

Enhancing photostability of 2D Ruddlesden–Popper perovskite via molecular acceptor passivation of metallic lead defects

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ABSTRACT

Two-dimensional (2D) Ruddlesden–Popper (RP) perovskites hold great potential for novel optoelectronic applications. However, their unconventional optoelectronic properties are often compromised by a vulnerability to light irradiation, which leads to the formation of metallic Pb (Pb⁰) defects. This study investigates the passivation mechanism of these Pb⁰ defects in phenylethylammonium lead iodide (PEA₂PbI₄) using a strong molecular acceptor, 2,2'-(perfluoronaphthalene-2, 6-diylidene) dimalononitrile (F6-TCNNQ). *In situ* x-ray photoelectron spectroscopy results demonstrate that F6-TCNNQ effectively removes the light-induced Pb⁰ states, leading to the recovery of photoluminescence intensity in photodegraded PEA₂PbI₄ samples and significantly improving the photostability of pristine PEA₂PbI₄. F6-TCNNQ protects the terrace edge of PEA₂PbI₄, which is the site of initial degradation, as evidenced by atomic force microscopy and scanning electron microscopy analyses. *In situ* ultraviolet photoelectron spectroscopy measurements confirm substantial electron transfer from Pb⁰ to F6-TCNNQ, causing the oxidation of Pb⁰ to Pb²⁺. Furthermore, the staggered energy level alignment prevents electron transfer from the valence band maximum of PEA₂PbI₄ to the lowest unoccupied molecular orbital of F6-TCNNQ, thereby preserving the pristine electronic structure of PEA₂PbI₄. These findings provide new insights into defect passivation in 2D RP perovskites and offer a design strategy for highly stable optoelectronic devices.

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I. INTRODUCTION

Organic–inorganic halide perovskites (referred to as perovskites hereafter) are a promising next-generation optoelectronic material for light-emitting diodes (LEDs), solar cells, and photodetectors because of their exceptional optoelectronic properties such as a high light absorption coefficient, tunable bandgap, outstanding carrier mobility, and long

carrier diffusion length.^{1–9} However, their inherent structural instability and susceptibility to environmental conditions (light,^{10–15} heat,^{16,17} oxygen,^{12,18} and moisture^{11,16,18}) can lead to performance degradation. To address this issue, two-dimensional (2D) Ruddlesden–Popper (RP) perovskites have been introduced because their unique structure provides heat and moisture stability and reduced ion migration compared to

conventional three-dimensional (3D) perovskites.^{19–23} Such an improved stability of 2D RP perovskites is attributed by their characteristic 2D structure, in which the corner-shared $[BX_6]^-$ octahedral sheets (B: metal cations, X: halide anions) are separated by bulky organic spacers.^{24,25} Furthermore, this structure also induces excellent optical properties owing to its charge and dielectric confinement effects.^{26,27}

However, ironically, photostability has become a major topic of discussion among researchers in the 2D perovskite research field, as it is a significant challenge to their application in optoelectronic devices.^{28–33} For example, the daily used fluorescent lamps, which emit also high-energy photons at extremely low intensities, can rapidly degrade the surface structure of 2D RP perovskites.²⁹ In many reports, it has been also revealed that the high-energy light irradiation on perovskites can disrupt crystalline structures, leading to undercoordinated Pb states that impede carrier transport and cause substantial loss of photoluminescence (PL).^{13–15,28,29,34–36} These photodegradation processes produce metallic Pb⁰ defects, which act as non-radiative recombination centers and accelerate undesired chemical reactions owing to their high reactivity.^{34–39} Hence, to achieve improved photostability, it is imperative to develop effective passivation or suppression techniques to prevent the formation of metallic Pb⁰ defects.

Researchers have tested various methods to passivate Pb⁰ in perovskites, such as controlling the annealing process,³⁷ optimizing the precursor ratios,⁴⁰ modifying the surface properties,³⁹ and incorporating additives.^{41,42} Among these, molecular surface passivation has shown promise in suppressing the formation of Pb⁰ states.^{43–45} It has been speculated that molecular electron acceptors stabilize perovskites by withdrawing electrons from unstable electron-rich Pb⁰ states. However, the electron transfer process and its potential to significantly enhance photostability are yet to be clearly demonstrated. Furthermore, despite the growing importance of 2D RP perovskites, studies of their molecular passivation are still scarce. To address the poor photostability in 2D RP perovskites, two fundamental questions must be answered regarding molecular surface passivation. (1) Is molecular surface passivation effective in improving the photostability of 2D RP perovskites? (2) What is the passivation mechanism and how does it differ from that of their 3D counterparts?

To answer these questions, we performed systematic experiments to investigate the validity of molecular surface passivation for 2D RP perovskites and the passivation mechanism, as summarized in Fig. 1. Specifically, we used x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) to analyze the interface formed between a representative 2D RP perovskite, phenylethylammonium lead iodide (PEA₂PbI₄), and a molecular electron acceptor with high electronic affinity (EA), 2,2'-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNNQ). We deposited an F6-TCNNQ layer stepwise on top of both pristine and photodegraded PEA₂PbI₄, and monitored the amount of Pb⁰ species and the valence band (VB) features during deposition. Our results provide direct evidence of how molecular acceptors interact with the produced Pb⁰ and reveal the passivation mechanism in 2D RP perovskites compared to their 3D counterparts.

II. RESULTS AND DISCUSSION

A. Photodegradation of PEA₂PbI₄

First, we investigated the photodegradation mechanism of PEA₂PbI₄ using XPS, atomic force microscopy (AFM), and scanning electron microscopy (SEM). PEA₂PbI₄ films were spin-coated onto an indium tin oxide (ITO) substrate (supplementary material Sec. 1).⁴⁶ The high quality of the samples was confirmed using x-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), and grazing-incidence wide-angle x-ray scattering (GIWAXS). The results are consistent with previous reports (supplementary material Sec. 2).^{6,46–48} Blue laser irradiation ($\lambda = 405$ nm, intensity = 50 mW cm^{-2}) was used to degrade the prepared PEA₂PbI₄ films since a higher photon energy causes more significant degradation.^{28,29} We also carefully controlled the irradiation time and dose of x-ray and UV sources to prevent undesired degradation of the PEA₂PbI₄ samples during measurements (supplementary material Sec. 3).

