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# Phase Transition in Halide Double Perovskites for Solar-To-Chemical Energy Conversion

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Halide double perovskites have recently garnered significant interest in solar energy conversion applications owing to their non-toxic and high solar absorption properties. However, unanticipated structural distortion within these materials can compromise their performance, suppressing the structural distortion is essential and remains challenging. Here, it is reported that using phenylethylamine triggering the disorder-order phase transition can largely increase the ordering extent of octahedra in double perovskite Cs<sub>2</sub>AgBiBr<sub>6</sub>, which can suppress self-trapped exciton and defect and enable rapid charge separation, leading to exceptional photo-physics/chemistry properties with over sixfold photoactivity enhancement in the photocatalytic C–H bond activation compared to less ordered structures. This work provides an effective strategy to solve the challenging problem of the disorder phenomenon of halide double perovskites for boosting solar-to-chemical energy conversion.

# 1. Introduction

Halide perovskites (HPs) have aroused tremendous attention in photoelectronic applications in the past decade owing to their fantastic optoelectronic properties.<sup>[1-3]</sup> Until now, HP solar cells power conversion efficiency has skyrocketed to 26%,<sup>[4]</sup> on par with silicon technology. Besides solar cells, HPs also hold huge promise in lightemitting diodes,<sup>[5,6]</sup> photodetectors,<sup>[7,8]</sup> photocatalysis,<sup>[9,10]</sup> and storage/memory devices.<sup>[11,12]</sup> Although lead-based perovskites, such as methylammonium lead halides, have demonstrated great potential for optoelectronic applications, the poor stability and toxicity of

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**Figure 1.** The effects of phase transition on charge dynamics. A) Schematic illustrating charges trapped within a distorted lattice and the charge localization resulting from non-periodic disorder and lattice defects. B) Diagram depicting the free exciton being self-trapped via deformation potential. C) Schematic representing the density of states (DOS) in a disordered semiconductor. D) Scheme of the PEA ligand-mediated disorder-order phase transition of the CABB material. Figure 1A: Reproduced with permission from Ref. [16] and Ref. [18] Copyright 2023, Wiley-VCH; Copyright 2020, The Royal Society of Chemistry. Figure 1B: Reproduced with permission from Ref. [16] Copyright 2023, Wiley-VCH.

most Pb-based HPs limit their further applications.<sup>[13,14]</sup> Recently, inorganic halide double perovskites A2BIBIIIX6 have emerged as promising lead-free alternatives. Among them, Cs<sub>2</sub>AgBiBr<sub>6</sub> (CABB), a compound with a suitable bandgap, microsecond carrier lifetime, and superior environmental stability, has triggered much attention.<sup>[13]</sup> Nevertheless, due to the solution synthesis process using cation precursors (i.e., CsBr, AgBr, and BiBr<sub>3</sub>), the formation of a partially disordered phase with random arrangements of [AgBr<sub>6</sub>]<sup>5-</sup> and [BiBr<sub>6</sub>]<sup>3-</sup> octahedra is inevitable and energetically favorable,<sup>[15]</sup> leading to an increased electrostatic repulsion between neighboring octahedra (Figure 1A),<sup>[16]</sup> distorting the crystalline structure originating from Jahn-Teller-like distortion.[15,17] Consequently, the strong interaction between electrons and phonons traps photogenerated charge carriers in distorted states, forming self-trapped excitons (STFs) that hinder charge transport (Figure 1B).<sup>[15,16,18]</sup> Moreover, the disorder in cation occupancies results in Ag<sub>Bi</sub> antisite defects within the bandgap, creating recombination centers for charge carriers (Figure 1C).<sup>[15,18,19]</sup>

Structural engineering has significantly advanced the efficient separation of photogenerated charge carriers in semiconductors.<sup>[17,20,21]</sup> Theoretically, density functional theory (DFT) is employed to investigate the disorder-order phase transition in mixed sublattices of the ordering parameter.<sup>[22-24]</sup> For instance, Zhang et al. conducted DFT to gain insight into how the configuration of Ag<sup>+</sup>/Bi<sup>3+</sup> cations influences the electronic structures of  $Cs_2AgBiX_6$  (X = Br, Cl).<sup>[24]</sup> Similarly, Yang et al. demonstrated that Ag-Bi disorder in CABB affects the band structure through band hybridization.<sup>[23]</sup> Experimentally, incorporating ligands/polymers as site-selective binders in double perovskite oxides has been shown to promote cation ordering. Especially, the phenyl  $\pi$ -electron cloud interacts with  $\sigma^*$  orbital of Bi-X via a push-electron-induced effect,<sup>[25]</sup> facilitating bonding with Bi<sup>3+</sup> ions. Additionally, the formation of enantioselective complex chiral macrocycles associated with enantiomeric recognition enhances the bonding of aromatic halogenated amines with Ag<sup>+,[26]</sup> Inspired by these findings, introducing suitable ligands could improve the lattice

