Hybrid Charge-Transfer Semiconductors: (C7H7)SbI4, (C7H7)BiI4, and Their Halide Congeners

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Submitted date: 10/03/2019 • Posted date: 11/03/2019
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The family of hybrid metal-halide semiconductors (C7H7)MX4 (M = Bi3+, Sb3+; X = Cl−, Br−, I−) was synthesized. The optical and electronic properties of the new compounds were elucidated, revealing electronic band gaps that span the visible region. The tropylium cations stack into columns separated by chains of edge-sharing M-X octahedra to yield a low dimensional crystal structure with electron and hole charge carriers confined to the organic and inorganic components, respectively.

File list (1)

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Hybrid Charge-Transfer Semiconductors: (C₇H₇)SbI₄, (C₇H₇)BiI₄, and Their Halide Congeners

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Abstract.

Hybrid metal halides yield highly desirable optoelectronic properties and offer significant opportunity due to their solution processability. This contribution reports a new series of hybrid semiconductors, (C₇H₇)MX₄ (M = Bi³⁺, Sb³⁺; X = Cl⁻, Br⁻, I⁻), that are composed of edge-sharing MX₆ chains separated in space by π-stacked tropylium (C₇H₇⁺) cations; the inorganic chains resemble the connectivity of BiI₃. The Bi³⁺ compounds have blue shifted optical absorptions relative to the Sb³⁺ compounds that span the visible and near-IR region. Consistent with observations, DFT calculations reveal that the conduction band is composed of the tropylium cation and valence band primarily the inorganic chain: a charge-transfer semiconductor. The band gaps for both Bi³⁺ and Sb³⁺ compounds decrease systematically as a function of increasing halide size. These compounds are a rare example of charge transfer semiconductors that also exhibit efficient crystal packing of the organic cations, thus providing an opportunity to study how structural packing affects optoelectronic properties.

Introduction.

Hybrid perovskites and their derivatives have emerged as highly efficient solution processable semiconducting materials, making them attractive for numerous applications such as light-emitting devices, photovoltaics, photodetectors, and radiation detectors.¹⁻⁸ These compounds combine many of the desirable properties of traditional inorganic semiconductors such as high carrier mobilities and absorption coefficients with the processability of organic electronics.⁶,⁹⁻¹⁰ However, many questions remain as to how the inorganic framework can influence or couple to the electronic behavior of the organic components. In the realm of hybrid perovskites, much focus has been on compounds containing small organic cations such as methylammonium or formamidinium.¹¹⁻¹⁵ Unlike smaller cations, organic cations with delocalized electrons can have electronic states near the valence and conduction band of the inorganic lattice, allowing for charge-transfer from the inorganic to organic subunits.
The templating of organic molecules within a complex crystal structure by inorganic frameworks remains underexplored. Such templating may give rise to properties from the cooperative behavior (e.g., electrical transport) not found in simple packings of the molecules,\textsuperscript{16} and spatial charge separation within the bulk of the material (e.g., (Pb\textsubscript{2}I\textsubscript{4})·(H\textsubscript{2}DPNDI)·(H\textsubscript{2}O)·(NMP)).\textsuperscript{17} A great diversity of compounds appears in the tetrathiofulvalene (TTF) based charge-transfer salts (e.g., TTF\subscript{3}SnCl\textsubscript{6}, (TTF)BiI\textsubscript{4}, (TTF)PbI\textsubscript{4}),\textsuperscript{18-21} in which the inorganic rarely shows spatial connectivity. A recent study has shown that the connectivity of the inorganic subunit can be modified in the compounds (TMP)[BiBr\textsubscript{3}], (TMP)[BiCl\textsubscript{3}], and (TMP)\textsubscript{1.5}[Bi\textsubscript{2}I\textsubscript{2}Cl\textsubscript{2}] (TMP = N,N,N′,N′-tetramethylpiperazine) by incorporation of multiple halides, showing that structural modification can be achieved, although the organic cation is not optoelectronically active.\textsuperscript{22} One of the few other reports describing hybrid metal halides with conjugated cations used the N-heterocyclic cations N-methylpyridinium and N-ethylpyridinium in specific molar ratios relative to BiI\textsubscript{3} to synthesize new structures with differing degrees of inorganic connectivity, such as the quasi-two-dimensional [Bi\textsubscript{3}I\textsubscript{10}]\textsuperscript{−} sub-structural unit that is bridged by neighboring iodine atoms.\textsuperscript{23} The layered perovskites, A\textsubscript{2}PbX\textsubscript{4}, where X is a halogen and A is an organic cation, host many conjugated organic molecules (e.g., (AEQT)PbI\textsubscript{4});\textsuperscript{24,25} though nearly all compounds rely on an ammonium salt to tether the molecule to the inorganic lattice. The diversity of chemical functionalities in conjugated molecules and the role that the inorganic lattice plays in templating such molecules beg to be expanded.