Figure 2(a) illustrates the Pb 4f core-level XPS spectra of PEA₂PbI₄ films at different blue laser irradiation times. The pristine film (0 s) shows two characteristic peaks stemming from the spin-orbit splitting at 138.0 eV for 4f_{7/2} and 142.8 eV for 4f_{5/2}, corresponding to fully coordinated Pb²⁺ ions (green shaded areas). However, as the blue

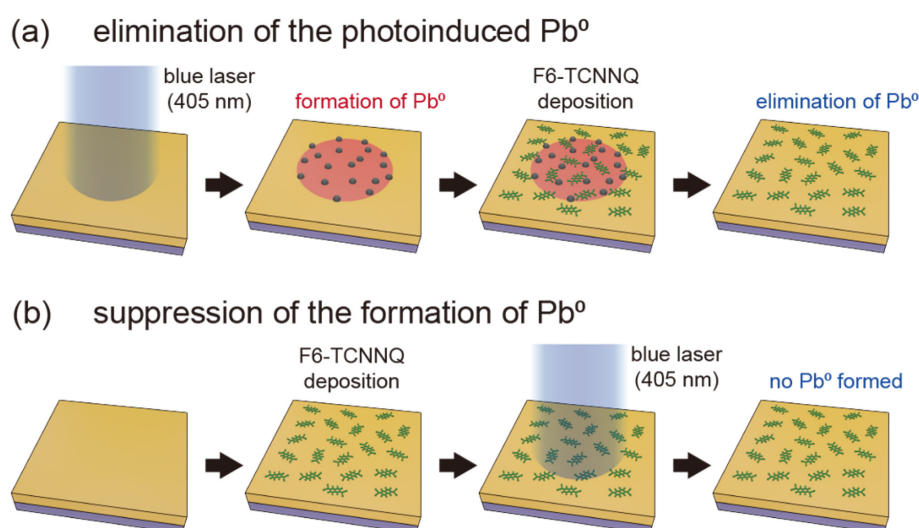


FIG. 1. Overview of the sample preparation method. Organic molecular dopant F6-TCNNQ was deposited on (a) light-irradiated PEA₂PbI₄ to eliminate already generated Pb⁰ (Secs. II A and II B) and (b) non-irradiated PEA₂PbI₄ to suppress future Pb⁰ formation under irradiation (Sec. II C). The region photodegraded by the blue laser irradiation is exhibited as red area. The black dots represent Pb⁰. The molecular structures depict deposited F6-TCNNQ (green). The blue laser irradiation is illustrated as a blue shade.

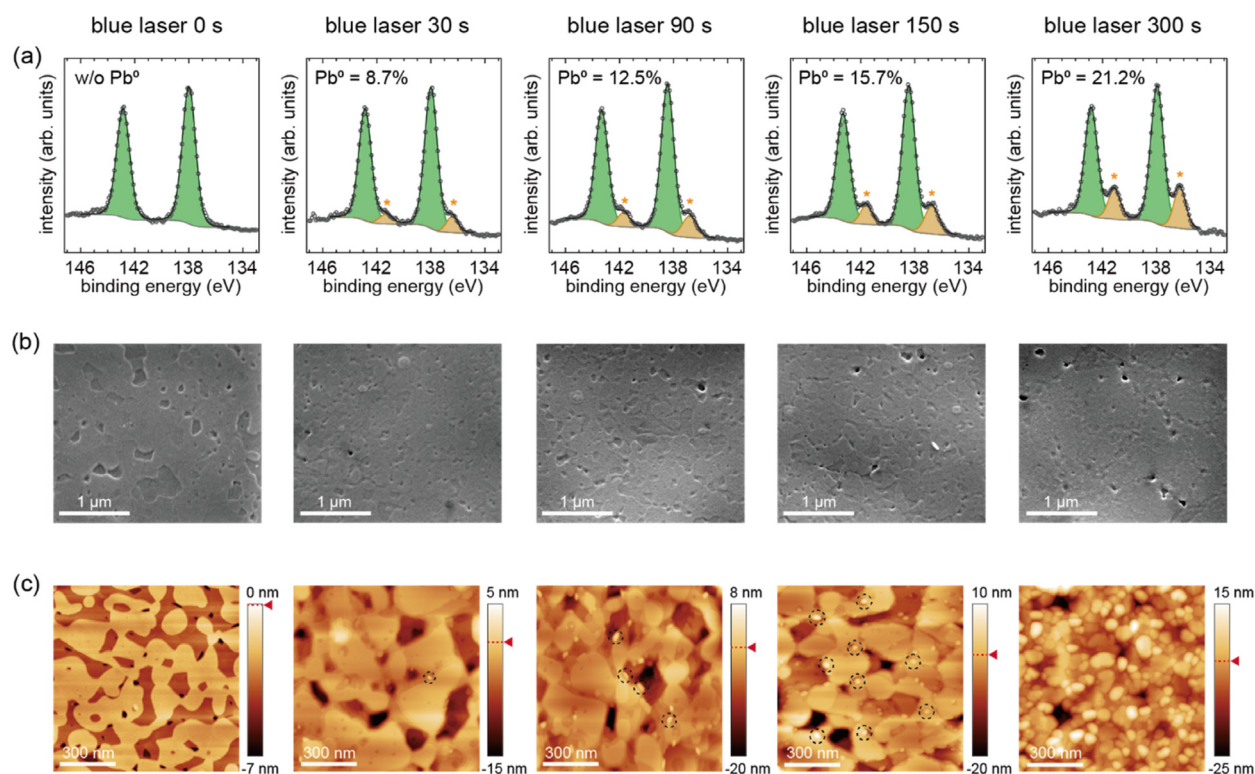


FIG. 2. (a) XPS spectra of Pb 4f core-level obtained at different blue laser irradiation times with corresponding deconvoluted peaks (green component: Pb^{2+} , yellow component: Pb^0); (b) SEM; and (c) AFM images of PEA_2PbI_4 films at varying blue laser irradiation times. Each column represents a different irradiation time: 0, 30, 90, 150, and 300 s. Red triangles and dashed lines on the scale bars indicate the heights of the top perovskite layer, excluding small bumps.

