Electronic Supplementary Material (ESI) for Chem Comm
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Supporting Information for:

# Structure-Directing Method to Semiconductive Zeolitic Cluster-Organic Frameworks with $Cu_3I_4$ Building Units

**Yao Kang, Wei-hui Fang, Lei Zhang,* and Jian Zhang**

*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

Corresponding Author
*E-mail: LZhang@fjirsm.ac.cn

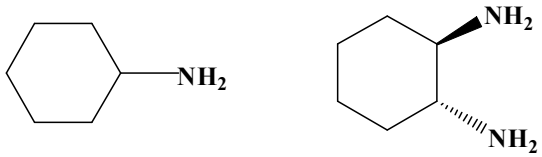
## Content

## Experimental Section:

**Materials and physical measurements.** All chemicals and solvents were commercially purchased and used without further purification. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400-4000 $cm^{-1}$. The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA $851^e$ analyzer in air atmosphere with a heating rate of 10 ºC/min from 30 ºC to 1000 ºC. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuK$\alpha$ radiation ($\lambda$ = 1.54056Å) under ambient conditions. The solid state photoluminescence spectra were measured on the Cary Eclipse fluorescence spectrophotometer. The UV diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm.

**X-Ray data collection.** Crystallographic data of complexes **1** and **2** were collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature. The structure was solved with direct methods using SHELXS-97 and refined with the full-matrix least-squares technique based on $F^2$ using the SHELXL-97. Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically. Contributions to scattering due to disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*.

## Supporting Figures:




Scheme S1. Schematic drawing for CHA (left) and DACH (right) ligands in compounds **1** and **2**.

