

***In situ* reduction from CuX₂ (X = Br, Cl) to Cu(I) halide clusters**

based on ligand bis(2-methylimidazo-1-yl)methane

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Experimental Section

Materials and Measurements. All chemicals were obtained commercially available and used as received without further purification. Ligand bis(imidazol-1-yl)methane (BIM) and bis(2-methylimidazol-1-yl)methane (2-mBIM) were prepared by literature's methods. The FT-IR spectra were recorded from KBr pellets in the range 4500-500 cm⁻¹ on a Nicolet 5700 infrared spectrometer. Thermogravimetric analysis (TGA) measurements were made using a Pyris diamond TG/DTA Thermogravimetric differential Thermal Analyzer. Samples were heated at 10 °C /min from 40 to 700°C in a dynamic nitrogen atmosphere. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The photoluminescence measurements were carried out on crystalline samples at room temperature and the spectra were collected with a Hitachi F-4500 spectrophotometer.

Cyclic voltammetric (CV) measurements were carried out using a CHI660 electrochemical workstation (CH Instruments, USA). The cell contained a glassy carbon working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. A salt bridge (containing supporting electrolyte, 0.1mol/L potassium nitrate dissolved in the solution of 6.0mol/L HCl) was used to connect the SCE with the electrochemistry solution. All experiments were carried out under a nitrogen atmosphere at RT and were uncorrected for junction potentials.

Synthesis of [Cu₂(2-mBIM)Cl₂] (1). The mixture of CuCl₂ · 2H₂O(85mg, 0.5 mmol), 1, 4-benzenedicarboxylic acid (83mg, 0.5mmol), NaOH (40mg, 1.0mmol) and ligand 2-mBIM (89mg, 0.5mmol) were dissolved in the solution of H₂O (8 mL) and ethanol (2ml), and the

resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel autoclave, under autogenous pressure at 160°C for 2 days and then slowly cooled to room temperature at a rate of 10°C /h. Light-yellow crystals of [Cu₂(2-mBIM)Cl₂] suitable for X-ray analysis were obtained in 55% yield based on Cu. Anal. Calcd for C₉H₁₂Cl₂Cu₂N₄. C, 28.89; H, 3.23; N, 14.97; Found: C, 29.33; H, 2.74; N, 15.33; IR (KBr, cm⁻¹): ν = 3119s, 2982w, 1593m, 1544s, 1508s, 1466m, 1403s, 1387w, 1270s, 1187m, 1145m, 1089w, 1008m, 794w, 744s, 669s, 618w.

Synthesis of [Cu(2-mBIM)Br] (2). The mixture of CuBr₂ (112mg, 0.5mmol), 1, 4-benzenedicarboxylic acid (83mg, 0.5mmol), NaOH (40mg, 1.0mmol) and ligand 2-mBIM (89mg, 0.5mmol) were dissolved in the solution of H₂O (8 mL) and ethanol (2ml), and the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel autoclave, under autogenous pressure at 160°C for 2 days and then slowly cooled to room temperature at a rate of 10°C /h. Light-yellow crystals of [Cu(2-mBIM)Br] suitable for X-ray analysis were obtained in 65% yield based on Cu. Anal. Calcd for C₉H₁₂BrCuN₄. C, 33.82; H, 3.78; N, 17.53; Found: C, 34.02; H, 3.41; N, 17.51; IR (KBr, cm⁻¹): ν = 3120m, 2978w, 1624m, 1543m, 1503m, 1457m, 1401s, 1263s, 1142m, 1082w, 1001w, 750s, 669m.

