



Colorimetric polarity chemosensor based on a organometal halide perovskite functional dye



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ABSTRACT

We have investigated polarity sensing of organometal halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite functional dye based on hydrogen bonds between alcohols and polar units in perovskite. Upon exposure of alcohol solvents, perovskite film showed a drastic visible color change with different changing time depending on the polarities of alcohols. From the kinetic study of the reaction between perovskite dye and alcohols having different polarities, efficiency of hydrogen-bonding interactions between them were clearly revealed to be the main sensing mechanism, which enables effective discrimination of polarities by naked eyes. This study suggests a novel and practical sensing platform for highly sensitive colorimetric polarity chemosensors.

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1. Introduction

Chemosensors are sensory receptor molecules that are capable of selective detection of interested analytes or chemical properties of interest with a measurable optoelectronic changes. Due to their simplicity, high sensitivity, and real-time detection for various analytes, chemosensors have attracted considerable attention during the past decade [1]. Among them, development of chemosensor systems that have precise and rapid recognizability of polarity of chemical compounds is of particular importance in the chemistry field because most chemical reactions and processes are significantly influenced by polarity of reactant molecules. In particular, choice of organic solvents with appropriate polarity values plays a critical role in organic synthesis, recrystallization, and chromatographic separation of compounds.

Recently, a large number of chemosensors detecting environmentally harmful volatile organic compounds (VOCs), biologically important anions, cations, acidity, and explosive or hazardous chemicals have been extensively developed [2]. Polarity-sensitive probes also have been reported, however, most of their detection mechanisms have been focused on fluorescence emission changes

rather than reflective color shifts, and there still remain technical challenges to overcome, such as limitations in marked color/emission wavelengths shifts enough to detect with naked eyes [3]. Even worse, chemosensors or sensing techniques for discriminating molecules having minute polarity differences by displaying distinct outputs color changes are rarely explored. One of the reasons for this research scarcity in the polarity-analyzing system lies in the lack of suitable probing materials satisfying two essential issues for the investigation; i) spontaneous interaction with polar analytes at a molecular level and ii) quick and drastic visible color conversion after detection.

Organometal halide-type hybrid perovskites with a structure of ABX_3 (A = organic cation, B = metal cation, and X = halogen anion) have emerged as a new functional dye due to their unprecedented optoelectronic properties such as intense broad-band UV/Vis light absorption (300–800 nm) and 10 times greater absorption coefficient ($\epsilon = 1.3 \times 10^5 \text{ cm}^{-1}$ at 550 nm) compared to that of the conventional light-absorbing ruthenium-based molecular dye [4]. Moreover, as shown in Fig. 1a, ionic interactions between the organic and inorganic portions in the structure of this hybrid perovskite dye, for example $\text{CH}_3\text{NH}_3\text{PbI}_3$, facilitate its sensitive interactions with polar molecules. This unique character allows spontaneous crystal structure conversion into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in response to polar environments concomitant with a fast and

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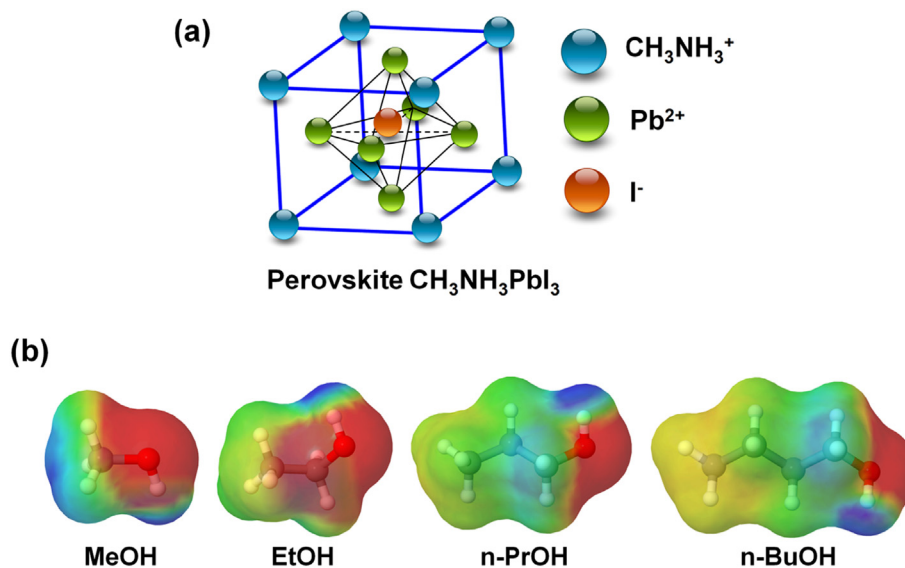
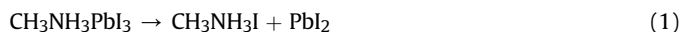


Fig. 1. (a) General (ABX₃) crystal structure of organometal halide perovskite (CH₃NH₃PbI₃). (b) Molecular electrostatic potential surface diagrams of MeOH, EtOH, n-PrOH, and n-BuOH.

discernible color conversion, according to the following chemical equation [5].



