Some New Luminescent Compounds Based on 4-Methylbenzylamine and Lead Halides

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Introduction

The low-dimensional (LD) semiconductors based on 2-phenylethylamine (C₆H₅CH₂CH₂NH₂) and metal halides, i.e., compounds of the type (CH₃NH₃)ₙ₋₁(CH₃CH₂NH₃H₃)₂MₓX₄₋ₙ, where M = Pb, Sn; X = I, Br, Cl, have been extensively studied (see refs 1, 2, 3,...) and characterized by X-ray crystal structure analysis. Their optical absorption and photoluminescence spectra exhibit excitonic bands, even at room temperature.

Experimental

Starting materials and apparatus

The following starting materials were used without further purification: PbO (Ferak 01-881), hydroiodic acid 25% (Merck 312), HCl 304), hydrochloric acid 25% (Merck 312), HClO₄ 50% (Fluka 9421), PbBr₂ (Johnson Matthey 976201), 4-methylbenzylamine (Fluka 73164) and methylamine solution (50%) in water (Fluka 65580). The precursors CH₃NH₃H₃, CH₃NH₃Br, CH₃CH₂NH₃H₃, CH₃CH₂NH₃Br and CH₃CH₂NH₃Cl were obtained by treating the precursors CH₃NH₃H₃, CH₃NH₃Br, CH₃CH₂NH₃H₃, CH₃CH₂NH₃Br and CH₃CH₂NH₃Cl were obtained by treating the amines with the corresponding acids.

Crystal X-ray intensity data were collected on a Crystal Logic [15] Dual Goniometer using graphite-monochromated Mo-Kα radiation. Unit cell dimensions were determined and refined by using the angular setting of 24°. Intensity data were recorded using a 2θ/2θ scan: for (CH₃CH₂NH₃H₃)$_2$PbI₄, θ range 0 - 25°, scan speed 3° min⁻¹, scan range 2.3 + θ, separation, 2583 / 2037 (Rint = 0.0780) / 1903 (Rint = 0.0800) / 0393; for (CH₃CH₂NH₃H₃)$_2$PbCl₂, θ range 0 - 25°, scan speed 3° min⁻¹, scan range 2.3 + θ, separation, 2583 / 2037 (Rint = 0.0452) / 2037; for (CH₃CH₂NH₃H₃)$_2$PbBr₂, θ range 0 - 25°, scan speed 2.5° min⁻¹, scan range 2.3 + θ, separation, 2583 / 2037 (Rint = 0.0780) / 1903.

Three standard reflections monitored every 97 reflections showed less than 3% variation and no systematic decay. Lorentz polarization and absorption corrections were applied using CrystalLogic Software. The structures were solved by Patterson methods using SHELXS-86 [16] and refined by full-matrix least-squares technique with SHELX-97 [17]. Hydrogen atoms were introduced at calculated positions as riding carbon atoms (except those of (CH₃NH₃H₃)$_2$PbI₄ which were not included). All non-hydrogen atoms were refined anisotropically. Crystallographic information files have been deposited in the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@chemistrys.cam.ac.uk). Deposition

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The mixture was heated at reflux temperature and the obtained clear solution was cooled slowly to 20 °C. The crystals obtained after several hours were filtered and dried in air; bright red plates, yield 77%. Analysis for C\textsubscript{16}H\textsubscript{24}N\textsubscript{2}Br\textsubscript{6}Pb: C 42.92, H 2.10, N 3.31, Br 46.01%. – Small deviations from the calculated values may be due to the presence of small amounts of (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{n-1}(CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}N\textsubscript{2}Cl\textsubscript{2}Pb\textsubscript{2}I\textsubscript{3n+1}, with n ≠ 3 (see [1 - 5] for C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{3} analogs).

