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

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Supporting Information

ABSTRACT: Low-dimensional metal halides have been researched as optoelectronic materials for the past two decades. Zero-dimensional halides of ns² 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-methyl-piperidinium 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 Bmpip2SnI₄ (peak at 730 nm). In the case of Sn(II) and Ge(II), both singlet and triplet excitonic emission bands have been observed. Furthermore, Bmpip2SnBr₄ and Bmpip2PbBr₄ exhibit X-ray-excited luminescence (radioluminescence) 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 MX₄⁻² anions of a rare disphenoidal geometry surrounded by 1-butyl-1-methyl-piperidinium (Bmpip) cations. Having homologue series of isostructural Bmpip₂MBr₄ 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 Bmpip₂SnI₄ extends into the near-infrared region.

Bmpip₂SnBr₄ and Bmpip₂PbBr₄ 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 ns² 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,
PbCl₂, PbBr₂, PbF₂, and SnCl₂. Such ns² 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). Bmpip₂PbBr₄, Bmpip₂SnBr₄, Bmpip₂GeBr₄, and Bmpip₂SnI₄ 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, C2/c; see Tables S2–S5 for further details).

Figure 1a illustrates the unit cell. The coordination of lead(II) with C₂ᵥ symmetry of the ns² 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 PL band of Bmpip₂PbBr₄ centers in the blue (470 nm), and that of germanium or tin counterparts shifts to red (peaks at 660–670 nm). The emission from the germanium complex is broader, likely due to stronger vibronic coupling. Bmpip₂SnI₄ is further shifted to the near-infrared (peak at 730 nm, Figure S3).

Bmpip₂SnBr₄ exhibits the highest PL QY of 75%, Bmpip₂PbBr₄ 24%, and Bmpip₂GeBr₄ display the lowest PL QY below 1% (Table S14). Fundamentally important is the observation of both singlet and triplet emission bands in all Bmpip₂MBr₄, 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 ¹P₁ → ¹S₀ transition, whereas the lower-energy emission band can be attributed to the ³Pₙ → ¹S₀ transitions (where n can be 0, 1, 2) (Scheme S1). For example, in Bmpip₂SnBr₄, this assignment is corroborated by emission decay times (Figure S5) of τ = 10 ns (singlet) and τ = 4 μs (triplet). Each singlet or triplet band in Bmpip₂GeBr₄ 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 Bmpip₂SnBr₄ 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.
than JT; this interplay is well-known for ns2-metal centered the splitting of the energy levels. For the Pb ion, however, (JT) perturbation of the ground state contributes the most to energy levels (Figure 2d). For Ge and Sn, the Jahn emission.13 This results in a smaller Stokes shift as well as more (Figure S13). The electronic density of states corroborates that in monoxides and monochalcogenides of Ge, Sn, and Pb.14

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: $\tau = 230$ ps and $\tau = 66$ 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 ns2 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 ns2-metal centered emission.13 This results in a smaller Stokes shift as well as more efficient mixing of 1P and 3P states for a heavier metal (Pb, Bi). In addition, the slower component of the emission at 470 nm ($\tau = 66$ ns) in Bmpip2PbBr4 can be attributed to the 3P0 → 1S0 transition, which becomes allowed only for Pb due to singlet/triplet mixing.

We have investigated electronic structures of the synthesized compounds on the density functional theory (DFT) level utilizing the Perdew–Burke–Ernzerhof (PBE) functional as implemented in the Vienna ab initio simulation package (VASP), initially without including SOC (Figure 3). When SOC and hybrid DFT functionals have been added, the qualitative picture remains the same (Figures S11 and S12). The electronic structure of Bmpip2MBr4 complexes is highly localized on MBr4 fragments, seen as flat electronic bands (Figure S13). The electronic density of states corroborates that the stereochemical activity of the lone pair depends not only on the metal but also on the halide. This dependence on both metal and anion has been previously theoretically investigated in monoxides and monochalcogenides of Ge, Sn, and Pb.14

Upon examining the projected density of states (PDOS, Figure 3), the main contribution of the metal s-states can be found below −5 eV. The contribution at the top of the valence band, around 0 eV, is smaller. This contribution determines the stereoactvity 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 $T_2$ 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 $C_{3v}$ 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 $C_{3v}$ 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 Bmpip2PbBr4 and red-emissive Bmpip2SnBr4 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 Bmpip2PbBr4 and Bmpip2SnBr4 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). X-ray

Figure 3. (a–c) Atomic-orbital-projected density of states for M s, M p, and Br p contributions in Bmpip2MBr4 (M = Ge, Sn, Pb). (d–f) Respective electron density maps at the top of the valence band (ground state), plotted between 0 and 0−0.011 e/Å3. (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, Bmpip$_2$PbBr$_4$, and Bmpip$_2$SnBr$_4$ 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

Figure 4. (a) X-ray fluorescence spectra under 50 kV Ag tube irradiation. (b) The normalized total amount of photons comparison with the same X-ray excitation source. NaI:Tl commercial scintillator, Bmpip$_2$PbBr$_4$, pellet, and Bmpip$_2$SnBr$_4$ pellet under (c) ambient light, (d) UV irradiation (365 nm), and (e) X-ray irradiation with a Rayme DG-073B-DC X-ray tube as an excitation source (70 kV, 1 mA, 1.8 s exposure time).

studied materials under daylight, UV light, and X-rays is presented in Figure 4c–e. The noteworthy performance of Bmpip$_2$MBr$_4$ 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, Bmpip$_2$MBr$_4$ (M = Ge, Sn, Pb) compounds feature unusual disphenoidal 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 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 from the ACS Publications website at DOI: 10.1021/jacs.9b02365.

Crystallographic data for C$_{36}$H$_{44}$N$_3$GeBr$_4$ (CIF)
Crystallographic data for C$_{36}$H$_{44}$N$_3$PbBr$_4$ (CIF)
Crystallographic data for C$_{36}$H$_{44}$N$_3$SnBr$_4$ (CIF)

Methods and additional features 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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Notes
The authors declare no competing financial interest.

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