Electronic Supplementary Information for Dalton Transactions

In situ Alkylation of N-Heterocycles in Organic Templated Cuprous Halides

Juan-Juan Hou, Shi-Li Li, Cui-Rui Li and Xian-Ming Zhang

Table S1. Bond lengths (Å) and angles (°) for **1-5.**

Compound 1

Cu(1)-I(1a)	2.655(4)	Cu(2)-I(1)	2.638(5)
Cu(1)-I(1)	2.655(4)	Cu(2)-I(1d)	2.655(4)
Cu(1)-I(2b)	2.672(3)	Cu(2)-I(2a)	2.690(3)
Cu(1)-I(2c)	2.672(3)	Cu(2)-I(2)	2.712(4)
Cu(1)-Cu(2c)	2.972(5)	Cu(2)-Cu(2a)	2.965(7)
Cu(1)-Cu(2b)	2.972(5)	Cu(2)-Cu(1e)	2.972(5)
I(1a)-Cu(1)-I(1)	98.56(18)	I(1d)-Cu(2)-I(2)	114.99(14)
I(1a)-Cu(1)-I(2b)	118.73(4)	I(2a)-Cu(2)-I(2)	100.33(12)
I(1)-Cu(1)-I(2b)	109.98(4)	Cu(2)-I(1)-Cu(1)	118.86(12)
I(1a)-Cu(1)-I(2c)	109.98(4)	Cu(2)-I(1)-Cu(2f)	118.94(13)
I(1)-Cu(1)-I(2c)	118.73(4)	Cu(1)-I(1)-Cu(2f)	117.97(15)
I(2b)-Cu(1)-I(2c)	101.86(18)	Cu(1e)-I(2)-Cu(2a)	67.33(10)
I(1)-Cu(2)-I(1d)	97.59(12)	Cu(1e)-I(2)-Cu(2)	67.01(10)
I(1)-Cu(2)-I(2a)	111.54(13)	Cu(2a)-Cu(2)-Cu(1e)	60.08(8)
I(1d)-Cu(2)-I(2a)	113.59(14)	Cu(2c)-Cu(1)-Cu(2b)	59.84(16)
I(1)-Cu(2)-I(2)	119.56(14)	Cu(2a)-I(2)-Cu(2)	66.58(13)

Symmetry codes: a)-x+1,-y,z; b)-x+1,-y,z+1; c)x,y,z+1; d)x+0,-y+1/2,z-1/2; e)x,y,z-1; f)x+0,-y+1/2,z+1/2; g)-x+3/2,y,z.

Compound 2

Cu(1)-Br(3)	2.4309(8)	Cu(1)-Br(1)	2.5914(8)
Cu(1)-Br(2)	2.4421(8)	Cu(1)-Br(1a)	2.5937(8)
Cu(1)-Cu(1a)	2.9445(13)	Cu(1)-Cu(1b)	2.9639(13)
Cu(1)-Cu(1c)	2.9887(13)		

Br(3)-Cu(1)-Br(2)	115.59(3)	Br(3)-Cu(1)-Br(1a)	106.88(3)
Br(3)-Cu(1)-Br(1)	108.09(3)	Br(2)-Cu(1)-Br(1a)	107.76(3)
Br(2)-Cu(1)-Br(1)	107.74(3)	Br(1)-Cu(1)-Br(1a)	110.79(3)

Symmetry codes: a) -x,-y,-z+1; b) x,-y+1/2,z; c) x,-y-1/2,z.

Compound 3

Cu(1)-I(1)	2.610(2)	Cu(1)-I(3a)	2.712(2)
Cu(1)-I(2)	2.621(2)	Cu(1)-I(3)	2.720(2)
Cu(1)-Cu(1a)	2.965(3)		
I(1)-Cu(1)-I(2)	113.22(7)	I(1)-Cu(1)-I(3)	106.75(7)
I(1)-Cu(1)-I(3a)	107.87(7)	I(2)-Cu(1)-I(3)	108.33(7)
I(2)-Cu(1)-I(3a)	106.98(7)	I(3a)-Cu(1)-I(3)	113.83(6)

Symmetry code: a) -x+1,-y,-z-1.