Tropylium, (C\textsubscript{7}H\textsubscript{7}\textsuperscript{+}), provides opportunities for the discovery of materials with optoelectronically-active cations at the frontier electronic states. The dielectric environment has been shown to have a profound impact on the charge-transfer based optical properties of simple tropylium salts.\textsuperscript{26} In our previous contribution, (C\textsubscript{7}H\textsubscript{7})PbI\textsubscript{3} and (C\textsubscript{7}H\textsubscript{7})\textsubscript{2}SnI\textsubscript{6} both form in solution and show activity of the π*-states derived from tropylium in the overall optical properties.\textsuperscript{27} It is therefore necessary to investigate other compounds containing cations of different structural and electronic character in order to find materials that show strong inorganic/organic coupling to establish structure-property relationships and the discovery of new emergent behavior.

Here, we report the synthesis and photophysical characterization of the new series of isostructural compounds, (C\textsubscript{7}H\textsubscript{7})MX\textsubscript{4} (M = Bi\textsuperscript{3+}, Sb\textsuperscript{3+}; X = Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}), that incorporates the tropylium cation into the structure with efficient π-stacking. We develop a simple synthesis that allows for growth of large single crystals across the series of compounds. Single crystal X-ray diffraction reveals edge-sharing [MX\textsubscript{4}] chains separated in space by π-stacked tropylium cations. UV-Visible diffuse reflectance spectroscopy reveals optical gaps that span the entire visible spectrum, from 3 eV for (C\textsubscript{7}H\textsubscript{7})BiCl\textsubscript{4} to 1.55 eV for (C\textsubscript{7}H\textsubscript{7})SbI\textsubscript{4}. Density functional calculations illustrate that halide p-orbitals comprise the valence band; π* orbitals of the tropylium cation make up the conduction band. The highly-ordered packing of the organic cations along
with the 1-D inorganic chains may result in enhanced charge transport, thus making them attractive materials for further exploration.

**Experimental.**

**Synthesis.**

(C₇H₇)BiCl₄. A 0.200 M Bi³⁺ stock solution in HCl was first made by dissolving 0.261 g (1.00 mmol) of BiOCl into 5 mL of concentrated HCl under magnetic stirring, resulting in a clear, colorless solution. After complete dissolution, tropylium tetrafluoroborate (0.356 g, 2.000 mmol) was dissolved into 1 mL of concentrated HCl and then transferred to the Bi³⁺ stock solution resulting in precipitation of a white microcrystalline powder. 2 mL of acetic acid was added as an antisolvent to increase yield. The solid was then filtered and washed with acetic acid and hexanes. Yield: 0.249 g (0.565 mmol); 56.5% based on Bi³⁺ content.

(C₇H₇)BiBr₄. A 0.200 M Bi³⁺ stock solution in HBr was first made by dissolving 0.261 g (1.00 mmol) of BiOCl into 5 mL of concentrated HBr under magnetic stirring, resulting in a yellow solution. After complete dissolution, tropylium tetrafluoroborate (0.356 g, 2.000 mmol) was dissolved into 1 mL of concentrated HBr and then transferred to the Bi³⁺ stock solution resulting in precipitation of a yellow microcrystalline powder. 2 mL of acetic acid was added as an antisolvent to increase yield. The solution was then allowed to stir for 15 min. The solid was then filtered and washed with acetic acid and hexanes. Yield: 0.385 g (0.625 mmol); 62.5% based on Bi³⁺ content.

(C₇H₇)BiI₄. A 0.200 M Bi³⁺ stock solution in stabilized HI (57 wt% in H₂O, <1.5% H₃PO₄) was first made by dissolving 0.261 g (1.00 mmol) of BiOCl into 5 mL of stabilized HI under magnetic stirring, resulting in a bright red solution. After complete dissolution, tropylium tetrafluoroborate (0.356 g, 2.000 mmol) was dissolved into 1 mL of stabilized HI and then transferred to the Bi³⁺ stock solution resulting in precipitation of a dark red microcrystalline powder. 2 mL of acetic acid was added as an antisolvent to increase yield. The solution was then allowed to stir for 15 min. The solid was then filtered and washed with acetic acid and hexanes. Yield: 0.552 g (0.687 mmol); 68.7% based on Bi³⁺ content.

(C₇H₇)SbCl₄. A 0.200 M Sb³⁺ stock solution in HCl was first made by dissolving 0.292 g (1.00 mmol) of Sb₂O₃ into 5 mL of concentrated HCl under magnetic stirring, resulting in a clear colorless solution. After complete dissolution, tropylium tetrafluoroborate (0.356 g, 2.000 mmol) was dissolved into 1 mL of concentrated HCl and then transferred to the Sb³⁺ stock solution resulting in precipitation of a yellow microcrystalline powder. 2 mL of acetic acid was added as an antisolvent to increase yield. The solution
was then allowed to stir for 15 min. The solid was then filtered and washed with acetic acid and hexanes to remove impurities. Yield: 0.212 g (0.602 mmol); 60.2% based on Sb\(^{3+}\) content.

