Supporting Information

$[Bmmim]_6[In_{10}Se_{16}Cl_4]\cdot(MIm)_2$: An Organic-ligand Free Discrete T3 Cluster for Efficient Hydrogen Evolution under Visible Light Irradiation

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Experimental section

Syntheses

Materials: Indium (99.99%) was purchased from Chengdu optoelectronic material Materials Co., Ltd. (Sichuan, China); selenium powder (AR) was purchased from Yingda Rare Chemical Regents Factory (Tianjin, China); zinc nitrate hexahydrate and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-butyl-2,3-dimethylimidazolium chloride ([Bmmim]Cl) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Science (Gansu, China); 1-methylimidazole (Mim, 99%) was purchased from Adamas; 1,5-Diazabicyclo[4,3,0]-5-nonene (DBN, 97%) was purchased from Damas-beta. All the chemicals were used without further purification.

In-Se-IL precursor: In-Se-IL precursor was prepared through a microwave-assisted ionothermal process. Microwave experiment was carried out on a microwave reactor Biotage Initiator™ EXP. The reactants consist of In (10 mmol, 1.1482 g), Se (22 mmol, 1.7358 g), (Bmmim)Cl (45 mmol, 8.4915 g). The mixed reactant was sealed in a 20 mL Biotage microwave quartz vessel. First, the microwave tube was placed on a magnetic heating stirrer and heated through a water bath (100 ^oC) until a mash-like mixture was formed. Then the program was set to heat reaction in a microwave reactor (Generally, the mixture was heated at 150 °C for 5 min followed by 200 °C for 1 h and then cooled to room temperature). Finally, a dark-red gel was formed.

$[Bmmim]_6[In_{10}Se_{16}Cl_4]\cdot(MIm)_2$: The as-synthesized 10 mmol (measured in indium) precursor was diluted with 5 mL DMF. Then one tenth of the mixture (wt.%) was mixed with 1 mmol $Zn(NO_3)_2\cdot 6H_2O$, 0.5 mL DBN and 1 mL 1-methylimidazole in a 20 mL Teflon-lined steel autoclave. The vessel was sealed and placed in a programmed temperature oven, heated to 160 °C for three hours, and then being kept at a constant temperature of 160 °C for six days before cooling to room temperature at a rate of 0.045 °C min^{-1}. Finally, the product was washed several times with absolute ethanol and light-yellow block-like crystals was obtained (Yield: 110.0 mg, 30.24% based on In). Elemental analysis: calculated for $(C_9H_{17}N_2)_6In_{10}Se_{16}Cl_4\,(C_4H_6N_2)_2$ (formula mass: 3637.04), C 20.47%, H 3.16%, N 6.16%; found, C 19.80%, H 3.00%, N 6.13%.

Characterization methods

Under the optical microscope, smooth and translucent single crystals were carefully selected. Single-crystal X-ray diffraction (SCXRD) intensity data of compound **1** was collected on a Rigaku Hypix with nitrogen-flow temperature controller (100 K) using graphite-monochromated Ga*K*α radiation (λ = 1.3405 Å). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-2018 program package. Powder X-rat diffraction (PXRD) was measured on a Rigaku Miniflex-II diffractometer with Cu $K\alpha$ radiation (λ = 1.54178 Å) in the angular range of 2θ = 3 - 65° with a scan speed of 0.12 $°\cdot min^{-1}$. The elemental analyses (EA) of C, H, and N were carried out on a German Elementary Vario EL III instrument. The energy dispersive spectroscopy (EDS**)** was observed and recorded on a JEOL JSM-6700F scanning electron microscope (SEM). The TGA was conducted using a NETZSCH STA 449F3 unit at a heating rate of 10 $K\cdot min^{-1}$ under a nitrogen atmosphere at the temperature of 25 - 800 °C. The solid-state optical diffuse reflectance spectrum was measured at room temperature using a Shimadzu UV-2600 spectrometer in the range of 200 - 800 nm with a $BaSO_4$ plate as a standard (100% reflectivity). The absorption spectrum was calculated from the reflection spectrum by using the Kubelka-Munk function.[1] ^1H NMR spectra of compound **1** was recorded on a Bruker AVANCE III spectrometer with Deuterated DMSO as the solvent (2 mg samples dispersed in 0.6 mL DMSO-d_6 after ultrasonic treatment in an ultrasonic cleaner for 5 min). ESI-MS was carried out on an Impact II UHR-TOF instrument (Bruker) with 1 mg samples dispersed in 1 mL DMSO after ultrasonic treatment in an ultrasonic cleaner.

