



## Research Highlight

# Hydrogen-bonded cation-composition-engineered color-stable blue PeLEDs

Fengjun Chun<sup>a,1</sup>, Kyung Yeon Jang<sup>a,1</sup>, Tae-Woo Lee<sup>a,b,c,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea

<sup>b</sup> School of Chemical and Biological Engineering, Seoul National University, Seoul 08826, Republic of Korea

<sup>c</sup> Institute of Engineering Research, Research Institute of Advanced Materials, Nano Systems Institute, Seoul National University, Seoul 08826, Republic of Korea

Perovskite light-emitting diodes (PeLEDs) have been considered to be the most promising candidate for solid-state lighting and high-definition full-color display due to their attractive properties such as tunable emission wavelengths, narrow full width at half maximum (FWHM), and high photoluminescence quantum yield (PLQY) [1–3]. The external quantum efficiencies (EQEs) of green- and red-emitting PeLEDs have exceeded 20%, rocketing toward the theoretical limit [4,5], but the blue PeLEDs still suffer from the obstacles of low efficiency and poor operational stability, which largely overshadows their real applications and industrial-scale adoption.

Composition engineering, preparing perovskites by adjusting the atomic ratio of chlorine and bromine, is a convenient and controllable method to prepare blue-emitting perovskites with desired wavelength and high PLQY [6]. However, the color stability of the blue PeLEDs under high voltage and long-term operation is still extremely low, resulting in that the electroluminescence (EL) spectrum shifts to the longer wavelength due to the inherent ionic nature of perovskite, that is, the ion migration-induced phase separation of mixed halide perovskite [7,8].

Many efforts have been paid to improve the color stability of the device, including cation composition engineering [9], ligand engineering [10], and interfacial engineering [11]. Among them, the cation composition engineering strategy, substitution of the original A cation ( $\text{Cs}^+$ ,  $\text{CH}(\text{NH}_2)_2^+$  ( $\text{FA}^+$ ),  $\text{CH}_3\text{NH}_3^+$  ( $\text{MA}^+$ )) in the  $\text{ABX}_3$  perovskites by other cations with similar radii, is beneficial to form a stable phase and to manipulate the conduction band of the perovskite layers [12]. As a result, the stability of PeLEDs is improved. For example, Xing et al. [13] reported that the phase monodispersity and crystallization of quasi-2D perovskite films can be enhanced by organic cation composition engineering. Jiang et al. [14] achieved a pure-blue PeLED with stable emission spectra by tuning the composition Rb and Cs in the A-site to form the Rb-Cs alloyed perovskites. The organic or inorganic cation composition engineering presents great potentials for color-stable blue PeLEDs.

Most recently, reporting in *Science Bulletin*, the research team led by Haibo Zeng [15] proposed the hydrogen-bonded cation composition engineering to prevent the phase separation of  $\text{CsPb}(\text{Br}/\text{Cl})_3$  mixed halide perovskite and then the color-stable sky-blue PeLEDs were realized (Fig. 1). Simple injection of guanidine (GA)-oleate or formamidine (FA)-oleate together with Cs-oleate into  $\text{PbX}_2$  precursor during the synthesis yielded doping of GA- or FA-doped into the A-site of  $\text{CsPb}(\text{Br}/\text{Cl})_3$  perovskite and partly replaced the  $\text{Cs}^+$ , as a result, the  $\text{N-H}\cdots\text{X}$  H-bonds between  $-\text{NH}_2$  and  $\text{Br}^-/\text{Cl}^-$  strengthened, and thereby increased the ion-migration barrier and effectively suppressed ion migration (Fig. 1a). This method reduces the ion migration caused by the weak interaction between  $\text{Cs}^+$  and  $\text{X}^-$  of the  $[\text{PbX}_6]^{4-}$  octahedron in  $\text{CsPb}(\text{Br}/\text{Cl})_3$  mixed halide perovskite and shows numerous positive effects on the optical properties and stability.

