Supporting Information

In situ amination and side group effect of multifunctional heterocyclic thione ligand toward discrete and polymeric cluster constructions

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Figure S1. The crystal packing of the adjacent hexanuclear copper molecules in compound 1.
**Figure S2.** The crystal packing of the adjacent (4,4) layers in compound 2.

**Figure S3.** The channel of 3 along the c axis features cross-shaped window.
**Figure S4.** TGA curve for an as-synthesized sample of 3 under a dinitrogen atmosphere.

**Figure S5.** Plots of $M$ vs $H$ for 3 at 1.8 K.
**Figure S6.** Simulated and experimental XRPD data of compound 1.

**Figure S7.** Simulated and experimental XRPD data of compound 2.

**Figure S8.** Simulated and experimental XRPD data of compound 3.
**Figure S9.** $^1$H NMR spectra of the complex 1.

**Figure S10.** $^1$H NMR spectra of the complex 2.

**Figure S11.** UV-Vis spectra of pure formic acid and the mother liquid collected after solvothermal synthesis of 1.