Experimental photocatalytic hydrogen production: The photocatalytic hydrogen production tests was carried out on a closed glass circulation system (CEL-SPH2N-D9). First, 90 mL of distilled water, 10 mL of triethanolamine, 33.5 µL of H_2PtCl_4 and 10 mg of solid sample were separately added to a 250 mL Poifelai reaction vessel in turn. 89 mL of distilled water, 10 mL of triethanolamine, and 33.5 µL of H_2PtCl_4 and 10 mg sample dissolved in 1 mL DMSO were separately added to a 250 mL Poifelai reaction vessel in turn. Next, the reaction system was evacuated, and then irradiated with a 300 W Xe lamp having a cut-off filter ($\lambda \geq 420$ nm). Last, the generated H_2 was measured by a gas chromatograph with Ar as a carrier gas.

Electrochemical experiment: All electrochemical tests were performed on the CHI660E electrochemical workstation. A three-electrode test system was used, with platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and T3 cluster (ITO) glass as the working electrode. The photocurrent density was measured using the Amperometric *i-t* Curve mode in the electrochemical test, and the Mott-Schottky curve was recorded by measuring the capacitance of the semiconductor-electrolyte interface at a frequency range of 500 to 3000 HZ using the Impedance-Potential mode. All test light sources were a 300 W Xe lamp with a cut-off filter ($\lambda \geq 420$ nm). Firstly, 5 mg sample was placed into the sample tube, and then 0.2 mL water, 40 μL absolute ethanol and 10 μL naphthol were added in turn. The mixture was ultrasonically shaken for 2 h in the ultrasound system. 40 μL of the mixed sample was selected and deposited on 1×4 cm^2 of conductive glass with the sample deposition area of 1×1 cm^2. Thus, photoelectric anode was fabricated. Finally, 0.05 $mol\cdot L^{-1}$ of a sodium sulfate salt solution was used as an electrolyte and electrochemical tests were carried out in a three-electrode system by electrochemical workstation.

Table S1 Crystallographic data and structural refinement details for compound 1.

Crystal	$[Bmmim]_6[In_{10}Se_{16}Cl_4]\cdot(MIm)_2$
Empirical formula	$C_{62}H_{114}N_{16}In_{10}Se_{16}Cl_4$
Formula Mass	3637.04
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a/Å	19.7255(4)
b/Å	19.7255(4)
c/Å	31.1693(6)
α/°	90
β/°	90
γ/°	120
V/Å^3	10503.0(5)
Z	4
λ/Å	1.3405
T/K	101(2)
$F(000)$	6800
Dc/g·cm^{-3}	2.300
μ/mm^{-1}	16.801
No. of Reflection collected	74688
No. of Reflection unique	4489
No. of parameters	61
R_{int}	0.0802
[a] R_1 value ($I > 2\sigma(I)$)	0.0731
[b] wR (F^2) value ($I > 2\sigma(I)$)	0.1510
R_1 value (all data)	0.0759
wR (F^2) value (all data)	0.1522
GOF	1.020
CCDC Number	1974812

[a] $R_1 = \sum \| F_o| - |F_c \| / \sum |F_o|$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

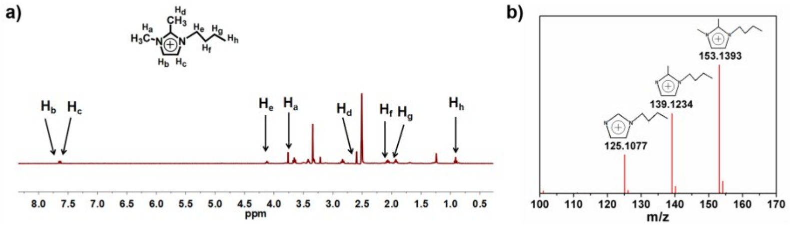
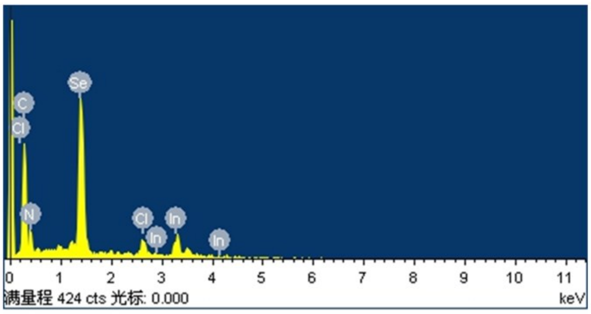


