bin Dong*

1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Acros) and used without further purification. Infrared (IR) spectrums were obtained in the 400-4000 cm^{-1} range using a Bruker ALPHA FT-IR Spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer. ^{1}H NMR data were collected on a Bruker Avance-300 spectrometer. Chemical shifts are reported in δ relative to TMS. All crystal data were obtained by Agilent SuperNova X-Ray single crystal diffractometer. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. XRD pattern was obtained on D8 ADVANCE X-ray powder diffractometer (XRPD) with Cu Kα radiation (λ = 1.5405 Å). The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope equipped with energy-dispersive X-ray detector (EDS). XPS were conducted on the ESCALAB 250. Raman spectra were collected at room temperature on a Horiba HR Evolution 800 Raman microscope system (laser wavelength 532 nm).

2. Synthesis and characterization of L

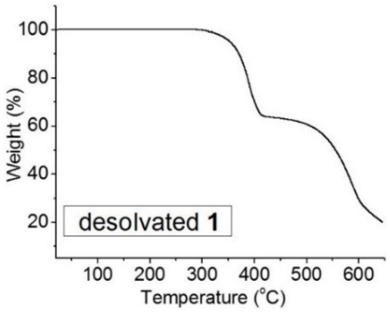


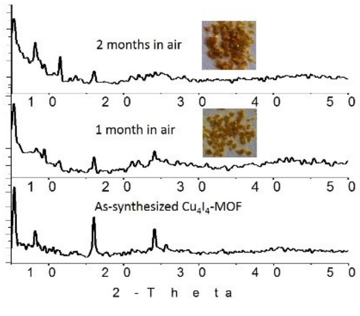
Scheme S1. Synthesis of **L**.

A mixture of 2, 4, 6-triethyl-1,3,5-benzenetricarbonyl trichloride[1] (3.48 g, 10 mmol), pyridine (10 mL) and 5-(3-pyridyl)-1H-tetrazole (4.41 g, 33 mmol) was heated at 120˚C for 2 h. After cooling to room temperature, the reaction mixture was poured into 100 mL water and filtered. The crude product was purified by column chromatography on silica gel using EtOAc as an eluent. After purification a light yellow solid of L was obtained. Yield 3.7 g, 58 %. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): 9.34 (s, 3H), 8.83 (d, *J* = 4.6 Hz, 3H), 8.42 (d, *J* = 7.9 Hz, 3H), 7.53 (d d, *J* = 7.8, 5.0 Hz, 3H), 2.47 (d d, *J* = 14.8, 7.3 Hz, 6H), 1.16 (t, *J* = 7.4 Hz, 9H). IR (KBr pellet) [(cm^{-1})]: 3051(w), 2979(m), 2875(w), 1693(w), 1615(s), 1572(s), 1475(m), 1411(s), 1217(m), 1103(s), 965(m), 877(s), 806(w), 690(s). Anal. Calcd for $C_{33}H_{27}O_3N_9$: C, 66.32; H, 4.59; N, 21.05. Found: C, 66.37; H, 4.56; N, 21.11.

3. Synthesis and characterization of 1-3

Synthesis of Cu_4I_4L (1): An acetonitrile (10 mL) solution of **L** (30 mg, 0.05 mmol) and CuI (40 mg, 0.2 mmol) was allowed to stand at ambient temperature for 12 h to generate as yellow crystals. The crystals were allowed to stand at ambient temperature for a while or heated at 60˚C for 2 h to generate guest free crystals of **1**. Yield, 77% based on L. IR (KBr pellet) [(cm^{-1})]: 3432(m), 3061(w), 2976(m), 2879(w), 1591(vs), 1548(m), 1467(s), 1437(m), 1212(w), 1100(s), 1057(m), 811(m), 694(m). Anal. Calcd for $C_{33}H_{27}O_3N_9Cu_4I_4$: C 29.16, H 2.00, N 9.27. Found: C 29.03, H 2.05, N 9.19.