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ordering of CABB. Encouragingly, phenylethylammonium (PEA) has been reported to assist crystal regulation in CABB by enhancing Ag<sup>+</sup>/Bi<sup>3+</sup> ordering,<sup>[15,17,27,28]</sup> leading to improved lattice structure and optoelectronic properties. This effect can be attributed to a combination of selective coordination, electrostatic interactions, and lattice strain relaxation. Specifically, PEA preferentially coordinates with Ag<sup>+</sup> and Bi<sup>3+</sup>, stabilizing their positions and reducing cation disorder. Furthermore, PEA could influence the local electrostatic environment, promoting a thermodynamically stable ordered structure. Despite these advances, the effects of the phase transition in CABB on its applications in solar-to-chemical energy conversion remain rarely unexplored.

In this work, we focused on typical halide double perovskites, CABB. In situ regulation of the order-disorder phase transition in the CABB using phenylethylamine bromide (PEABr) ligand was used to improve  $Ag^+/Bi^{3+}$  cations ordering, which brings about dramatic differences in photoelectric and catalytic properties. Specifically, the ordered structure exhibits improved charge separation and reduced barrier energy in surface photoredox reactions compared to the less ordered one. Benefiting from the phase transition, the modified CABB drastically improves the photocatalytic performance when testing benzylic C(sp<sup>3</sup>)–H bond activation in toluene under simulated solar light.

## 2. Results and Discussion

Figure 1C illustrates the effect of PEA on the arrangements of [AgBr<sub>6</sub>]<sup>5-</sup> and [BiBr<sub>6</sub>]<sup>3-</sup> octahedra of CABB (PEA-CABB). Theoretical investigations using DFT calculations were first performed to examine changes in electronic structures of CABB influenced by cation ordering,<sup>[29,30]</sup> including band structure, density of states (DOS), and charge distribution (Figure 2; Figure S1, Supporting Information). Examining the CABB and PEA-CABB structures cell characteristics (a) and volumes reveal that following PEA modification of the CABB, the "a" value increased marginally from 11.23 to 11.28 Å, and the volume increased from 1417.50 to 1433.65 Å<sup>3</sup>. Looking at the relative stabilities of these two systems shows that the PEA-CABB structure is more stable than the CABB, with a total energy of -119.0963 eV for the PEA-CABB structure and -118.93057 eV for the CABB. The total density of state (TDOS) and atomic-resolved projected density of state (PDOS) spectra provide a more detailed electronic structure analysis. Figure 2A, B illustrates the PEA effects in PEA-CABB, wherein the Ag 4d orbitals hybridize with Br 4p orbitals to jointly contribute to the VBM while the Bi 6p orbitals occupy the CBM. The introduction of the PEA leads to a slightly enhanced bandgap, changing from 2.15 to 2.19 eV, where the bandgap for both structures is indirect (Figure 2C,D). This supports the experiments regarding the evolution of a wider bandgap upon introducing PEA (vide infra). The CBM and VBM-associated charge density maps of the primitive cells of CABB and PEA-CABB are shown in Figure 2C,D. In contrast to the charge density of CABB, the PEA-CABB exhibits greater and more dispersive CBM and VBM-associated charge densities, which are attributed to the better-ordered arrangement of Ag<sup>+</sup> and Bi<sup>3+</sup>.<sup>[17]</sup>

Next, we move to synthesize the materials and examine their photoelectronic properties experimentally. The synthetic process

of the CABB is described in the Experimental section. A similar procedure was adopted to synthesize ordered CABB, except utilizing the complexing ability of PEA<sup>+</sup> ligand with Ag<sup>+</sup> and Bi<sup>3+</sup> ions to promote cation occupancy ordering. Specifically, the  $\pi$  electron clouds of the phenyl group in PEA<sup>+</sup> tend to bond with the  $\sigma^*$  orbital of Bi<sup>3+</sup> due to a push electron-induced mechanism.<sup>[25]</sup> Meanwhile, the ammonium group of PEA<sup>+</sup> forms a bond with Ag<sup>+</sup> through a noncovalent intermolecular force. This preferred linkage is facilitated by the similarity in distance between the phenyl and ammonium groups in PEA<sup>+</sup> (6.4 Å),<sup>[17]</sup> and the distance between Ag<sup>+</sup> and Bi<sup>3+</sup> in CABB (6.5 Å). As a result, [AgBr<sub>6</sub>]<sup>5-</sup> and [BiBr<sub>6</sub>]<sup>3-</sup> octahedra are structured periodically, ultimately forming an ordered CABB.

