Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Information

General Procedures and Physical Measurements. All manipulations were performed in air using purified solvents. The $K_2Zn(CN)_4$ salt, ethylenediamine (en) and all other reagents were obtained from commercial sources and used as received. IR spectra were obtained using a Thermo Nicolet Nexus 670 FT-IR spectrometer. Microanalyses (C, H, N) were performed at Simon Fraser University by Mr. Miki Yang. Solid-state visible reflectance data were obtained using an Ocean Optics SD2000 spectrometer with reflectance fibre-optics cables and converted into absorbance data. Variable temperature magnetic susceptibility data were collected using a Quantum Design MPMS XL-7 Evercool magnetometer at a 1 T field from 300-2 K, using a low-background gelcap and straw as a sampleholder. The data were corrected for the diamagnetism of the constituent atoms.

*Synthesis of **1**:* CAUTION! Although we have experienced no difficulties, perchlorate salts are potentially explosive and should only be used in small quantities and handled with care. To a 15 ml aqueous solution of $Cu(ClO_4)_2 \cdot 6\ H_2O$ (0.037 g, 0.1 mmol) was added a 3 mL aqueous stock solution (0.100 M) of ethylenediamine (en). While stirring, a 10 ml aqueous solution of $K_2Zn(CN)_4$ (0.025 g, 0.1 mmol) was added to this purple solution. The resulting solution was partially covered and allowed to slowly evaporate for a week. Large, dark purple blocks of $[Cu(en)_2][Zn(NC)_4(CuCN)_2]$ (**1**) were collected by vacuum filtration, washed with H_2O, followed by methanol, and left to air-dry. Yield based on copper: 0.009 g (50.7%). Anal. Calcd. For $C_{10}H_{16}N_{10}Cu_3Zn$: C, 22.56; H, 3.03; N, 26.31. Found: C, 22.81; H, 3.10; N, 26.48. IR (KBr, cm^{-1}): 3333(m), 3283(m), 2136(m), 2128(vs), 2111(vs), 2089(m), 2082(m), 2067(m), 1573(m), 1383(w), 1275(w),

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1161(w), 1091(m), 1042(vs), 973(w), 685(m), 530(m), 473(w), 460(w), 443(w). Solid-state visible absorbance: 541 nm. μ_{eff} (300 K) = 1.8 μ_B.

*Solid-state NMR spectroscopy of **1***. NMR spectra were recorded at 150.79 MHz (^{13}C) and 60.77 MHz (^{15}N) on a Varian Inova 600. The sample (47 mg) was spun in a 3.2 mm rotor at 20 kHz. A single-channel (i.e., no cross-polarization) spin-echo sequence was used to suppress the probe background signal. Due to very short relaxation times induced by the paramagnetic metal centers, the recycle delay was 300-500 ms and each spectrum is the result of 50000 (^{13}C) and 250000 (^{15}N) averaged transients. Chemical shifts are referenced to TMS (^{13}C) and NH_3(l) (^{15}N) using secondary, external references.