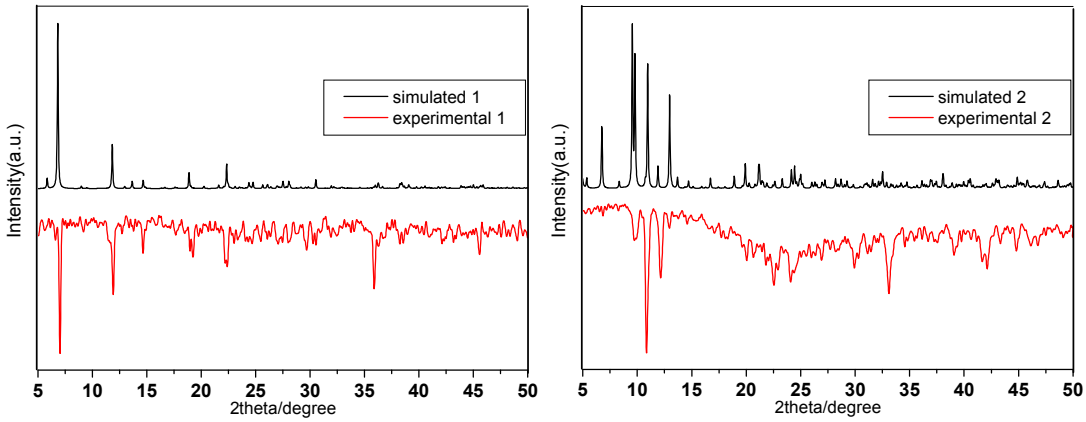



**Fig. S1** The simulated and experimental PXRD patterns of compounds **1** (left) and **2** (right).

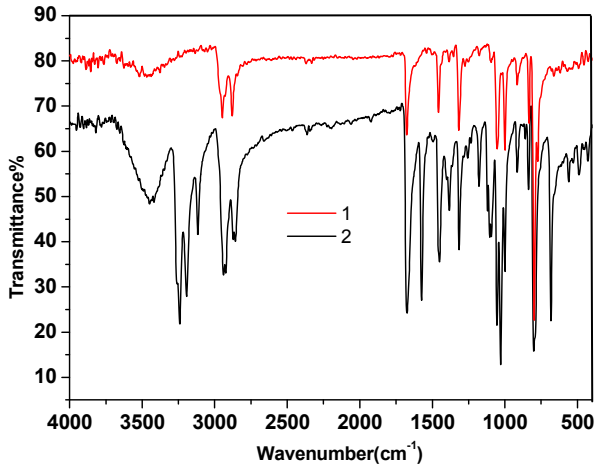



**Fig. S2** The IR spectra of the two compounds.

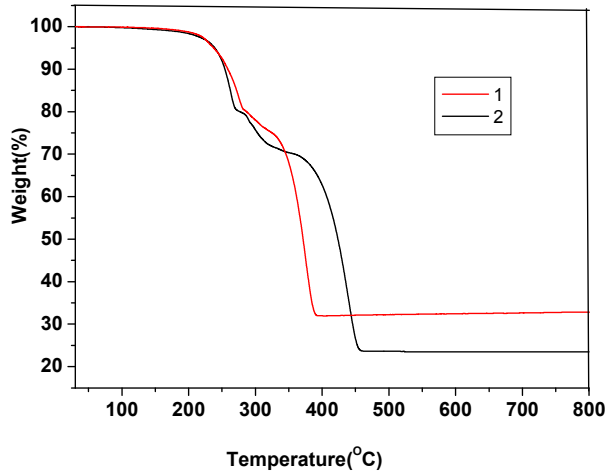



**Fig. S3** The TGA curves of the two compounds, indicating that they can keep stable up to 200 °C.

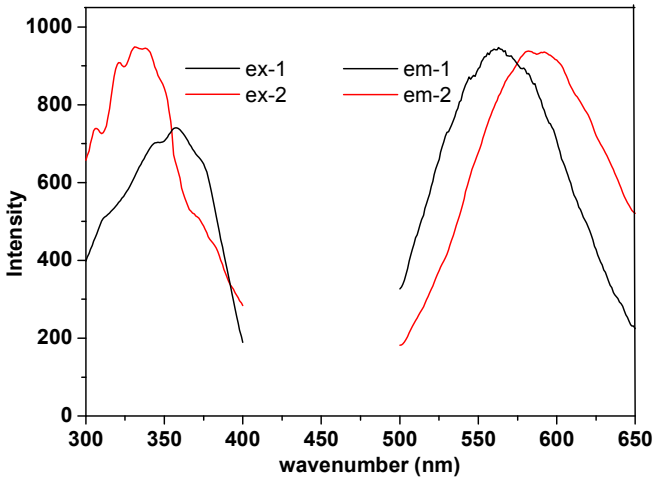



**Fig. S4** The emission and excitation spectra of the two compounds.

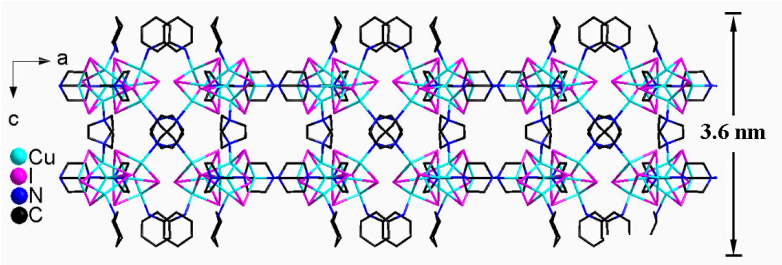



**Fig. S5** Side view of the double-decker structure of compound **1**.

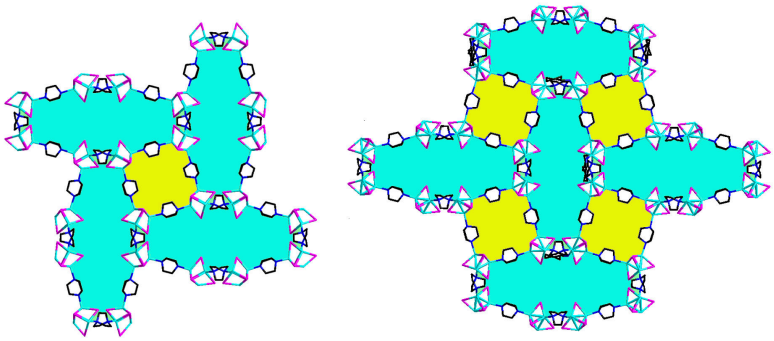


**Fig. S6** The coordinate environment of the 4-membered (left) and twisted 8-membered rings (right). The terminal CHA ligands are omitted for clarity.