\((C_7H_7)SbBr_4\). A 0.200 M Sb\(^{3+}\) stock solution in HBr was first made by dissolving 0.292 g (1.00 mmol) of Sb\(_2\)O\(_3\) into 5 mL of concentrated HBr under magnetic stirring, resulting in a yellow solution. After complete dissolution, tropylium tetrafluoroborate (0.356 g, 2.000 mmol) was dissolved into 1 mL of concentrated HBr and then transferred to the Sb\(^{3+}\) stock solution resulting in precipitation of an orange microcrystalline powder. 2 mL of acetic acid was added as an antisolvent to increase yield. The solution was then allowed to stir for 15 min. The solid was then filtered and washed with acetic acid and hexanes to remove impurities. Yield: 0.340 g (0.645 mmol); 64.5% based on Sb\(^{3+}\) content.

\((C_7H_7)SbI_4\). A 0.200 M Sb\(^{3+}\) stock solution in stabilized HI (57 wt% in H\(_2\)O, <1.5% H\(_3\)PO\(_2\)) was first made by dissolving 0.292 g (1.000 mmol) of Sb\(_2\)O\(_3\) into 5 mL of stabilized HI under magnetic stirring, resulting in a bright red solution. After complete dissolution, tropylium tetrafluoroborate (0.356 g, 2.000 mmol) was dissolved into 1 mL of stabilized HI and then transferred to the Sb\(^{3+}\) stock solution resulting in precipitation of a black microcrystalline powder. 2 mL of acetic acid was added as an antisolvent to increase yield. The solution was then allowed to stir for 15 min. The solid was then filtered and washed with acetic acid and hexanes to remove impurities. Yield: 0.514 g (0.715 mmol); 71.5% based on Sb\(^{3+}\) content.

**Molar Solubility Studies.** Molar solubilities were determined by adding ~0.050 g of each compound to a vial followed by titrating with the respective hydrohalic acid until completely dissolved. Results and details of these experiments are provided in Table S1.

**Single Crystal Growth and Optimization.** Single crystals of the compounds were grown by dissolving the synthesized micro-crystalline powders in their respective hydrohalic acid, heating to boiling, and slow cooling to room temperature. The optimal concentration for each compound \((C_7H_7)MX_4\) (M = Bi\(^{3+}\), Sb\(^{3+}\); X = Cl\(^-\), Br\(^-\), I\(^-\)) was determined based on the molar solubility studies. In general, approximately 50% molar excess of the room temperature molar solubility leads to large crystals up to ~2 mm in length after slow cooling the solution from boiling, then allowing the solution to stand at room temperature for ~24 h.

**Powder X-ray Diffraction.** Laboratory powder X-ray diffraction data were collected on a Bruker D8 Discover DaVinci Powder X-ray Diffractometer using Cu K\(\alpha\) radiation and a Lynxeye XE-T position-sensitive detector. Samples were prepared on a zero-diffraction Si wafer by sprinkling the microcrystalline powder directly onto the substrate. TOPAS6 was used for Rietveld and Pawley refinements of the data. The data were refined using two methods: first using idealized organic cation positions for use in DFT calculations, and the second using a rigid body refinement of the tropylium cation. For the latter, the organic cations were located through simulated annealing of rigid bodies. Initial refinements of parameters relevant
to the inorganic framework, background, and profile terms were performed with C$_7$H$_7^+$ in an idealized position. We then constructed a z-matrix consisting of the seven-membered carbon ring, requisite hydrogen atoms, and two dummy atoms at the center of the ring and 90 degrees from the center of the ring to preserve symmetry. Bond lengths, bond angles and dihedral angles were determined by relaxation of DFT-calculated forces (using GAMESS;\textsuperscript{28} minimal basis set and the B3LYP hybrid functional). After allowing the position and orientation of the rigid body to refine, parameters relevant to the inorganic framework, background, and profile terms were refined again using a least-squares refinement. The process was iterated until changes in statistics and visual fit were negligible.

**Single Crystal X-ray Diffraction.** Laboratory Singe Crystal X-ray diffraction data for (C$_7$H$_7$)BiI$_4$ was collected at room temperature using a Bruker D8 Quest ECO diffractometer equipped with a microfocus Mo K$\alpha$ radiation source and Photon 50 CMOS half-plate detector. Single crystals were mounted onto a MiTeGen tip using paratone oil. Bruker SAINT was used for integration and scaling of collected data and SADABS was used for absorption correction.\textsuperscript{29} Starting models for the compounds were generated using the intrinsic phasing method in SHELXT.\textsuperscript{30} SHELXL2014 was used for least-squares refinement.\textsuperscript{31} The PLATON suite was used to determine higher symmetry and for structural validation.\textsuperscript{32} Structural details of the refinement and crystallographic parameters are listed in Table 1; Atomic positions are provided in the Supporting Information, Tables S2 and S3.