Compound 4

Cu(1)-Br(9)	2.331(4)	Cu(4)-Br(7)	2.746(4)
Cu(1)-Br(2a)	2.427(4)	Cu(5)-Br(8)	2.360(4)
Cu(1)-Br(1a)	2.465(4)	Cu(5)-Br(6)	2.387(4)
Cu(2)-Br(9)	2.394(4)	Cu(5)-Br(3b)	2.616(4)
Cu(2)-Br(5)	2.423(4)	Cu(5)-Br(7)	2.762(5)
Cu(2)-Br(7)	2.476(4)	Cu(6)-Br(4)	2.345(4)
Cu(2)-Br(3)	2.837(4)	Cu(6)-Br(6)	2.403(4)
Cu(3)-Br(7)	2.426(4)	Cu(6)-Br(1b)	2.668(5)
Cu(3)-Br(2)	2.444(4)	Cu(6)-Br(3b)	2.707(4)
Cu(3)-Br(3)	2.493(4)	Cu(7)-Br(4)	2.358(4)
Cu(3)-Br(1)	2.646(4)	Cu(7)-Br(2)	2.449(3)
Cu(4)-Br(8)	2.402(3)	Cu(7)-Br(5b)	2.493(4)
Cu(4)-Br(1)	2.494(3)	Cu(7)-Br(3b)	2.895(4)
Cu(4)-Br(5)	2.500(3)	Cu(3)-Cu(4)	2.847(4)
Cu(1)-Cu(2)	3.024(8)	Cu(3)-Cu(1b)	2.644(5)
Cu(1)-Cu(3b)	2.644(5)	Cu(4)-Cu(5)	2.910(5)
Cu(2)-Cu(3)	3.047(4)	Cu(6)-Cu(7)	2.792(5)

Cu(2)-Cu(4)	2.870(4)		
Br(9)-Cu(1)-Br(2a)	122.53(17)	Br(8)-Cu(5)-Br(6)	129.19(18)
Br(9)-Cu(1)-Br(1a)	116.50(17)	Br(8)-Cu(5)-Br(3b)	115.36(15)
Br(2a)-Cu(1)-Br(1a)	118.88(17)	Br(6)-Cu(5)-Br(3b)	101.11(14)
Br(9)-Cu(2)-Br(5)	117.96(15)	Br(8)-Cu(5)-Br(7)	104.21(14)
Br(9)-Cu(2)-Br(7)	117.62(15)	Br(6)-Cu(5)-Br(7)	106.28(16)
Br(5)-Cu(2)-Br(7)	114.85(14)	Br(3b)-Cu(5)-Br(7)	95.41(13)
Br(9)-Cu(2)-Br(3)	103.26(13)	Br(4)-Cu(6)-Br(6)	129.9(2)
Br(5)-Cu(2)-Br(3)	100.52(13)	Br(4)-Cu(6)-Br(1b)	103.54(17)
Br(7)-Cu(2)-Br(3)	97.32(12)	Br(6)-Cu(6)-Br(1b)	108.99(16)
Br(7)-Cu(3)-Br(2)	115.63(15)	Br(4)-Cu(6)-Br(3b)	116.27(16)
Br(7)-Cu(3)-Br(3)	108.63(14)	Br(6)-Cu(6)-Br(3b)	98.16(15)
Br(2)-Cu(3)-Br(3)	105.60(14)	Br(1b)-Cu(6)-Br(3b)	94.64(14)
Br(7)-Cu(3)-Br(1)	113.39(14)	Br(4)-Cu(7)-Br(2)	125.62(16)
Br(2)-Cu(3)-Br(1)	111.62(13)	Br(4)-Cu(7)-Br(5b)	116.09(15)
Br(3)-Cu(3)-Br(1)	100.46(13)	Br(2)-Cu(7)-Br(5b)	107.98(13)
Br(8)-Cu(4)-Br(1)	115.48(13)	Br(4)-Cu(7)-Br(3b)	109.27(14)
Br(8)-Cu(4)-Br(5)	114.61(13)	Br(2)-Cu(7)-Br(3b)	94.47(12)
Br(5)-Cu(4)-Br(7)	103.68(12)	Br(5b)-Cu(7)-Br(3b)	97.28(12)

Symmetry codes: a) -x+1/2, y+1/2,-z+1/2, b) -x+1/2, y-1/2,-z+1/2.

