Electronic Supporting Information

A quasi-D_3-symmetrical metal chalcogenide cluster constructed by corner-sharing of two T3 supertetrahedral

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Contents

Experimental Section:

Chemicals and Materials

Indium powder (In, 99.99%), sulfur powder (S, ≥ 99.5%), (1,5-Diazabicyclo [4.3.0]-5-nonene) ($C_7H_{12}N_2$, 98%), and methanol absolute all used without any further purification.

Synthesis of $(HDBN)_6[In_{20}S_{33}(DBN)_6]$

A mixture of indium powder (36.8 mg, 0.32 mmol), sulfur powder (48.0 mg, 1.5 mmol), 1,5-Diazabicyclo [4.3.0]-5-nonene (DBN) 1.5 mL and MeOH 0.5 mL was prepared and stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 ^oC for 8 days, and then the autoclave was cooled to room temperature naturally without any other operations. Light yellowish green block crystal was obtained with a few impurities. The raw products were washed three times by ethanol and distilled water, and then filtered off, and further purified by hand with a yield of 37.4 mg (52.3% based on indium).

X-ray Crystallography

Data collection for $(HDBN)_6[In_{20}S_{33}(DBN)_6]$ was carried on an Agilent Technologies SuperNova Single Crystal Diffractometer using Cu Kα radiation (λ = 1.54178 A) at 150 K. Absorption corrections were applied by using the program CrysAlis[1] (multi-scan). The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 within OLEX2[2].

Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) of the compound was obtained using a Bruker Model D8Avance powder diffractometer at room temperature with Cu K_α radiation (λ= 1.5418 Å). The patterns were record in the range of 5−60° (2θ) with the scanning step width of 0.02°.

Elemental Analysis

Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) detector. An accelerating voltage of 25 kV and 40s accumulation time were applied. EDS results clearly confirmed the presence of In and S elements. Elemental analysis of C, H, and N was performed on VARIDEL III elemental analyzer {Calcd. (*wt* %): C 20.80; N 6.93; H 3.12, Found: C 20.72; N 7.13; H 3.307} for compound **1.**

Thermogravimetric (TG) Measurement

A Shimadzu TGA-50 thermal analyzer was used to measure the TG curve by heating the sample from room temperature to 800 ^{o}C with heating rate of 10 ^{o}C/min under N_2 flow.

Fourier-Transform Infrared Absorption

Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with Potassium bromide optics allowing the instrument to observe from 500-4000 cm^{-1}.

UV-Vis Absorption Measurement

The UV−vis−NIR reflectance date for five compounds were collected on an EVOLUTION 220 UV−vis−NIR spectrophotometer in the wavelength range from 240-800 nm at room temperature with $BaSO_4$ powder as the standard of 100% reflectance. The absorption spectra were calculated from the reflectance spectra using the Kubelka−Munk function: $F(R) = (1-R)^2/(2R) = K/S$, where K, R and S represent the absorption, reflectance and scattering, respectively.[3]

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian09 software package[4] and analyzed with Multiwfn software[5]. DFT calculations using the hybrid density functional PBE0-1/3[6] have been performed during the geometry optimization and estimating electron charges distribution process. The metal atoms (In) were treated using LanL2DZ basis set[7] while for other atoms (S, N, C, H), standard Pople basis set 6-31G(d,p)[8] was used.

Table S1 Crystal data and structure refinement parameters for compound **1**.

Compound	**1**
Formula	$C_{84}H_{150}In_{20}N_{24}S_{33}$
M_r	4850.65
Temp (K)	150
Formula Weight	4850.65
Wavelength (Å)	1.54184
Cryst syst	monoclinic
Space group	$P2_1/c$
a (Å)	25.7960(3)
b (Å)	19.9108(3)
c (Å)	32.7481(5)
α (deg)	90
β (deg)	108.707(2)
γ (deg)	90
V (Å^3)	15931.5(4)
Z	4
ρ (g cm^{-3})	1.864
μ (mm^{-1})	26.937
F(000)	9320
Collected reflns	114386
Unique reflns (R_{int})	0.0739
Completeness (%)	99.8
GOF on F^2	1.057
$R_1{}^a/wR_2{}^b$ [I> 2(I)]	0.0752/0.2051
$R_1{}^a/wR_2{}^b$ (all data)	0.0865/0.2143

$^aR_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $^bwR2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$.

PLAT602_ALERT_2_A Solvent Accessible VOID(S) in Structure ..... ! Check

Response：Packing of molecular clusters create large holes, so the existence of "solvent accessible voids" is not a problem to be resolved.