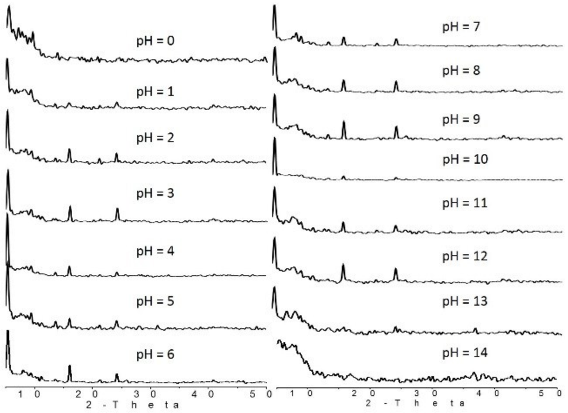


Fig. S1 Top left: TGA trace of **1** allowed for standing at room temperature for a while. Top right: the Cu_4I_4-MOF can be stable for at least two months at room temperature which is confirmed by the corresponding XRPD patterns. Bottom: XRPD patterns of **1** soaked in aqueous solution with different pH values, indicating it is stable in a wide pH range of 0-13.

Synthesis of micro-sized of Cu_4I_4L (1). An acetonitrile solution (3 mL) of CuI (40 mg) was quickly added to a hot acetonitrile (2 mL) solution of L (30 mg). The mixture was refluxed for 1 h to provide the yellow micro-sized crystals. The product was collected by centrifugation.

Synthesis of $0.5I_2\subset Cu_4I_4L$ (2). 1 was exposed to gaseous HCl (200 ppm) in air, dark crystals of 2 were obtained in quantitative yield. IR (KBr pellet) [(cm^{-1})]: 3443(m), 3067(w), 2975(m), 2879(w), 1588(vs), 1548(m), 1467(s), 1423(m), 1212(w), 1102(m), 1056(m), 812(w), 692(m). Anal. Calcd for $C_{33}H_{27}O_3N_9Cu_4I_4Cl$: C 28.41, H 1.95, N 9.04. Found: C 27.93, H 1.96, N 9.07. Ion chromatography analysis: Cl 2.54 % (calculated), Cl 2.57 % (measured).

Synthesis of $0.75I_2\subset Cu_4I_4L$ (3). When **1** was placed in I_2 ($p(I_2)$ is ca. 0.3 mm Hg) atmosphere for 5 min., dark crystals of **3** was obtained in quantitative yield. IR (KBr pellet) [(cm^{-1})]: 3421(m), 3062(w), 2975(m), 2879(w), 1591(vs), 1549(m), 1467(s), 1420(m), 1213(w), 1100(m), 1031(m), 811(m), 693(m). Calcd for $C_{33}H_{27}O_3N_9Cu_4I_{5.5}$: C 25.57, H 1.76, N 8.13. Found: C 25.07, H 1.73, N 7.97.

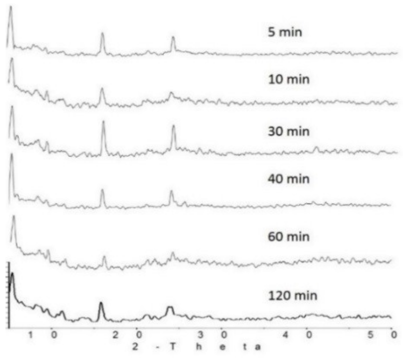


Fig. S2 The XRPD patterns of **1** in HCl (200 ppm), indicating the structural integrity of **1** is maintained during the process.