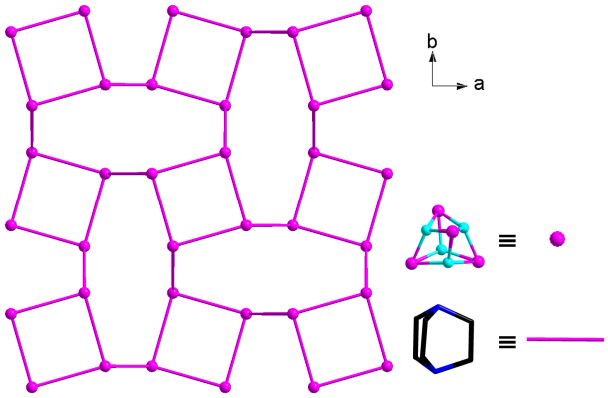



**Fig. S7** Topological view of the 2D layers showing the 3-connected network in compound **1**.

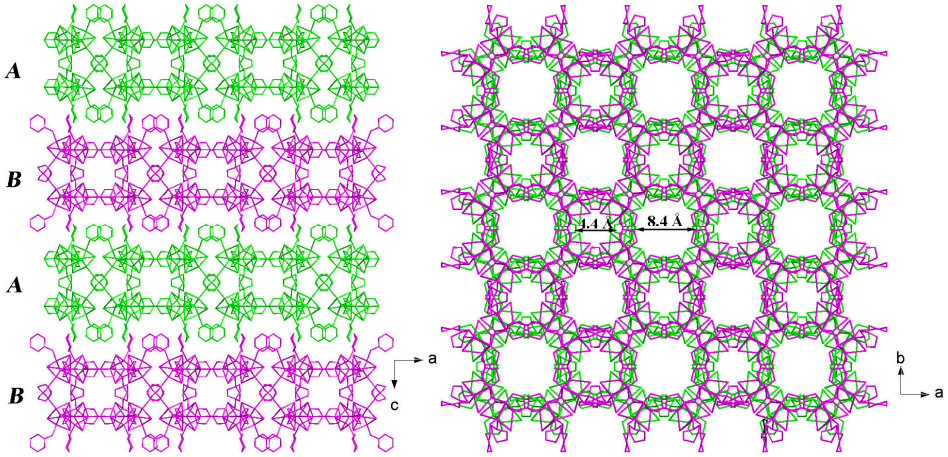



**Fig. S8** The side (left) and top (right) view of the packing of compound **1**.

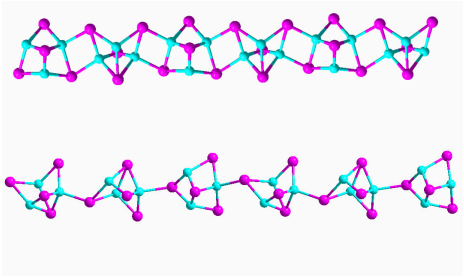


**Fig. S9** The comparison chains assembled by $Cu_3I_4$ clusters in ref. 23 (top) and complex **2** (down).

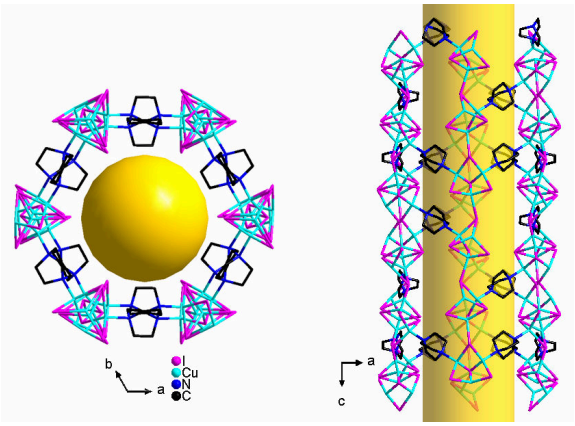



**Fig. S10** The 1D hexagonal channel viewing down along the *c* and *b* axis direction.

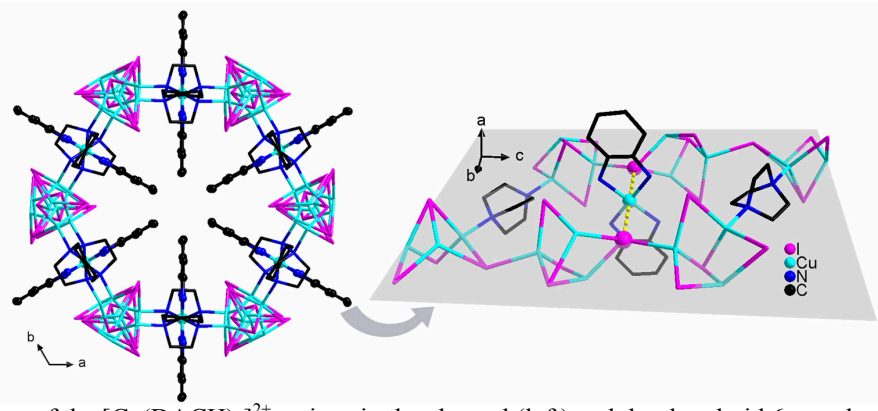