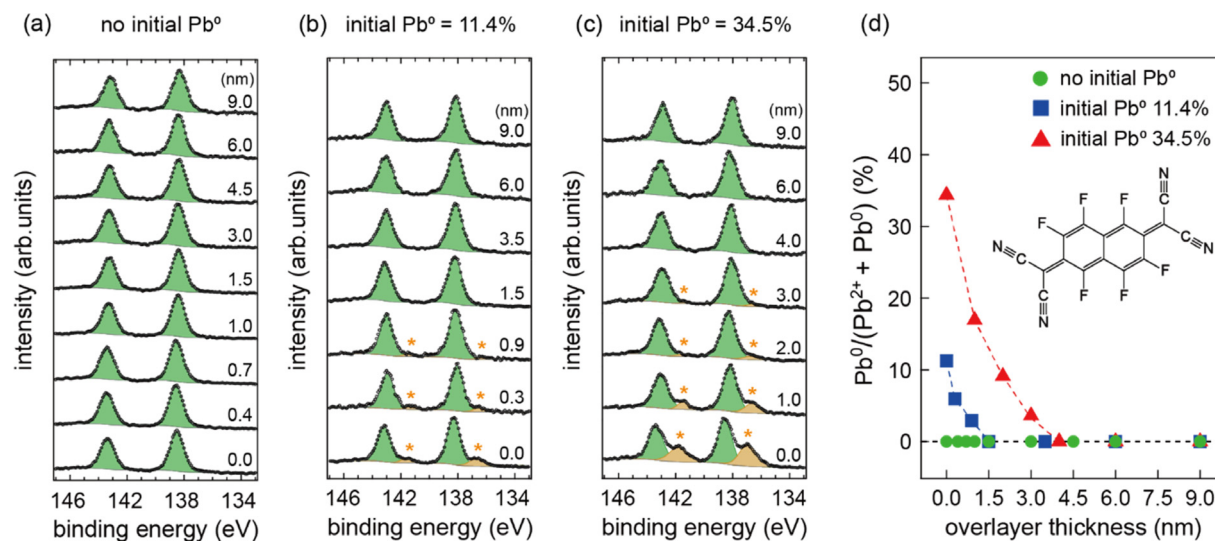


FIG. 3. Changes in Pb 4f core-level XPS spectra of PEA_2PbI_4 films with stepwise F6-TCNNQ deposition on (a) pristine PEA_2PbI_4 and photodegraded PEA_2PbI_4 containing (b) 11.4% Pb^0 and (c) 34.5% Pb^0 . The green fitted peak indicates Pb^{2+} state and the orange fitted peak with asterisk (*) indicates the Pb^0 state. The thickness of the deposited F6-TCNNQ is shown at the right end of each spectrum. The degree of degradation was controlled with blue laser irradiation time. (d) $\text{Pb}^0/(\text{Pb}^{2+} + \text{Pb}^0)$ ratio as a function of the F6-TCNNQ thickness. Inset in (d): structure of F6-TCNNQ, a molecular acceptor used for the passivation of perovskite surface.

laser irradiation time increases, new peaks (yellow shaded areas marked with asterisks) with lower binding energies gradually appear at 136.3 and 141.1 eV. These peaks are attributed to the Pb^0 state because of the loss of I^- ions.^{37,49–51} The rapid increase in the Pb^0 state with light irradiation time confirms the light vulnerability of PEA_2PbI_4 .

Figure 2(b) shows SEM images of PEA_2PbI_4 films with different amounts of the Pb^0 state. The pristine film has a flat, pinhole-free surface with clear terrace edges, demonstrating its solid planar structure. With increasing light irradiation time, the flat and clear surface becomes blurred, and the number and size of pinholes both increase. Figure 2(c) shows the topography of the PEA_2PbI_4 films determined by AFM. The pristine film has an extremely flat surface, confirming its 2D structure. The AFM line profile exhibits sharp terrace edges with heights that are integer multiples of approximately 1.65 nm, which is consistent with the thickness of a PEA_2PbI_4 monolayer (see supplementary material Sec. 4).^{28,52} At longer blue laser irradiation times, small bumps appear, and both the size and depth of pinholes increase. Only a few bumps appear at 30 s, but at 300 s the entire surface area is covered with bumps. Note that the bumps primarily appear at the terrace edge (dashed circles), suggesting that photodegradation starts at the terrace edges, which are reactive sites owing to the broken periodicity that provides dangling bonds including undercoordinated Pb states. We speculate that these small bumps are degraded fragments from PEA_2PbI_4 such as metallic Pb^0 or PbI_2 .^{28,34,53} Moreover, the Pb^0 state is well-known as a non-radiative recombination center, significantly reducing the efficiency and stability of solar cells and LEDs.^{49,54,55} Therefore, suppressing the formation of the Pb^0 state by passivating unstable terrace edges and eliminating any formed Pb^0 states are essential for maximizing the optoelectronic properties of perovskites. In Sec. II B, we demonstrate how a molecular acceptor can efficiently passivate the degraded surface.