Quantitative assessment of cation ordering in double perovskites can be achieved by evaluating X-ray diffraction (XRD) patterns of the samples.<sup>[15,17]</sup> Generally, CABB belongs to the Fm $\overline{3}$ m space group and the crystal structure deviates from the conventional extinction law for (111) and (022) planes. For the fully disordered Ag<sup>+</sup> and Bi<sup>3+</sup>, the (111) plane would be extinct.<sup>[17]</sup> Therefore, studying the intensities of the (111) and (022) planes (i.e., I<sub>111</sub>/I<sub>022</sub>) is a powerful approach to analyzing the extent of ordering in the CABB. The higher the ratio, the better the ordering of the [AgBr<sub>6</sub>]<sup>5-</sup> and [BiBr<sub>6</sub>]<sup>3-</sup> octahedra and fewer Ag<sub>Bi</sub> antisite defects. This has been accredited in such double perovskite structures.<sup>[31,32]</sup>

Figure 2E shows the XRD patterns of CABB and PEA-CABB samples with various concentrations of PEABr precursor. All the samples exhibit the same diffraction peaks, where no PEA-based material such as PEA<sub>4</sub>AgBiBr<sub>8</sub> is formed, indicating that PEA introduction does not affect the intrinsic structure of CABB. Additionally, all the PEA-CABB samples show negligible peak shifts compared to pristine CABB, suggesting minimal strain effects. Note that the PEA<sup>+</sup> may remain attached to the compound with coordinate bonds after the formation of ordered CABB, and the ligand can be desorbed at a high temperature like 280 °C.<sup>[15]</sup> However, changes are visible when quantitatively analyzing the peak intensity and width in detail. The intensity of the (111) plane relative to the (022) plane increases with the increase of PEA concentration (Figure 2F), indicating an enhancement in the ordering of Ag<sup>+</sup> and Bi<sup>3+</sup> occupancies.<sup>[17]</sup> Meanwhile, the full width at half maximum (FWHM) of the (111) plane decreases as the PEA+ concentration increases, suggesting improved cation ordering and reduced density of  $Ag_{Bi}$  defects in the PEA-CABB samples.<sup>[17]</sup> This is collaborated by Raman measurements (Figure 2G). Based on the maximum structural ordering and photocatalytic activity observed within the range tested (vide infra), the 10% PEA-CABB sample was selected for the experimental characterization. The Raman spectrum of the original CABB shows a strong peak at 180 cm<sup>-1</sup>, attributed to a longitudinal optical (LO) phonon mode A<sub>1g</sub>, in conjunction with the symmetric stretching vibration of Br around Bi atoms.<sup>[33]</sup> Another two peaks at the lower wavenumber were also detected. The peak at 139 cm<sup>-1</sup> is assigned to the  $E_{1g}$ mode, corresponding to the asymmetric stretching vibrations of Br around the Bi atoms. Meanwhile, the  $\rm T_{2g}$  mode at 74  $\rm cm^{-1}$  is linked to the scissoring motion of Cs around Br atoms. Here, we focus on the  $A_{\rm 1g}$  mode as it is responsible for electron–phonon coupling and crystalline lattice distortion.<sup>[15]</sup> Compared to pristine disordered CABB, a noticeable decrease in the FWHM of LO mode in the representative 10%PEA-CABB sample and a

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**Figure 2.** Structural investigation combining theoretical calculations and experimental characterization. A,B) Band structure and PDOS and C,D) charge distributions of CBM and VBM of CABB and PEA-CABB systems, respectively. E) XRD patterns CABB and a series of PEA-CABB samples with different concentrations of PEA<sup>+</sup> precursor. F) The peak corresponds to the (111) plane relative to the intensity of the (022) plane. G) Raman spectra and H) FWHM of the  $A_{1g}$  mode and Raman shift of CABB and 10%PEA-CABB samples.

slight peak shift toward higher energy were observed (Figure 2H). This observation has also been reported in other systems,<sup>[34]</sup> reinforcing the inference of increasing order in the cation occupancy.

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the chemical structure and valence state of the materials. Figure S2B (Supporting Information) shows the two characteristic Cs 3d peaks at 738.1 and 724.1 eV, corresponding to Cs 3d<sub>3/2</sub> and Cs 3d<sub>5/2</sub>, respectively.<sup>[35]</sup> No changes were observed for the PEA-CABB sample. Similar shifts were also noted in Ag 3d, Bi 4f, and Br 3d (Figure S2C–E, Supporting Information). Furthermore, the absence of N 1s peak in the PEA-CABB (Figure S2F, Supporting Information) indicates that PEA is not incorporated in the lattice or forming PEA-based compounds. Ultraviolet pho-

toelectron spectroscopy (UPS) revealed slight alterations in secondary electron cutoff and valence band edge of these two systems (Figure S3, Supporting Information). Fourier transform infrared (FTIR) spectroscopy showed the interaction between PEA and Ag<sup>+</sup>/Bi<sup>3+</sup> (Figure S4, Supporting Information). Scanning electron microscope (SEM) revealed similar surface morphology for both CABB and PEA-CABB materials (Figure S5, Supporting Information), and energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of the same elements. Transmission electron microscope (TEM) images showed that CABB and PEA-CABB possess comparable particle structures (Figure S6, Supporting Information), with in-plane (200) lattice spacings of 0.32 nm, aligning with the known lattice parameters of CABB.<sup>[36]</sup> EDS mapping demonstrated the Cs, Ag, Bi, and Br