Table S2 Detailed data of hydrogen bonds of compound **1.**

D-H···A	N• • •S distances (Å)	H• • •S distances (Å)	N-H• • •S angles (°)
N(13)-H• • •S(18)	3.23(2)	2.38(3)	163.1(1)
N(15)-H• • •S(18)	3.23(2)	2.38(3)	160.8(1)
N(17)-H• • •S(18)	3.22(1)	2.35(3)	168.1(9)

Table S3 ADCH fragment charges (in *a.u.*) associated with amount of intramolecular electron transfers of twelve DBN groups for different connection sites.

Edge sites	Transferred electrons	Middle sites	Transferred electrons	Side sites	Transferred electrons
0.368	0.632	0.651	0.349	0.636	0.364
0.368	0.632	0.662	0.338	0.695	0.305
0.367	0.633	0.598	0.402	0.677	0.323
0.359	0.641				
0.388	0.612				
0.359	0.641				

Table S4 MBO analysis for In-N bonds and neighboring In-S bonds at edge connection sites.

In-N	In-S(1)	In-S(2)	In-S(3)
0.352	0.880	0.789	0.828
0.357	0.852	0.820	0.848
0.351	0.948	0.808	0.775
0.363	0.837	0.789	0.855
0.368	0.804	0.766	0.920
0.356	0.788	0.881	0.818

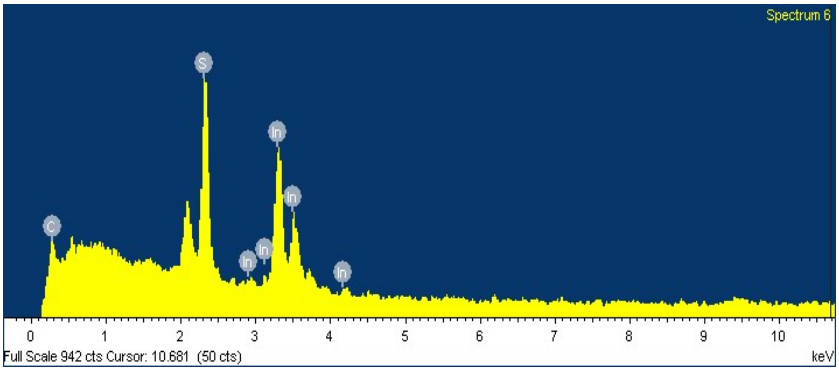


Fig. S1 Energy dispersive X-ray spectra (EDS) for compound **1.**

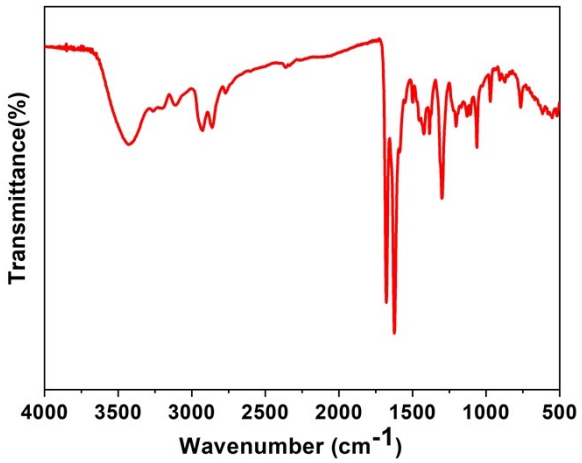


Fig. S2 FTIR spectrum of compound **1**.

