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.
Thermal gravimetric (TG) analysis was carried out in flowing N₂ 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. S9** TGA curves for 1-3.

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

**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$_3$OH solution. b) The fitting Abs value vs concentration of I$_2$ with the relatively good linearity satisfies Lambert-Beer Law.