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**Figure 3.** Optical and electronic properties. A) UV-vis DRS spectra of CABB and a series of PEA-CABB samples. B) Steady-state PL spectra, C) timeresolved PL decay, D,E) pseudocolor temperature-dependent PL, F) FWHM of PL peaks as a function of temperature, G,H) AFM and KPFM potential images in dark and under light irradiation, and I) the corresponding SPV curves of CABB and 10%PEA-CABB materials, respectively.

elements across the PEA-CABB sample (Figure S7, Supporting Information).

The optical absorption properties of the pristine CABB and PEA-CABB were examined using UV–vis diffuse reflection spectroscopy. The absorption spectrum of CABB shows an absorption band edge at 595 nm (**Figure 3**A). Upon introducing PEA, a slight blue shift was observed (optical photos are shown in Figure S8, Supporting Information), which may be attributed to enhanced cation ordering in the double perovskite structure.<sup>[17]</sup> This observation is in line with previous findings,<sup>[23,37]</sup> in which an ordered system exhibits a higher light absorption threshold than a disordered one.

The photophysical properties of CABB and PEA-CABB materials were further investigated through photoluminescence (PL) spectroscopy. The steady-state PL spectrum of CABB shows an emission peak at around 646 nm (Figure 3B). No changes in defect-related PL emissions in PEA-CABB samples were observed, indicating that the defect density remains relatively unchanged. A lower PL intensity was observed in PEA-CABB compared to CABB, indicating suppressed radiative recombination and thus a reduction in unwanted recombination pathways for the photogenerated charge carriers.<sup>[38,39]</sup> This is supported by the time-resolved PL data (Figure 3C), where the PL decay of the samples was analyzed using a bi-exponential model, with the extracted decay constants  $\tau_1$  and  $\tau_2$  corresponding to bound exciton and free exciton recombination, respectively.<sup>[10,40]</sup> The PEA-CABB sample showed a longer lifetime than pure CABB, with the contribution of  $\tau_1$  decreasing from 43.2% (64 ns) to 37.7% (85 ns), while  $\tau_2$  contribution increased from 56.8% to 62.3% with  $\tau_2$  extending from 635 to 976 ns. The suppressed exciton recombination and enhanced carrier lifetime are attributed to the fast electron-hole separation, providing clear evidence of more effective charge separation for PEA-CABB. Previous studies have suggested that the disordered arrangements of Ag<sup>+</sup> and Bi<sup>3+</sup> in

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**Figure 4.** Photocatalytic activity evolution and reaction mechanism study. A) The photocatalytic performance of toluene oxidation over CABB and x%PEA-CABB catalysts. B) Control experiments with different scavengers. C) Comparison of the photocatalytic activity of toluene oxidation over the 10%PEA-CABB material and other recently reported photocatalysts. D) Charge density difference plots of the toluene adsorption on catalysts and Bader charge analysis (left panel), and the adsorption energy between the catalyst and the BAD product (right panel). E) Gibbs free energy for CABB and PEA-CABB. F) Schematic illustration of the toluene photooxidation processes over PEA-CABB catalyst.

the double perovskite compound lead to strong electron–phonon interactions.  $^{\left[ 15\right] }$ 

To better understand the effect of Ag<sup>+</sup>/Bi<sup>3+</sup> ordering in our case, temperature-dependent PL measurements were performed (Figure 3D,E; Figure S9, Supporting Information). The electron–phonon coupling was quantitatively evaluated using the Huang–Rhys factor (S), derived from the FWHM of the PL peaks according to the equation:<sup>[17]</sup>

$$FWHM = 2.36\sqrt{S}H\omega_{phonon}\sqrt{\coth\frac{H\omega_{phonon}}{2\kappa_{B}T}}$$
(1)

where  $\omega$  phonon is phonon frequency, T is temperature, and  $k_{\rm B}$  is the Boltzmann constant. As shown in Figure 3F, the S values of pristine CABB and PEA-CABB are determined to be 48.2 and 43.6, respectively. Normally, a higher S value indicates a greater tendency for the formation of STEs.<sup>[17]</sup> The above analyses reveal the improved photoelectric properties in PEA-CABB systems.