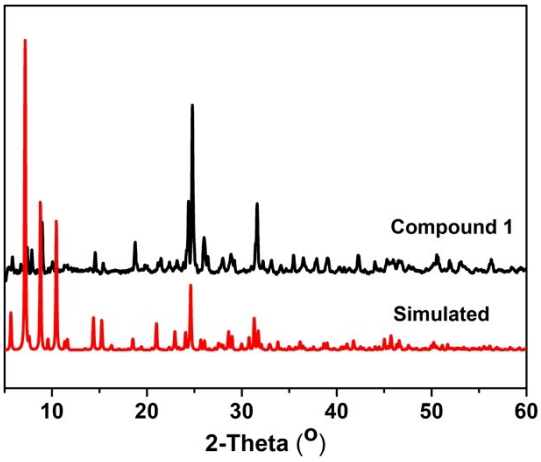


Fig. S3 Simulation and experimental PXRD diagrams of compound **1.**

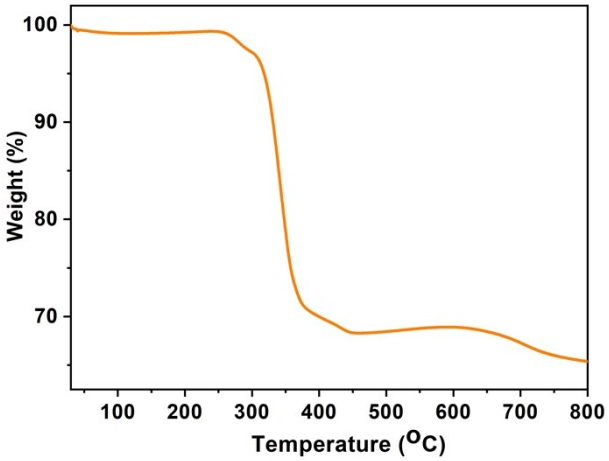


Fig. S4 TGA curve of compound **1**. The sharp weight loss of 31.1 % between 253-452 °C is attributed to the carbonization of organic molecules.

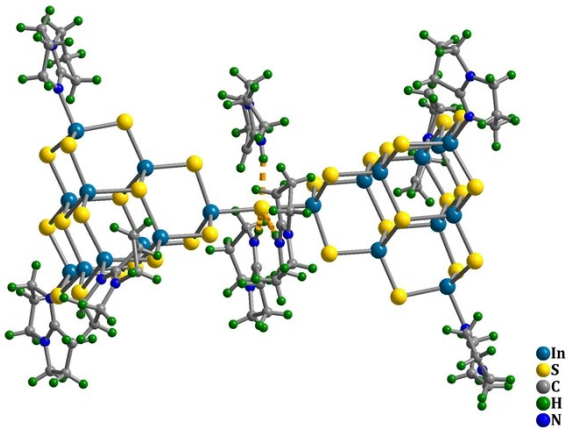


Fig. S5 Hydrogen bonds between HDBN and μ_2-S in compound **1.**

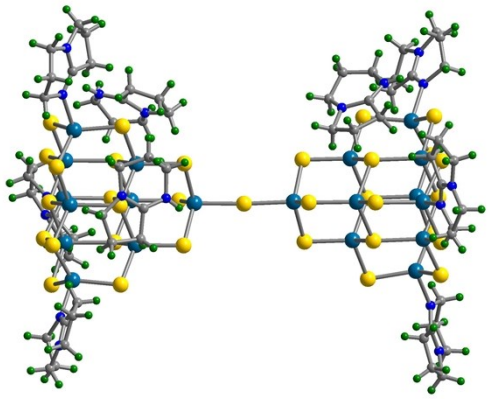


Fig. S6 Distribution of HDBN on the surface of supertetrahedral in compound **1.**