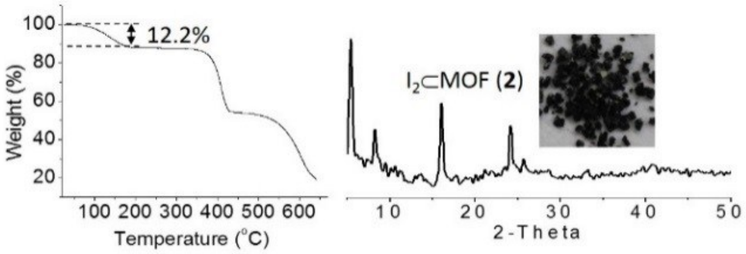


Fig. S3 Left: TGA trace of $0.75I_2{\subset}Cu_4I_4L$ (**3**). Right: XRPD pattern of **3**. The photograph is inserted. The desolvated **1** can uptake I_2 at ambient temperature in the vapor phase with retention of its structure, meanwhile the colour of **1** changed to dark brown. The iodine content of up to 12.2 % based on thermogravimetric analysis (TGA) which is consistent with the formula of $0.75I_2@Cu_4I_4L$ (**3**).

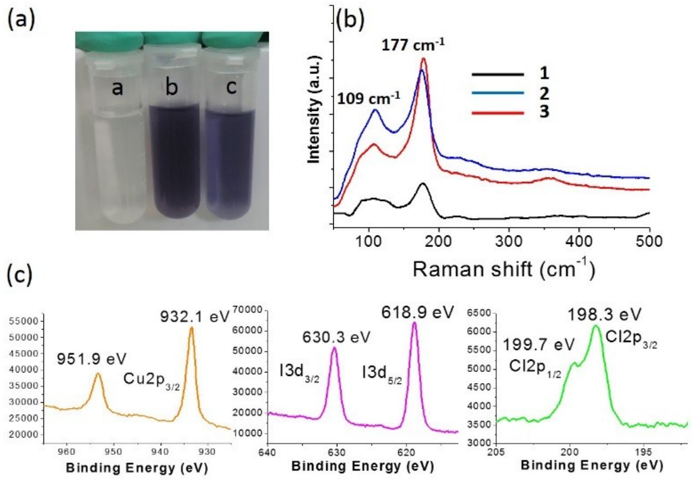
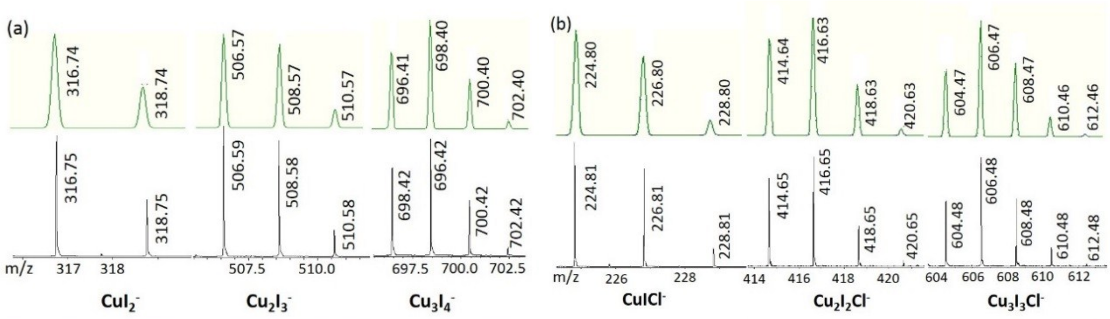


Fig. S4 (a) a-c: aqueous starch solution of KI, aqueous starch solution of KI/I_2 and aqueous starch solution of KI with **2**. (b) Raman spectra of **1-3**. (c) XPS spectra of **2**.



Ion fragment	Calculated	Measured
$Cu_3I_4^-$	698.40	698.42
$Cu_2I_3^-$	506.57	506.59
CuI_2^-	316.74	316.75

Ion fragment	Calculated	Measured
$Cu_3I_3Cl^-$	606.47	606.48
$Cu_2I_2Cl^-$	416.63	416.65
$CuCl^-$	224.80	224.81

Fig. S5 ESI-MS spectra for **1** (a) and **2** (b). The result indicates that the Cl/I ion-exchange reaction occurred during the HCl sensing process.