Kelvin-probe force microscopy (KPFM) was further conducted to observe the surface potential of CABB and PEA-CABB before and after exposure to light.<sup>[41]</sup> AFM images (Figure 3G,H) show CABB with comparable nanoparticle sizes of several hundred nanometers. The corresponding line profiles of the contact potential difference (CPD) of images in the dark and under light illumination of PEA-CABB is about 176.2 mV (Figure 31), significantly higher than that of CABB (34.2 mV), verifying that more accumulation of photogenerated charges on the surface of PEA-CABB as the enhanced charge separation. To better understand the mechanism behind the improved charge separation, electrochemical impedance spectroscopy (EIS) was employed to investigate the changes in charge-transfer properties of the samples (Figure S10, Supporting Information). According to the Nyquist plot, the charge-transfer resistance ( $R_{ct}$ ) of PEA-CABB (11.3 k $\Omega$ ) is significantly lower than that of CABB (21.1 M $\Omega$ ), indicating that the incorporation of PEA enhances electrical conductivity in CABB,<sup>[10]</sup> thereby improving charge transport.

The photoelectronic properties of the samples were then assessed using photocatalytic toluene oxidation as a model reaction (Figure S11, Supporting Information, see Experimental section), with the photocatalytic performance summarized in Figure 4A. No reaction products were detected in the absence of photocatalyst and light irradiation. After 4 h of light irradiation, pristine CABB yielded benzaldehyde (BAD) at a production rate of 905.2  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>, with minor amounts of benzyl alcohol

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(BA) as the main side product (125.3  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>), resulting in a BAD selectivity of 87.8%. By contrast, the PEA-CABB materials showed a significant enhancement in photoactivity. The highest BAD production rate of 5801.6  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> was achieved with the 10%PEA-CABB compound with a selectivity of 92.8%, which represents a 6.4-fold improvement over the original CBB. GC-MS measurements confirmed the generated BAD and BA products (Figure S12, Supporting Information), and no other potential byproducts (e.g., benzoic acid) were detected. Note that the PEA beyond 20% leads to a decrease in photocatalytic performance, possibly due to the lower charge separation and reduced active sites. Importantly, the optimized 10%PEA-CABB sample outperforms the most recently reported photocatalysts (Figure 4B; Table S1, Supporting Information).

To elucidate the mechanism of this reaction, isotope labeling experiments were performed. Using deuterated toluene (d<sub>8</sub>toluene) as the reactant revealed a kinetic isotope effect (KIE) with a  $k_{\rm H}/k_{\rm D}$  ratio of 3.3 (Table S2, Supporting Information), indicating that the cleavage of the C(sp<sup>3</sup>)-H bond in toluene is the rate-determining step.<sup>[42,43]</sup> Also, the GC-MS spectra of the deuterated products were summarized in Figure S13 (Supporting Information). Control experiments with scavengers were further conducted to better understand the reaction mechanism (Figure 4C). Ammonium oxalate (AO), silver nitrate (AgNO<sub>3</sub>), 1,4-benzoquinone (p-BQ), t-butanol (t-BA), and butylated hydroxytoluene (BHT) were used as scavengers for holes (h<sup>+</sup>), electrons (e<sup>-</sup>), superoxide (°O<sub>2</sub><sup>-</sup>), hydroxyl (°OH<sup>-</sup>), and carboncentered radicals (\*R), respectively, to investigate their effects on the toluene photooxidation.<sup>[44-46]</sup> Scavenging the photogenerated holes with AO led to a significant decrease in toluene conversion efficiency. The presence of AgNO3 electron scavengers reduced the reaction rate but did not completely stop it. The addition of p-BQ also resulted in diminished conversion rates. On the other hand, replacing O<sub>2</sub> with Ar nearly halted the reaction altogether. Note that AgNO<sub>3</sub> has a more significant inhibitory effect on the reaction rate than Ar gas. A similar effect was observed with the introduction of BHT radical scavengers, whereas the addition of t-BA had minimal impact on the reaction rate. These experiments highlight the importance of free radicals and indicate that photogenerated electrons and holes play a pivotal role in toluene activation.

Electron paramagnetic resonance (EPR) was employed to identify the generated reactive oxygen species, using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping agent (Figure S14, Supporting Information). In the dark, extremely weak DMPO- ${}^{\bullet}O_{2}^{-}$  signals were recorded, with no toluene conversion occurring under these conditions. Upon exposure to light irradiation, the EPR signals of  ${}^{\bullet}O_2^{-}$  species were detected, with the signal strength increasing as the illumination time extended, indicating that photogenerated electrons in the PEA-CABB catalyst reduce  $O_2$  to  $O_2^{-}$ . Additionally, a strong signature corresponding to the nitroxide radical was detected after prolonged irradiation, resulting from the cleavage of the N-C bond and the ring opening of the DMPO-•O<sub>2</sub><sup>-</sup> adduct. Based on these observations, a plausible mechanism for the selective photooxidation of toluene to BAD over the PEA-CABB photocatalyst is proposed:[45,46] under light irradiation, PEA-CABB absorbs solar light with certain photon energy, generating electron-hole pairs. The electrons transfer to the photocatalyst's surface, reducing absorbed molecular oxygen

into  ${}^{\circ}O_{2}^{-}$  species; meanwhile, the holes oxidize the toluene substrates into carbocations. The toluene radical carbocations then react with  ${}^{\circ}O_{2}^{-}$  species to generate the BAD product.