**DFT calculations.**

To gain insight in to the electronic states of all compounds, density functional theory calculations within the plane-wave code VASP (Vienna Ab initio Simulation Package) were performed.\textsuperscript{33-34} To treat the effects of exchange and correlation, the PBEsol functional, a version of the Perdew, Burke and Erzorhof (PBE) functional revised for solids was used.\textsuperscript{35-36} Valence-core interactions were described with the projector augmented wave method. The experimental crystals structures of all compounds were relaxed in the Niggli-reduced cell by allowing all ions to move and allowing the unit cell shape and size to vary; convergence was achieved when forces on all the ions were less than 0.001 eV Å$^{-1}$. Relaxations of the ionic positions were conducted using 8x6x6 k-point meshes generated using the Monhorst-Pack scheme and using an energy cutoff of 530 eV.

Densities of states (DOS) and band structures were calculated with explicit inclusion of spin orbit coupling (SOC). DOS were calculated using 10x8x8 k-point meshes; the band structure was calculated across two main paths across high symmetry points as defined by Setyawan and Curtarolo.\textsuperscript{37} DOS and band structures were visualized using the sumo package.\textsuperscript{38} Band-decomposed charge densities were computed from the highest occupied and lowest unoccupied bands and visualized using VESTA.\textsuperscript{39}
Optical Diffuse Reflectance Spectroscopy. UV-visible diffuse reflectance spectroscopy was performed on powdered samples of each compound diluted to ~10 wt % with BaSO₄, using BaSO₄ as a baseline. Spectra were acquired using a Thermo Nicolet Evolution 300 spectrophotometer with a Praying Mantis mirror setup from λ = 200 to 1100 nm at a scan rate of 240 nm/min.

Photoluminescence Spectroscopy. Bulk phase photoluminescence spectra were collected using a Horiba Jobin-Yvon Fluorolog-3 Spectrofluorometer from 375 nm to 800 nm at room temperature. Powdered samples were mounted in a quartz tube and then loaded into an evacuated quartz dewar for all samples.

Thermal Gravimetric Analysis. Thermal analysis of all compounds was performed on a TA TGA Q500 Thermogravimetric analyzer from 30 °C to 450 °C at a ramp rate of 10°C per minute. Thermal decomposition curves are shown in Figure S1.

Infrared Spectroscopy. Fourier transform infrared spectroscopy (FT-IR) was performed on powdered samples on a Thermo Nicolet iS50 FT-IR spectrometer from 1000 to 4000 cm⁻¹. Infrared spectra comparing tropylium tetrafluoroborate and each compound are shown in Figure S2.

Results and Discussion.


The synthesis of the title compounds is achieved by generating solvated Bi³⁺ or Sb³⁺ cations in the respective hydrohalic acid followed by addition of a solution containing dissolved tropylium tetrafluoroborate in the hydrohalic acid. This leads to spontaneous precipitation of the targeted compounds as microcrystalline powders with colors ranging across the visible spectrum (Figure 1(a-f)). Dissolving tropylium tetrafluoroborate in the necessary hydrohalic acid prior to addition to the Bi³⁺/Sb³⁺ solution ensures the cation remains protonated throughout the reaction. The starting reagents BiOCl and Sb₂O₃ readily dissolve into each acidic media with minimal heating. We find that using a 0.2 M [M³⁺] solution is ideal for targeting these compounds as it allows for moderate to high yields and minimizes potential precipitation of unwanted side products, such as BiX₃ or SbX₃ (X = Cl, Br, I) phases. The experimentally determined molar solubilities as seen in Table S1 range from ~0.008 M for (C₇H₇)SbI₄ to ~0.128 M for (C₇H₇)BiCl₄. The solubilities of the compounds in their respective hydrohalic acid decreases as a function of increasing halogen size for both bismuth and antimony-containing compounds resulting in slightly lower product yields for the chlorides and bromides. The Sb³⁺-compounds have lower solubilities than the Bi³⁺-compounds for each halide, again leading to lower yields for the latter than the former for each respective halide. Nonetheless, these molar solubilities are well below the starting molar concentration (0.2 M) of the trivalent metal in our synthesis, ensuring precipitation of the product for each compound. The addition of
excess tropylum (2:1 molar excess relative to $M^{3+}$) ensures that each metal cation has sufficient organic cation present; we have not observed any other potential phases with higher C$_7$H$_7^+:M^{3+}$ ratios, ensuring the only product formed are those targeted; use of lower ratios leads to a decreased yield of the targeted phases. The addition of excess C$_7$H$_7^+$ cation further lowers the molar solubilities of the targeted products via the common ion effect, leading to higher yields based on metal content than if stoichiometric ratios are used. Lastly, the addition of ~28 vol% glacial acetic acid increases product yield due to the lower molar solubilities of the targeted compounds in acetic acid.