Synthesis of [Cu(BIM) (1, 4-BDC)] (3). The mixture of CuCl₂ • 2H₂O (85mg, 0.5 mmol), 1, 4-benzenedicarboxylic acid (1, 4-H₂BDC, 83mg, 0.5mmol), NaOH (40mg, 1.0mmol) and ligand BIM (75mg, 0.5mmol) were dissolved in the solution of H₂O (8 mL) and ethanol (2ml), and the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel autoclave, under autogenous pressure at 160°C for 2 days and then slowly cooled to room temperature at a rate of 10°C /h. Purple crystals of [Cu(BIM)(1, 4-BDC)] suitable for X-ray analysis were obtained in 59% yield based on Cu. Anal. Calcd for C₁₅H₁₂CuN₄O₄. C, 47.94; H, 3.22; N, 14.91; Found: C, 47.67; H, 2.78; N, 14.76; IR (KBr, cm⁻¹): ν = 3136s, 3031m, 1605s, 1591s, 1559w, 1498s, 1401m, 1378m, 1361s, 1268s, 1228s, 1143w, 1081s, 1017w, 951m, 883w, 826s, 751s, 695m, 655m, 588m.

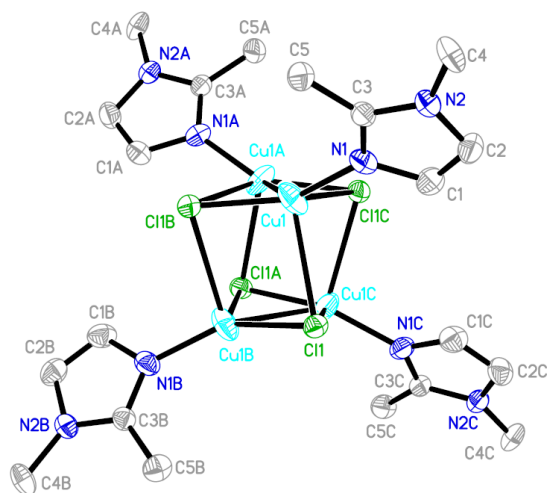


Figure 1. View of the coordination environment of Cu(I) in **1**.

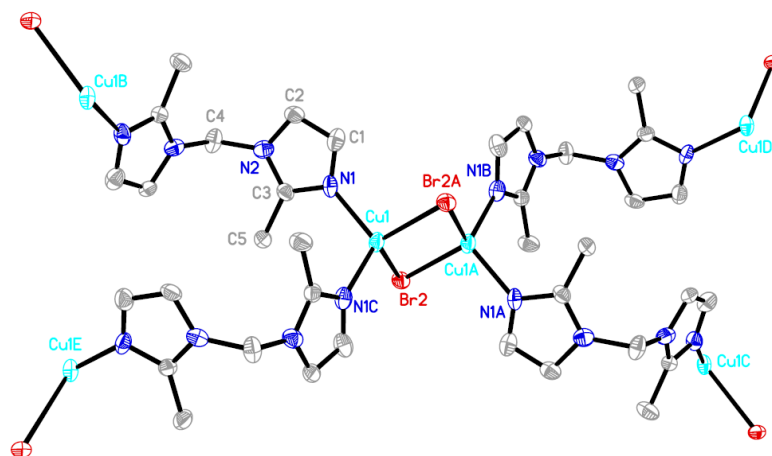


Figure 2. Thermal ellipsoid (30%) plot of **2**, showing the coordination environments of the Cu centers.

