Lead Halide-based Layered Perovskites Incorporated with a *p*-Terphenyl Laser Dye

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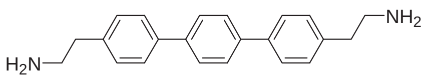
An attempt to incorporate a representative laser dye, *p*-terphenyl, into the layered organic–inorganic perovskite structure was made. From PbX_2 (X = Cl, Br) and the corresponding 4,4″-bis(2-aminoethyl)-*p*-terphenyl (AETP) hydrogen halide salt (AETP-2HX), two kinds of AETP-PbX_4 crystals were prepared, and their structural and optical properties were investigated. Emission color of the crystals was fluorescent blue for X = Cl, while phosphorescent orange for X = Br, suggesting different emission processes dependent on the different energy levels of PbX_4 perovskite layers.

Owing to much effort on developing organic light-emitting diodes (OLEDs), the part of them has reached the level of practical use at present. In OLED materials, where the individual molecules are weakly held together by van der Waals forces, however, the drastic raising of OLED performances especially in term of carrier-transport property cannot be expected. This makes it difficult to realize a next-generation OLED device, that is, the organic laser diode (OLD); the major obstacle to making a OLD is the charged-carriers-induced absorption-loss problem that is originated from inherent low carrier mobility of organics.[1]

Organic–inorganic hybrid materials are considered to be an alternative and potential candidate for attaining the performance that laser devices demand. From such a viewpoint, we have been focusing on the organic–inorganic layered perovskites (OILPs). The OILP compound is a single molecular-scale composite where organic sheets formed by assembling molecules and inorganic perovskite sheets of corner-sharing metal halide octahedra are alternatively stacked.[2] So far, OILPs have attracted considerable interests, not only in the quantum and dielectric confinement effects of excitons formed within inorganic semiconducting layers[3] and their related phenomena,[4] but also in the applications to optoelectronic[5] and electronic[6] devices. For the purpose of developing OLDs, we intend that carrier transport will resort to inorganic layers with potentially superior transport property. Namely, on the premise of constructing organic layers by use of a laser dye, we assume that electrically pumped lasing could be attained through the following three steps: (1) carrier injection, transport, and recombination (i.e., exciton formation) in inorganic layers, (2) exciton energy transfer from inorganic to organic layers,[7] and (3) occurrence of stimulated emission from organic layers. Toward creation of such a model system, we first selected *p*-phenylene-based laser dyes, since they have good stimulated emission performance even in crystalline state.[8] Here we report the structural and optical properties of the PbX_4-based layered perovskites (X = Cl, Br) incorporated with *p*-terphenyl laser dyes.



Scheme 1. Structure of 4,4″-bis(2-aminoethyl)-*p*-terphenyl (AETP).

The chemical modification of organic molecules with ethylamino groups is a conventional way to incorporate into OILP structures. Thus, the synthesis of 4,4″-bis(2-aminoethyl)-*p*-terphenyl (AETP) shown in Scheme 1 was attempted in the following procedure: first, the precursor of AETP was synthesized by the Suzuki coupling of 1,4-phenylenediboronic acid and 2-(4-bromophenyl)ethylamine with its amino group protected by a Boc group. The Boc groups at the both sides of the precursor were then deprotected by addition of aqueous hydrogen halide solution, and AETP was obtained as hydrogen halide salts, AETP-2HX (X = Cl, Br). These salts and their corresponding lead halides were mixed together at a molar ratio of 1:1 with water, and dissolved by heating. Slow cooling to room temperature yielded aggregates of very thin platelet-like white crystals of AETP-PbX_4 (X = Cl, Br);[9] AETP is incorporated as a diammonium cation.

The formation of OILP structures was confirmed by X-ray diffraction (XRD) method. Figure 1 shows the XRD profiles of AETP-PbX_4 (X = Cl, Br). These profiles are clearly different from those of the corresponding AETP-2HX salts (data not shown). In both cases, one can see the (*l*00) series of reflections, which corresponds to a *d*-spacing of 21.69 Å and 18.32 Å, for X = Cl and Br, respectively; the ground samples deposited on a substrate are preferentially oriented with their *a*-axes perpendicular to the substrate. Assuming that the *a*-axis is in accordance with the layer staking direction, the crystal packing diagrams can be reasonably drawn as shown in Figure 2. On the basis of the values of the *d*-spacings, the Pb–X bond lengths (X = Cl, 2.83; X = Br, 2.95 Å),[2b] and the molecular length of AETP (18.5 Å), it is roughly estimated that the molecular long axis of AETP tilts at angles of about 30° and 47° from the *a*-axis, for X = Cl and Br, respectively. Such a difference in AETP ar-

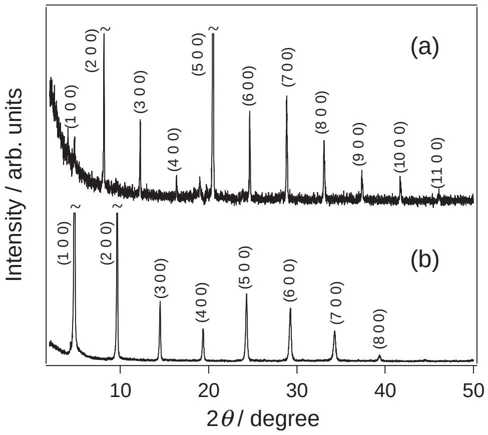


Figure 1. XRD patterns of AETP-PbX_4: (a) X = Cl, (b) X = Br.

