

Accessing Copper Selenide Nanostructures Through A 1D Coordination Polymer of Copper(II) with 4,4'-dipyridyl diselenide as Molecular Precursor

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Experimental

Materials and methods

Anhydrous Cupric acetate $\text{Cu}(\text{CH}_3\text{COO})_2$, oleylamine (OAm) and analytical grade solvents were procured from commercial sources. 4,4'-dipyridyl diselenide, i.e., $(\text{SeC}_5\text{H}_4\text{N})_2$ was prepared according to a literature method with slight modification [1].

Elemental analyses were carried out on a Thermo Fischer Flash EA-1112 CHNS analyzer. Thermogravimetric analysis (TGA) was carried out on a Nitzsch STA 409 PC-Luxx TG-DTA instrument, which was calibrated with $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The TG curve was recorded at a heating rate of $10^\circ\text{C min}^{-1}$ under flow of argon. X-Ray powder diffraction patterns were obtained on a Philips PW-1820 diffractometer using Cu-K_α radiation. Optical diffuse reflectance measurements in the range 200–1800 nm (0.68 to 6.2 eV) was conducted on a two-beam spectrometer (V-670, JASCO) with a diffuse reflectance (DR) attachment consisting of an integration sphere coated with BaSO_4 which was used as a reference for the same. Measured reflectance data were converted to absorption (A) using Kubelka-Munk remission function [2]. The band gaps of the nanostructures were calculated by extrapolating the linear portion of the plot to X (energy) axis. SEM and EDS and 2-D elemental mapping measurements were carried out on ULTRA 55 FESEM of Zeiss and Oxford Inca instruments, respectively. A Zeiss Libra 200 FE Transmission electron microscope (TEM) operating at accelerating voltage of 200 kV was used for bright field TEM studies. The

samples for TEM were prepared by placing a drop of sample dispersed in chloroform on a carbon coated copper grid.

Preparation of $[\{\text{Cu}_2(\mu(\text{O},\text{O}')\text{-OAc})_4\}(\mu(\text{N},\text{N}')\text{-4,4'}\text{-py}_2\text{Se}_2)]_n$ (*1D-CupySe*):

A solution of $\text{Cu}(\text{OAc})_2$ (58.7 mg, 0.32 mmol) in 20 mL methanol was layered onto a 10 mL solution of 4,4'-dipyridyl diselenide (101.5 mg, 0.32 mmol) in the same solvent. The solution was allowed to stand for one day to give insoluble green colored crystals (Yield: 208 mg, 95%), m.p. 220°C (dec.). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{Cu}_2\text{N}_2\text{O}_8\text{Se}_2$: C, 31.92; H, 2.98; N, 4.14%. Observed: C, 31.65; H, 3.08; N, 4.00 %.

X-ray Crystallography:

The single crystal of $[\text{Cu}_2(\mu\text{-OAc})_4(4,4'\text{-py}_2\text{Se}_2)]_n$ was mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 100 K. A BRUKER Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite [3]. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a $\text{Cu}\text{-}\mu\text{sX}$ -ray tube ($K_\alpha = 1.5418\text{\AA}$ with a potential of 50 kV and a current of 1.0mA).

Synthesis of copper selenide nanocrystals

Copper selenide nanocrystals were prepared utilizing *1D-CupySe* as a precursor. The synthesis process involves thermolysis of *1D-CupySe* in high boiling solvents OAm and ODE using heat up method. In a typical heat-up method, 10 mL of the high boiling solvent was taken in a three-necked round bottom flask along with 200 mg of *1D-CupySe*. The reaction mixture was then degassed at 120°C under nitrogen flow for 30 min to remove residual moisture. Subsequently, the temperature was elevated to 200°C and the reaction was continued for 10 minutes while maintaining the temperature, after which the heat source was removed and the reaction mixture was allowed to cool to 60°C followed by addition of 5 mL of methanol to ensure complete precipitation of the nanocrystals. The synthesized materials were collected after repeated washing with methanol and toluene mixture followed by centrifugation at 8000 rpm for 10 minutes to remove excess capping agent. Finally, all the nanostructures were isolated as black residue.

