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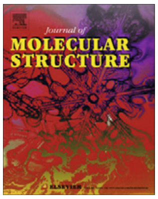

A combined experimental and theoretical study of an semi-conductive iodoargentate hybrid induced by large conjugate cation

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ABSTRACT

A hybrid iodoargentate $[(\text{APHEN-H})_2(\text{Ag}_4\text{I}_6)]_n$ (**1**) (APHEN = 5-amino-1,10-phenanthroline) has been obtained by the routine synthetic reaction and structurally determined. In **1**, a $(\text{Ag}_4\text{I}_6)_n^{2-}$ chain was defined by edge-sharing of Ag_4I_6 units, and its quasi-three-dimensional hybrid structure was constructed from π–π interactions and C—H···I hydrogen bonds. Experimental band gap of about 2.30 eV indicates its semiconductor nature. Strong luminescence can be detected in the title compound, which has been assigned by theoretical calculation with DFT method.

1. Introduction

The controllable synthesis of organic–inorganic hybrid materials using idea of molecular engineering and energy band engineering presents an attractive new direction in solid state chemistry [1–3]. Our current research is focused on the synthesis of organic/metal halide hybrids with the aim of enhancing useful physical properties associated with hyperpolarizable organic and inorganic components, such as molecule switches [4,5]. In this field, silver halides directed by organic cations have captured continuous interests, whose structures present variable dimensions and topologies. Among them, organic–inorganic Ag–I/amine hybrid systems with organic amine not coordinating to metal centers are much less and most of them present zero-dimensional or one-dimensional structures [6–17]. Specially, the band gaps, i.e., charge carrier mobilities of organic/iodoargentate hybrids can be tuned with the aim at achieving a special functional property. In order to improve the charge carrier mobility of a given halogenometallate network, the following strategies have been considered: (a) to achieve hybrids with higher structural dimensionality and (b) to tune the band gap associated with inorganic layer by incorporating selected cations which are able to impact the bonding features of the inorganic framework [18]. This can be accomplished by incorporating certain organic moieties with low-dimensional inorganic networks. Kept this in mind, we think that usage of the large conjugate system, for example, phenanthroline derivative possessing hydrogen bonding-donating abilities could help to achieve corresponding reduced band gap hybrids. Herein, by modifying phenanthroline into 5-amino-1,10-phenanthroline, we introduce H-bond donor to obtain a new hybrid iodoargentate $[(\text{APHEN-H})_2(\text{Ag}_4\text{I}_6)]_n$ (**1**). As expected, in **1**, the dimensional extension and a reduced band gap can be achieved.

2. Experimental

2.1. General remarks

All chemicals were analytically pure and used without any purification. Elemental analysis was performed on a Vario MICRO instrument. Infrared spectra of single crystals was recorded with a Perkin-Elmer Spectrum-2000 FTIR spectrophotometer (4000–400 cm^{-1}) on powdered sample spread on KBr plate. Optical diffuse-reflectance spectrum was measured on a PE Lambda 35 UV–vis spectrophotometer equipped with an integrating sphere at 293 K, and the BaSO_4 plate was used as the reference. Fluorescence spectrum was carried out on a PW2424 spectrometer. X-ray powder diffraction (XRD) was performed on a Rigaku X-ray MiniFlexII diffractometer.

Electronic structure calculation was based on density function theory (DFT) [19], in which wave functions were explained in a plane wave basis set and the spin polarized version of the PW-91 GGA was employed for the exchange–correlation functional in the CASTEP code [20]. Ultrasoft pseudo-potentials, known for their high efficiency in calculating the structural and electronic properties, are used for the electron–ion interactions. In this case, a 3 × 3 × 2 Monkhorst–Pack grid and a total number of 6 k points in the irreducible Brillouin zone are adopted, and the cutoff energy

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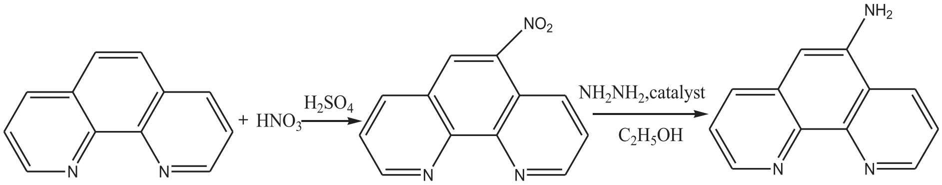
is 270 eV. The calculations of linear optical properties described in terms of the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ were also made in this work.

2.2. Preparation of APHEN and 1

5-amino-1,10-phenanthroline (APHEN) was synthesized via two steps with 1,10-phenanthroline as starting material according to literature method [21]:



Fifteen milliliter condensed H_2SO_4 was droped into a 250 mL three-neck flask, and 10 g 1,10-phenanthroline was added slowly. Afterwards, 30 mL H_2SO_4/HNO_3 mixture was droped into the reaction system slowly and heated to 150 °C for 8 h. Then the solution was poured into ice water with pH being adjusted to 6.0 using 10% NaOH, the resultant yellow depositions (5-nitro-1,10-phenanthroline) was washed and re-recrystallized with methanol (yield 65%). In the second step, catalytic amount NH_2NH_2 and palladium carbon were used as reduction catalysts in 50 mL methanol. The methanol solution containing NH_2NH_2 and palladium carbon was heated to 70 °C, and then 5.0 g 5-nitro-1,10-phenanthroline was added and kept reacting for 8 h. The raw product was re-recrystallized with methanol (yield: 54%).

