



Preparation and optical characteristics of layered perovskite-type lead-bromide-incorporated azobenzene chromophores

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ABSTRACT

Lead bromide-based layered perovskite powders with azobenzene derivatives were prepared by a homogeneous precipitation method. From the diffuse reflectance (DR) and photoluminescence (PL) spectra of the hybrid powder materials, the present hybrids exhibited sharp absorption and PL peaks originating from excitons produced in the PbBr_2 layer. When the present hybrid powder was irradiated with UV light at 350 nm, the absorption band from the *trans*-azobenzene chromophore, observed around 350 nm, decreased, while the absorption band from the *cis*-azobenzene chromophore, observed around 450 nm, increased. These results indicate that azobenzene chromophores in the present hybrid materials exhibit reversible photoisomerization. Moreover, it was found that the PL intensity from the exciton also varied due to photoisomerization of the azobenzene chromophores in the present hybrid. Thus, for the first time we succeeded in preparing the azobenzene derivative lead-bromide-based layered perovskite with photochromism before and after UV light irradiation.

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1. Introduction

Metal halide-based layered perovskites with chemical formulas such as $(\text{R-NH}_3)_2\text{MX}_4$ (R-NH₃: organic ammonium such as alkylammonium; M: Pb, Sn, Ge, and so on; and X: Cl, Br, and I) is well known as one of the natural two-dimensional (2D) superlattice compounds [1–16]. A strong quantum-confinement effect appears in the 2D semiconductor layer, and then a stable exciton with a large binding energy of several hundred meV is formed. As a result, metal halide-based layered perovskites exhibit attractive optical properties such as photoluminescence (PL), electroluminescence (EL), and nonlinear optical effects originating from these excitons. In earlier studies, halide-based layered perovskites that used simple alkyl ammonium molecules as organic ammonium ions were investigated [4,6,14]. In this hybrid system, organic ammonium plays only the role of an insulating barrier layer. Recently, various halide-based layered perovskite materials with not only simple alkylammonium cations but also with various functional organic ammonium ions such as chromophores, polymers, and compounds with π -conjugated systems have been reported [2,3,10,15,16]. In these reported hybrid systems, unique optical, electronic, and magnetic properties could be observed. These experimental facts indicate that the properties of these

types of hybrid systems can be controlled by using selected functional organic ammonium as cations.

It is well known that the azobenzene chromophores exhibit reversible photoisomerization from *trans*- to *cis*- forms, enabling the optical and electronic properties of azobenzene chromophores to be significantly varied by the same photoisomerization process. Thus, the photoswitching of various properties and functions by the photoisomerization of azobenzene chromophores has been attempted by many researchers [18–23]. Halide-based layered perovskites with azobenzene chromophores have also been investigated, and a photoinduced energy transfer from the *trans*-azobenzene chromophore to a lead halide semiconductor layer was reported [8,16,17]. However, photoisomerization of azobenzene chromophores and changes to the optical and/or electronic properties of a metal halide semiconductor layer by photoisomerization is yet to be achieved. In this study, we attempted to synthesize a lead-bromide-based layered perovskite, which is a typical compounds, with azobenzene ammonium derivatives, and the spectroscopic characteristics of the synthesized hybrid powder was investigated both before and after UV and/or visible light irradiation.

2. Experimental

2.1. Materials

Lead(II) bromide (Kojundo Chemical Laboratory Co., Ltd.), 4-(phenylazo)phenol (Sigma-Aldrich Co. LLC.), *n*-dibromoalkane

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(TCI), and potassium phthalimide and hydrobromic acid (Nacal Tesque) were all used without further purification. Hydrazine monohydrate, silver nitrate aqueous solution, *N,N*-dimethylformamide (DMF), and sodium hydroxide were purchased from Kishida Chemical Co., Ltd. and also used without further purification. All other solvents were reagent grade.