Photo electrochemical cell experiment

Photo-responsivity of the nanostructures was measured in a photo electrochemical cell prepared by using silicon/copper selenide geometry as the working electrode, Pt wire as counter and pseudo reference electrodes, respectively and aqueous Na₂S (0.6 M): aqueous Na₂SO₃ (0.8 M) (1:2) as the electrolyte. The working electrode (silicon/Cu_{1.8}Se or silicon/Cu_{1.75}Se) were prepared by spin coating a colloidal solution of the copper selenide nanostructures in toluene on the rough surface of n-type Si wafer of (100) orientation having thickness of 200 μm and resistivity of 1-10 Ωcm. The spin coated film was dried at 150°C for 2 h under air. The process was repeated many times till a uniform coating was obtained on the silicon surface. Fluorescent white lamp (36 W, UV content < 3%) was used as radiation source with light intensity at the cell being 200 μWcm⁻².

Table S1: Crystallographic and structure refinement data for **1D-CupySe**.

Compounds	[{Cu₂(μ(O,O')-OAc)₄}(μ(N,N')-4,4'-py₂Se₂)_n
Chemical Formula	C ₁₈ H ₂₀ Cu ₂ N ₂ O ₈ Se ₂
Formula weight	677.36
Crystal Size (mm ³)	0.123 x 0.071 x 0.012
Diffractometer	BRUKER Venture
T/K	99.99
λ/Å	1.5418
Crystal system	Orthorhombic
Space group	P _{ccn}
a/Å	12.7110 (4)
b/Å	25.3176 (8)
c/Å	8.7136 (3)
α/°	90
β/°	90
γ/°	90
V/Å ³	2804.14 (16)
ρ _{calc} /g cm ⁻³	1.604
Z	4
μ/mm ⁻¹	5.185
Reflection collected	49402
Data/restraints/parameters	2651/0/147
Final R ₁ , wR ₂ indices	R1 = 0.0235 wR2 = 0.0613
R ₁ , wR ₂ (all data)	0.0280 / 0.0632
Largest diff. peak & hole [eÅ ⁻³]	0.288 and -0.330

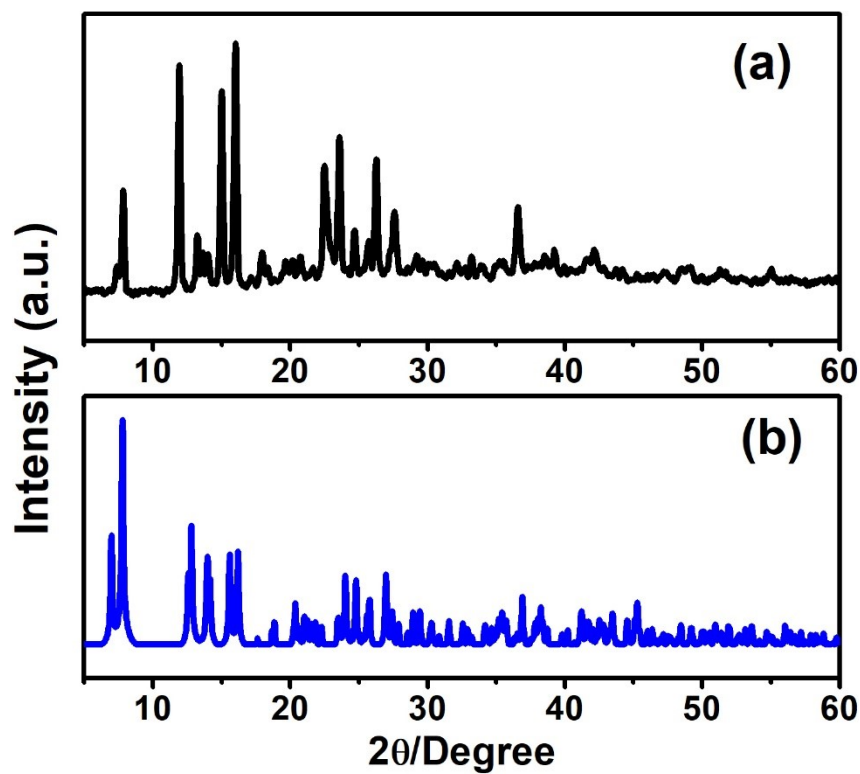


Figure S1. (a) XRD pattern of powder *1D-CuPySe* and (b) simulated XRD pattern of *1D-CuPySe* generated from single crystal data.