Optical properties after GA or FA doping were investigated. The positive effect of  $\text{N-H}\cdots\text{X}$  interaction by A-site cation doping was proved by our group [4] which obtained PLQY of 93.3% and  $\text{EQE}_{\text{max}}$  of 23.4% after GA doping in  $\text{FAPbBr}_3$ . In Zeng group's work [15], PLQY increased nearly 200% and photoluminescence (PL) lifetime of GA- or FA-doped  $\text{CsPb}(\text{Br}/\text{Cl})_3$  increased compared to the non-doped counterpart. This result reveals that non-radiative channels and defects were suppressed after doping. GA or FA doping into  $\text{CsPb}(\text{Br}/\text{Cl})_3$  also decreased the loss of PL and PL shift under external electric field. These results mean that the doping enhanced the structure and color stability.

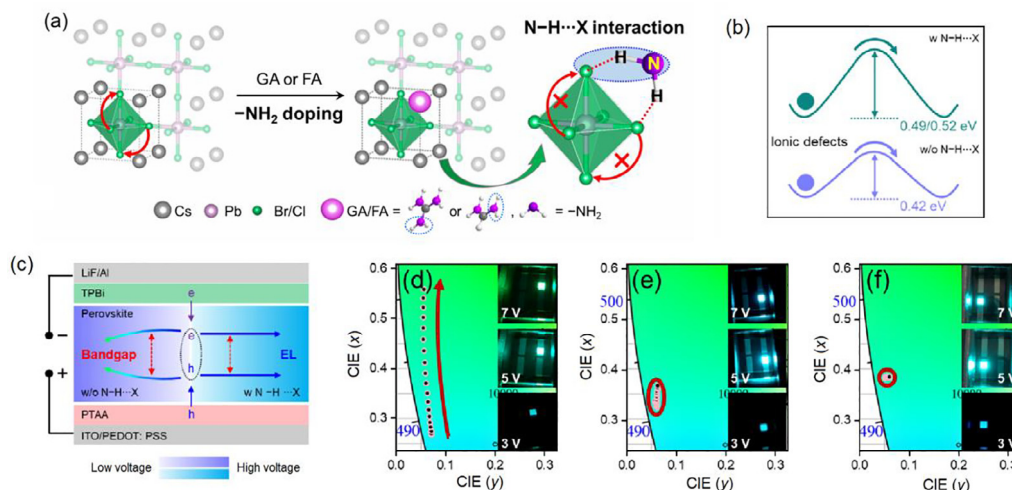
The authors further confirmed the mechanism of  $\text{N-H}\cdots\text{X}$  interaction for inhibiting the color shift of the device from the materials and device perspectives. From the materials perspective, the authors engaged in the Fourier transform infrared spectroscopy (FTIR) measurement to verify the existence of the doping group, and in which  $\text{C}=\text{N}$  vibrational spectra were observed and  $\text{N-H}$  stretching vibration peak was broadened and shifted, revealing the strong interaction between the amine-group and the halogen anion ( $\text{N-H}\cdots\text{X}$  interaction).

The ion migration is the immediate reason that causes a color-shift of mixed halide perovskite. Density functional theory (DFT) and climbing image nudged elastic band (CI-NEB) calculation were used to measure the ion migration barrier energy. The authors calculated which anion was the major kind of migration, and it

\* Corresponding author.

E-mail address: [twlees@snu.ac.kr](mailto:twlees@snu.ac.kr) (T.-W. Lee).

<sup>1</sup> These authors contributed equally to this work.



**Fig. 1.** (Color online) Hydrogen-bonded cation composition engineered color-stable blue PeLEDs. (a) N-H...X doping to inhibit ion migration of CsPbBr<sub>3-x</sub>Cl<sub>x</sub> QDs. (b) Demonstration of the energy barrier for ionic migration influenced by N-H...X interaction. (c) Schematic illustration of EL stability enhancement under external electric fields. (d) The color coordinates of blue PeLEDs without H-bonds. (e) The color coordinates of blue PeLEDs with FA doping. (f) The color coordinates of blue PeLEDs with GA doping [15]. Copyright © 2021, Elsevier B. V.

