Supporting Information

Incorporation of heterovalent copper-oxo and copper-halide clusters for fabrication of three porous cluster organic frameworks: syntheses, structures and iodine adsorption/release study

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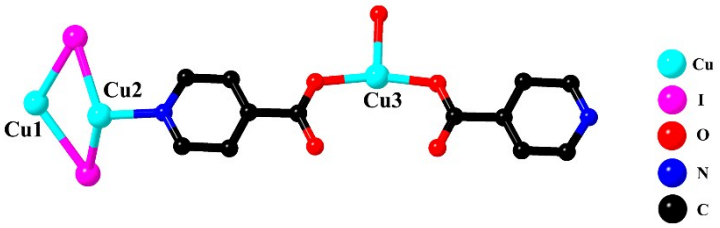

Fig. S1 The asymmetric unit of **1.**

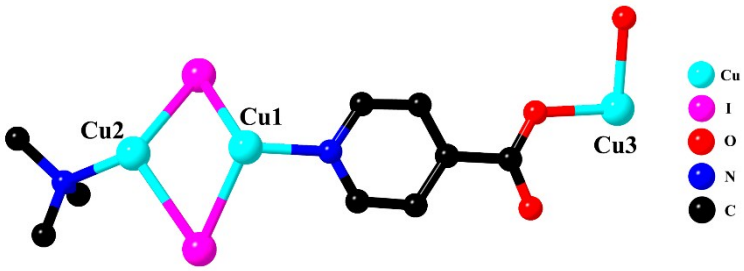

Fig. S2 The asymmetric unit of **2.**

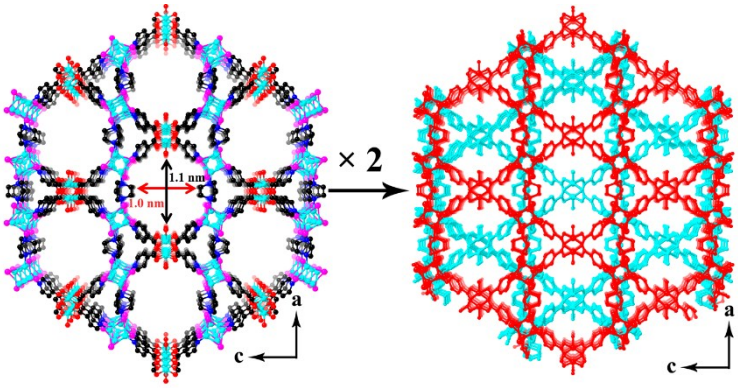

Fig. S3 View of the channels of the framework of **2** along *b* axis.