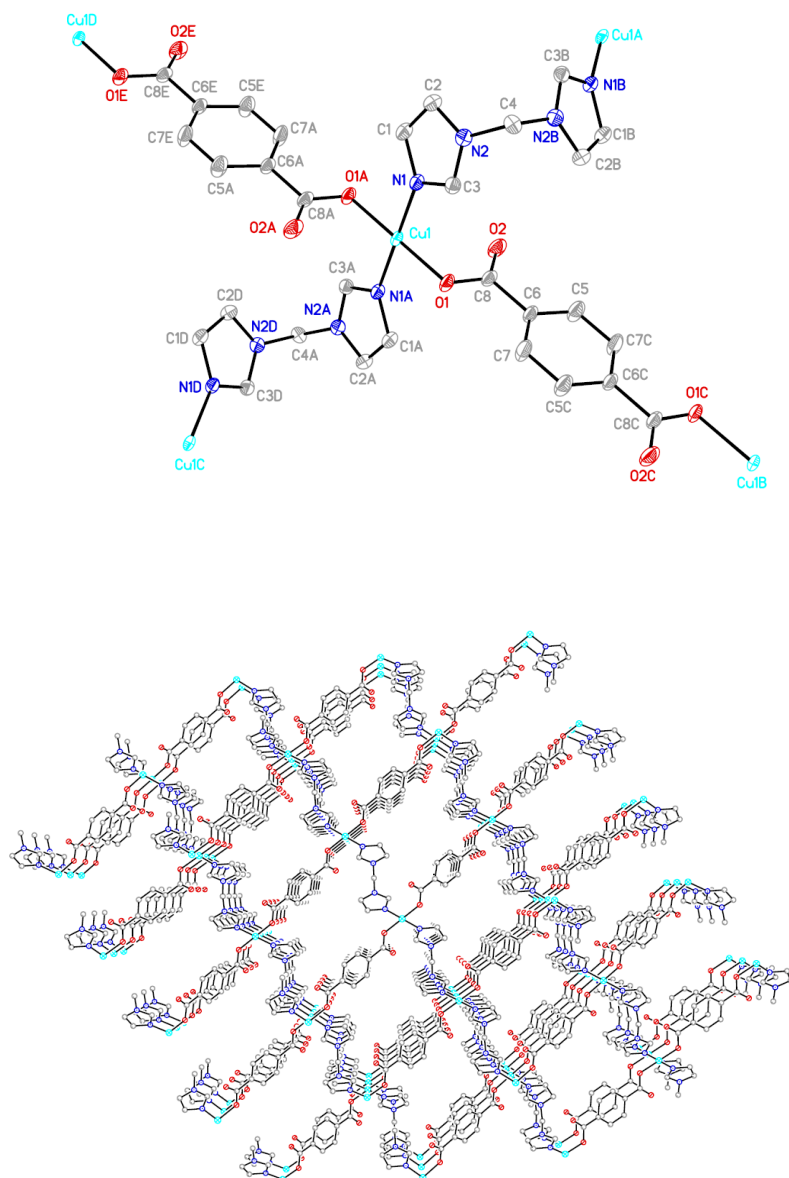


Figure 3. (a) Thermal ellipsoid (30%) plot of **3**, showing the coordination environments of the Cu centers. (b) View of 3D porous network in **3**.

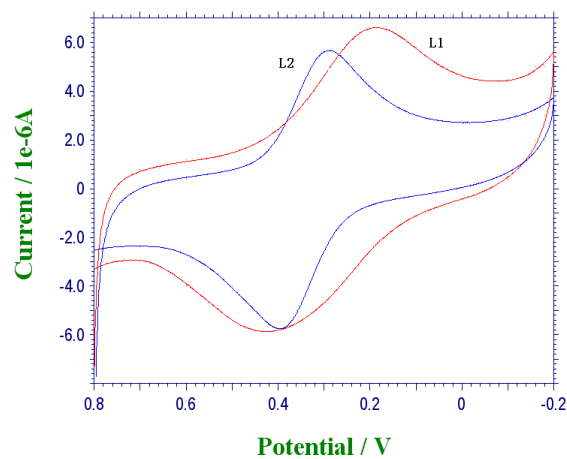


Figure 4. Cyclic voltammogram of BIM and 2-mBIM in HCl solution using a glassy carbon electrode.

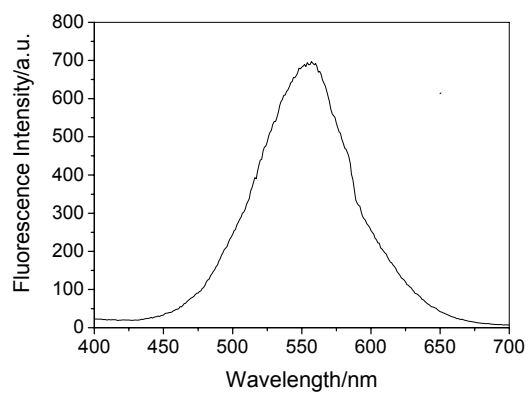


Figure 5. Emission spectrum of compound **2** measured in the solid state at room temperature.