B. Elimination of Pb^0 in photodegraded PEA_2PbI_4 by molecular passivation

We examined the impact of molecular surface passivation on PEA_2PbI_4 by investigating the interface between PEA_2PbI_4 and F6-TCNNQ. To achieve this, we generated PEA_2PbI_4 samples with varying degrees of photodegradation, as outlined in Sec. II A. Then, we deposited F6-TCNNQ stepwise on both pristine and degraded PEA_2PbI_4 films and monitored the Pb 4f core-level XPS spectra of PEA_2PbI_4 during the deposition process. In Fig. 3(a), the spectrum of pristine PEA_2PbI_4 remains unchanged throughout the deposition process, indicating that F6-TCNNQ does not strongly interact with pristine PEA_2PbI_4 . When starting with a photodegraded film containing 11.4% of surface Pb^0 , the Pb 4f XPS spectrum changes with F6-TCNNQ deposition [Fig. 3(b)]: the Pb^0 state (orange shading) remarkably decreases after the first deposition step (0.3 nm F6-TCNNQ) and entirely disappears at 0.9 nm. Figure 3(c) shows the corresponding results for a more photodegraded PEA_2PbI_4 film (34.5% Pb^0). The Pb^0 state also rapidly diminishes in this case and disappears after depositing 3.0 nm of F6-TCNNQ. At the same time, we observed peak shifts toward lower binding energy in both Pb 4f and I 3d (Fig. 3 and supplementary material Sec. 7). These shifts can be attributed to changes in electron density resulting from the high electron-withdrawing property of F6-TCNNQ. Compared to Fig. 3(b), the photodegraded PEA_2PbI_4 film in Fig. 3(c) contains

three times of the Pb^0 and requires three times the thickness of the F6-TCNNQ overlayer to eliminate Pb^0 . To assess the passivation effect of F6-TCNNQ, we evaluated the $\text{Pb}^0/(\text{Pb}^{2+} + \text{Pb}^0)$ ratio from the Pb 4f XPS data in Fig. 3(d). These ratios clearly show a dramatic decrease in the amount of the Pb^0 state as F6-TCNNQ is deposited on the photodegraded PEA_2PbI_4 surface. These findings suggest that F6-TCNNQ can effectively eliminate existing Pb^0 defects in photo-degraded PEA_2PbI_4 .

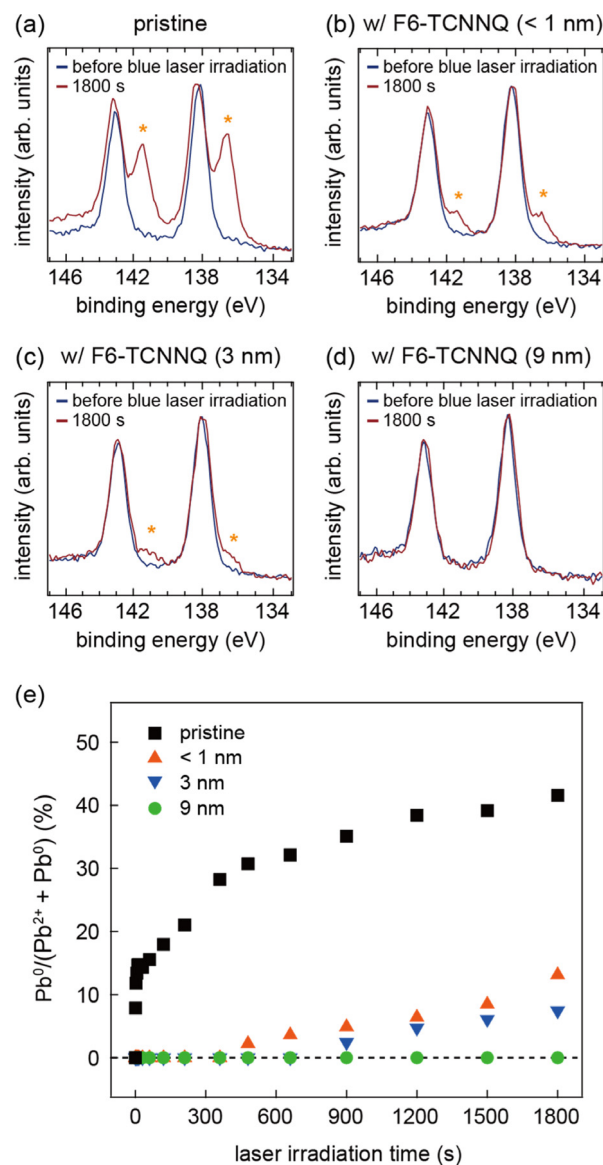


FIG. 4. Pb 4f core-level XPS spectra of PEA_2PbI_4 films before (blue lines) and after (red lines) blue laser irradiation for 1800 s. To clearly exhibit the Pb^0 state, it is marked with orange asterisks. Different amounts of F6-TCNNQ were deposited: (a) pristine PEA_2PbI_4 , (b) sub-monolayer (<1 nm) (c) 3 nm, and (d) 9 nm F6-TCNNQ. (e) $\text{Pb}^0/(\text{Pb}^{2+} + \text{Pb}^0)$ ratios of pristine and F6-TCNNQ-covered (<1, 3, and 9 nm) PEA_2PbI_4 as a function of blue laser irradiation time, calculated using XPS data.

C. Enhancing the photostability of PEA_2PbI_4 by F6-TCNNQ surface passivation

To investigate whether F6-TCNNQ can prevent the photodegradation of PEA_2PbI_4 in the first place, we next examined the photostability of F6-TCNNQ-covered PEA_2PbI_4 . Here, surface passivation was assessed in terms of suppressing the formation of a new Pb^0 state. Changes in the Pb^0 state were analyzed by comparing the pristine and F6-TCNNQ-deposited PEA_2PbI_4 films after irradiating these films with blue laser for 1800 s. Figure 4(a) shows the Pb 4f core-level XPS spectra of pristine PEA_2PbI_4 before and after irradiation. No features of Pb^0 were observed before the irradiation, while 41% of the Pb^{2+} species was converted to the Pb^0 state after irradiation. Figure 4(b) shows the corresponding results when the PEA_2PbI_4 film was covered by a sub-monolayer of F6-TCNNQ. Surprisingly, the photostability was significantly enhanced even when its surface was not yet fully covered with F6-TCNNQ; the Pb^0 ratio was only 13% after 1800 s of irradiation, less than one-third the amount when starting with the pristine sample. This passivation effect was further enhanced when using a

3-nm-thick F6-TCNNQ layer, as shown in Fig. 4(c); the corresponding sample only contained 7% Pb^0 after irradiation. Finally, a 9-nm-thick F6-TCNNQ layer achieved full passivation, as the PEA_2PbI_4 film underneath displayed no spectral changes after the same irradiation [Fig. 4(d)].