Large, high quality single crystals (up to ~2 mm on a side) suitable for single crystal diffraction and physical properties measurements can be grown by heating a solution containing the microcrystalline product in the respective hydrohalic acid to boiling followed by slow cooling and allowing to stand at room temperature for 24 h. As the molar solubilities of each compound are different, it is necessary to tailor the crystal growth of each compound to optimize crystal size and quality. We find that using a ~50% excess molar amount of the room temperature molar solubility of a given compound leads to high quality specimens. For example, as the molar solubility of (C$_7$H$_7$)SbI$_4$ at room temperature is ~0.008 M, using a total molar concentration of ~0.0112 M [(C$_7$H$_7$)SbI$_4$] in stabilized HI results in black, well faceted crystals such as the those seen in Figure 1(g,h).

![Figure 1](image_url)

**Figure 1.** (a-f) Brightfield photographs of ground powders of (C$_7$H$_7$)MX$_4$ ($M = Bi^{3+}, Sb^{3+}; X = Cl^-, Br^-, I^-$) compounds. (g) Small (C$_7$H$_7$)SbI$_4$ single crystals grown by slow cooling from a saturated solution over a period of ~5 h. (h) Larger (C$_7$H$_7$)SbI$_4$ single crystals grown by slow cooling from a saturated solution over a period of ~24 h.
We note that the habit of the crystals depends on the size of the particles: smaller crystallites tend to adopt a needle-like habit, while larger crystals grown by cooling more slowly form plates (Figure 1(g,h)). In both cases, the crystallographic c-axis is parallel to the long axis of the crystal, indicating the 1-D chains grow lengthwise throughout the crystallites.

Thermal gravimetric analysis was used to determine the thermal stability of the compounds studied. Figure S1 show the thermal decomposition curves of each compound. Each compound is stable up to ~200 °C, with relatively steep drops in their weight-%, indicating that these compounds decompose relatively rapidly in a single step. The lack of any substantial weight loss around 100 °C ensures that these compounds do not appear to have any significant water adsorption (whether physi- or chemisorption) such as that seen in 3-D perovskite materials such as CH$_3$NH$_3$PbI$_3$. Additionally, to assess if these compounds directly decompose or sublime during the heating process, we exposed (C$_7$H$_7$)SbI$_4$ to a thermal gradient (240 °C at the hot zone and ~50 °C at the cold zone) while under vacuum (~5 x 10$^{-2}$ torr) to attempt sublimation of the compound onto a glass substrate located at the cold zone. We observed a significant amount of C$_7$H$_7$I on the substrate, evident by a dark orange-red solid. No evidence of a black solid was present on the substrate, which is what would be expected if the compound was thermally evaporating and depositing onto the substrate. This suggests that these compounds decompose upon heating.

Crystal Structure.

The compounds (C$_7$H$_7$)MX$_4$ (M = Bi$^{3+}$, Sb$^{3+}$; X = Cl$^-$, Br$^-$, I$^-$) are isostructural to one another, adopting a unique monoclinic structure with space group C2/c; The crystallographic parameters are provided in Table 1, with atomic positions listed in Tables S2 and S3. Powder X-ray diffraction (Figure 2) confirms the phase purity of each sample and consistent structural model with the single crystal diffraction data. Describing (C$_7$H$_7$)BiI$_4$, the structure is composed of 1-dimensional sub-structural units: edge-sharing [MX$_6$] octahedral chains are separated in space by π-stacked tropylium cations (Figure 3a) to form a close-packed iodine lattice between chains with an interchain I•••I distance of 4.0899(2) Å. The [MX$_6$] units resemble the layers of BiI$_3$ that have been broken up into 1-D chains (Figure 3b) by the tropylium cations. The crystal structures of the compounds (C$_7$H$_7$)MX$_4$ (M = Bi$^{3+}$, Sb$^{3+}$; X = Cl$^-$, Br$^-$, I$^-$) were solved by Rietveld refinement of the powder X-ray diffraction data using the single crystal model obtained for (C$_7$H$_7$)BiI$_4$ as the initial input. Given the poor X-ray contrast of the organic molecules against the heavy elements in the inorganic framework, the absolute positions of the tropylium ring were treated lightly. We attempted to find the simplest and highest fidelity description of the structure by refining the structural coordinates using two methods: (i) “idealized” refinements wherein the organic cation positions are refined one atom at a time in order to relax the C$_7$H$_7^+$ ring in order to avoid an otherwise poor convergence of the refinement; the organic atom positions were then fixed for the final Rietveld refinement;
(ii) rigid body refinements to refine the position of the organic cations. The ‘idealized’ models were used as inputs for DFT calculations and are reported here, as the rigid body refinements did not lead to improved descriptions of the observed data (either on an absolute scale or from Hamilton’s analysis of the R-ratio).\textsuperscript{42}