Compound 5

I(1)-Cu(1)	2.695(2)	I(10)-Cu(5)	2.688(2)
I(1)-Cu(2)	2.737(2)	I(10)-Cu(6)	2.706(2)
I(2)-Cu(2)	2.669(2)	I(11)-Cu(7)	2.618(2)
I(2)-Cu(1)	2.680(2)	I(11)-Cu(6)	2.624(2)
I(3)-Cu(3)	2.654(2)	I(12)-Cu(6)	2.635(2)
I(3)-Cu(2)	2.662(2)	I(12)-Cu(7)	2.647(2)
I(4)-Cu(2)	2.642(2)	I(13)-Cu(8)	2.674(2)
I(4)-Cu(3)	2.657(2)	I(13)-Cu(7)	2.688(2)
I(5)-Cu(3)	2.683(2)	I(14)-Cu(7)	2.667(2)

I(5)-Cu(4)	2.692(2)	I(14)-Cu(8)	2.709(2)
I(6)-Cu(4)	2.666(2)	I(15)-Cu(8)	2.643(2)
I(6)-Cu(3)	2.725(2)	I(16)-Cu(8)	2.627(2)
I(7)-Cu(5)	2.646(2)	Cu(1)-I(16a)	2.631(2)
I(7)-Cu(4)	2.653(2)	Cu(1)-I(15a)	2.651(2)
I(8)-Cu(5)	2.651(2)	Cu(1)-Cu(2)	2.787(3)
I(8)-Cu(4)	2.657(2)	Cu(3)-Cu(4)	2.787(3)
I(9)-Cu(6)	2.655(2)	Cu(5)-Cu(6)	2.768(3)
I(9)-Cu(5)	2.679(2)	Cu(7)-Cu(8)	2.731(3)

I(16a)-Cu(1)-I(15a)	103.28(7)	I(6)-Cu(4)-I(5)	107.62(7)
I(16a)-Cu(1)-I(2)	117.46(7)	I(7)-Cu(5)-I(8)	105.35(7)
I(15a)-Cu(1)-I(2)	105.37(7)	I(7)-Cu(5)-I(9)	105.63(7)
I(16a)-Cu(1)-I(1)	113.52(8)	I(8)-Cu(5)-I(9)	115.92(8)
I(15a)-Cu(1)-I(1)	110.89(7)	I(7)-Cu(5)-I(10)	109.72(7)
I(2)-Cu(1)-I(1)	106.01(7)	I(8)-Cu(5)-I(10)	113.35(7)
I(2)-Cu(1)-Cu(2)	58.40(6)	I(9)-Cu(5)-I(10)	106.54(7)
I(1)-Cu(1)-Cu(2)	59.87(6)	I(11)-Cu(6)-I(12)	104.16(7)
I(4)-Cu(2)-I(3)	105.84(7)	I(11)-Cu(6)-I(9)	106.98(7)
I(4)-Cu(2)-I(2)	115.44(7)	I(12)-Cu(6)-I(9)	113.95(7)
I(3)-Cu(2)-I(2)	106.80(7)	I(11)-Cu(6)-I(10)	108.27(7)
I(4)-Cu(2)-I(1)	115.35(7)	I(12)-Cu(6)-I(10)	116.29(7)
I(3)-Cu(2)-I(1)	107.78(7)	I(9)-Cu(6)-I(10)	106.70(7)
I(2)-Cu(2)-I(1)	105.15(7)	I(11)-Cu(7)-I(12)	103.97(7)
I(3)-Cu(3)-I(4)	105.64(7)	I(11)-Cu(7)-I(14)	113.52(7)
I(3)-Cu(3)-I(5)	113.94(7)	I(12)-Cu(7)-I(14)	108.48(7)
I(4)-Cu(3)-I(5)	107.09(7)	I(11)-Cu(7)-I(13)	114.74(7)
I(3)-Cu(3)-I(6)	115.69(8)	I(12)-Cu(7)-I(13)	107.92(7)
I(4)-Cu(3)-I(6)	107.85(7)	I(14)-Cu(7)-I(13)	107.87(7)
I(5)-Cu(3)-I(6)	106.20(7)	I(16)-Cu(8)-I(15)	103.62(7)
I(7)-Cu(4)-I(8)	104.94(7)	I(16)-Cu(8)-I(13)	108.86(7)

I(7)-Cu(4)-I(6)	108.67(7)	I(15)-Cu(8)-I(13)	111.35(7)
I(8)-Cu(4)-I(6)	108.89(7)	I(16)-Cu(8)-I(14)	106.08(7)
I(7)-Cu(4)-I(5)	119.82(7)	I(15)-Cu(8)-I(14)	119.36(8)
I(8)-Cu(4)-I(5)	106.50(7)	I(13)-Cu(8)-I(14)	107.06(7)

Symmetry code: a) x, y, z-1.

