Supporting Information for

An unusual cuprous iodide polymer incorporating I⁻, I₂ and I₃⁻ structural units

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General Remarks

All reagents in the preparation procedure were of analytical reagent grade and used without any purification or degassing of solvents. Elemental analyses (C, N and H) were performed using a PE2400 II elemental analyzer. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000–400 cm⁻¹ range. Powder X-ray diffraction (PXRD) patterns was recorded in the angular range of $2\theta = 5.70^{\circ}$ on a Bruker D₈ advance diffractometer using CuK α radiation. UV spectra were performed with a U-4100 spectrometer at room temperature. Photoluminescence spectrum was carried out on an Edinburgh FLS 980 analytical instrument equipped with a 450 W xenon lamp and a μ F900H high-energy microsecond flash-lamp as the excitation source.

Computational description.

The band structure and density of state (DOS) of **1** were theoretically calculated by the CASTEP. The total energy is calculated with the density functional theory (DFT) using the Perdew–Burke– Ernzerhof generalized gradient approximation (GGA). The following orbital electrons are treated as valence electrons: H 1s1, C 2s22p2, N 2s22p3, I 5s²5p⁵, and Cu 3d¹⁰4s¹. The number of plane waves included in the basis is determined by a cutoff energy of 270 eV, and the numerical integration of the Brillouin zone is performed using a Monkhorst-Pack k point sampling: $1 \times 2 \times 1$. The Fermi level (E_f = 0 eV) was selected as the reference of the energy.

Electrode preparation and photocurrent measurement.

The working electrodes for photocurrent measurements were prepared by following processes. 10.1 mg of microcrystal sample was dispersed into a mixed solution of H₂O (2 mL) and Nafion (50 μ L), and followed by ultrasonic treatment for 0.5 h. Then, 200 μ L of above slurry was coated onto the FTO glass (F-doped SnO₂) with an effective area of 1 cm² and dried naturally at room temperature. The photocurrent experiment was performed on a CHI650E electrochemistry work station in a three-electrode system, the sample coated FTO glass as the working electrode, a Pt slice as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte solution was 0.5 mol/L Na₂SO₄ aqueous solution (500 mL). A 450 W high pressure Xe lamp with 420 nm was used as the illumination source. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light. The sample was typically irradiated at intervals of 100 s.

X-ray Crystallography

Single-crystal X-ray diffraction data for **1** were recorded on a Rigaku Mercury CCD diffractometer using a ω -scan method with graphite monochromated Mo K α radiation (λ = 0.71073 Å). Absorption corrections were applied using multi-scan technique. The structures of all compounds were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-H atoms were refined with anisotropic displacement parameters. The H atoms bonded to C/N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal collection data parameters and refinement results can be found in Table S1.

-	
	1
formula	$C_{10}H_8Cu_2I_8N_6$
Fw	1354.52
crystal system	Monoclinic
space group	$P2_1/n$
<i>a</i> , Å	15.105(7)
b, Å	9.426(2)
<i>c</i> , Å	17.316(8)

Table 1 Cr	ystallographic	data for 1.

β , deg	94.93(5)
<i>V</i> , Å ³	2456.2(17)
Ζ	4
Т, К	293(2)
Calcd density, Mg.m ⁻³	3.662
F(000)	2368
$2\theta(\max), \deg$	55.84
Total reflns collected	44323
Unique reflns	5869
No. of param	235
$R1[I>2\sigma(I)]$	0.0374
wR2(all data)	0.0803
GOF on F^2	1.008



Fig. S1 Simulated and experimental powder XRD patterns of 1.



Fig. S2 The asymmetric unit of 1 with labeling scheme.



Fig. S3 The coordination environment of Cu⁺ ions.



Fig. S4 3-D 3-D cuprous polyiodide network built up from the linkages of 1-D unsaturated cuprous coordination polymers $[Cu_2(\mu_4-L)]_n$ and 1-D $[(I^-)\cdot 2I_2\cdot (I_3)^-]_n$ polyiodide ribbons.



Fig. S5 the photo of one single crystal.



Fig. S6 Thermogravimetric analyse curve of 1.



Fig. S7 N₂ adsorption-desorption isothermal curve of 1.



Fig. S8 Pore size distribution curve of 1.

 N_2 adsorption–desorption isotherms were measured to characterize BET surface areas and the porosity of **1**. The obtained type IV isotherm with a typical hysteresis loop shifted to a high relative pressure range of 0.97–1.0. The corresponding pore size distribution curve calculated by BJH methods reveals average distribution around 4.88 nm, and the BET surface areas of **1** is calculated to be about 13.0218 m²·g⁻¹.