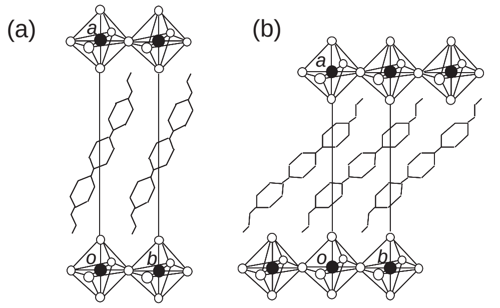


Figure 2. Schematic representations of the packing arrangements in AETP-PbX_4, predicted by XRD measurements: (a) X = Cl, (b) X = Br. Considering that AETP is a diammonium cation, eclipsed arrangement of layers (i.e., Pb-over-Pb arrangement between perovskite layers) is assumed. (see Ref. 2b)

rangement might be related to hydrogen-bonding fashion between terminal ammonium groups of AETP and halogen atoms of lead halide octahedra.[2b]

Figure 3a shows the photoluminescence (PL) spectrum for crystalline sample of AETP-$PbCl_4$. For excitation, light with wavelength of 300 nm was used, by which both AETPs and perovskite sheets could be excited. The spectral profile and region with maximum around 390 nm are similar to those for AETP-2HCl (dotted line in Figure 3). It can be thus said that the PL origin of AETP-$PbCl_4$ is attributed to fluorescence from AETP. On the other hand, no observation is available for the sharp peak characteristic of $PbCl_4$ perovskite sheet excitons occurring at around 330 nm. Therefore, exciton energy transfer from the $PbCl_4$ perovskite sheet to the AETP molecules is suggested.

While in the PL spectrum for AETP-$PbBr_4$ (Figure 3b), a sharp peak at 420 nm, characteristic of exciton formed in $PbBr_4$ perovskite layer, is confirmed. On the contrary, fluorescence from AETP is not observed, and a weak band is seen at around 550 nm probably due to phosphorescence from AETP; in practice, emission color of the AETP-$PbBr_4$ crystals appears dimly orange, not blue to the naked eye. Such an assignment should be also supported by the previous reports on observations of the room-temperature phosphorescence in OILPs containing a chromophore.[10]

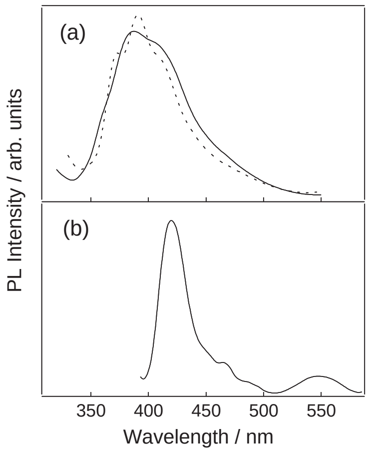


Figure 3. Photoluminescence spectra for the crystalline samples of (a) AETP-$PbCl_4$ (solid line), AETP-2HCl (dotted line) and (b) AETP-$PbBr_4$. Excitation wavelengths are 300 and 330 nm, for (a) and (b), respectively.

For explanation of the spectral difference between X = Cl and Br, it might be reasonable to consider the order in energy of two excited states S_1 and EB, where S_1 is the singlet excited state of AETP and EB is the excitonic band of lead halide perovskite sheet; namely, assuming $S_1 < \mathrm{EB}$ for X = Cl and $\mathrm{EB} < S_1$ for X = Br, and energy transfer from the higher to the lower excited state, the only observable emission is from the lower excited state, which is consistent with the experimental results. In the case of X = Br, energetically matching of EB and the triplet excited state of AETP (T_1) might make possible the electron exchange energy transfer from EB to T_1, leading to phosphorescence from AETP. More detailed investigation is, however, needed to verify this explanation.

In this work, the PbX_4-based layered perovskites (X = Cl, Br) incorporated with a *p*-terphenyl laser dye were synthesized, and their structural and optical properties were investigated. For the purpose of developing OLD devices, it is quite significant not only to optimize the three steps for electrically pumped lasing mentioned above, but also to fabricate device structures by using OILP thin film deposition technique.[11] Work in these directions is in progress.

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References and Notes

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9 Aggregates of very thin and small crystals made us difficult to measure their absorption spectra. Although exciton absorption of $PbBr_4$ layers could be observed with a peak of 407 nm, that of $PbCl_4$ layers could not be confirmed owing to strong light scattering.

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