Fig. S1 (a) ^1H NMR spectra (400 MHz, DMSO-d_6, 298 K) of compound **1**; (b) positive mode ESI-MS spectrum of compound **1** in solution.



Element	Weight percentage	Atom percentage	Atomic ratio obsvd (calcd)
Cl K	14.18	5.97	1.00 (1.00)
Se L	53.76	50.36	3.79 (4.00)
In L	32.06	43.67	2.26 (2.50)
Total	100.00		

Fig. S2 Energy dispersive spectroscopy (EDS) of compound **1**.

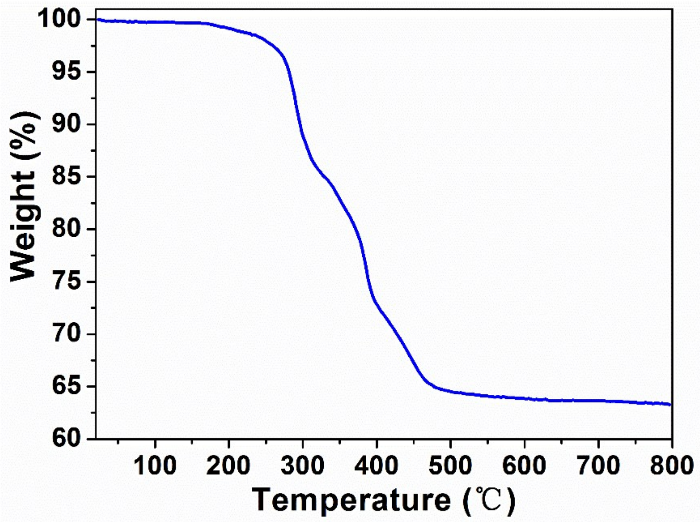


Fig. S3 Thermogravimetric curve of compound **1**.

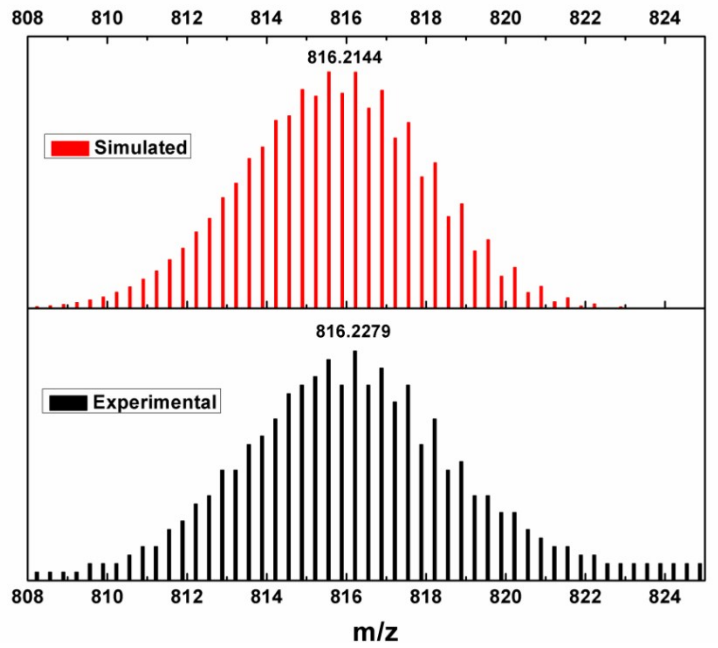


Fig. S4 The measured mass spectrum (bottom) of the $[In_{10}Se_{16}Cl]^{3-}$ cluster is comparable with that simulated from isotopic patterns (top).

Reference:

1. J. Tauc, *Mater. Res. Bull.* 1970, **5**, 721-729.