The stability of the 10%PEA-CABB material was also assessed. Figure S15A (Supporting Information) shows the uncompromised photoactivity after five successive cycles compared to its initial performance, suggesting the good stability of this material. XRD patterns (Figure S15B, Supporting Information) further confirm the well-maintained crystal structure of the catalyst, indicating its high stability.

To develop an in-depth understanding of photoactivity enhancement in the PEA-CABB system at the molecular level, DFT calculations were performed to detail the surface photoredox reactions. Charge density difference and Bader charge analysis were first computed to examine the charge population and transfer between the catalyst and adsorbed reactant (Figure 4D; Figures S16 and S17, Supporting Information). The results indicated that the charges transfer from PEA-CABB to toluene molecules are greater than that of the CABB sample, suggesting the better activation of the reactant and thus facilitating the conversion of toluene to the main BAD product.<sup>[47,48]</sup> Furthermore, PEA-CABB exhibits a stronger adsorption ability of the reactant intermediates (Figure S18, Supporting Information) and weaker desorption of BAD compared to CABB (Figure 4D, right panel), which is beneficial for improving photoactivity.<sup>[49]</sup> The Gibbs free energy of the elementary steps was further investigated, with the energy diagram shown in Figure 4E. Electron charge density difference studies show the unobservable surface interactions between adsorbed toluene molecules and catalytic surfaces (Figures S16 and S17, Supporting Information). PEA-CABB exhibits stronger interaction between H and Bi atoms due to their shorter distance (2.71Å) and localized charge distribution. This tilts the toluene molecule toward the Bi atom, facilitating C-H bond dissociation (Figure 4F). The Gibbs free energies for toluene molecule absorption and activation on CABB and PEA-CABB were computed. The negative adsorption energies indicate that the adsorption of toluene molecules on these catalysts is more energy-efficient. Although C-H bond dissociation is a slightly uphill process, PEA-CABB has a lower activation energy barrier (1.22 eV) than CABB (1.47 eV), indicating a much faster toline conversion process on PEA-CABB. Bader charge analysis was used to explain this variation in activation energy. The charge transferred from the PEA-CABB to the \*PhCH<sub>2</sub> intermediate is greater than that of the CABB (Figure 4D), suggesting that the touline molecule reactant is better activated and that \*PhCH<sub>3</sub> is converted to \*PhCH<sub>2</sub> more easily. Furthermore, all subsequent reaction steps are energetically favorable (Figure 4E) except for the production of \*PhCH<sub>2</sub>O. Notably, the PEA-CABB system shows a lower energy barrier for the formation of intermediates, including the rate-limiting step of \*PhCH<sub>2</sub> generation (Figure S19, Supporting Information), compared to the original CABB, thereby reducing the energy barrier for the overall oxidation processes. As a result, the adsorption and activation of toluene molecules are thermodynamically favored, enhancing the photocatalytic oxidation of toluene.<sup>[49]</sup> Based on the results, the conversion pathways of toluene photooxidation over PEA-CABB photocatalyst, with adsorption structures of intermediates, are illustrated in Figure 4F and Figure S20 (Supporting Information).

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# 3. Conclusion

In summary, regulating the arrangement  $[AgBr_6]^{5-}$  and  $[BiBr_6]^{3-}$ octahedra improved the ordering extent of the octahedra in CABB. This improvement eliminates the self-trapped excitons and the Ag<sub>Bi</sub> antisite defects, thereby reducing the strong localization of electron-hole pairs and charge recombination. Experimentally, this phase transition was achieved through the modification of the PEA ligand. The reorganized material demonstrated superior charge separation efficiency compared to the original CABB. As a result, the enhanced intrinsic photoelectric properties of the phase-ordered material led to a significant improvement in photocatalytic toluene oxidation performance, over sixfold higher than the less-ordered sample. Overall, the selective coordination of the functionalized phenyl and ammonium ion in PEA<sup>+</sup> facilitates the formation of an alternating ordered arrangement of Ag<sup>+</sup> and Bi<sup>3+</sup> ions. This enhanced ordering of [AgX<sub>6</sub>]<sup>5-</sup> and [BiX<sub>6</sub>]<sup>3-</sup> octahedra, both theoretically and experimentally validated, plays a crucial role in modulating the bandgap and reducing defect density compared to pristine Cs<sub>2</sub>AgBiBr<sub>6</sub>. Furthermore, the high degree of Ag<sup>+</sup>/Bi<sup>3+</sup> ordering significantly suppresses self-trapped exciton formation, leading to an increase in carrier mobility, a key factor in improving optoelectronic performance. This study highlights the relationship between crystal structure and photoactivity in halide double perovskites, offering valuable insights into understanding the photoelectric properties of these materials, which may also inform research involving artificial intelligence.<sup>[50]</sup>

# 4. Experimental Section

*Materials*: Cesium bromide (CsBr, 99.9%), bismuth(III) bromide (BiBr<sub>3</sub>,  $\geq$ 98%), silver bromide (AgBr,  $\geq$ 99.9%), phenylethylamine bromide (PEABr,  $\geq$ 98%), dimethyl sulfoxide (DMSO, anhydrous,  $\geq$ 99.9%), isopropanol (IPA,  $\geq$ 99.5%, ACS reagent), and toluene (anhydrous, 99.8%) were purchased from Sigma–Aldrich. All chemicals were used without further purification.