1 was synthesized with solution evaporation method. In 10 mL DMF, AgI (0.117 g, 0.5 mmol), NaI (0.225 g, 1.5 mmol), and APHEN (0.195 g, 1.0 mmol) with molar ratio of 1:3:2 was dissolved and stirred at 60 °C for 1 h. The pH of resultant suspension was adjusted to pH = 5.0 with 10% HI solution. During the course of stirring, small amount of NaI was added till the solution became colorless clear and then filtered. The filtrate was allowed to stand for two days at room temperature with red block crystals of **1** **obtained** **(0.129** g, yield 65.2% based on Ag). Anal. Calcd. for $C_{24}H_{20}Ag_4I_6N_6$ (1585.34): C, 18.1; H, 1.26; N, 5.30%. Found: C, 18.6; H, 1.36; N, 5.20%. IR (KBr, cm^{-1}): 3457m, 3352m (ν_{N-H}), 3046w (ν_{Ar-H}), 1628s, 1581s ($\nu_{C=C}$, $\nu_{C=N}$), 1257s (ν_{C-N}), 828s, 782s, 713s (γ_{C-H}).

2.3. Crystallography

A red block crystal with dimensions of 0.35 mm × 0.12 mm × 0.11 mm was mounted on a glass fiber. The data collection was performed at 293(2) K on a SIEMENTS SMART CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation by using an $\omega/2\theta$ scan in the range of $3.08 \leqslant \theta \leqslant 27.51°$. Out of the total reflections of 27,682, 7500 were independent with $R_{int} = 0.0593$, of which 6973 were considered to be observed ($I \geqslant 2\sigma(I)$) and used in the succeeding refinement. The intensity data were corrected with empirical absorption and the structure was solved by direct method in SHELXS-97 program [22]. All of the non-hydrogen atoms and some of the hydrogen atoms were located by successive difference Fourier synthesis, and the anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 calculation for 361 parameters. Hydrogen atoms were calculated at theoretical positions. The final cycle of refinement gave rise to $R_1 = 0.0713$, $wR_2 = 0.2048$, $w = 1/[\sigma^2(F_O)^2 + (0.0912P)^2 + 33.3227P]$, where $P = (F_O^2)_{max} + 2F_c^2)/3$, $S = 1.271$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 2.309$, $(\Delta\rho)_{min} = -1.721$ e/Å^3.

3. Results and discussion

3.1. Description of crystal structure

The organic–inorganic hybrid structure of **1** is composed by protonized 5-amino-1,10-phenanthroline cations and $(Ag_4I_6)_n^{2-}$ chain polyanion chains, π–π interaction and C—H···I hydrogen bonds between cations and polyanions contribute to the formation of a quasi-three-dimensional network. In the inorganic polymeric skeleton, $(Ag_4I_6)_n^{2-}$ polyanion can be discussed with Ag_4I_8 unit with cubane-type Ag_4I_4 core. The cubane-type Ag_4I_4 core structure is similar with Mo–S cubane. The Ag_4I_8 unit is defined by four edge-sharing AgI_4 tetrahedra and argentophilic interactions. If

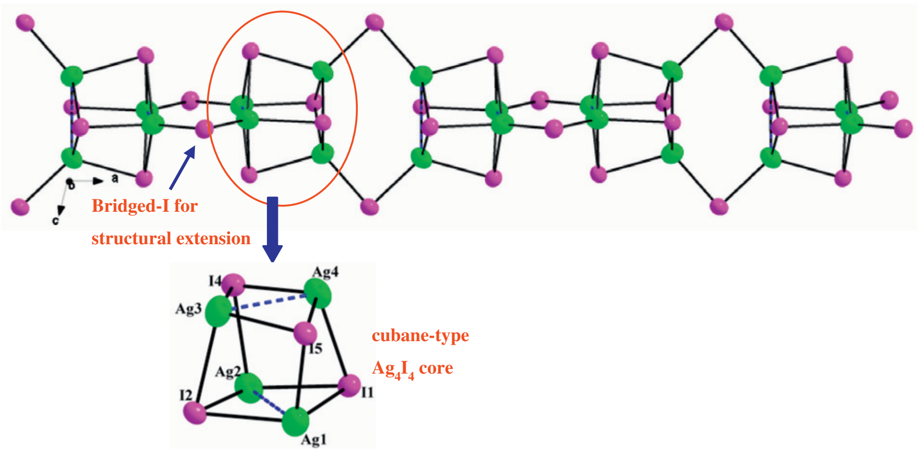


Fig. 1. The structure of $(Ag_2I_4)_n^{2-}$ chain and cubane-type Ag_4I_4 core.