The compound (CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}N\textsubscript{2}Cl\textsubscript{2}Pb\textsubscript{2}I\textsubscript{3n+1} was prepared as follows: In 5 ml of aq. HBr (47%), 9 ml of CH\textsubscript{3}OH, 44.8 mg of CH\textsubscript{3}NH\textsubscript{3}Br, 121.2 mg of CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}NH\textsubscript{2}Br, and 183.5 mg of PbBr\textsubscript{2} were added. The mixture was heated at reflux temperature and the obtained clear solution was cooled slowly to ca. 20 °C. The crystals obtained after several hours were filtered and dried in air; bright yellow plates, yield 77%. Analysis for C\textsubscript{16}H\textsubscript{24}N\textsubscript{2}Br\textsubscript{6}Pb: C 42.92, H 2.10, N 3.31, Br 46.01%. – Small deviations from the calculated values may be due to the presence of small amounts of (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{n-1}(CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}N\textsubscript{2}Cl\textsubscript{2}Pb\textsubscript{2}I\textsubscript{3n+1}, with n ≠ 3 (see [1 - 5] for C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{3} analogs).

The compound (CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}N\textsubscript{2}Cl\textsubscript{2}Pb\textsubscript{2}I\textsubscript{3n+1} was prepared as follows: In 2 ml of aq. HCl (35%), 44.8 mg of PbO, and 63.0 mg of CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}Cl were added. The mixture was heated at reflux temperature and the obtained clear solution was cooled slowly to ca. 20 °C. The crystals obtained after several hours were filtered and dried in air; bright white plates, yield 63%. Analysis for C\textsubscript{16}H\textsubscript{24}N\textsubscript{2}Cl\textsubscript{2}Pb: C 42.38, H 4.08, N 4.72. Found C 42.31, H 4.13, N 4.65%.

Attempts for the preparation of (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{n-1}(CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}H\textsubscript{2}N\textsubscript{2}Cl\textsubscript{2}Pb\textsubscript{2}I\textsubscript{3n+1}, were unsuccessful.
Structures, Optical Properties and Discussion

A summary of the crystal, intensity collection and refinement data of compounds (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbI$_4$ (1), (CH$_3$NH$_3$)(CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$-Pb$_2$I$_7$ (2), (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbBr$_4$ (3), (CH$_3$-C$_6$H$_4$CH$_2$NH$_3$)$_2$PbCl$_4$ (4), are given in Table 1.

Crystals of the compounds (CH$_3$NH$_3$)$_2$(CH$_3$-C$_6$H$_4$CH$_2$NH$_3$)$_2$Pb$_3$Br$_{10}$ were not good enough for X-ray crystal structure solution. However, the elemental analysis results, given above, and the optical properties, which are described below, indicate a 2D-structure, similar to those observed for the C$_6$H$_5$CH$_2$CH$_2$NH$_2$ analogs [1 - 8].

Compounds 1, 3 and 4 are isostructural. The packing diagram of (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbI$_4$ (1) is shown in Fig. 1. The structures of 1, 3 and 4 consist of corner sharing PbX$_6$ octahedra (X = I, Br, Cl for 1, 3 and 4, respectively) forming two-dimensional (2D) anionic / inorganic networks parallel to the $ab$ plane, which alternate with layers of organic cations. The PbX$_6$ octahedra are centrosymmetric with the Pb-X$_{axial}$ bond distances being 3.213(2), 2.996(2) and 2.868(4) Å for 1, 3 and 4, respectively, while the Pb-X$_{equatorial}$ bond distances are 3.180(1) and 3.193(1) Å for 1, 2.978(2) and 2.979(2) Å for 2, and 2.847(3) and 2.853(3) Å for 3. The Pb-X-Pb bridging angle between two neighbouring octahedra significantly deviates from linearity (154.49(2), 145.70(5) and 149.1(1)$^\circ$ for 1, 3 and 4, respectively).