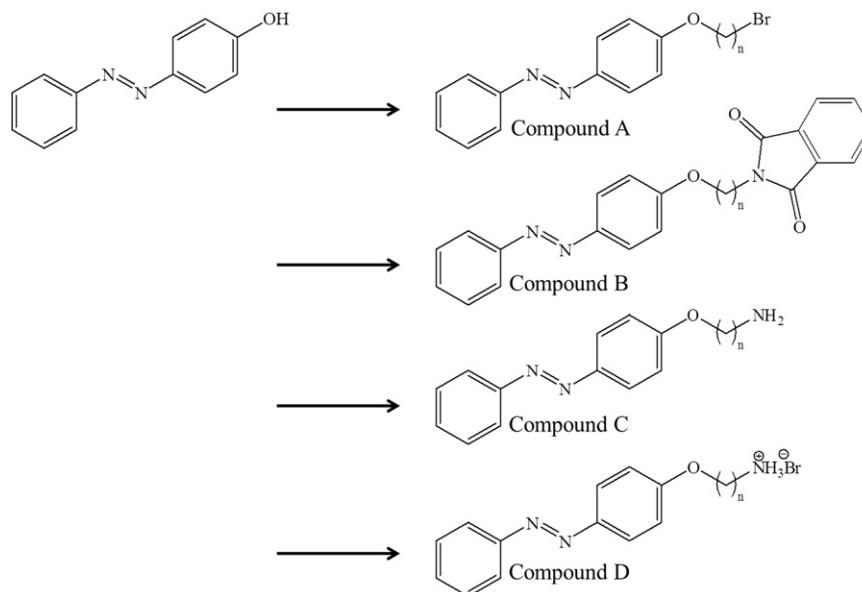
2.2. Synthesis of azobenzene derivatives

The azobenzene derivatives (compound D) used in this study were synthesized according to Scheme 1. Compound A: 4-(phenylazo)phenol (30 mmol) and 1,*n*-dibromoalkane (60 mmol, carbon number: $n=2, 4, 6$) were added to 30 cc of a 1 mol/dm³ NaOH aqueous solution, and then this mixture was refluxed with vigorous stirring overnight. After confirming a neutral pH, the products were extracted by chloroform. After dehydrating the chloroform solution by MgSO₄, compound A as a yellow powder was obtained by evaporating the solvent [$n=2$: yield=76.0%, ¹H NMR (500 MHz, CDCl₃) δ 7.93 (td, 2H), 7.88 (td, 2H), 7.51 (t, 2H), 7.45 (t, 1H), 7.03 (td, 2H), 4.38 (tt, 2H), 3.68 (tt, 2H). $n=4$: yield=38.2%, ¹H NMR (500MHz, CDCl₃) δ 7.92 (td, 2H), 7.88 (td, 2H), 7.50 (tt, 2H), 7.44 (tt, 1H), 7.00 (td, 2H), 4.09 (t, 2H), 3.51 (t, 2H), 2.31–2.08 (m, 2H), 2.02–1.97 (m, 2H). $n=6$: yield=56.4%, ¹H NMR (500 MHz, CDCl₃) δ 7.91 (td, 2H), 7.87 (td, 2H), 7.50 (tt, 2H), 7.43 (tt, 1H), 7.00 (td, 2H), 4.05 (t, 2H), 3.44 (t, 2H), 1.92 (quint, 2H), 1.85 (quint, 2H), 1.54 (quint, 4H)]. Compound B: compound A (15 mmol) and potassium phthalimide (18 mmol) was added to 200 cc of a DMF, and then this mixture was heated at 363 K for 3 h. After evaporating the solvent, the product was extracted by hot water and chloroform, and then the product was rinsed with hot water until bromide ions could no longer be observed by the AgNO₃ method. After dehydrating the chloroform solution by MgSO₄, compound B as an orange powder was obtained by evaporating the solvent [$n=2$: yield=97.6%, ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.90–7.84 (m, 6H), 7.75–7.72 (m, 2H), 7.49 (tt, 2H), 7.43 (tt, 1H), 6.99 (td, 2H), 4.32 (t, 2H), 4.16 (t, 2H). $n=4$: yield=98.5%, ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.91–7.84 (m, 5H), 7.71 (sext, 2H), 7.50 (tt, 2H), 7.43 (tt, 1H), 6.98 (td, 2H), 4.09 (t, 2H), 3.79 (t, 2H), 1.96–1.85 (m, 4H). $n=6$: yield=98.8%, ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.91–7.84 (m, 6H), 7.71 (q, 2H), 7.50 (t, 2H), 6.98 (d, 2H), 4.03 (t, 2H), 3.71 (t, 2H), 1.82 (quint, 2H)]. Compound C: compound B (8 mmol) and