4. Sensing and selectivity

Sensing. Dilute HCl aqueous solution (0.083 mg/mL) was used in the sensing experiment. 1-16ppb gaseous HCl atmosphere was prepared by heating (~ 90˚C) the corresponding amount of the HCl solution in a sealed big conical flask, respectively. The gaseous HCl concentration was obtained according to the following equation:

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

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

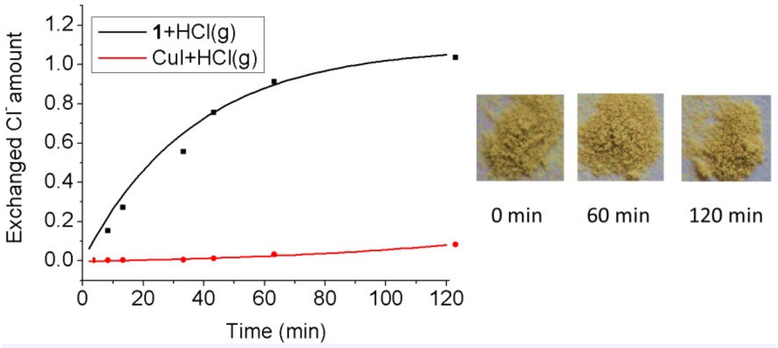
When **1** was placed in gaseous HCl with different concentrations, and exposed to air, the colour of the crystals of **1** changed from orange to dark brown. It is noteworthy that if **1** was in HCl gas in inert atmosphere (N_2 or Ar), no colour change was observed. The colour change, however, occurred again once it exposed to air for a while.

1

1 in HCl without air

Exposed to air again

Fig. S6 The comparison of **1**, **1** in HCl without air and it was exposed to air again.



0 min

60 min

120 min

Fig. S7 Left: Comparison the Cl-I exchange of **1** and CuI in HCl (g). Right: Photos of CuI in HCl (g) at different time and no colour change was observed.

When **1** was placed in various other kinds of acidic gases such as HI, HBr, HF, HOAc, HNO_3 and $HClO_4$ in air, no colour change occurred was observed, indicating that **1** is a highly selective sensor for HCl gas. Notably, the sensing parallel experiment of HF was carried out in a plastic vial.