**Fig. S11** The location of the $[Cu(DACH)_2]^{2+}$ cations in the channel (left) and the rhomboid 6-membered circuits (right).

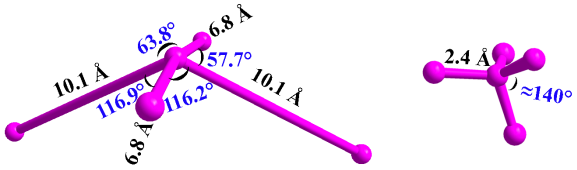



**Fig. S12** The comparison of 4-connected node in complex **2** (left) and in typical zeolites (right).

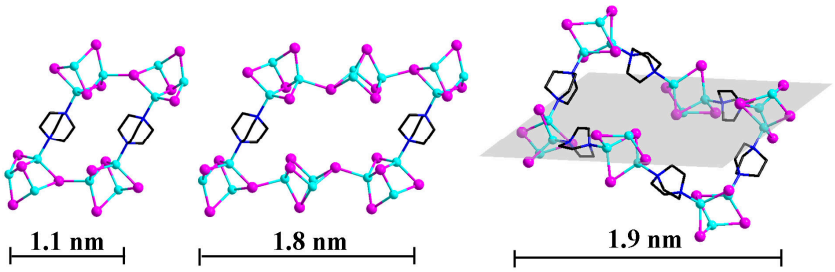



**Fig. S13** Three types of unusual configuration windows in complex **2**.

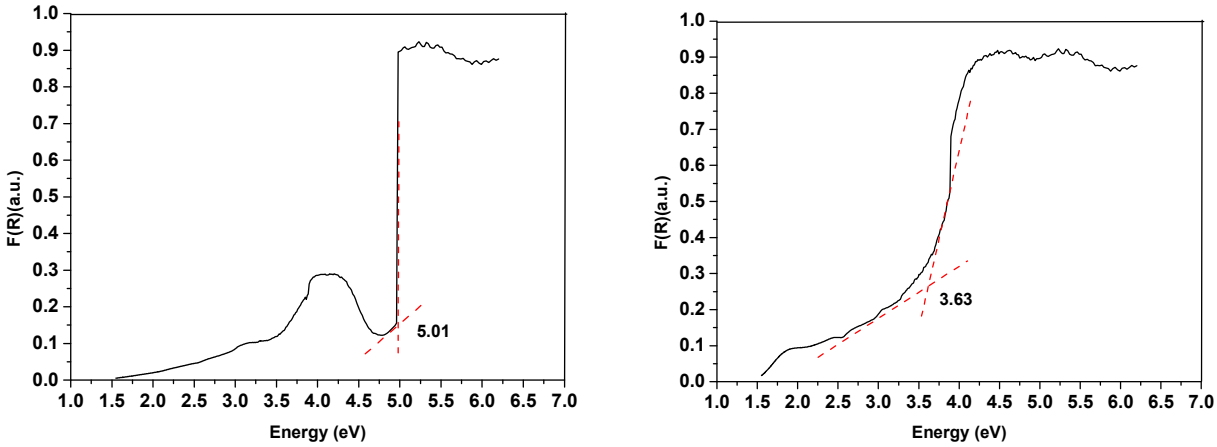



**Fig. S14** The bands gap of the compound **1** (left) and complex **2** (right).