Supporting Information

Spontaneous Resolution of Four-Coordinate Zn(II) Complexes in the Formation of Three-Dimensional Metal-Organic Frameworks †

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Experimental Section:

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1** was measured at 293 K on a Rigaku D/max-IIIA diffratometer (Cu-Kα, λ = 1.54056 Å). The crushed single-crystalline powder samples were prepared by crushing the crystals and scanned from 5-60^o with a step of 0.4^o/s. Calculated pattern of **1** were generated with Mercury. The CD spectra of **1a** and **1b** were obtained on a Circular Dichroism Spectrometer [J810] at room temperature. The photoluminescent spectra of **1** were carried out with Combined Fluorescence Lifetime and Steady State Spectrometer [FLSP920] at room temperature.

Hydrothermal Synthesis.

Zn(bdt) (**1a**) and (**1b**). A mixture of $ZnCl_2 \cdot nH_2O$ (0.2 mmol, 0.027 g) and H_2bdt (0.1 mmol, 0.025 g) and distilled H_2O (10 mL) was sealed in a 23-mL Teflon-liner autoclave. Heated in an oven to 160 ^{o}C for 120 hs, and then cooled to room temperature at a rate of 5 ^{o}C h^{-1}, yielded colorless block crystals of **1** (yields 8 mg, calcd. 28.8 %, based on H_2bdt) Elemental analysis calcd. (%) for $C_8H_4N_8Zn$: C 34.62, H 1.45, N 40.37; Found: C 34.79, H 1.973, N 40.20; IR (4000 – 400 cm^{-1}): 3432 w, 2355 w, 1697 w, 1552 m, 1445 s, 1367 m, 1242 m, 1158 s, 1049 m, 851 s, 751 s, 555 m, 481 m.

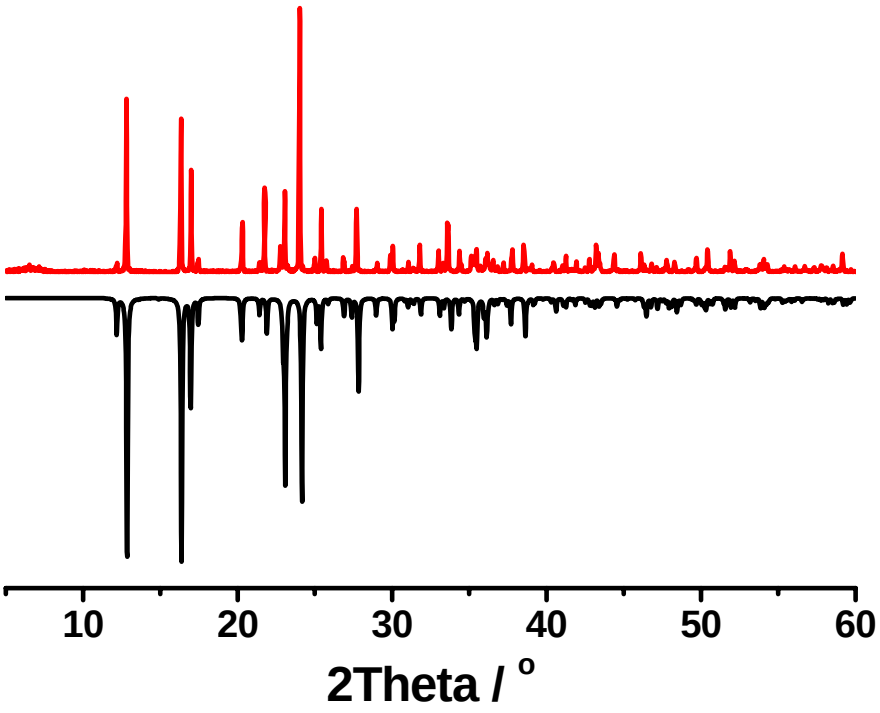

Fig. S1. XRD patterns of **1** (red) and simulated (balck).

