Synthesis, crystal and electronic structures and optical properties of (HIm)$_2$Hg$_3$Cl$_8$ and (HIm)HgI$_3$ (HIm = imidazolium)

Hariharan Nhalil[a], Vincent R. Whiteside[b], Ian R. Sellers[b], Wenmei Ming[c], Mao-Hua Du[c], Bayrammurad Saparov[a,*]

[a] Department of Chemistry and Biochemistry, University of Oklahoma, 101 Stephenson Parkway, Norman, OK 73019, USA
[b] Homer L. Dodge Department of Physics & Astronomy, University of Oklahoma, 440 W. Brooks St., Norman, OK 73019, USA
[c] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ARTICLE INFO

ABSTRACT

We report synthesis, crystal and electronic structures, and optical properties of two new Hg-based zero-dimensional hybrid organic-inorganic halides (HIm)$_2$Hg$_3$Cl$_8$ and (HIm)HgI$_3$ (HIm = imidazolium). (HIm)$_2$Hg$_3$Cl$_8$ crystallizes in the triclinic P-1 space group with a pseudo-layered structure made of organic imidazolium cation layers and anionic inorganic layers containing [Hg$_2$Cl$_6$]$^{2-}$ units and linear [HgCl$_2$]^0 molecules. (HIm)HgI$_3$ crystallizes in the monoclinic $P2_1/c$ space group featuring anionic [HgI$_3$]$^-$ units that are surrounded by imidazolium cations. Based on density functional theory calculations, (HIm)$_2$Hg$_3$Cl$_8$ has an indirect band gap, whereas (HIm)HgI$_3$ has a direct band gap with the measured onsets of optical absorption at 3.43 and 2.63 eV, respectively. (HIm)$_2$Hg$_3$Cl$_8$ and (HIm)HgI$_3$ are broadband light emitters with broad photoluminescence peaks centered at 548 nm (2.26 eV) and 582 nm (2.13 eV), respectively. Following the crystal and electronic structure considerations, the PL peaks are assigned to self-trapped excitons.

1. Introduction

Hybrid organic-inorganic halide materials (HOIMs) have been attracting attention in the past several decades owing to their rich crystal chemistry afforded by the low temperature solution synthesis, and resultant broadly tunable physical properties [1]. At present, HOIMs are being considered for a variety of technologies including photovoltaics [2], non-linear optics [3], photodetectors [4], light-emitters [5], ferroelectric [6], magnetic [4,7] and multiferroic [8,9] applications. The flexibility in structural design, and tunability of their physical properties derive from the rich selection of metal and organic ions that can be effectively incorporated into crystal structures to form novel functional materials. The resultant HOIMs carry attributes of organic and inorganic constituents within a single compound.

The recent focus of the HOIMs research has been primarily on the visible light absorbing Pb- and Sn-based hybrid perovskites [10,11]. Given the compositional and structural diversity of HOIMs, further research into scarcely studied metal, inorganic and organic ion combinations is expected to yield new families of functional materials for optoelectronic applications. Among the systems that are currently receiving a limited attention are the Hg-based halides. Given the fact that the states around the Fermi level in HOIMs are dominated by metal

and halogen states, the Hg-based compounds are expected to have larger band gaps compared to the Pb- and Sn-based hybrids due to the large difference in electronegativities of Hg and halogens [12]. Low temperature solution processability of large band gap hybrid halides makes them prospective candidates for inexpensive high-light-yield scintillator and light-emitter applications [13,14]. In fact, the binary parent HgX$_2$ halides (X = Cl, Br, I) have already been considered for high-power electronic transition lasers, X-ray and gamma-ray detection applications [15–18]. In contrast, for most of the reported Hg-based HOIMs [19], detailed studies including characterization of optoelectronic properties and electronic band structure calculations are lacking. The literature reports so far have primarily focused on structural studies including reports on (CH$_3$NH$_3$)HgX$_3$ (X = Cl, Br, I) [20] and (R)$_2$HgX$_4$ (R = CH$_3$NH$_3$$^+$, (CH$_3$)$_2NH_2$$^+$, C$_8H_9NH_3$$^+$) families [21], to name just a few. From the light-emission standpoint, the use of low dimensional Hg-based HOIMs could be advantageous due to the confinement of charges within dimensionally-reduced inorganic substructures [1,14]. The presence of highly-localized charges in low dimensional HOIMs [22], in turn, results in unusually high exciton binding energies exceeding 0.5 eV that could provide room-temperature stable excitons [1,13,22]. Exciton binding energy plays a crucial role in determining the viability of materials for specific optoelectronic applications. Technologies that are