### Table 1. (C\textsubscript{7}H\textsubscript{7})Bi\textsubscript{4} Experimental Crystallographic Parameters From Single Crystal Diffraction

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\textsuperscript{a}R\textsubscript{1} = Σ||F\textsubscript{o}|| - |F\textsubscript{c}||/ Σ|F\textsubscript{o}|, \textsuperscript{b}wR\textsubscript{2} = [Σ[w(F\textsubscript{o}\textsuperscript{2} - F\textsubscript{c}\textsuperscript{2})\textsuperscript{2}]/ Σ[w(F\textsubscript{o}\textsuperscript{2})\textsuperscript{2}]\textsuperscript{1/2}.

### Table 2. Experimental Parameters for Structures Solved from Rietveld Refinement

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<th>(C\textsubscript{7}H\textsubscript{7})BiCl\textsubscript{4}</th>
<th>(C\textsubscript{7}H\textsubscript{7})BiBr\textsubscript{4}</th>
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<td>13.8564(3)</td>
<td>14.5631(4)</td>
<td>13.4555(8)</td>
<td>13.9264(4)</td>
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<td>c (Å)</td>
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<td>7.5399(2)</td>
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<td>7.3354(3)</td>
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<td>β (°)</td>
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<td>120.494(2)</td>
<td>118.249(2)</td>
<td>119.461(3)</td>
<td>118.519(1)</td>
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<td>V (Å\textsuperscript{3})</td>
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<td>1430.87(8)</td>
<td>1151.83(11)</td>
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<tr>
<td>(Z)</td>
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<td>(\chi^2)</td>
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<td>1.52</td>
<td>1.55</td>
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<tr>
<td>(R_p^{a})</td>
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<td>7.28%</td>
<td>7.11%</td>
<td>6.83%</td>
<td>5.22%</td>
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<tr>
<td>(R_{wp}^{b})</td>
<td>10.53%</td>
<td>9.69%</td>
<td>9.50%</td>
<td>8.98%</td>
<td>7.03%</td>
</tr>
</tbody>
</table>

\[ aR_p = \sqrt{\frac{\sum |Y_{o,m} - Y_{c,m}|}{\sum Y_{o,m}}} \]
\[ bR_{wp} = \sqrt{\frac{\sum w_m(Y_{o,m} - Y_{c,m})^2}{\sum w_mY_{o,m}^2}} \]

Figure 2. Powder X-ray diffraction and Rietveld refinement of \((C_7H_7)MX_4\) \((M = Bi^{3+}, Sb^{3+}; X = Cl^-, Br^-, I^-)\). Data are shown as black spheres; calculated patterns from Rietveld analysis shown as colored lines, with difference curves below.

These relatively short intermolecular contacts may lead to charge transport facilitated by the \(\pi\)-interactions of the tropylium cations. In the compounds \((C_7H_7)PbI_3\) and \((C_7H_7)SnI_6\) we have previously investigated,\(^2^7\) the nearest neighbor tropylium cations are not parallel to one another, but rather they adopt a \(\pi\cdots H\) interaction that minimizes overlap between neighboring molecules, which may contribute to their poor charge transport properties. Remarkably, the compounds presented here have a nearly un-interrupted closed-packed lattice of halogens, and ideal characteristic in itself for transport. We note that the C-H stretching vibrational mode (ca. 2990 – 3030 cm\(^{-1}\)) seen in the ATR-IR data (Figure S2) shifts to lower energy as a function of increasing halide size, consistent with that expected for a C–H\(\cdots X\) interaction. This indicates that there exist significant interactions between the inorganic chains and tropylium cations, which helps to stabilize the structure and allow for charge transfer between the two substructural units.
Figure 3. Top: Crystal structure of \((\text{C}_7\text{H}_7)\text{BiI}_4\) showing \([\text{BiI}_{4/2}\text{I}_{2/1}]^–\) chains separated by \(\pi\)-stacked tropylium cations. Bottom: Single \([\text{BiI}_{4/2}\text{I}_{2/1}]^–\) chain shown with neighboring tropylium cations.