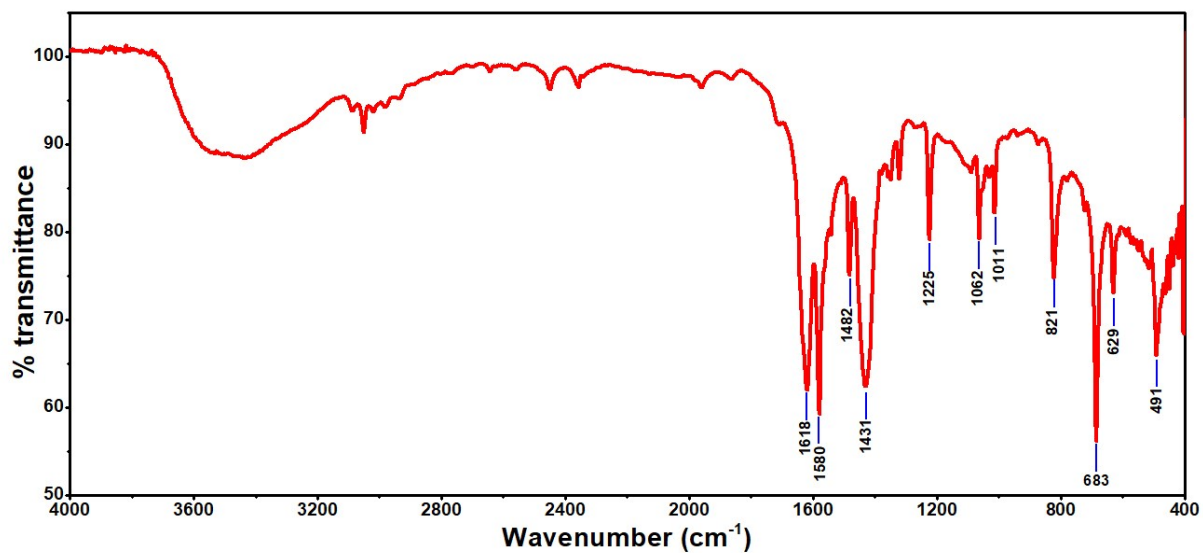


Figure S2. FT-IR spectra of *1D-CuPySe*.