Figure 4(e) summarizes the $\text{Pb}^0/(\text{Pb}^{2+} + \text{Pb}^0)$ ratios as a function of blue laser irradiation time (details are given in supplementary material Sec. 5). In pristine PEA_2PbI_4 , Pb^0 was formed almost immediately (8% after 1 s) and rapidly accumulated with the irradiation time. On the other hand, the PEA_2PbI_4 film covered with the sub-monolayer F6-TCNNQ took 480 s to generate a noticeable Pb^0 signal, for the film covered with 3 nm F6-TCNNQ it took 900 s, and the film covered with 9-nm F6-TCNNQ showed no Pb^0 states at all. Therefore, we conclude that F6-TCNNQ effectively suppresses the photoinduced Pb^0 states, resulting in dramatically enhanced photostability.

To elucidate the origin of the passivation effect further, we investigated another organic molecule, *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB, supplementary material Sec. 6).

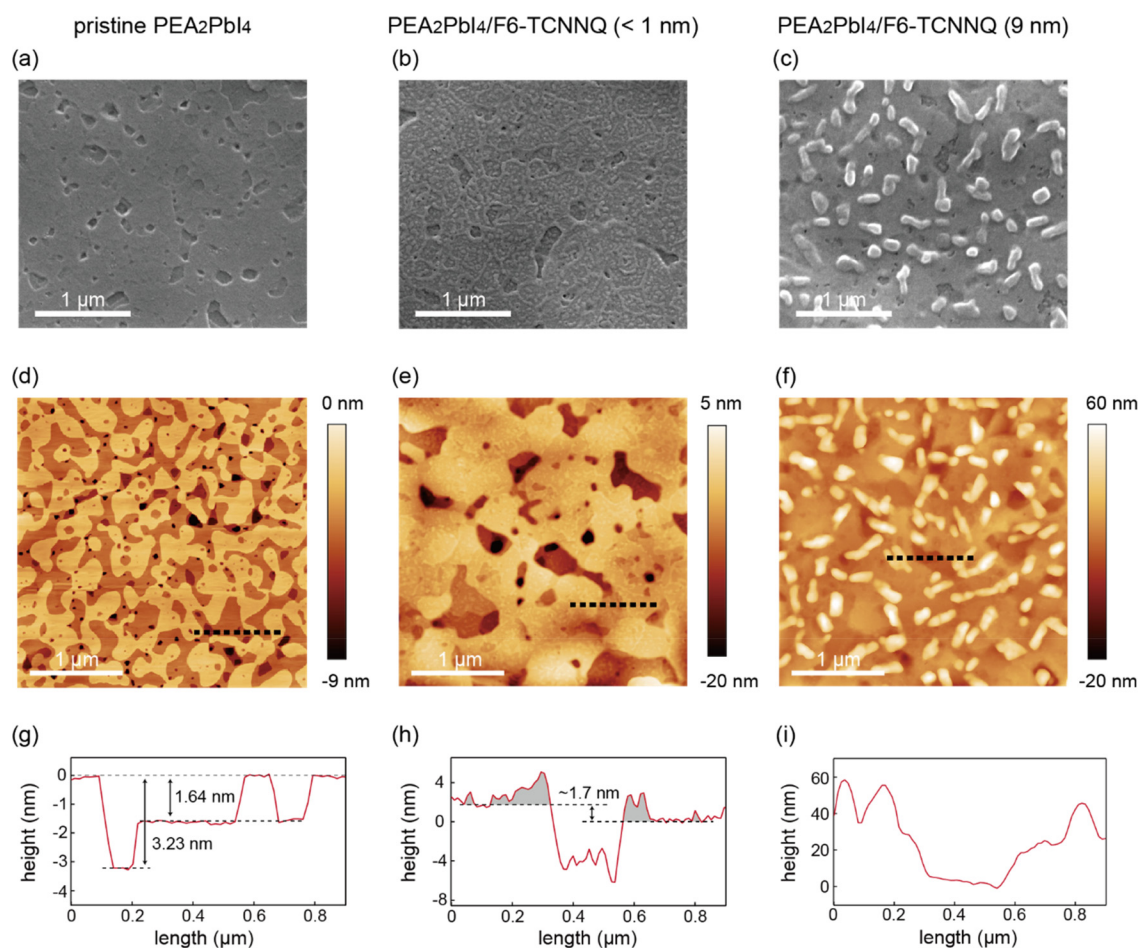


FIG. 5. SEM and AFM images of different PEA_2PbI_4 films: (a), (d), and (g) in the pristine state, (b), (e), and (h) covered by sub-monolayer F6-TCNNQ, and (c), (f), and (i) fully passivated with a 9-nm-thick F6-TCNNQ layer. Height profiles along black dashed lines in AFM images are shown in (g), (h), and (i). Horizontal dashed lines in (g) and (h) indicate monolayer (terrace) planes of PEA_2PbI_4 . Gray shaded area in (h) represents F6-TCNNQ adsorbed on the terrace edge of PEA_2PbI_4 .

Unlike F6-TCNNQ, an NPB overlayer neither eliminated the existing Pb^0 state nor improved the photostability of PEA_2PbI_4 after its deposition. This is due to the energetics between different organic molecules and Pb^0 . The ionization energy (IE) (5.30 eV) and EA (1.25 eV) of NPB^{56,57} are not favorable for withdrawing electrons from the Pb^0 states in PEA_2PbI_4 . This issue is further discussed in Sec. II E.