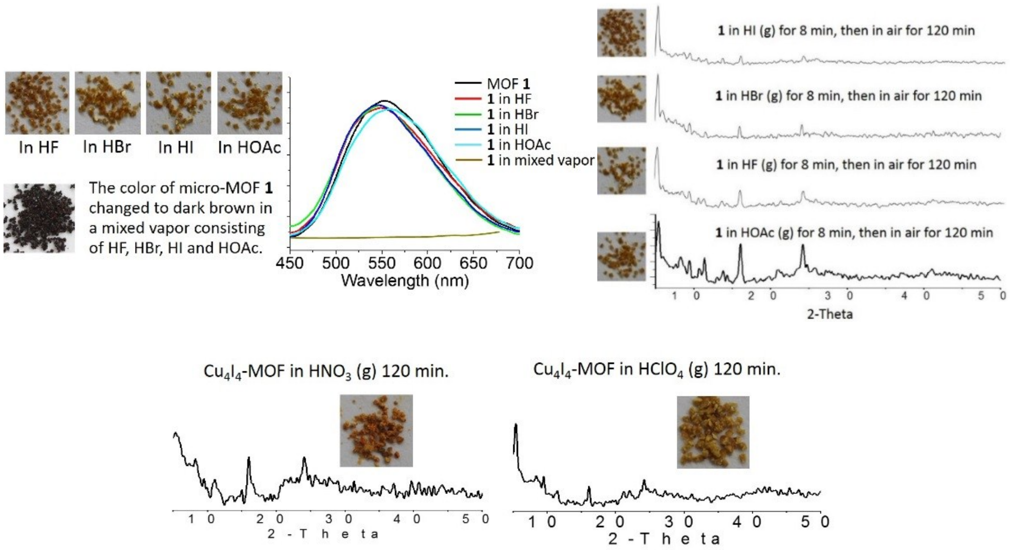


Fig. S8 Top left: Emission spectra of Cu(I)-MOF (**1**) in HF, HBr, HI, HOAc and the HF/HCl/HBr/HI/HOAc mixed acid gases. The corresponding photographs are inserted. Top right: The XRPD patterns of **1** in different acidic gases, indicating its structural integrity was retained. However, no colour change of **1** was found in these acidic gases. The corresponding sample pictures are inserted. Bottom: **1** was in gaseous HNO_3 and $HClO_4$, and then exposed to air, no obvious colour change was detected. In addition, **1** is not very stable in gaseous HNO_3 after 10 min based on the XRPD pattern.

5. Preparation of Cu_4I_4-MOF-based MMM

Preparation of Cu_4I_4-MOF-based MMM: **L** (83 mg, 0.138 mmol) was dissolved in DMF (1 mL) solution of PVDF (7.5 wt %) and the solution was preheated to 90˚C. Acetonitrile (5 mL) solution of CuI (106 mg, 0.555mmol) was added to above solution with continuous stirring (1 h). Then the solution was evaporated under vacuum to remove acetonitrile and a homogeneous ink of micro-Cu_4I_4-MOF in the DMF solution of PVDF polymer was obtained. The ink was casted on microscope slide with a glass rod and dried at 90˚C to remove the solvents. The membrane on the slide can be delaminated by immersing in methanol through the swelling at the MMM/substrate interface. The free standing MMM was dried in air.

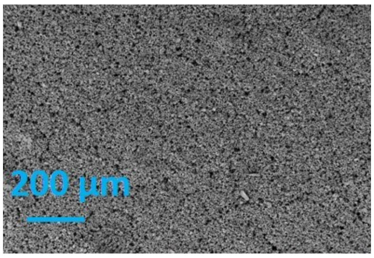


Fig. S9 SEM image of the Cu_4I_4-MOF-based MMM.

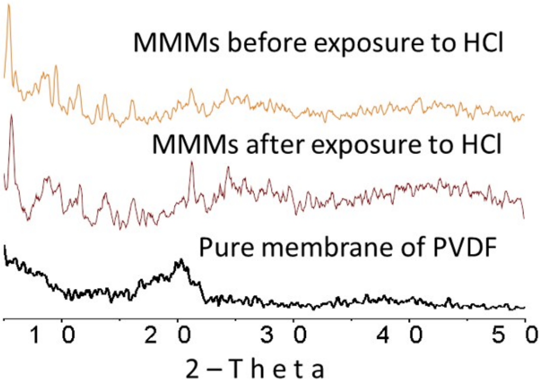


Fig. S10 The XRPD patterns of Cu_4I_4-MOF-based MMM before and after exposure to gaseous HCl, which indicates the MOF structure was retained in the MMM.

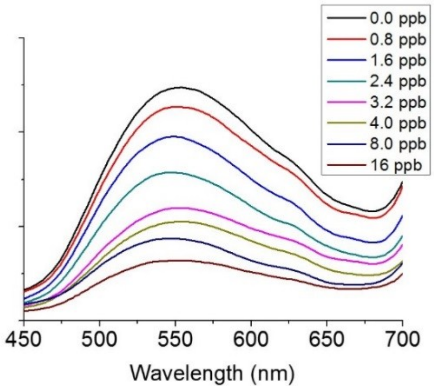


Fig. S11 The emission spectra of Cu_4I_4-based MMM in HCl (g) with different concentrations (551 nm upon exciated at 370 nm).

6. Crystal data[2]

Crystal data. $C_{33}H_{27}Cu_4I_4N_9O_3$, Monoclinic a = 19.4538 (5), b = 32.5779 (7), c = 22.6155 (6) Å, β = 103.876 (2)°, V = 13914.6 (6) Å^3, ρ = 1.297 g/cm^3, space group *P 1 21/c 1*, 2θ = 67.08°, λ = 1.54184 Å, data/restraints/parameters 24785/528/955, R_1 = 0.0946, wR_2 = 0.2549. CCDC 1413643 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requeat/cif.