Sample Preparation: Synthesis of Cs<sub>2</sub>AgBiBr<sub>6</sub>: Cs<sub>2</sub>AgBiBr<sub>6</sub> was synthesized using a room temperature solution process via an anti-solvent precipitation approach. Specifically, 319.2 mg of CsBr, 336.5 mg of BiBr<sub>3</sub>, and 140.8 mg of AgBr were first dissolved in 5 mL of DMSO solution in a stoichiometric molar ratio (i.e., CsBr:AgBr:BiBr<sub>3</sub> = 2:1:1) at a concentration of 0.15 M to form the Cs<sub>2</sub>AgBiBr<sub>6</sub> precursor. Then, the prepared precursor solution was added to 40 mL of IPA to get the Cs<sub>2</sub>AgBiBr<sub>6</sub> suspension through the anti-solvent precipitation method. The suspension was subsequently centrifugated to collect the Cs<sub>2</sub>AgBiBr<sub>6</sub>, which was then dried overnight in a vacuum oven at 60 °C. As a result, 796.5 mg of Cs<sub>2</sub>AgBiBr<sub>6</sub> powder with a yield of nearly 100% can be obtained.

Synthesis of PEA-Cs<sub>2</sub>AgBiBr<sub>6</sub>: The synthesis of PEA-Cs<sub>2</sub>AgBiBr<sub>6</sub> followed the same procedure as Cs<sub>2</sub>AgBiBr<sub>6</sub>, with the exception that a portion of CsBr was replaced by PEABr (in 2, 5, 10, and 20 mol% ratios). To be specific, the PEABr (6.1, 15.2, 30.5, and 31.0 mg for 2, 5, 10, and 20% PEA-Cs<sub>2</sub>AgBiBr<sub>6</sub> samples, respectively) together with CsBr (312.8, 303.2, 287.3, and 255.4 mg for 2, 5, 10, and 20% PEA-Cs<sub>2</sub>AgBiBr<sub>6</sub> samples, respectively), BiBr<sub>3</sub> (329.8, 319.7, 302.9, and 269.2 mg for 2, 5, 10, and 20% PEA-Cs<sub>2</sub>AgBiBr<sub>6</sub> samples, respectively) and AgBr (138.0, 133.9, 126.7, and 112.6 mg for 2, 5, 10, and 20% PEA-Cs<sub>2</sub>AgBiBr<sub>6</sub> samples, respectively) powders were then dissolved in 5 mL DMSO to form the precursor solution.

*Characterization*: XRD data were obtained using an X-ray diffractometer (Cu K $\alpha$ 1 radiation,  $\lambda = 1.5406$  Å) with a 100 mg sample mounted on a powder sample holder. Scanning electron micrographs (SEM) were

recorded using a FEI-Q FEG250 scanning electron microscope, in which 10 mg powder was put on a sample stub with conductive carbon tape. Transmission electron microscopy (TEM) images were captured on a JEOL ARM200F, using a 5 mg powder sample dispersed in a 5 IPA solution and drop-casted 10 µL solution onto a TEM copper grid. Steady-state photoluminescence (PL) measurements were performed using an Edinburgh FLS980 spectrometer, scanning the powder sample (100 mg in quartz cuvette) from 500 to 900 nm in 2 nm steps with an integration time of 1 s, under excitation at 405 nm. Time-resolved PL data were recorded using a confocal FLIM microscope, with a 50 mg powder sample on a quartz glass substrate. Excitation was provided by a pulsed 405 nm laser diode (LDH-D-C-485), with a bandpass filter (Chroma ET485/20x). The laser repetition rate was set to 1 MHz using the PDL 828 Sepia2 driver (PicoQuant). Optical absorption spectra were obtained using a UVvis diffuse reflectance (DRS) spectrophotometer (Shimadzu UV-2600i) with a detection range of 400-800 nm, with a 50 mg powder sample and barium sulfate (BaSO<sub>4</sub>) as the reference. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific Nexsa instrument with a monochromatized Al K $\alpha$  X-ray source at 1486.68 eV, using 20 mg powder sample, and the peaks were calibrated by C 1s spectrum at 284.8 eV. Atomic force microscopy (AFM) measurements were performed using atomic force microscopy (Seiko, Bioscope system) with the semicontact mode, where 25 mg powder was coated on the quartz glass substrate, Contact potential difference (CPD) data were acquired using Kelvin probe force microscopy (KPFM) in dual-pass AM-SKM mode. Femtosecond transient absorption spectroscopy was carried out on optical pump-probe spectroscopy with a mode locked Ti-sapphire laser amplifier, and the samples were prepared by spin-coating a 50  $\mu L$  0.1 M precursor solution onto a quartz substrate. Radical scavenging experiments were conducted by using ammonium oxalate (AO), silver nitrate ( $AgNO_3$ ), 1,4-benzoquinone (p-BQ), t-butanol (t-BA), and butylated hydroxytoluene (BHT) as scavengers for holes ( $h^+$ ), electrons ( $e^-$ ), superoxide ( ${}^{\bullet}O_2^{-}$ ), hydroxyl (°OH<sup>-</sup>), and carbon-centered radicals (°R), respectively, in which 0.5 mm scavengers was added the reaction systems with a reaction time of 4 h.

