Disphenoidal Zero-Dimensional Lead, Tin, and Germanium Halides: Highly Emissive Singlet and Triplet Self-Trapped Excitons and X-ray Scintillation

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ABSTRACT: Low-dimensional metal halides have been researched as optoelectronic materials for the past two decades. Zero-dimensional halides of ns\(^2\) elements (Sn, Pb, Sb) have recently gained attention as highly efficient broadband light emitters. These compounds comprise discrete metal halide centers, isolated by bulky organic cations. Herein, we report isostructural halide complexes of Ge(II), Sn(II), and Pb(II) with a 1-butyl-1-methylpiperidinium cation (Bmpip), featuring unusual disphenoidal coordination with a highly stereoactive lone pair. Spectrally broad, bright emission from highly localized excitons, with quantum efficiencies of up to 75%, is observed in blue to red spectral regions for bromides (for Pb, Sn, and Ge, respectively) and extends into the near-infrared for Bmpip\(_2\)SnI\(_4\) (peak at 730 nm). In the case of Sn(II) and Ge(II), both singlet and triplet excitonic emission bands have been observed. Furthermore, Bmpip\(_2\)SnBr\(_4\) and Bmpip\(_2\)PbBr\(_4\) exhibit X-ray-excited luminescence (radio luminescence) with brightness being commensurate with that of a commercial inorganic X-ray scintillator (NaI:Tl).

Diverse metal halides are increasingly recognized for their potential as versatile classical light sources (lighting, displays\(^1\)) and quantum light emitters (single-photon sources, entangled photon).\(^2\) Recent years have seen a surge of reports on lead and tin halide perovskites, whose atomistic structure comprises corner-sharing metal halide octahedra, leading to a delocalized electronic structure with large Wannier-type excitons characterized by small binding energies (10–40 meV): the attributes most suited for light harvesting purposes (solar cells, photodetectors).\(^3\) For a related but rather orthogonal purpose—enhancing the light emissivity—engineering the electronic dimensionality for controlling the formation and radiative recombination of the excitons had been a major thrust. This can be accomplished either morphologically, that is, by tuning the crystal size in one or more dimensions (e.g., nanocrystals),\(^4\) or structurally, i.e., by controlling the connectivity of metal halide polyhedral anions.\(^5\) As the structural dimensionality decreases, so also does the electronic structure, favoring the formation of the smaller, strongly bound excitons already at room temperature (RT), starting from 2-dimensional (2D) compounds.\(^6\) Electronic localization culminates in 0D metal halides: a photoexcited electron–hole pair resides within one anionic entity, and its formation and subsequent relaxation can be described as electronic transitions in the central metal atom,\(^7\) perturbed by the field of halide ligands. Luminescence from 0D metal halides is typically characterized by large Stokes shifts and broad emission line widths: both features in agreement with the strong coupling of the excitons to multiple phonons (e.g., structural distortions of the metal halide anions). Herein, we report on highly luminescent 0D hybrid organic—inorganic germanium(II), tin(II), and lead(II) bromides and tin(II) iodide, comprising MX\(_4^−\) anions of a rare disphenoidal geometry surrounded by 1-butyl-1-methylpiperidinium (Bmpip) cations. Having homologue series of isostructural Bmpip\(_2\)MBr\(_4\) allowed for assessment of the effect of the central metal, in particular, stereoactivity of its lone pair. These compounds also exhibit pronounced singlet exciton emission at RT, in addition to triplet emission (also known as self-trapped excitons). All presented compounds are bright broadband emitters in the visible spectral region, with photoluminescence quantum yields (PL QYs) of up to 75%. PL of Bmpip\(_2\)SnI\(_4\) extends into the near-infrared region.

Bmpip\(_2\)SnBr\(_4\) and Bmpip\(_2\)PbBr\(_4\) also exhibit intense emission under X-ray excitation, motivating further work on the exploration of low-dimensional metal halides for X-ray scintillation.

The electronic spectra of ns\(^2\) ions in solid matrices and solutions have been widely investigated over the past century. Singlet and triplet bound excitons, as well as emission from defects, were observed at low temperatures in, for instance,
PbCl$_2$, PbBr$_2$, PbF$_2$, and SnCl$_2$. Such ns$^2$ metals possess a lone pair that can be either inert or stereochemically active, depending on the efficiency of s- and p-orbital mixing. The mixing of states for the Pb lone pair is recognized to give rise to important phenomena in lead halide perovskites, including defect tolerance. However, the toxicity of lead motivates the quest for benign alternatives such as its electronic analogues—tin and germanium.