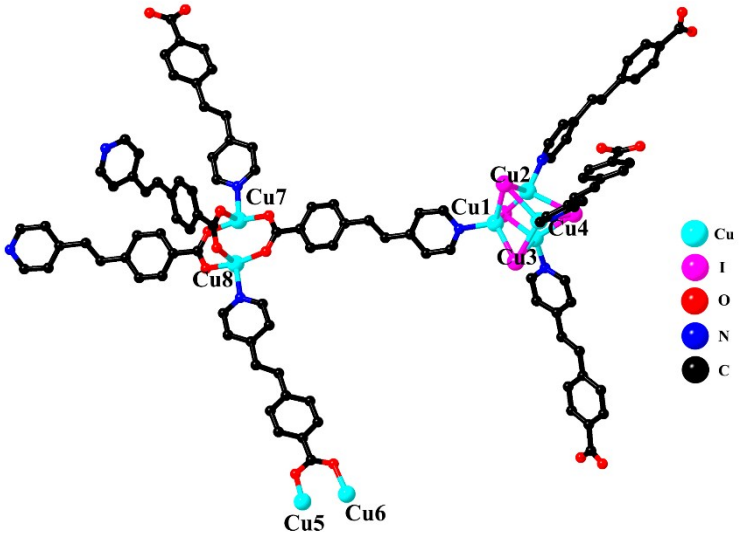

Fig. S4 The asymmetric unit of **3.**

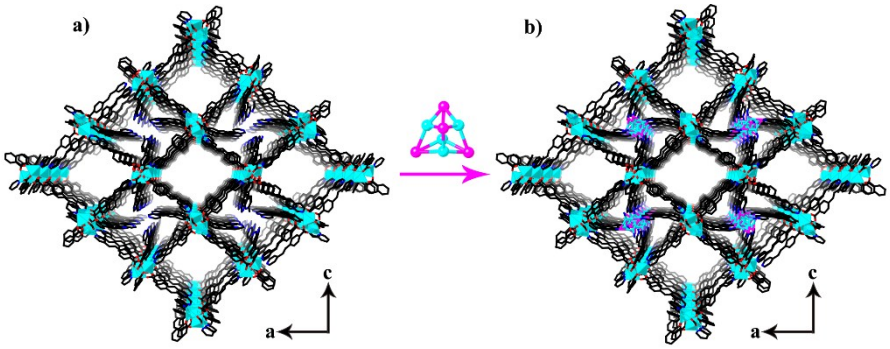

Fig. S5 a) View of the framework based on $Cu_2(CO_2)_4$ clusters and $PVBA^-$ bridges. b) View of the framework of **3**.

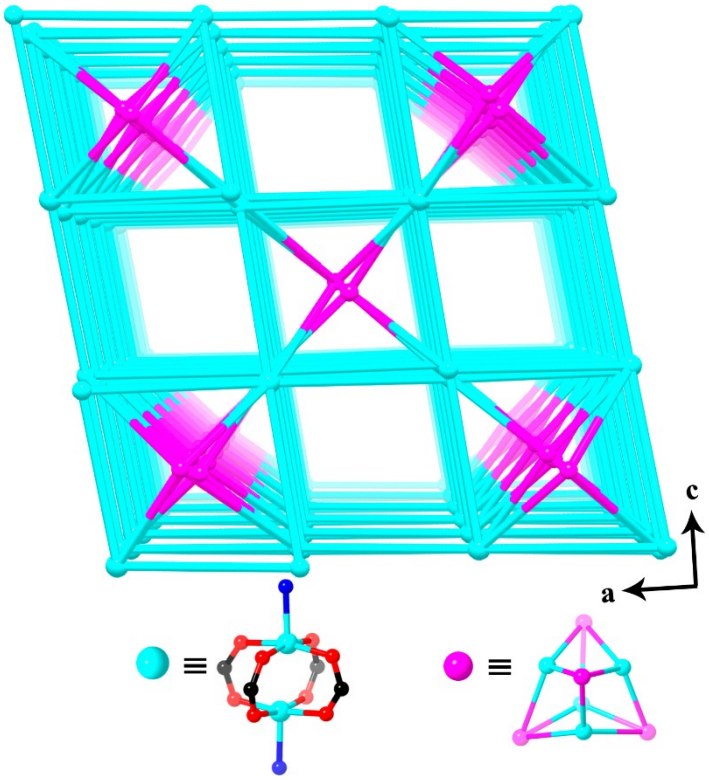

Fig. S6 The topological representation of the 3D framework of **3** along the *b* axis.

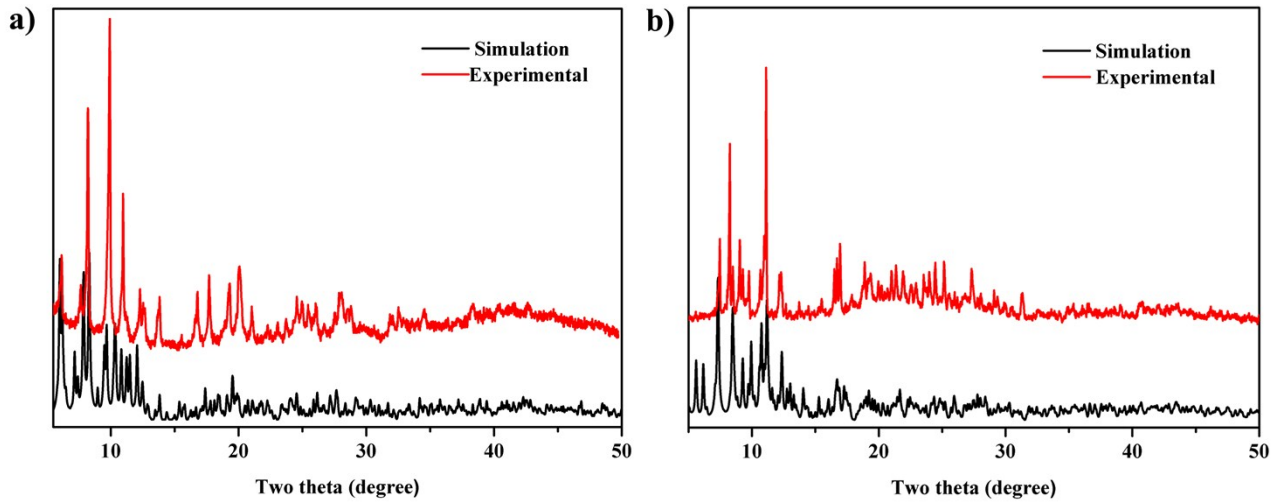

Fig. S7 Powder XRD patterns for **1** a) and **3** b).