hydrazine monohydrate (400 mmol) was added to 160 cc of a tetrahydrofuran (THF)/ethanol (EtOH) mixed solution (80/20, v/v), and then this mixture was heated at 353 K for 3 h. After removing the white precipitate (phthalic salt), the product was extracted by chloroform. After dehydrating the chloroform solution by MgSO₄, impurities were removed from the concentrated filtrate by diethylether. Compound C as an orange powder was collected by concentrating the obtained filtrate [$n=2$: yield=99.7%, ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, 2H), 7.88 (d, 2H), 7.50 (t, 2H), 7.44 (t, 1H), 7.03 (d, 2H), 4.09 (t, 2H), 3.13 (t, 2H), 1.53 (br, 2H). $n=4$: yield=68.4%, ¹H NMR (500 MHz, CDCl₃) δ 7.91 (td, 2H), 7.87 (td, 2H), 7.50 (tt, 2H), 7.43 (tt, 1H), 7.00 (td, 2H), 4.07 (t, 2H), 2.80 (t, 2H), 1.88 (quint, 2H), 1.65 (quint, 2H), 1.52 (br, 2H). $n=6$: yield=70.0%]. Compound D: compound C (2 mmol) was added to 100 cc of diethylether under N₂ atmosphere. Hydrobromic acid (2.4 mmol of 47%) was dropped to the mixed solution in an ice bath, producing an orange precipitate. Filtrated compound D as an ochre powder was obtained by a small amount of acetone [$n=2$: yield=99.1%, ¹H NMR (500 MHz, DMS-*d*₆) δ 7.97 (br, 3H), 7.93 (d, 2H), 7.85 (d, 2H), 7.60–7.52 (m, 3H), 7.20 (d, 2H), 4.29 (t, 2H), 3.29 (t, 2H) $n=4$: yield=83.6%, ¹H NMR (500 MHz, DMS-*d*₆) δ 7.90 (td, 2H), 7.84 (td, 2H), 7.68 (br, 3H), 7.58 (tt, 3H), 7.53 (tt, 1H), 7.14 (td, 2H), 4.12 (t, 2H), 2.88 (sext, 2H), 1.82 (quint, 2H), 1.72 (quint, 2H). $n=6$: yield=36.6%, ¹H NMR (500 MHz, DMS-*d*₆) δ 7.89 (td, 2H), 7.84 (td, 2H), 7.63 (br, 3H), 7.58 (tt, 3H), 7.52 (tt, 1H), 7.13 (td, 2H), 4.10 (t, 2H), 2.80 (sext, 2H), 1.77 (quint, 2H), 1.57 (quint, 2H), 1.46 (quint, 2H), 1.39 (quint, 2H)]. Hereafter, synthesized azobenzene derivatives are abbreviated as AzoCnA⁺Br⁻ ($n=2, 4, 6$).

2.3. Preparation of layered perovskite compounds with lead (II) bromide and azobenzene derivatives

AzoCnA⁺Br⁻ (0.10 mmol) and lead(II) bromide (0.05 mmol) were completely dissolved in 0.3 cc of DMF. After irradiating this DMF solution with near UV light (450 nm) for 10 min, precipitates were produced by adding sufficient quantities of acetone to this DMF solution under light shielding. These precipitates were collected by filtration, and then dried under reduced pressure at room temperature. Hereafter, obtained hybrid powders are abbreviated as PbBr-AzoCnA ($n=2, 4, 6$).



Scheme 1. Synthesis routes of AzoCnA ($n=2, 4, \text{and } 6$).

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