*Photocatalytic Activity Evaluation*: Toluene photooxidation experiments were performed in a 25 mL quartz reactor under simulated solar light illumination. Specifically, 10 mg of photocatalyst was added to 2.5 mL of toluene with saturated molecular oxygen, followed by irradiation for 4 h under stirring. After that, the mixture was centrifuged, and the liquid was analyzed by GC (Shimadzu 2010).

Density Functional Theory Calculation: All calculations were performed using the projector augmented wave (PAW) method and the spinpolarized density functional theory (DFT) as it is implemented in the Vienna ab-initio simulation package (VASP). The same number of atoms was used in CABB and PEA-CABB systems. The exchange-correlation interaction between electrons was described using the Perdew-Burke-Ernzerhof (PBE) the variation of the generalized-gradient approximation (GGA). For optimal stress tensor convergence during parameter relaxations, a plane wave cut-off of 550 eV was chosen. The Brillouin zone was sampled with a size-dependent G-centered k-point mesh, i.e.,  $3 \times 3 \times 3$  for the unit cells of Cs<sub>8</sub>Ag<sub>4</sub>Bi<sub>8</sub>Br<sub>24</sub> and PEA doped Cs<sub>8</sub>Ag<sub>4</sub>Bi<sub>8</sub>Br<sub>24</sub> and for the super cell  $Cs_8Ag_4Bi_8Br_{24}(001)$  and PEA- $Cs_8Ag_4Bi_8Br_{24}(001)$  structures,  $1 \times 3 \times 1$  is used. To prevent interaction between the periodic images, a vacuum area of around 15 Å was created above the surface layer. The lattice parameters and atomic positions were fully relaxed until the variation of total energy was within  $10^{-4}$  eV and the final force on each atom was less than  $0.01 \text{ eV} \text{ } \text{\AA}^{-1}$ . A van der Waals correction was examined for vdW functionals using the Grimme method in conjunction with Becke–Jonson damping.<sup>[51]</sup> Bader charge analysis was carried out by analyzing the electronic charge density using Henkelman's Bader scheme.[52] The electrical properties, particularly the density of states (DOS), were predicted using HSE12 functionals. Generally, hybrid functionals (such as HSE06) predict more realistic bandgaps and electrical structures than pure functionals (such as PBE). The computations were performed using the HSE12 functional with a 12% precise exchange contribution. Because the HSE12 requires a lot of processing power, only the Gamma point was sampled in the Brillouin zone for the HSE12 calculations.

The equation used to determine the adsorption energy of organic molecules (OM) on  $Cs_8Ag_4Bi_8Br_{24}(001)$  and  $PEA-Cs_8Ag_4Bi_8Br_{24}(001)$  these surfaces is as follows:

$$\Delta E_{\text{Comp}} = E_{\text{Surf}+\text{OM}} - E_{\text{Surf}} - E_{\text{OM}}$$
<sup>(2)</sup>

where  $E_{\rm OM}$  stands for the total energy of an isolated organic molecule in the gas phase and  $E_{\rm Surf+OM}$  and  $E_{\rm Surf}$  are the total energies with and without organic-molecule adsorption on surfaces, respectively.

In addition, the difference between the 2D and 3D-charge density differences of these structures ( $\Delta_{\rho}$ ) was calculated. The charge density difference is calculated using the following equation:

$$\Delta \rho = \left[\rho_{[Surf+OM]} - \left[\rho_{[Surf]} + \rho_{[OM]}\right]$$
(3)

here,  $\rho_{[Surf+OM]}$  is the total charge densities of organic molecules adsorption on surface corresponding complexes,  $\rho_{[Surf]}$  and  $\rho_{[OM]}$  are charge densities of Cs<sub>8</sub>Ag<sub>4</sub>Bi<sub>8</sub>Br<sub>24</sub>(001) and PEA-Cs<sub>8</sub>Ag<sub>4</sub>Bi<sub>8</sub>Br<sub>24</sub>(001) surface slabs, and each organic molecule, respectively.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

## Keywords

charge dynamics, halide double perovskite, phase transition, photocatalysis, photoelectric property

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