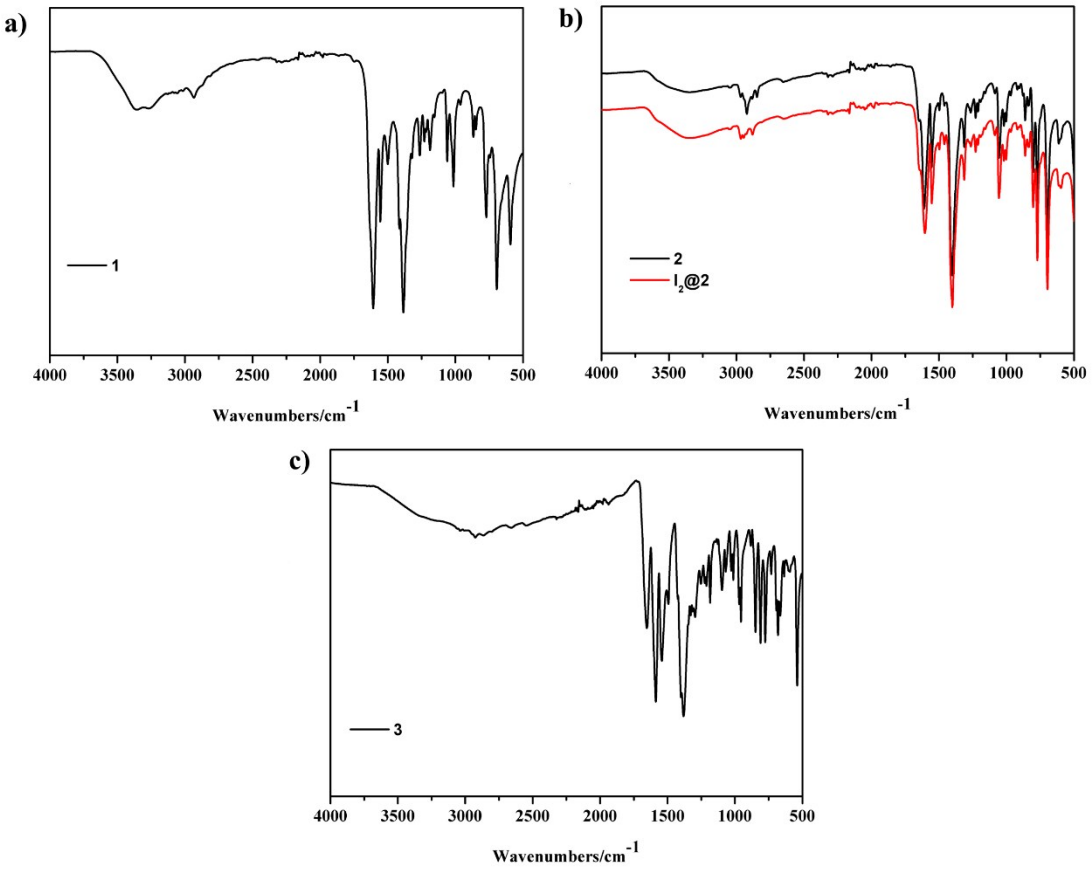

Fig. S8 IR spectra for **1**-**3**.