resulted that the migration barrier energy of Br<sup>-</sup> is calculated to be 0.58 eV which is lower than that of Cl<sup>-</sup> (0.7 eV) because the bonding energy of Pb-Br is weaker than that of Pb-Cl. The main migration element is Br<sup>-</sup>, so the migration barrier was calculated on CsPbBr<sub>3</sub> and GA- or FA-doped CsPbBr<sub>3</sub>. The maximum barrier for migration was confirmed to be 0.58 eV in CsPbBr<sub>3</sub>, 0.67 eV in FA-doped CsPbBr<sub>3</sub>, and 0.85 eV in GA-doped CsPbBr<sub>3</sub>. These results indicate that N-H...X interaction efficiently inhibits halide migration. Additionally, ion conduction activation energy ( $E_a$ ) was experimentally extracted by measuring the temperature-dependent conductivity.  $E_a$  of CsPb(Br/Cl)<sub>3</sub> was 0.42 eV, while the increased  $E_a$  of 0.49 and 0.52 eV for GA-doped CsPb(Br/Cl)<sub>3</sub> and FA-doped CsPb(Br/Cl)<sub>3</sub> were confirmed, which signified that N-H...X interaction could suppress the ion migration effectively (Fig. 1b).

From the device perspective, as the external bias voltage is increased, the weak van der Waals interaction between the Cs<sup>+</sup> and X<sup>-</sup> permits ion migration in the non-doped perovskite layer. As a result, a bromide-rich phase with narrow bandgap appears, and the emission spectrum redshifts with continuous operation of the device. Nevertheless, by introducing the cations with amine-groups into the perovskites, the strong H-bond binding restricts the ion migration and further stabilizes the bandgap and emission spectrum (Fig. 1c). As a benefit of the low ion migration rate, PeLEDs that use GA- or FA-doped CsPb(Br/Cl)<sub>3</sub> perovskite have excellent color stability (Fig. 1d-f). For blue PeLEDs without H-bonds, the EL spectrum red-shifted 15 nm from 487 to 502 nm as operating voltage was increased from 3 to 7 V. However, the introduction of the H-bond into the perovskite layer yielded a constant of the EL spectra at 490.5 and 492.5 nm for GA- and FA-doped CsPb(Br/Cl)<sub>3</sub> based PeLED, respectively.

Overall, this work by Zeng and co-workers [15] provides an effective and promising strategy to achieve high-efficiency and color-stable blue PeLEDs. The results not only deepen the understanding of the impact of A-site substitution on halide ion diffusion in perovskites, but also provide a platform for high-performance and stable perovskite optoelectronic devices. So far, there are few candidates for the A-site cations, and further work focusing on the substitution of new cations will be needed to expand the range of perovskite materials. Moreover, developing multiple cations doped perovskite materials and understanding the interaction mechanism of the ions may guide development of ways to signifi-

cantly increase the optoelectronic properties and stability of the PeLEDs and to facilitate their commercialization.

### Conflict of interest

The authors declare that they have no conflict of interest.

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Fengjun Chun is pursuing her doctor's degree under the supervision of Prof. Weiqing Yang at Southwest Jiaotong University. In 2019, she joined Seoul National University as a visiting scholar under the supervision of Prof. Tae-Woo Lee. Her research focuses on perovskite nanocrystals and their applications in optoelectronic devices.



Tae-Woo Lee is a full professor in Materials Science and Engineering at the Seoul National University. He received his Ph.D. degree in Chemical Engineering from the Korea Advanced Institute of Science and Technology in 2002. After his doctorate, he joined Bell Laboratories, USA as a postdoctoral researcher and then worked at Samsung Advanced Institute of Technology as a senior member of research staff (2003–2008). He was an associate professor in Materials Science and Engineering at the Pohang University of Science and Technology (POSTECH) until 2016. His research focuses on flexible or printed electronics based on organic and organic-inorganic hybrid materials for displays, solid-state lighting, solar energy conversion devices and neuro-morphic bioelectronics.



Kyung Yeon Jang is studying his Ph.D. course and received his B.S. degree at the Department of Materials Science and Engineering, Seoul National University. His research focuses on synthesis of blue-emitting perovskite quantum dot and fabrication of perovskite LED for displays.