In general, organic−inorganic metal halide hybrids achieve greater structural versatility due to the structural engineerability of the organic moiety: its bulkiness and symmetry dictate the anionic framework of the structure. Bmpip is an example of a bulky cation with weak intermolecular interactions (lack of hydrogen-bonding or π-stacking capabilities), explaining the low melting points of the obtained compounds (Table S1). Bmpip$_2$PbBr$_4$, Bmpip$_2$SnBr$_4$, Bmpip$_2$GeBr$_4$, and Bmpip$_2$SnI$_4$ were synthesized from precursor solutions of metal(II) halide and BmpipX in organic solvents and have been structurally studied by single-crystal and powder X-ray diffraction (Figure S1; space group, C$_2$/c; see Tables S2−S5 for further details). Figure 1a illustrates the unit cell. The coordination of lead(II) with C$_2$v symmetry of the ns$^2$ ion had been previously described in the systems with bulky phosphonium salts. It results from the deviation from Td tetrahedral symmetry due to HOMO stabilization. For the tin(II) bromide anion, a similar coordination has been recently reported.

All three complexes exhibit broadband luminescence at room temperature (RT) upon excitation with UV light (Figure 1c, Table S14 and Figure S2). While the excitation bands of all compounds are peaked at similar energies (ca. 3.5 eV), the low PL QY of 24%, and Bmpip$_2$GeBr$_4$ display the lowest PL QY below 1% (Table S14).

Fundamentally important is the observation of both singlet and triplet emission bands in all Bmpip$_2$MBr$_4$, well-pronounced for Sn and Ge at RT, when sufficiently high-energy photons are used for excitation (above 3.9 eV, Figure 2a−c, Figure S4). The blue emission band (singlet) can be attributed to the $^1P_1 \rightarrow ^1S_0$ transition, whereas the lower-energy emission band can be attributed to the $^3P_n \rightarrow ^1S_0$ transitions (where n can be 0, 1, 2) (Scheme S1). For example, in Bmpip$_2$SnBr$_4$, this assignment is corroborated by emission decay times (Figure S5) of $\tau = 10$ ns (singlet) and $\tau = 4 \mu$s (triplet). Each singlet or triplet band in Bmpip$_2$GeBr$_4$ consists of two components (Figure S5). Cooling from 300 to 150 K resulted in the disappearance of the shorter component (Figures S6a and S7, streak-camera experiments). This could be explained by the shorter component of the decay originating from the efficient exciton coupling to a phonon mode activated above 150 K. For Bmpip$_2$SnBr$_4$, no such pronounced temperature effect is observed (Figures S6b and S8). Both compounds exhibit a large Stokes shift (ca. 1.7 eV) for the dominant triplet emission.

Figure 1. (a) Crystal structure of Bmpip$_2$MBr$_4$ viewed along the [110] crystallographic direction. (b) Disphenoidal coordination of lead, tin, and germanium, demonstrating a different degree of repulsion between axial bromide atoms and the lone pair, which occupies one of the equatorial positions. (c) RT spectra of PL (color-shaded) and PLE for Bmpip$_2$PbBr$_4$ (blue), Bmpip$_2$SnBr$_4$ (red), and Bmpip$_2$GeBr$_4$ (yellow) and (inset) a photograph of Bmpip$_2$PbBr$_4$ and Bmpip$_2$SnBr$_4$ under UV excitation.

Figure 2. (a−c) PL spectra of Bmpip$_2$MBr$_4$ at different excitation wavelengths, showing both singlet and triplet emission bands for Sn, Ge (RT), and Pb (inset, 10 K) cases. (d) Single coordinate diagram demonstrating the accessibility of both singlet and triplet bound excitonic states in Bmpip$_2$MBr$_4$. LD, lattice distortion; ISC, intersystem crossing.
In the analogous Pb compound, the Stokes shift is almost two times smaller (ca. 0.9 eV), and there is one pronounced emission band at RT, centered at 470 nm. The emission decay function consists of two very distinct components: \( \tau = 230 \text{ ps} \) and \( \tau = 66 \text{ ns} \) (Figure S5). The faster emission becomes dominant upon cooling from 300 to 10 K (Figure S9). In addition, the streak-camera captures the emergence of a fast, sub-100 ps singlet emission at 435 nm, coexisting with the 470 nm peak (Figure S10). The optical properties of all three compounds can be explained on the basis of the ns\(^2\) free ion energy levels (Figure 2d). For Ge and Sn, the Jahn–Teller (JT) perturbation of the ground state contributes the most to the splitting of the energy levels. For the Pb ion, however, spin–orbit coupling (SOC) perturbation is much stronger than JT; this interplay is well-known for ns\(^2\)-metal centered emission.\(^{13}\) This results in a smaller Stokes shift as well as more localized emission centers, and large emission bands (Figure S13). The electronic density of states corroborates that the stereoactivity of the lone pair. In the case of Sn, s-states near the Fermi level are broader and better mixed with Br p-states. The mixing is additionally mediated by empty M p-states. This corroborates the assumption that the lone pair is more active in the case of Sn. The lone pair stereoactivity manifests itself also through the repulsion with the axial halide atoms, adjusting the bond angles (Tables S6–S13).