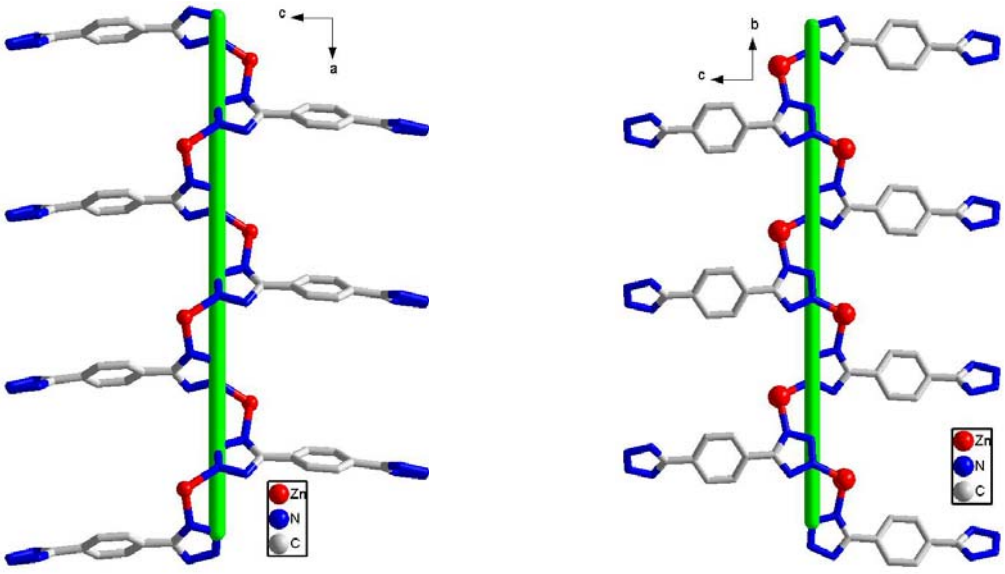

Fig. S2. View of the helical chains running along the *a* (left) and *b* axis(right) in **1a**.

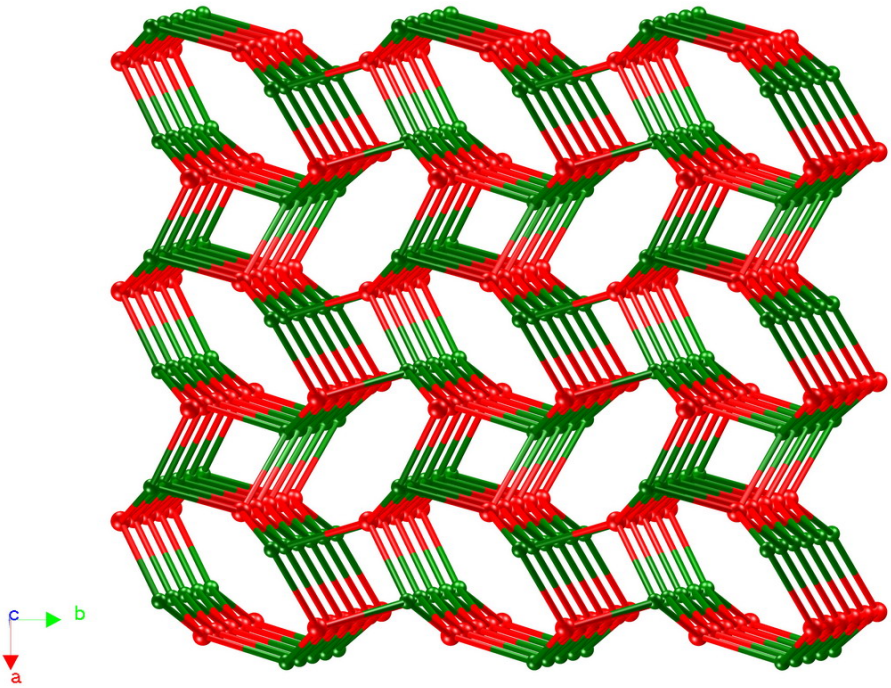

Fig. S3. Topological view showing an unc network based on the 3D framework of **1b** (red and green balls represent two kinds of four-connected nodes, zinc centers and bdt ligands).

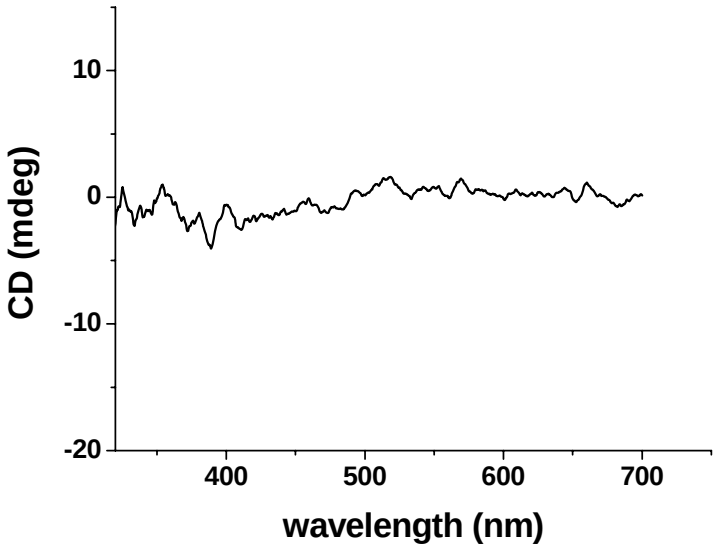

Fig. S4. The solid -state CD spectra of bulky sample of **1**(**1a** and **1b**).