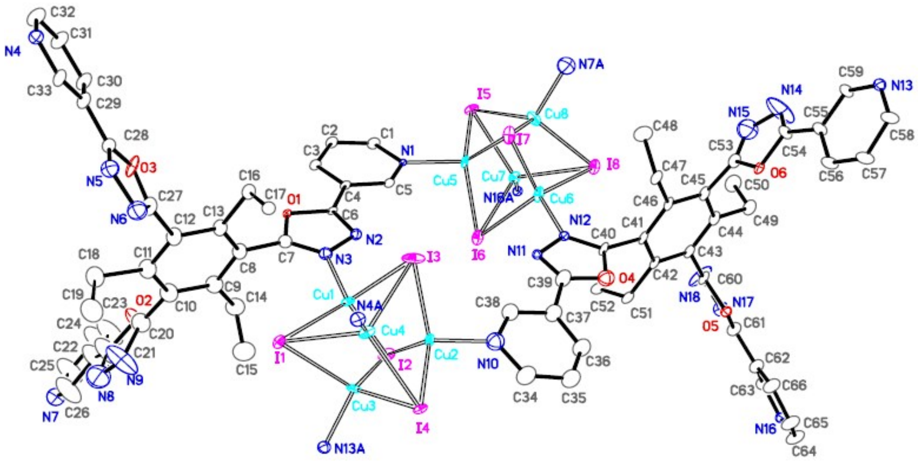


Fig. S13 ORTEP figure of Cu(I)-MOF.

Table S1. Crystal data of Cu_4I_4-MOF (**1**)

Empirical formula	$C_{33}H_{26.50}Cu_4I_4N_9O_3$
Fw	1358.89
Cryst syst	Monoclinic
a (Å)	19.4538 (5)
b (Å)	32.5779 (7)
c (Å)	22.6155 (6)
α (°)	90
β (°)	103.876 (2)
γ (°)	90
V (Å^3)	13914.6 (6)
Space Group	*P 1 21/c 1*
Z value	8
ρcalc. (g/cm^3)	1.297
μ (Cu Kα) (mm^{-1})	15.531
Temp (K)	100.01 (10)
Data / restraints / parameters	24785 / 528 / 955
final *R* indices [I > 2sigma(I)]	*R1* = 0.0946 *wR2* = 0.2549

Table S2. Selected bond lengths [Å] and angles [°] for Cu_4I_4-MOF (**1**)