---

based on the electron-hole recombination for light emission such as scintillators, light-emitting diodes, or phosphors could benefit from high binding energies while technologies such as photodetectors and solar photovoltaics where the performance depend on the flow of charge carriers in the opposite directions, need low exciton binding energy for charge separation [1,23,24].

Herein, we report the synthesis of two new Hg-based hybrid organic-inorganic halides $(HIm)_2Hg_3Cl_8$ and $(HIm)HgI_3$ (HIm = imidazolium cation $C_3H_5N_2^+$) featuring 0D inorganic cluster structures. $(HIm)_2Hg_3Cl_8$ crystallizes in the triclinic P-1 space group with a pseudo-layered crystal structure made of cationic organic layers and anionic inorganic layers made of dimeric $[Hg_2Cl_6]^{2-}$ units and neutral linear $[HgCl_2]^0$ molecules. $(HIm)HgI_3$ crystallizes in the monoclinic $P2_1/c$ space group featuring trigonal planar anionic $[HgI_3]^-$ units that are surrounded by imidazolium cations. Optical diffuse reflectance studies show onsets of optical absorption at 3.43 eV and 2.63 eV for $(HIm)_2Hg_3Cl_8$ and $(HIm)HgI_3$, respectively, which corroborate with the white and yellow colors of the powdered samples. The nature of the band gap is indirect for $(HIm)_2HgCl_8$ and direct for $(HIm)HgI_3$, as based on electronic structure calculations. Room temperature photoluminescence (PL) spectra exhibit a broad peak with full width at half maximum (FWHM) value of 220 nm at 548 nm (2.26 eV) for $(HIm)_2Hg_3Cl_8$ while the PL peak for $(HIm)HgI_3$ is located at 582 nm (2.13 eV) with FWHM = 208 nm. Weak band dispersion near the Fermi level and strong localization of charges due to the low dimensionality of these materials could be inferred from their calculated band structures.

2. Experimental

2.1. Synthesis

High purity starting materials, imidazole (99.9%, Aldrich) and mercury halides (99.9%, Fisher Scientific) were used as commercially available without further purification. Single crystals of $(HIm)_2Hg_3Cl_8$ were obtained serendipitously while targeting $(HIm)HgCl_3$. For the targeted synthesis of $(HIm)_2Hg_3Cl_8$, 13.3 mg (2 mmol) of imidazole was dissolved in 400 μl methanol (reagent grade, Aldrich) in a 5 ml glass vial and 159.2 mg (6 mmol) of $HgCl_2$ was added. This was followed by an addition of 100 μl concentrated hydrochloric acid (11.6 M) to obtain clear colorless solution. The solution was kept undisturbed and mm-size colorless block crystals of $(HIm)_2Hg_3Cl_8$ could be harvested after 24 h. We were successful in growing large sized crystals (∼ 3 × 3 × 2 mm) over a week's period (Fig. S1(a)).

Single crystals of $(HIm)HgI_3$ were grown largely following the procedure described above: 20.9 mg (3 mmol) of imidazole was dissolved in 400 μl methanol and 139.7 mg (3 mmol) of HgI_2 was added. Finally, the solution was acidified by adding 100 μl hydroiodic acid (57 wt% in H_2O). The as-prepared clear yellow solution becomes black (due to presence of iodine in solution) in color overnight and needle like yellow crystals of $(HIm)HgI_3$ were obtained within 4–5 days (Fig. S1(b)). Trapping of mother liquor (dark brown) in the crystal grain boundaries was also noted.

2.2. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku MiniFlex600 system with a D/tex detector using a Ni-filtered Cu-Kα radiation (Cu-Kα$_1$: 1.540562 Å; Cu-Kα$_2$: 1.544398 Å). X-ray data collection experiments were performed at room temperature in the 3–80° (2θ) range, with a step size of 0.02° and the accumulation time of 0.5 s/step.