The crystal structure of (CH$_3$NH$_3$)(CH$_3$C$_6$H$_4$-CH$_2$NH$_3$)$_2$Pb$_2$I$_7$ (2) is shown in Fig. 2. It consists of corner-sharing PbI$_6$ octahedra forming 2D anionic / inorganic bilayer networks parallel to the $ab$ plane, which alternate with layers of organic cations. Each Pb$^{2+}$ cation is bridged to four neighbouring metal ions of the same layer through the four equatorial positions (Pb-I(2) = 3.189(1), Pb-I(2') = 3.180(1), Pb-I(3) = 3.190(1), Pb-I(3') = 3.165(1) Å, Pb-I(2)-Pb' = 155.39(4), Pb-I(3)-Pb" = 158.86(4)$^\circ$; 1(2'): 0.5 - x, 0.5 + y, z, 1(3'): -x, y, 0.5 - z, Pb': 0.5 - x, y - 0.5, z, Pb": -x - 0.5, y - 0.5, z) and to one Pb$^{2+}$ cation of
the adjacent layer through the axial I(1) bond (Pb-I(1) = 3.260(1) Å, Pb-I(1)-Pb' = 178.28(6)°; Pb': -x, y, 0.5 - z). The second axial position is occupied by I(4) (Pb-I(4) = 3.146(1) Å).

Fig. 3 shows the optical absorption (OA) and photoluminescence (PL) spectra of (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbI$_4$, (CH$_3$NH$_3$)$_2$(CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$Pb$_2$I$_7$, (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbBr$_4$, and of a single crystal (c) before (c) and after rubbing (a, b, d); excitation 457.9 nm. Vertical bars indicate the PL peak positions with the same excitation; N ≥ 20.

Fig. 4 shows the OA (a, b) and PL (c, d) spectra of (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbBr$_4$ (a) and (CH$_3$NH$_3$)$_2$(CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$Pb$_2$Br$_{10}$ (b, c, d) thin deposits on quartz plates (a, b, d) and of a single crystal (c) before (c) and after rubbing (a, b, d); excitation 457.9 nm. Vertical bars indicate the PL peak positions with excitation 310 nm; N ≥ 60.

Fig. 5. OA (a, b) spectra of (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbCl$_4$ (a) and CH$_3$C$_6$H$_4$CH$_2$NH$_3$Cl (b). Vertical bar indicates the PL peak position of (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbCl$_4$; excitation 300 nm.

NH$_3$)$_{n-1}$(CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$Pb$_n$Br$_{3n+1}$ (n ≥ 2) exhibit excitonic peaks at longer wavelengths than those of (CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$PbBr$_4$. The intensity of the peaks varies from sample to sample. The PL spectrum of (CH$_3$NH$_3$)$_2$(CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$Pb$_2$Br$_{10}$ single crystals exhibits an excitonic peak at ca. 471 nm. After intensive rubbing of (CH$_3$NH$_3$)$_2$(CH$_3$C$_6$H$_4$CH$_2$NH$_3$)$_2$Pb$_2$Br$_{10}$ single crystals on quartz plates (or paper) very thin deposits are obtained. They exhibit a strong blue-green photoluminescence with a maximum at ca. 513 nm.
Fig. 5 shows the OA spectra of \((\text{CH}_3\text{C}_6\text{H}_4-\text{CH}_2\text{NH}_3)_2\text{PbCl}_4\) and the corresponding spectrum of \((\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Cl}\) for comparison. One can see that the excitonic peaks are close to the OA electronic band of \((\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Cl}\), as in the case of \((\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Cl}\) analogs \([8]\).

The effects observed in the OA and PL spectra of compounds based on \((\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Cl}\) are more pronounced than those observed for similar compounds based on \((\text{C}_10\text{H}_{21})\text{NH}_2\), \((\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2)_2\) etc. (see also \([1 - 8]\)). Strong PL bands are observed after grinding of the neat compounds (or of their suspensions in \((\text{C}_6\text{H}_5\text{CH}_3\text{CH}_2\text{Br}, \text{CCl}_4\) etc.). Perhaps, this result is due to quantum confinement of excitons, as in the case of \((\text{CsPbX}_3\) \([18]\), and / or to some rearrangement of Pb and I or Br atoms in the corresponding lattices (i.e., in \((\text{Pb}_2\text{I}_{3n+1}\) and \((\text{PbI}_3\) or \((\text{Pb}_3\text{Br}_{3n+1}\) and \((\text{PbBr}_3\) networks). Details on the optical absorption, photoluminescence and photoconductivity spectra of these materials as well as the spectra of Sn analogs will be reported elsewhere.