Table S2. Calculated energies and oscillator strength of $Cu_3I_8^{5-}$ in **1**.

	Transition Type	Coefficients of the function	Energy(eV)	Oscillator Strength
Excited State 1	59 ->60	0.65388	2.8518	0.0376
Excited State 2	59 -> 61	0.65524	2.8643	0.0321

Table S3. Calculated molecular orbitals and orbital energies of HOMO, LUMO and LUMO+1.

	E(eV)	Electron occupied
59 (HOMO)	0.35442	Cu(2) 6PZ: 2.60, 7D: 5.52, 7D-: 2.46, 7D+: 1.35; Cu(6) 6PY: 3.28, 7D-: 10.89, 8D-: 1.16; Cu(7) 6PZ: 2.60, 7D: 5.52, 7D-: 2.46, 7D+: 1.35; I (1) 3PY: 1.18, 3PZ: 2.20, 4PY: 1.50, 4PZ: 3.51; I (4) 3PZ: 3.13, 4PZ: 4.41; I (8) 3PY: 3.72, 4PY: 5.58; I (9) 3PY: 3.72, 4PY: 5.58; I (10) 3PY: 1.18, 3PZ: 2.20, 4PY: 1.50, 4PZ: 3.51; I (11) 3PZ: 3.13, 4PZ: 4.41.
60 (LUMO)	0.47940	Cu(2) 3S: 24.58, 6PY: 17.21, 6PZ: 5.32; Cu(7) 3S: 24.58, 6PY:17.21, 6PZ: 5.32.
61 (LUMO+1)	0.48002	Cu(2) 3S: 7.67, 6PY: 5.20, 6PZ: 3.28; Cu(6) 3S :34.46, 6PZ:28.32; Cu(7) 3S : 7.67, 6PY: 5.20, 6PZ: 3.28.

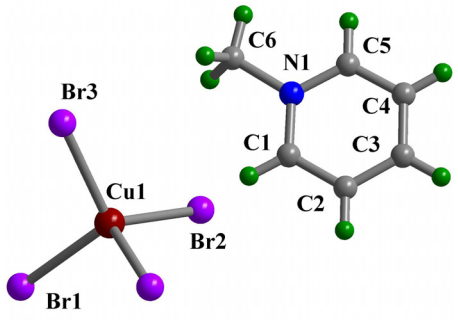

Figure S1. View of the coordination environment of copper atoms in **2**.

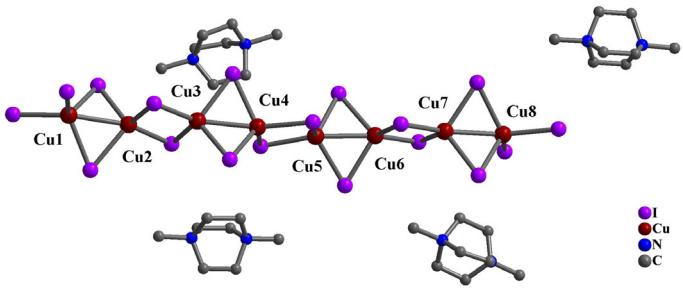

Figure S2. The coordination environment of copper atoms in **5**.

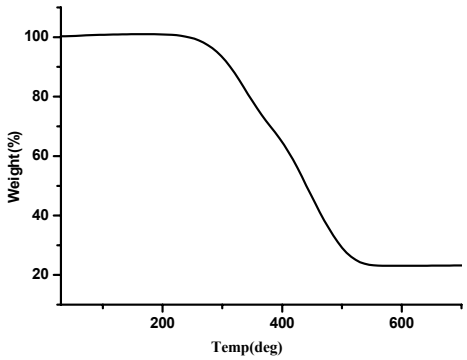

Figure S3. TGA curves of **1** in nitrogen atmosphere and at the heating rate of 10 °C/min.

Thermal gravimetric analyses (TGA) were performed under nitrogen atmosphere using a SETARAM LABSYS thermo-gravimetric analyzer with a heating rate of 10°C/min from 30 to 700°C. The TGA curve (Fig. S3) shows a continuous weight loss of 76.6% in the range of 200-570 °C, indicating the removal of etpy and iodine. The remaining weight percentage of 23.4% at 570 °C is in agreement with the theoretical value of elemental Cu.