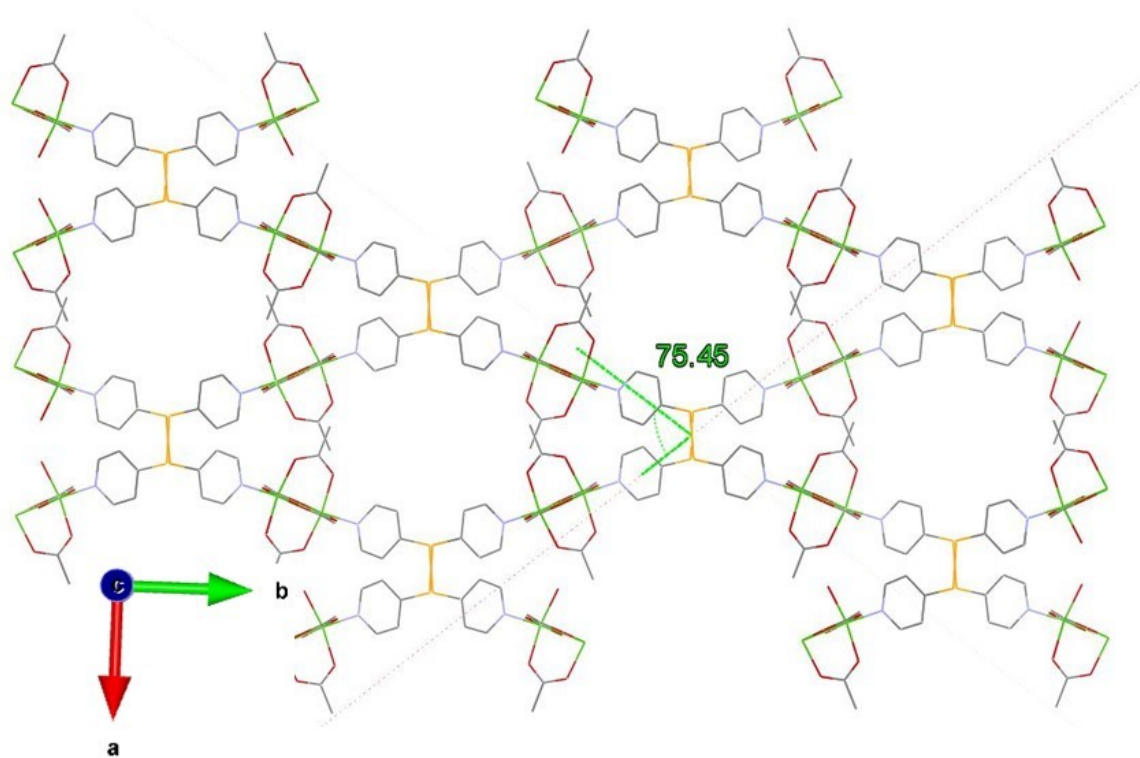


Figure S3. View of crystal packing along *c*-axis featuring the crossing angle of the 1D chain assemblies forming the 3D structure of *1D-CupySe*.

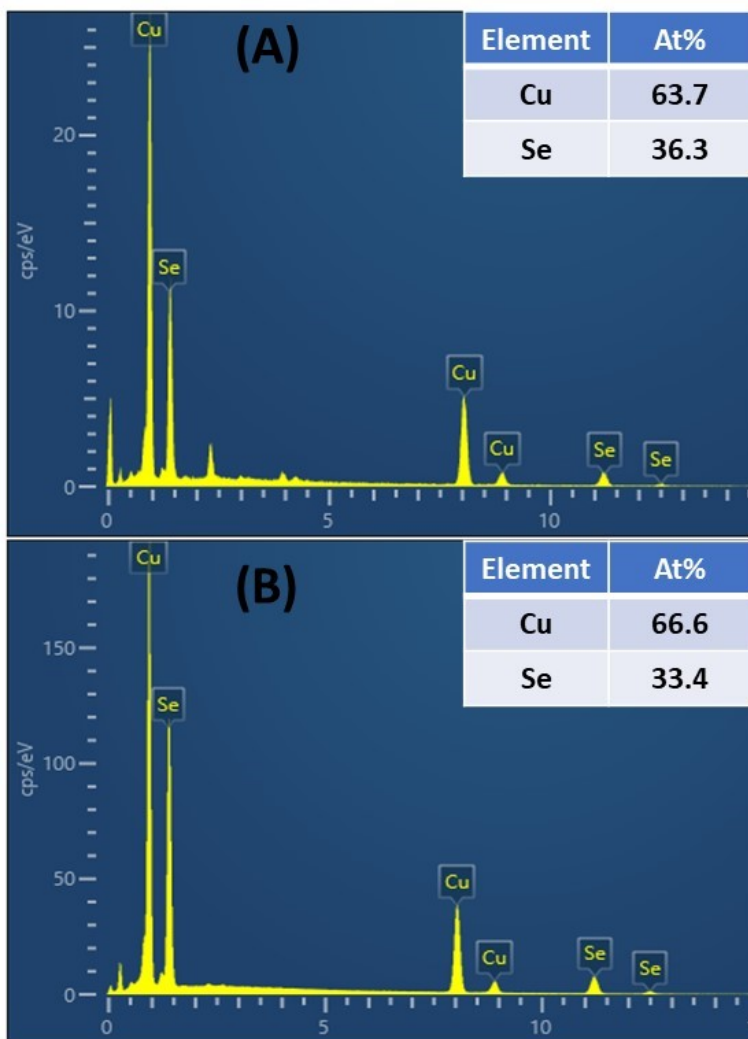


Figure S4. EDS spectra of (a) $\text{Cu}_{1.75}\text{Se}$ and (d) Cu_2Se nanoparticles synthesized from **1D-CuPySe** by thermolysis in ODE and OAm respectively.

