## **Supplementary Information**

# Mutual Restriction-Driven Anomalous Multistage Piezochromic Behavior in Copper(I) Thiocyanate/Isoquinoline Coordination Polymers

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#### Experimental

The synthesis of the  $[Cu(SCN)(iqi)]_n$  (iqi=isoquinoline) sample follows the procedure outlined in the literature<sup>1</sup>. In brief, a suspension of CuSCN(I) (12.1 mg, 0.1 mmol) in acetonitrile (50 mL) was vigorously stirred for 10 min and subsequently filtered. To the resulting filtrate was added isoquinoline (0.0585 mL, 0.5 mmol), followed by brief stirring (1 min). After filtration, the solution was allowed to undergo slow solvent evaporation under ambient conditions for 3-4 days, yielding yellow crystalline [Cu(SCN)(iqi)]<sub>n</sub> as the final product. The resulting fine powdered samples were characterized by X-ray diffraction (XRD) using a MicroMax-007HF (Rigaku, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). High-pressure studies were conducted using a 300 µm diamond anvil cell (DAC). A T301 stainless steel gasket was preindented to a thickness of 40-60 µm, with a 100 µm diameter hole used as the sample chamber. Pressure calibration was performed using the R1-line emission from a tiny ruby ball. Potassium bromide (KBr) was used as the pressure-transmitting medium (PTM) for all measurements, except for XRD, where no PTM was employed. Photoluminescence (PL) measurements were carried out using a Raman spectrometer (Renishaw in Via) in fluorescence mode, with a 514 nm excitation line from a Cobolt Fandango TM laser operating at a total power of 36.8 mW. High-pressure UV-visible absorption spectra were collected using a custom-built fluorescence microscope, equipped with a deuterium-halogen light source and a Horiba Jobin Yvon iHR320 spectrometer. High-pressure XRD patterns were obtained with a Rigaku Synergy Custom FR-X ( $\lambda$ =0.7093 Å). High-pressure infrared (IR) spectra were measured using a Bruker VERTEX 80v spectrometer. Raman measurements were performed on a micro-Raman spectrometer (HR Evolution) with a 785 nm excitation wavelength.

### **Computational method**

We used the CP2K software package to perform geometry optimization using the PBE/DZVP-MOLOPT-SR-GTH level with the dispersion-corrected density functional (DFT-D3(BJ)), with a grid cutoff of 500 Ry. The unit cell parameters a, b, c, and  $\beta$  shown in Figures 2c-d were obtained through experimental XRD data analysis under pressure. We calculated the lattice constants from peak locations and miller indices by using JADE, then conducted first-principles calculations (DFT with van der Waals corrections) to optimize atomic coordinates and obtain a stable structural model. The projected energy band dispersion (PBAND) and partial density of states (PDOS) calculations were performed by using HSE06/DZVP-MOLOPT-SR-GTH in the CP2K. The crystal structures at different pressures used for all calculations were obtained based on high-pressure XRD characterization. The CP2K input files, Hirshfeld-I charge analysis and Interaction Region Indicator (IRI) analysis were performed by the Multiwfn program.



Fig. S1 (a) The molecular packings of the  $[Cu(SCN)(iqi)]_n$ . (b) PL and (d) absorption spectra of  $[Cu(SCN)(iqi)]_n$  during the decompression process. The initial and released (c) PL and (e) absorption spectra. "d" represents depressurized.



Fig. S2 High-pressure XRD patterns CuSCN. New peaks are marked by asterisks.



Fig. S3 High-pressure Raman spectrum of CuSCN.



Fig. S4 The Hirshfeld-I charge analyses of [Cu(SCN)(iqi)]<sub>n</sub>.



**Fig.S5** The sign( $\lambda 2$ ) $\rho$  colored isosurfaces (isovalue=0.05) of [Cu(SCN)(iqi)]<sub>n</sub> at (a) 1.67 GPa, (b) 3.55 GPa and (c) 8.94 GPa.



Fig.S6 Labeling of related atoms surrounding copper and numerical quantification of their interaction strengths.

## References

1 T. Nishiyama, H. Kitoh-Nishioka, S. Tanaka, M. Maekawa, T. Kuroda-Sowa, M. Yoshida, M. Kato and T. Okubo, A Copper(I) Thiocyanate-Based Photoresponsive Semiconducting 2D Coordination Polymer, *Dalton Trans.*, 2024, **53**, 1445–1448.