The metal-halide interatomic distances within the series of compounds \((\text{C}_7\text{H}_7)\text{BiX}_4\) \((\text{X} = \text{Cl}, \text{Br}, \text{I})\) contracts following the shrinking of the ionic radii when going from iodine, to bromine, to chlorine. The octahedra of each compound are distorted, with two of the equatorial \(\text{M}–\text{X}\) bonds being significantly longer than the other two (Figure 4). For instance, two of the \(\text{Bi}–\text{I}\) bonds have short distances of 2.9668(1) Å while the other two are much longer at 3.2841(7) Å. This distorted octahedron contrasts with the slightly-distorted \([\text{BiI}_6]\) units in \(\text{BiI}_3\) \((\text{C}_3\text{V} \text{ symmetry})\), where three of the \(\text{Bi}–\text{I}\) distances are 3.0455(13) Å and the others are 3.1204(13) Å. The \(\text{Bi}–\text{I}\) distances are all near or within the summed ionic radii of a \(\text{Bi}^{3+}\) cation and \(\text{I}^–\) anion (1.17 Å and 2.06 Å, respectively). The distorted nature of the octahedra could be due to slight or dynamic stereochemical activity of a lone pair on the \(\text{Bi}^{3+}\) center, which has been observed in other bismuth or tin halide compounds previously.43-45 Additionally, the moderately large thermal parameters for the halide atoms further suggests the presence of an active lone pair. We note that the anisotropic displacement parameters obtained from the single crystal diffraction model of \((\text{C}_7\text{H}_7)\text{BiI}_4\) show slight elongation of the ellipsoids directed toward the nearest hydrogen on the tropylium cation, indicating that hydrogen bonding exists in the structure.
The compounds (C\(_7\)H\(_7\))SbX\(_4\) (X = Cl\(^-\), Br\(^-\), I\(^-\)) follow similar structural motifs as those observed in the bismuth analogues. The Sb–X bond lengths shorten as a function of halide (Figure 4); however, they have significantly more distorted octahedra. This further implicates the role of lone-pair stereoactivity, which is expected to strengthen when more the metal s and ligand p orbitals become closer in energy,\(^{46-47}\) as consistent with the trends observed in CsMX\(_3\)-based compounds, where M spans from Ge, Sn, and Pb and X is a halogen.\(^{44, 48-51}\) In fact, the longest Sb–Cl and Sb–Br bond lengths (3.02090(5) Å and 3.171(7) Å, respectively) are longer than the longest Bi–Cl and Bi–Br lengths (2.96689(11) Å and 3.1057(3) Å respectively), highlighting the large degree of octahedral distortion in the Sb-compounds.

![Figure 4](image.png)

**Figure 4.** Isolated [MX\(_6\)] (M = Bi\(^{3+}\), Sb\(^{3+}\); X = Cl\(^-\), Br\(^-\), I\(^-\)) octahedra showing the different bond lengths and trends throughout the series.

**Optical Diffuse Reflectance.**

UV-visible diffuse reflectance spectra were collected on each sample to determine the optical band gaps and assess their absorbance properties. These compounds exhibit intense physical colors as shown in Figure 1, indicating strong absorbance of the visible region. The Kubelka–Munk transform of the diffuse reflective shown in Figure 5 shows similar light absorption for each compound, but with a systematic change in absorption edge.

The spectra reveal significant absorption of visible light with relatively sharp edges for all compounds. The absorption edges for compounds (C\(_7\)H\(_7\))SbX\(_4\) (X = Cl, Br, I) are all red shifted relative to (C\(_7\)H\(_7\))BiX\(_4\) (X = Cl, Br, I) for their respective halides. For instance, (C\(_7\)H\(_7\))SbI\(_4\) has an optical absorbance...
edge centered around 1.55 eV (800 nm) versus 1.83 eV (790 nm) for (C\textsubscript{7}H\textsubscript{7})BiI\textsubscript{4}. (C\textsubscript{7}H\textsubscript{7})BiBr\textsubscript{4} and (C\textsubscript{7}H\textsubscript{7})BiI\textsubscript{4} have slightly sharper features near the absorption edge than the Sb-analogues. No photoluminescence was detectable in the samples at room temperature (Figure S4).

![Figure 5](image_url)

**Figure 5.** Kubelka-Munk transformed UV-visible diffuse reflectance showing the absorption edges for each compound across the visible spectrum. The TrSbX\textsubscript{4} (X = Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}) compounds (left) are significantly red-shifted (~100 nm) relative to their bismuth congeners (right).