We used SEM and AFM to investigate the initial morphology and topography of the F6-TCNNQ-deposited PEA_2PbI_4 surface. To minimize degradation by air exposure, the SEM and AFM images were obtained within 300 s after F6-TCNNQ-layer deposition. Figure 5(a) shows the flat surface and sharp terrace boundaries of the pristine PEA_2PbI_4 film, and Fig. 5(d) reveals its 2D layered structure. The topography profile along the black dashed line [Fig. 5(g)] shows sharp step terrace edges with a monolayer height of 1.64 nm. Figures 5(b) and 5(e) present the SEM and AFM images of PEA_2PbI_4 covered with sub-monolayer F6-TCNNQ, respectively. The characteristic planar structure of PEA_2PbI_4 remains and its terrace edges are still visible. Yet, most of the surface area is covered with tiny bumps that we attribute to molecular aggregation of F6-TCNNQ, which is consistent with previous studies.^{58–60} We confirmed that F6-TCNNQ is mostly adsorbed on the terrace edge rather than the terrace of PEA_2PbI_4 , and the AFM images in Fig. 5(e) and corresponding height profile [Fig. 5(h)] support this observation. Previous studies have suggested that the terrace edges of PEA_2PbI_4 are the initial degradation site because of their instability.²⁸ The crystal structure of PEA_2PbI_4 indicates that the organic spacers protect the $[\text{PbI}_6]^-$ octahedra in the terrace region, while at the terrace edge the undercoordinated octahedra are directly exposed to the environment.⁶¹ These undercoordinated octahedra are unstable and tend to coordinate with nearby molecules. The adsorption of F6-TCNNQ at the terrace edge [Fig. 5(h)] supports this interpretation, and such preferential adsorption eliminates Pb^0 states that mainly exist at those locations, as observed in Fig. 4. Further studies are required to provide a more detailed mechanism of F6-TCNNQ adsorption at the terrace edges. Figures 5(c), 5(f), and 5(i) show the SEM image, AFM image, and topography profile of PEA_2PbI_4 covered with 9 nm F6-TCNNQ, respectively, confirming that the surface is fully covered with F6-TCNNQ aggregates.

D. Impact of passivation on optical properties of PEA_2PbI_4

We measured steady-state PL to investigate the effect of F6-TCNNQ passivation on the optical properties of PEA_2PbI_4 . The PL spectra were measured after a controlled degradation and passivation process. The photodegraded film had $\text{Pb}^0/(\text{Pb}^0 + \text{Pb}^{2+}) = 32\%$, while this ratio was recovered to 0% in the film passivated with a 3 nm-thick F6-TCNNQ layer. Figure 6(a) shows the steady-state PL spectra of pristine, photodegraded, and F6-TCNNQ-passivated PEA_2PbI_4 . The peak position and full width at half maximum remain unchanged among the three cases, but the intensities decrease after photodegradation and recover with F6-TCNNQ passivation. Figure 6(b) shows box plots of the PL intensities of ten samples normalized by the results of pristine PEA_2PbI_4 . After photodegradation, the normalized PL intensity (red) is $0.85 (\pm 0.03)$, indicating that the induced Pb^0 acts as a non-radiative recombination center. Notably, the normalized PL intensity recovers to $0.92 (\pm 0.06)$ after surface passivation with F6-TCNNQ. These results indicate that eliminating the Pb^0 state reduces non-radiative recombination in PEA_2PbI_4 .

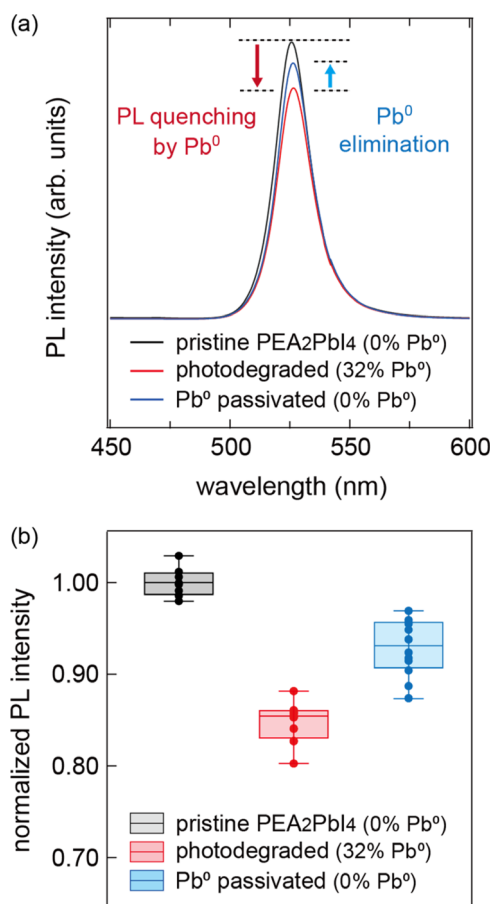


FIG. 6. (a) Steady-state photoluminescence (PL) spectra of pristine (0% Pb^0 ; black line), photodegraded (32% Pb^0 ; red line), and F6-TCNNQ-passivated PEA_2PbI_4 (0% Pb^0 ; blue line). (b) Box plots of steady-state PL intensity normalized to that of pristine PEA_2PbI_4 . Each set of data was collected on ten samples. The boxes display minimum, maximum, and mean along with upper and lower standard deviation ($\pm 1\sigma$) of PL intensities for each individual sample, which indicated by circular dots.