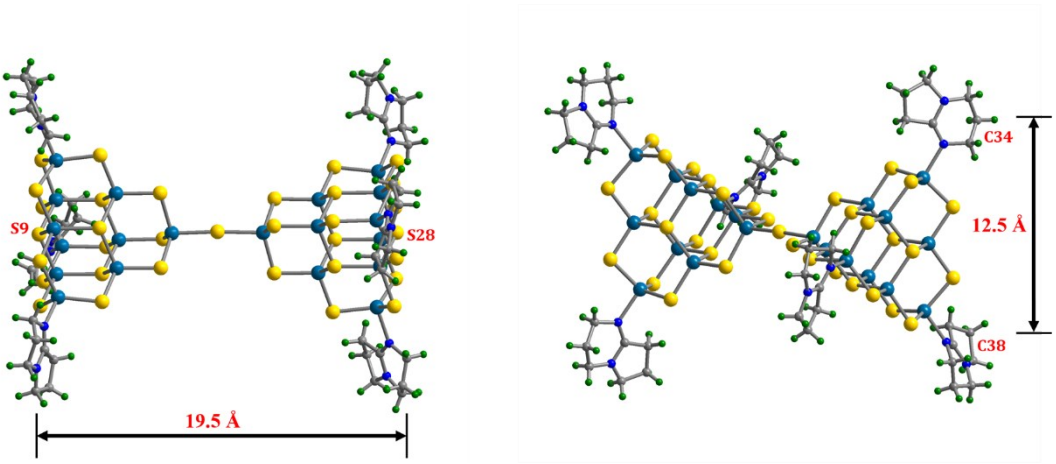


Fig. S7 The maximum and minimum of dimensional size of the cluster

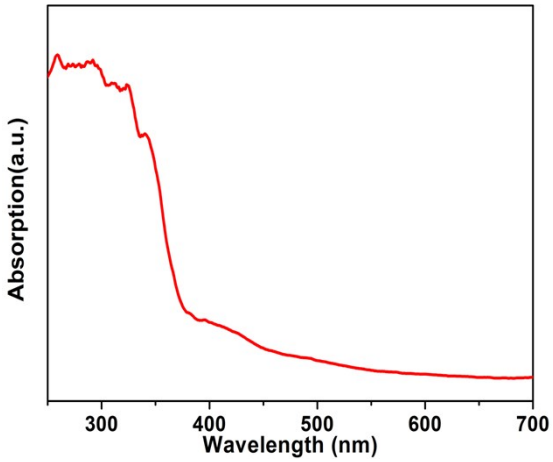
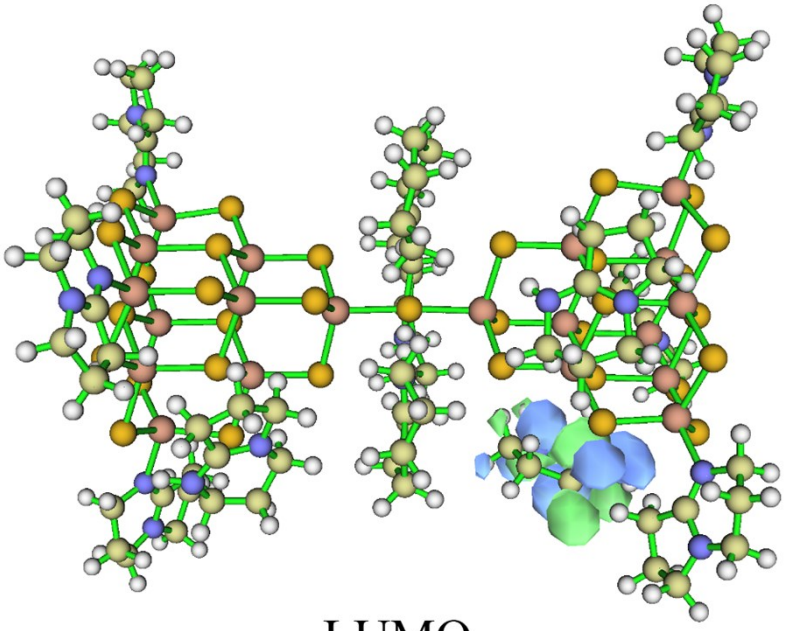
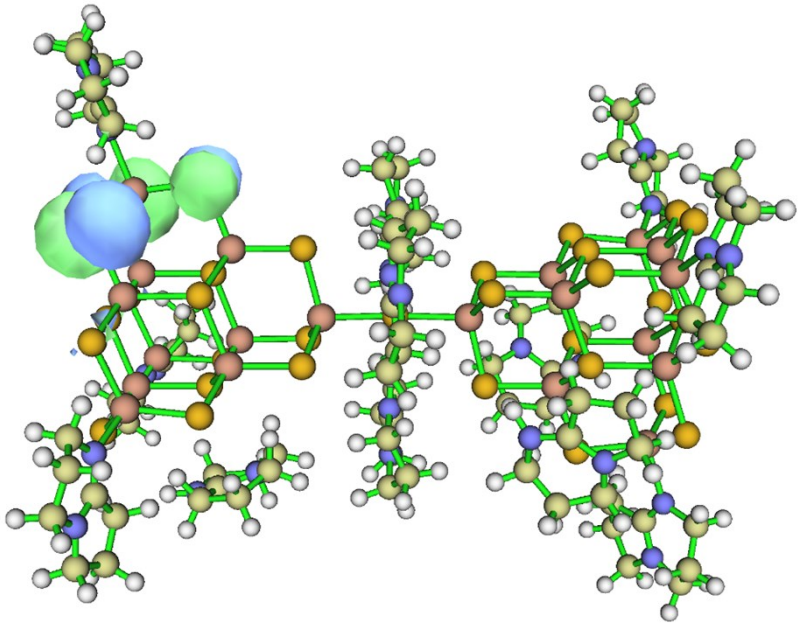


Fig. S8 UV-vis absorption spectra of compound **1**.



LUMO



HOMO

Fig. S9 HOMO and LUMO for **c**ompound **1.**

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