**Electronic Structure Calculations.**

Density functional calculations provide direct support of inorganic-organic charge transfer and agree with the observed periodic trends. Only minimal deviations of the structure result from relaxation of the DFT-calculated forces of the crystallographically-determined structures (Table S4). Figure 6 shows the densities of states (DOS) of (C\textsubscript{7}H\textsubscript{7})SbI\textsubscript{4} and (C\textsubscript{7}H\textsubscript{7})BiI\textsubscript{4}. The calculations reveal indirect band gaps of $E_g = 0.68$ eV ($E_g$\textsubscript{direct} = 0.71 eV) and $E_g = 0.98$ eV ($E_g$\textsubscript{direct} = 1.01 eV), respectively. The valence band is composed of primarily iodine $p$-orbitals with a vanishingly small contribution also from the Sb $s$-orbitals (Figure 6a) and Bi $s$-orbitals (Figure 6b) at the band edge. Shown in Figure 7 for (C\textsubscript{7}H\textsubscript{7})BiI\textsubscript{4}, the bands have relatively low dispersion, as expected from the anisotropic 1-D structure. Furthermore, the valence band states resemble the non-dispersive halogen-character valence band of BiI\textsubscript{3},\textsuperscript{52} which is reasonable given the close structural resemblance. The flat, localized conduction band is composed of $\pi^*$ states from the tropylium cation, as illustrated by the band-decomposed charge density (Figure 7b). Projection of the valence band
charge densities onto the peripheral iodines (Figure 7c) illustrates that the primary electronic transition is a charge transfer from the inorganic chains to the tropylion cation. These results are similar to those observed in (C$_7$H$_7$)PbI$_3$, (C$_7$H$_7$)$_2$SnI$_6$,\textsuperscript{27} and (Pb$_2$I$_6$)·(H$_2$DPNDI)·(H$_2$O)·(NMP).\textsuperscript{17}

While underestimated relative to the experimental optically-determined gap from the diffuse reflectance data, the calculations reflect the observed periodic trends. There is an increase in band gap from iodine to chlorine and from Sb to Bi. Shown in Figure 8, we observe the role of the halogens in pulling down the valence band maximum (VBM) the conduction band minima (e.g., $\pi^*$ states) are equated to $E = 0$ eV. We also observe that the VBM of the Bi-based compounds is lower in energy relative to that of the Sb-based compounds, giving rise to a larger band gap for the Bi-based compound. This is similar to the trend observed in (CH$_3$NH$_3$)PbI$_3$ (~1.6 eV) and (CH$_3$NH$_3$)SnI$_3$ (~1.2 eV), where the increased relativistic effects on Pb 6s electrons bring down the conduction band relative to the valence band, thus increasing the band gap.\textsuperscript{53}

Figure 6. Densities of states and their orbital projections for (a) (C$_7$H$_7$)SbI$_4$ and (b) (C$_7$H$_7$)BiI$_4$. 
Conclusions.

We report a new isostructural family of compounds \((\text{C}_7\text{H}_7)\text{MX}_4\) \((\text{M} = \text{Bi}^{3+}, \text{Sb}^{3+}; X = \text{Cl}^-, \text{Br}^-, \text{I}^-)\). These compounds are composed of edge sharing 1-D \([\text{MX}_6]\) chains in a close-packed halogen lattice interspersed with chains of \(\pi\)-stacked tropylium cations. UV-Visible diffuse reflectance reveals sharp absorption edges with a systematic change to higher energy from iodine to chlorine. Band structure calculations confirm the trend observed in the absorbance data, as well as show that the primary electronic transition is from the halide to the \(\pi^*\) orbital of the tropylium cation. The compounds \((\text{C}_7\text{H}_7)\text{BiI}_4\) and
(C\textsubscript{7}H\textsubscript{17})SbI\textsubscript{4} show significant visible light absorbance due to their low band gaps (1.8 eV and 1.55 eV, respectively), indicating potential for use as absorbers in photovoltaic devices.

Acknowledgements

This work was supported by grant DE-SC0016083 funded by the U.S. Department of Energy, Office of Science. JRN acknowledges additional support from Research Corporation for Science Advancement through a Cottrell Scholar Award, and JRN thanks the A.P. Sloan Foundation for assistance provided from a Sloan Research Fellowship. This work utilized the RMACC Summit supercomputer, which is supported by the National Science Foundation (awards ACI-1532235 and ACI-1532236), the University of Colorado Boulder and Colorado State University. The RMACC Summit supercomputer is a joint effort of the University of Colorado Boulder and Colorado State University. J.R.N. gratefully acknowledges the support of NVIDIA Corporation with the donation of the Tesla K40 GPU used for this research.

Supporting Information

The supporting information includes details of the molar solubility experiments, thermal properties, ATR-FTIR spectra, Photoluminescence spectra, and atomic positions derived from powder and single crystal X-ray diffraction. Also included are supplementary crystal information files (cif) of new structures.

References.


Synopsis.

The family of hybrid metal-halide semiconductors \((\text{C}_7\text{H}_7)\text{MX}_4\) \((M = \text{Bi}^{3+}, \text{Sb}^{3+}; X = \text{Cl}^-, \text{Br}^-, \text{I}^-)\) was synthesized. The optical and electronic properties of the new compounds were elucidated, revealing electronic band gaps that span the visible region. The tropylium cations stack into columns separated by chains of edge-sharing M-X octahedra to yield a low dimensional crystal structure with electron and hole charge carriers confined to the organic and inorganic components, respectively.

![Diagram of the crystal structure](image)