E. Mechanism of molecular acceptor-induced Pb^0 elimination/passivation on PEA_2PbI_4

To investigate the mechanism of Pb^0 elimination (or passivation), we conducted UPS measurements on photodegraded PEA_2PbI_4 with stepwise deposition of F6-TCNNQ, using a process similar to the XPS measurements. Evolution of the secondary electron cutoff (SEC) and VB region spectra during the stepwise F6-TCNNQ deposition is shown in Figs. 7(a) and 7(b), respectively. The bottommost spectrum (green) represents the pristine PEA_2PbI_4 , with a work function (Φ) of 4.71 eV and a VB maximum (VBM) of 1.18 eV from the linear extrapolation of the VB curve. The ionization energy (IE) of PEA_2PbI_4 was calculated by $\text{IE} = \Phi + \text{VBM}$ to be 5.89 eV, in good agreement with previous reports.^{62–64} The black spectrum (0.0 nm) shows that unpassivated PEA_2PbI_4 is degraded by blue laser irradiation and contains 11.4% Pb^0 as determined by XPS. After degradation, Φ decreases by 0.10 eV, while VBM shifts by 0.10 eV toward a higher binding energy

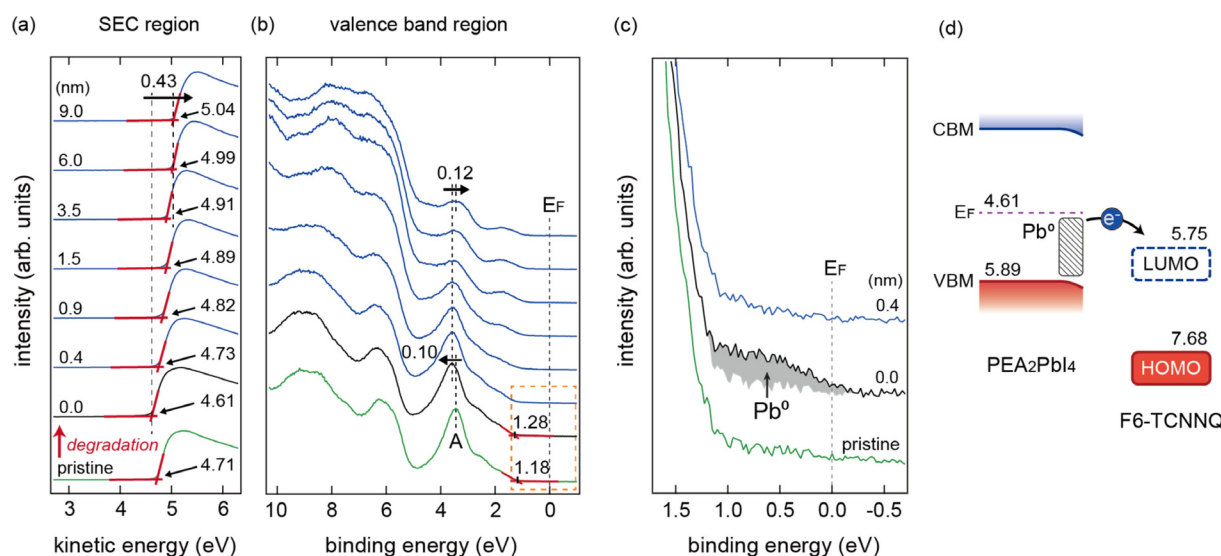


FIG. 7. (a) Secondary electron cutoff (SEC) and (b) valence band (VB) region spectra of pristine PEA₂PbI₄ film (green), photodegraded PEA₂PbI₄ film (black), and photodegraded PEA₂PbI₄ film with stepwise F6-TCNNQ deposition (blue); (c) magnified view of the Fermi-edge region (indicated by an orange dashed box in b); and (d) energy level diagram of F6-TCNNQ on degraded PEA₂PbI₄ containing metallic Pb⁰ state.

because the accumulated Pb⁰ acts as donor-like states.⁶⁵ As more F6-TCNNQ is deposited (blue spectra), the VB spectral shape gradually changes from that of PEA₂PbI₄ to that of F6-TCNNQ owing to the surface-sensitive nature of UPS measurements. Concurrently, Φ significantly increases by 0.43 eV. The VB peak of PEA₂PbI₄ at 3.1 eV (mark A) was tracked to evaluate the energy level shift. This peak was continuously observed even when the deposition exceeded 3.5 nm because of F6-TCNNQ aggregation, as confirmed in Fig. 5. The VB gradually shifts toward the Fermi level (E_F) by 0.12 eV, in good agreement with the core-level shift shown in supplementary material Sec. 7. The VB shift at the surface toward a higher binding energy due to Pb⁰ would also imply a modification in the interfacial energetics. This alteration raises the barrier height for electrons in the VBM of PEA₂PbI₄ to be transferred. Figure 7(c) shows a magnified view near the E_F , highlighted by the orange dashed box in Fig. 7(b). The spectrum of pristine PEA₂PbI₄ (green) shows a flat and straight baseline near the E_F without any spectral features. After photodegradation, broad spectral features (gray area) emerge between the E_F and VBM, indicating a small but definite E_F crossing due to the metallic Pb⁰ states.^{37,66} The broad occupied density of states crossing the E_F indicates that the Pb⁰ defect states possess an electron-rich character, resembling a donor-like state. With a 0.4-nm-thick F6-TCNNQ layer (blue), the Pb⁰ states disappear, and the spectrum completely recovers to that of pristine PEA₂PbI₄. This recovery clearly demonstrates electron transfer from Pb⁰ to F6-TCNNQ and the reversion of metallic Pb⁰ states to Pb²⁺ states.

Figure 7(d) displays the energy level diagram of PEA₂PbI₄ evaluated based on the measured VBM and Pb⁰ states of PEA₂PbI₄. The diagram also includes the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of F6-TCNNQ (see supplementary material Sec. 8 for details), as well as the vacuum level reference. The F6-TCNNQ LUMO (5.75 eV) is positioned below the Pb⁰ top states (4.61 eV) but higher than the VBM of PEA₂PbI₄ (5.89 eV). This arrangement favors electron transfer from