Cu(1)-N(3)	2.035(9)	Cu(1)-I(1)	2.6590(16)
Cu(1)-I(3)	2.7030(17)	Cu(1)-I(2)	2.7096(16)
Cu(2)-N(10)	2.005(11)	Cu(2)-I(3)	2.6570(18)
Cu(2)-I(4)	2.6765(16)	Cu(2)-I(2)	2.6922(17)
Cu(3)-N(13)#1	2.031(9)	Cu(3)-I(4)	2.6621(16)
Cu(3)-I(2)	2.6662(16)	Cu(3)-I(1)	2.6995(17)
Cu(4)-N(4)#2	2.033(10)	Cu(4)-I(4)	2.6747(16)
Cu(4)-I(1)	2.6760(17)	Cu(4)-I(3)	2.6822(18)
Cu(5)-N(1)	2.019(8)	Cu(5)-I(5)	2.6689(16)
Cu(5)-I(7)	2.6863(16)	Cu(5)-I(6)	2.6901(17)
Cu(6)-N(12)	2.012(9)	Cu(6)-I(8)	2.6602(17)
Cu(6)-I(6)	2.7089(18)	Cu(6)-I(7)	2.7213(19)
Cu(7)-N(16)#3	2.015(9)	Cu(7)-I(6)	2.6581(17)
Cu(7)-I(8)	2.6831(16)	Cu(7)-I(5)	2.7152(17)
Cu(8)-N(7)#4	2.020(12)	Cu(8)-I(5)	2.6367(17)
Cu(8)-I(7)	2.6446(17)	Cu(8)-I(8)	2.7040(19)
N(3)-Cu(1)-I(1)	114.1(3)	N(3)-Cu(1)-I(3)	102.9(3)
I(1)-Cu(1)-I(3)	113.91(6)	N(3)-Cu(1)-I(2)	99.9(3)
I(1)-Cu(1)-I(2)	112.79(6)	I(3)-Cu(1)-I(2)	112.11(6)
N(10)-Cu(2)-I(3)	107.8(3)	N(10)-Cu(2)-I(4)	106.7(3)
I(3)-Cu(2)-I(4)	113.41(6)	N(10)-Cu(2)-I(2)	99.7(3)
I(3)-Cu(2)-I(2)	114.15(6)	I(4)-Cu(2)-I(2)	113.65(6)
N(13)#1-Cu(3)-I(4)	107.1(3)	N(13)#1-Cu(3)-I(2)	104.8(3)
I(4)-Cu(3)-I(2)	114.99(6)	N(13)#1-Cu(3)-I(1)	102.3(3)
I(4)-Cu(3)-I(1)	113.30(6)	I(2)-Cu(3)-I(1)	112.88(6)
N(4)#2-Cu(4)-I(4)	105.1(3)	N(4)#2-Cu(4)-I(1)	106.3(3)

I(4)-Cu(4)-I(1)	113.66(6)	N(4)#2-Cu(4)-I(3)	103.9(3)
I(4)-Cu(4)-I(3)	112.65(6)	I(1)-Cu(4)-I(3)	114.04(6)
N(1)-Cu(5)-I(5)	106.8(2)	N(1)-Cu(5)-I(7)	106.3(2)
I(5)-Cu(5)-I(7)	110.39(6)	N(1)-Cu(5)-I(6)	101.7(2)
I(5)-Cu(5)-I(6)	114.64(6)	I(7)-Cu(5)-I(6)	115.86(5)
N(12)-Cu(6)-I(8)	112.9(2)	N(12)-Cu(6)-I(6)	101.8(2)
I(8)-Cu(6)-I(6)	112.78(6)	N(12)-Cu(6)-I(7)	101.1(2)
I(8)-Cu(6)-I(7)	113.02(7)	I(6)-Cu(6)-I(7)	114.07(6)
N(16)#3-Cu(7)-I(6)	107.0(3)	N(16)#3-Cu(7)-I(8)	104.6(2)
I(6)-Cu(7)-I(8)	113.69(6)	N(16)#3-Cu(7)-I(5)	103.8(2)
I(6)-Cu(7)-I(5)	114.16(6)	I(8)-Cu(7)-I(5)	112.45(6)
N(7)#4-Cu(8)-I(5)	107.5(3)	N(7)#4-Cu(8)-I(7)	107.4(3)
I(5)-Cu(8)-I(7)	112.73(6)	N(7)#4-Cu(8)-I(8)	99.5(3)
I(5)-Cu(8)-I(8)	114.32(6)	I(7)-Cu(8)-I(8)	114.09(7)

Symmetry transformations used to generate equivalent atoms:
#1 x+1, y, z #2 x, -y-1/2, z+1/2 #3 x, -y+1/2, z-1/2 #4 x-1, y, z

7. Reference

(1) C.-W. Zhao, J.-P. Ma, Q.-K. Liu, Y. Yu, P. Wang, Y.-A. Li, K. Wang, Y.-B. Dong, *Green Chem.* 2013, **15**, 3510.

(2) (a) CrysAlisPro, Agilent Technologies,Version 1.171.36.32 (release 02-08-2013 CrysAlis171. NET) (compiled Aug 2 2013,16:46:58). (b) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool. University of Utrecht, Utrecht, The Netherlands, 1998.