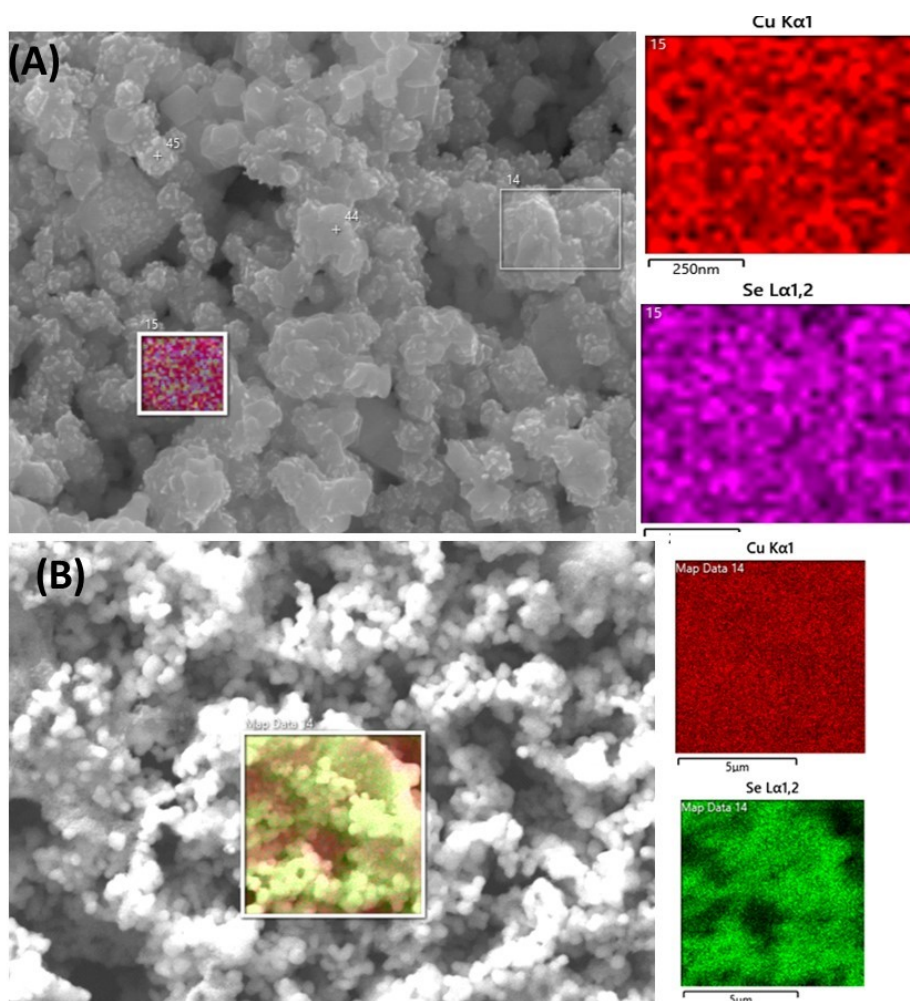


Figure S5. 2D elemental mapping of (a) $\text{Cu}_{1.75}\text{Se}$ and (d) Cu_2Se nanoparticles synthesized from *1D-CuPySe* by thermolysis in ODE and OAm respectively.

References

1. B. Boduszek, R. Gancarz, *J. Prakt. Chem.* 1996, 338, 186–189.
2. P. Kubelk and F. M. Aussig, *Zeitschrift für Technische Physik*, 1931, **12**, 593-601.
3. APEX3 ‘Program for Data Collection on Area Detectors’ Bruker AXS Inc., 5465 East Chery Parkway, Madison, WI 53711-5373 USA.