In the excited state, the sp-mixing of the HOMO no longer stabilizes the lone pair: the energy gain of HOMO stabilization is compensated by the energy of the electron promoted to the LUMO. For similar Sb(III) chloride complexes in acetonitrile, Nikol et al. have argued that the structure, therefore, relaxes toward \( T_d \) symmetry upon excitation.\(^{15}\) The energy loss associated with this change is reflected in the Stokes shift. We have calculated the excited-state geometry using the PBE functional and unrestricted Kohn–Sham approach with triplet multiplicity as implemented in the cp2k code. The results suggest that in the excited state the structure changes from \( C_{2v} \) symmetry to another lower symmetry derivative of \( T_d \), e.g., \( D_{2d} \) (Figure 3g). In this symmetry, the gain in energy from the promotion of an electron from the HOMO to LUMO overcomes the HOMO stabilization in the \( C_{2v} \) geometry.

The scope of applications for luminescent zero-dimensional metal halides has thus far been limited to solid-state lighting, exploiting their broadband emission.\(^{7b,16}\) Herein, we outline yet another perspective application—X-ray detection by scintillation—that harnesses specific advantages of these compounds; namely, high X-ray absorptivity by heavy elements, highly localized emission centers, and large emission Stokes shifts for efficient light out-coupling. As a showcase example, blue-emissive Bmpip\(_2\)PbBr\(_4\) and red-emissive Bmpip\(_2\)SnBr\(_4\) has been compared with the typical commercial NaI:Tl scintillator. In such an X-ray excited PL comparative experiment, about one half of a gram of Bmpip\(_2\)PbBr\(_4\) and Bmpip\(_2\)SnBr\(_4\) was pressed into pellets (13 mm × 2.5 mm, see the Supporting Information) and illuminated with a 50 kV Ag X-ray tube. The thickness of such pellets is estimated to ensure nearly complete absorption of X-rays, based on calculated X-ray absorptivities of these materials (Figure S14).

**Figure 3.** (a–c) Atomic-orbital-projected density of states for M s, M p, and Br p contributions in Bmpip\(_2\)MBr\(_4\) (M = Ge, Sn, Pb). (d–f) Respective electron density maps at the top of the valence band (ground state), plotted between 0 and \(-0.011 \text{ e/Å}^3\). (g) Schematics for the ground-state and excited-state geometries.
transmittance images (Figure S15) convey that the pellets do absorb more than 90% of the incident X-ray photons. The radioluminescence spectra of NaI:Tl, Bmpip2PbBr4, and Bmpip2SnBr4 excited by a 50 kV Ag tube and corrected for background and spectral sensitivity of the system exhibit similar intensities (Figure 4a,b). A visual comparison of the studied materials under daylight, UV light, and X-rays is presented in Figure 4c–e. The noteworthy performance of Bmpip2MBr4 compounds warrants further detailed investigations. Future practical avenues include the engineering of the optically homogeneous medium, such as sufficiently large single-crystals or fine dispersions in polymers. These forms of low-dimensional metal halides will allow for accurate measurements of the radioluminescence quantum yields.

In conclusion, Bmpip2MBr4 (M = Ge, Sn, Pb) compounds feature unusual dispheonidal coordination. Ge and Sn compounds display both singlet and triplet exciton emission. The computational study emphasized the contribution of the lone pair. In the practical context, Pb and Sn compounds have been shown to be potent X-ray fluorophores, comparable to NaI:Tl. Future work should focus on the systematic exploration of such metal halides as scintillators for hard radiation detection.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b02365.

Crystallographic data for C20H44N2PbBr4 (CIF)

Crystallographic data for C20H44N2GeBr4 (CIF)

Crystallographic data for C20H44SnBr4 (CIF)

Methods and additional figures including XRD patterns, photoluminescence measurement spectra, 2D PL vs PLE map, luminescence decay, temperature-dependent emission decay curves, time-resolved emission, energy level diagram, total energy comparison, DOS comparison, X-ray absorbance vs photon energy, and transmission image (PDF)

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