For air stability studies, powder samples of $(HIm)_2Hg_3Cl_8$ and $(HIm)HgI_3$ were left in ambient air on a laboratory bench for a period of 5 weeks. During this time, PXRD measurements were regularly performed using the conditions described above.

Table 1
Single crystal X-ray data collection and refinement parameters for $(HIm)_2Hg_3Cl_8$ and $(HIm)HgI_3$ (HIm = Imidazolium cation $C_3H_5N_2^+$).

Formula	$(C_3H_5N_2)_2Hg_3Cl_8$		$(C_3H_5N_2)HgI_3$	
Formula weight	1023.55 g/mol		650.38 g/mol	
Temperature	100(2) K		100(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Triclinic		Monoclinic	
Space group	P-1		$P2_1/c$	
Z	1		8	
Unit cell dimensions	$a =$ 6.9115(9) Å	$\alpha = 100.966(2)°$	$a =$ 8.728(9) Å	$\alpha = 90°$
	$b =$ 7.9194(11) Å	$\beta = 107.393(2)°$	$b =$ 16.72(2) Å	$\beta = 91.05(2)°$
	$c =$ 9.9721(13) Å	$\gamma = 102.590(2)°$	``$c =$ 14.92(2) Å	$\gamma = 90°$
Volume	488.86(11) Å^3		2178(4) Å^3	
Density	3.477 g/cm^3		3.968 g/cm^3	
Absorption coefficient	24.583 mm^{-1}		22.581 mm^{-1}	
$\theta_{min} - \theta_{max}$	2.23–29.13°		1.83 – 27.10°	
Reflections collected	12,101		41,280	
Independent reflections	2629		4800	
R^a indices ($I > 2\sigma(I)$)	$R_1 = 0.019$		$R_1 = 0.0396$	
	$wR_2 = 0.0458$		$wR_2 = 0.0984$	
Goodness-of-fit on F^2	1.143		1.034	
Largest diff. peak/hole	2.073/−1.108 e$^-$/Å^3		1.890/−1.264 e$^-$/Å^3	

^{a} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \left[\sum \left| w(F_o^2 - F_c^2)^2 \right| / \sum \left| w(F_o^2)^2 \right| \right]^{1/2}$, where

$w = 1/[\sigma^2 F_o^2 + (AP)^2 + BP]$, with $P = (F_o^2 + 2F_c^2)/3$ and weight coefficients A and B.

2.3. Single crystal X-ray diffraction

The X-ray intensity measurements were carried out on a Bruker Apex CCD area detector diffractometer using a graphite-monochromated Mo-Kα (0.71073 Å) radiation source. A colorless block crystal of $(HIm)_2Hg_3Cl_8$ and a yellow needle-like crystal of $(HIm)HgI_3$ were cut into suitable sizes (less than 0.3 mm in all dimensions) inside Paratone N oil. The crystals were then cooled to the data collection temperature of 100(2) K under a cold stream of nitrogen. Preliminary unit cell determination and subsequent structure refinement were carried out using the APEX3 software package [25]. SAINT [26] and SADABS programs [27] were employed for frame integration and absorption correction using the multi-scan method, respectively. The structure solution and refinements were performed using SHELXS and SHELXL programs [28,29]. Hydrogen atom positions were determined by geometry. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and structure refinement results are provided in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are given in Tables 2 and 3. Relevant interatomic distances and bond angles are summarized in Tables 4 and 5. Crystallographic Information Files (CIF) for these new compounds have been deposited in The Cambridge Crystallographic Data Centre (CCDC) and can be found under deposition numbers 1,576,893 for $(HIm)_2Hg_3Cl_8$ and 1,576,892 for $(HIm)HgI_3$.

2.4. UV−Vis diffuse reflectance

UV−vis diffuse reflectance was measured on crushed single crystals employing a high-resolution UV−Vis−NIR spectrometer (PerkinElmer LAMBDA 750) equipped with 100 mm diameter integrating sphere attachment for measuring powder samples. The diffuse reflection