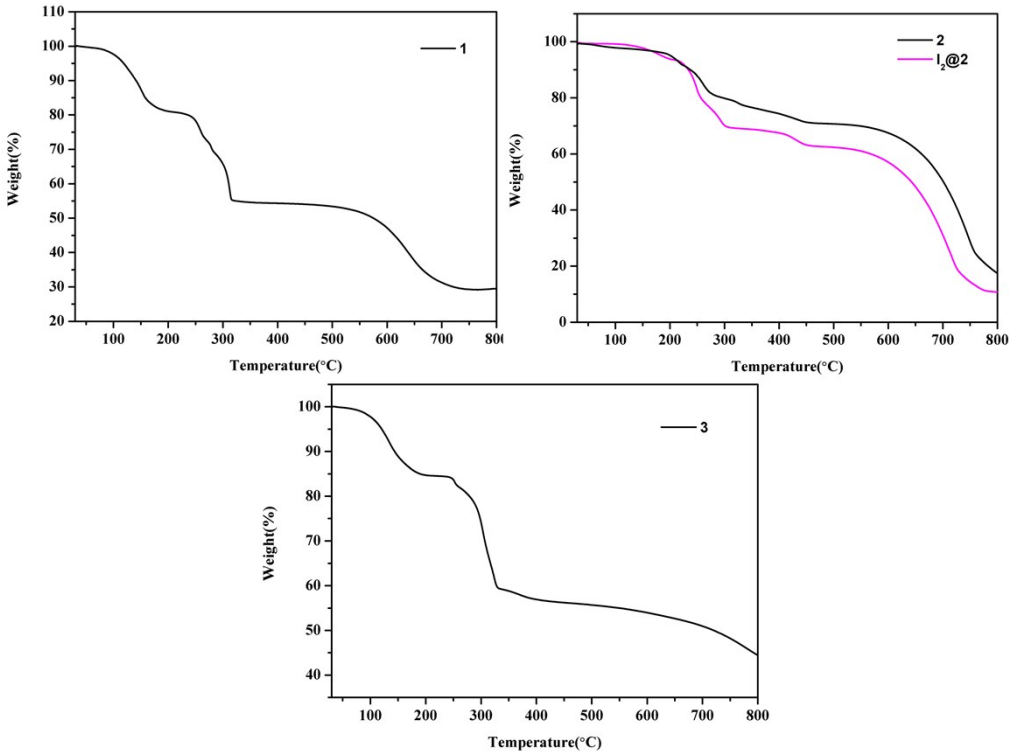

Fig. S9 TGA curves for **1**-**3**.

Thermal gravimetric (TG) analysis was carried out in flowing N_2 with a heating rate of 10 °C min^{-1} in the temperature range 30-800 °C to check the thermal stability of **1-3**. Three distinct weight loss stages are observed on the TGA curve of **1** and **3**. The first step weight loss (20 % for **1** and 15% for **3**) in the temperature range ca. 82-200 °C and 84-177 °C, corresponds to the removal of disordered solvent molecules (DMA and EDF for **1** and DMF for **3**), respectively. The remainder two stages weight loss in the temperature range ca. 242-800 °C and 250-800 °C are attributed to the collapse of structure. The TG curve of **2** displays two stages of continuous weight loss. The first weight loss is 18 % from 196-270 °C, corresponding to the disordered DMA molecules. The second weight loss in the temperature range ca. 558-800 °C is attributed to the collapse of structure (Fig. S9).