Taking advantages of these satisfactory optical and chemical properties which are compatible with the investigation on the molecule's polarity, herein, we introduced CH₃NH₃PbI₃ perovskite dye as a polarity sensing probe in attempt to develop an effective colorimetric polarity chemodosimeter. We demonstrate a simple but very effective method to distinguish polarities of alcohol solvents with minute difference in polarity values. The differences in optical responses and kinetics of hydrogen bonding interactions between perovskite and alcohols with different polarity provide insights into the photophysical polarity-sensing mechanism of perovskite.

2. Experimental section

2.1. Materials

Chemical reagents used in this study were used without any further purification. Methylammonium iodide (CH₃NH₃I) and lead (II) iodide (PbI₂) were purchased from Tokyo Chemical Industry (TCI). Dimethyl sulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH), and n-butanol (n-BuOH) were purchased from Sigma-Aldrich.

2.2. Film preparation and characterization

CH₃NH₃PbI₃ perovskite precursor solution was prepared using CH₃NH₃I and PbI₂ following the reported method [6], and the perovskite films in this study were prepared on the glass substrates. The substrates were rinsed by sonication in detergent and deionized water, acetone and isopropyl alcohol before film coating. Then, uniform and large-area (10 cm²) perovskite films were prepared in ambient condition by using a blade-coater and homogeneous CH₃NH₃PbI₃ precursor solution in DMSO. The wet films formed immediately after solution blading were kept at room temperature for 40 min before annealing to wait for the majority of DMSO

solvent to be dried and evaporated. Finally, the substrates were annealed at 100 °C for 15 min to complete perovskite film fabrication. ~400 nm-thick perovskite layers were obtained by blade-coating the precursor solution with a coating speed of 10 mm/s with the gap between blade and substrate of 10 μm at room temperature (Blade-coating was performed using a knife-coating device (KP-3000H, KIPAE). UV–vis absorption spectra were obtained using an Agilent 8457 UV–vis spectrophotometer. X-ray diffraction (XRD) data were recorded using a Rigaku D/max-2500 diffractometer. Electrostatic potential surface of alcohols were calculated using Avogadro and Jmol softwares.

3. Results and discussion

The crystal structure of perovskite dye (CH₃NH₃PbI₃) used in this study can be described by the general formula ABX₃, as shown in Fig. 1a. These organic-inorganic hybrid crystals are fixed together by the interaction between organic cation (CH₃NH₃⁺) and inorganic anion (PbI₃⁻) component through hydrogen bonds between the hydrogens on the NH₃⁺ and the iodide atoms (N–H/I⁻) and the hydrogens on the CH₃ and iodide atoms (C–H/I⁻) [4].

We prepared CH₃NH₃PbI₃ films using mixed precursor (CH₃NH₃I/PbI₂ in DMSO) solution using a blade-coating method, which is convenient and effective technique for large-area printing. The wet films deposited by a blade-coater were dried under room-temperature before annealing for crystallization at 100 °C. Formation of CH₃NH₃PbI₃ from wet film to the crystallized structure was clearly confirmed from the gradual evolution of absorption spectra and film color changes as shown in Fig. 2.

Firstly, to demonstrate the potential applications of CH₃NH₃PbI₃ perovskite films to colorimetric probes for the polarity detection of organic molecules, absorption spectral studies of CH₃NH₃PbI₃ film in the presence of alcohol solvents with different polarities were performed. For this study, the time course of the reaction between CH₃NH₃PbI₃ film and EtOH was investigated by monitoring the absorption intensities of the CH₃NH₃PbI₃ at λ_{max} (420 nm). As shown in Fig. 3, it was observed that strong intensity of absorption band at 420 nm quickly decreased to 60.2% of its initial one in less than 5 min, accompanied by a significant color changes from dark brown to yellow, with exposure to the EtOH solvent.

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