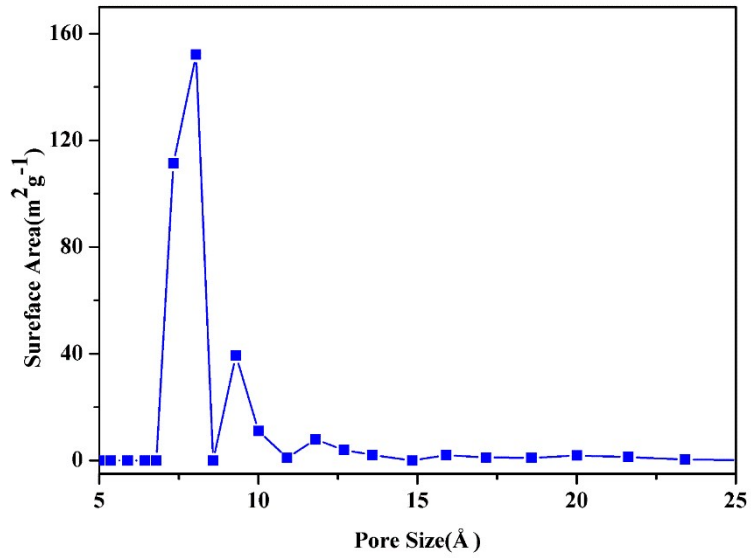

Fig. S10 The pore size distribution of **2.**

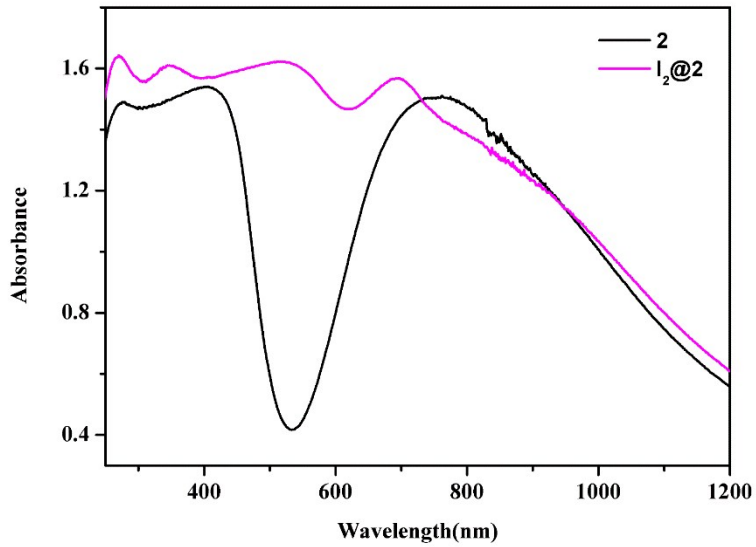

Fig. S11 Solid-state UV-Vis absorption spectra of **2** and **I_2@2.**

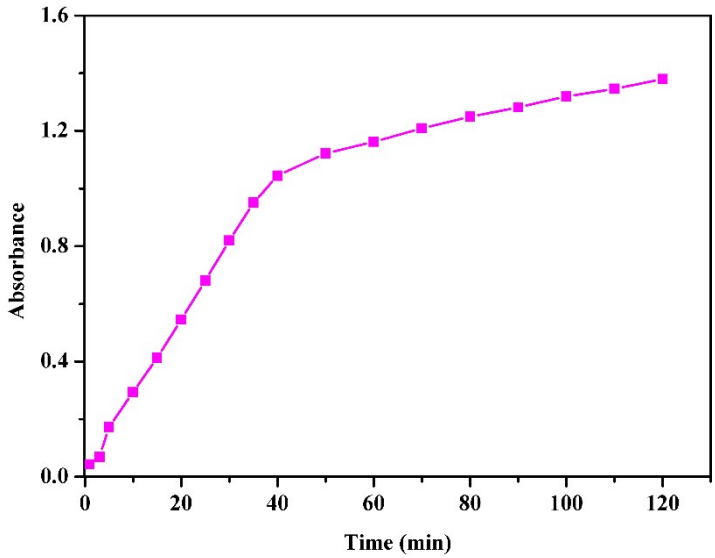

Fig. S12 The release rate of I_2@**2** (monitored at 202 nm).

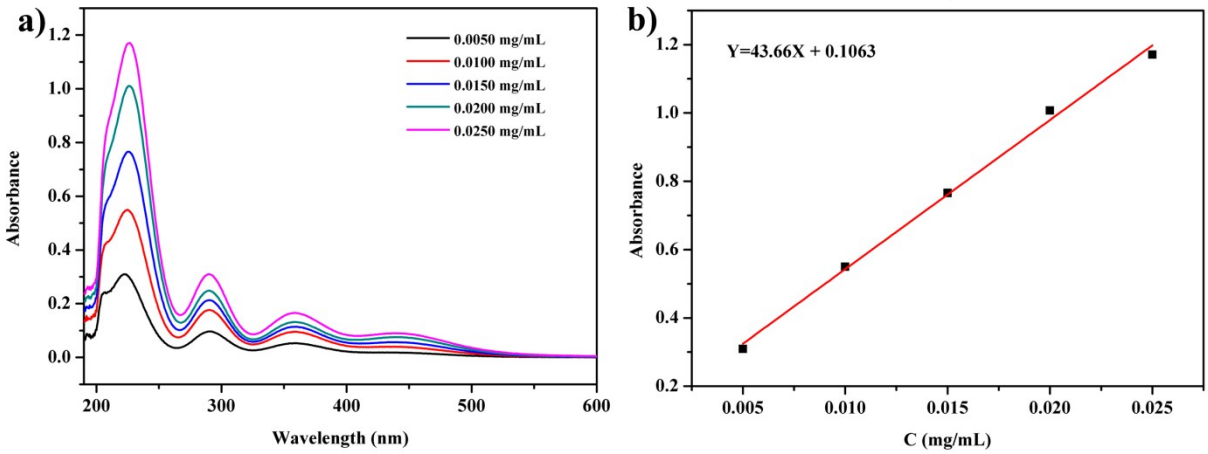

Fig. S13 a) Calibration plot of standard iodine determined by UV/vis spectra in CH_3OH solution. b) The fitting Abs value vs concentration of I_2 with the relatively good linearity satisfies Lambert-Beer Law.