the Pb⁰ states to the F6-TCNNQ LUMO while making electron transfer from the PEA₂PbI₄ VBM to F6-TCNNQ LUMO unfavorable. Moreover, PEA organic spacers on the surface of pristine PEA₂PbI₄ substantially decrease the orbital overlap between the F6-TCNNQ LUMO and the PEA₂PbI₄ VB, impeding direct electron transfer.⁶⁷ The small band shift observed in PEA₂PbI₄ (0.12 eV) in Fig. 7 matches this finding, and it is much smaller than data measured in similar ways on the 3D perovskite MAPbI_{3-x}Cl_x (0.71 eV), indicating minimal electron transfer from PEA₂PbI₄ to F6-TCNNQ.⁶⁵ In contrast, the VBM of MAPbI_{3-x}Cl_x is reported to be situated between 5.39 and 5.73 eV, thereby allowing electron transfer from the VBM to the acceptor LUMO level.^{65,66,68,69} In the current case, however, F6-TCNNQ can selectively extract electrons from the Pb⁰ states without disrupting the pristine PEA₂PbI₄. This likely explains the superior optoelectronic properties of PEA₂PbI₄, which are preserved despite the presence of F6-TCNNQ. The energy level diagrams based on these observations are summarized in supplementary material Sec. 9. To verify the electron transfer further, we performed UV-Vis measurements to determine the existence of charged F6-TCNNQ. When F6-TCNNQ was deposited on degraded PEA₂PbI₄ containing Pb⁰, we observed new sub-bandgap absorption between 700 and 1000 nm, which is attributed to the absorption of anionic F6-TCNNQ (supplementary material Sec. 10).⁷⁰

Our observations indicate a fundamental distinction in electron transfer between 2D and 3D perovskites, attributed to surface molecular doping. In 2D perovskites, organic spacers spatially separate the dopants from the metal-halide octahedral layers. This spatial separation hinders the overlap between the valence orbitals of 2D perovskites and the conduction orbitals of dopants or vice versa. In contrast, in 3D perovskites, the dopants come into direct contact with the octahedral layers, facilitating electron transfer at the interface. Furthermore, it is worth noting that the ionization energy of 2D PEA₂PbI₄ is greater than that of F6-TCNNQ, promoting selectively favorable electron extraction from photodegraded sites comprising metallic leads.

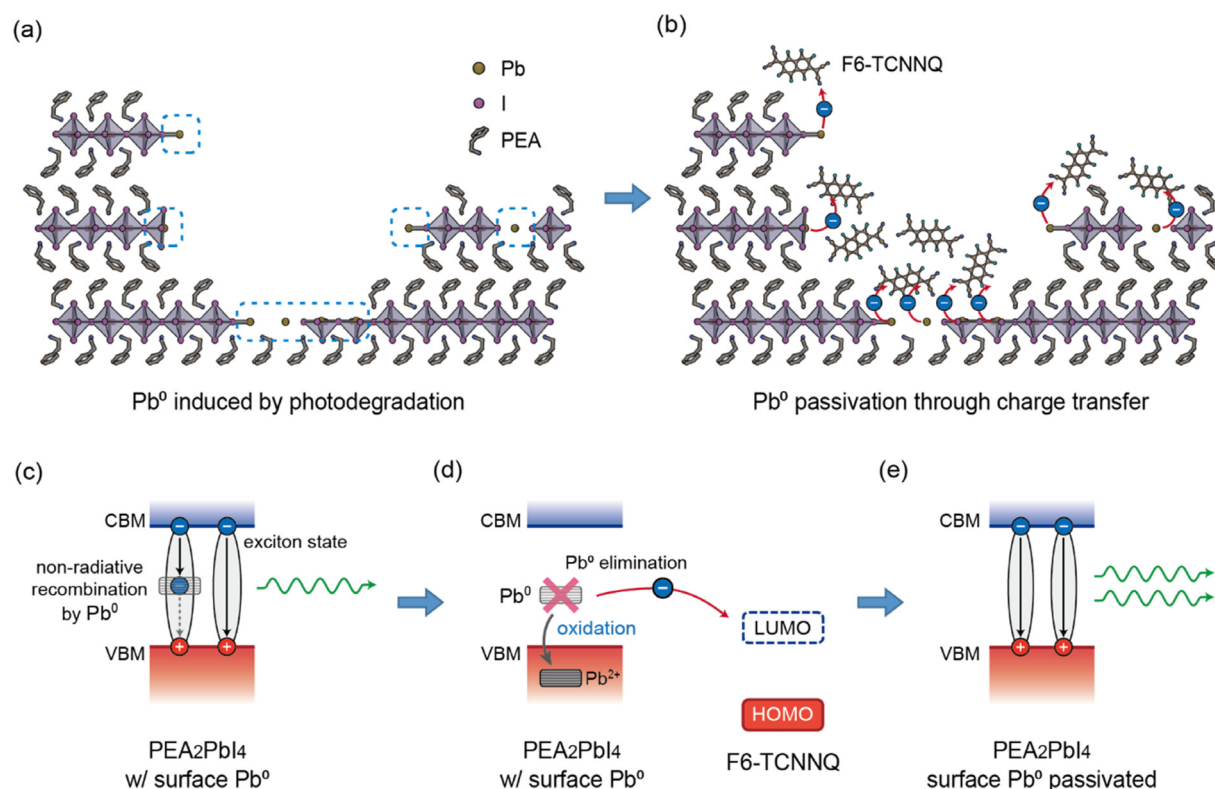


FIG. 8. Surface passivation process using a molecular acceptor: (a) Pristine PEA₂PbI₄ is irradiated with a blue laser, which causes the loss of I[−] ions and formation of metallic Pb⁰. (b) F6-TCNNQ is then adsorbed on the terrace edge nearby, withdraws electrons from Pb⁰, oxidizes Pb⁰ into Pb²⁺, and prevents further degradation. (c) Energy level diagram of PEA₂PbI₄ in the presence of Pb⁰. This system shows a reduced photoluminescence (PL) intensity due to non-radiative recombination. (d) However, F6-TCNNQ withdraws electrons from the Pb⁰ states and oxidizes them into Pb²⁺. (e) As a result of Pb⁰ elimination, the PL intensity recovers.

Figure 8 illustrates the photodegradation process in PEA₂PbI₄ and subsequent surface passivation via the deposition of a molecular acceptor (F6-TCNNQ). The overall process is described in Figs. 8(c)–8(e). Light irradiation causes degradation of the PEA₂PbI₄ surface, resulting in the formation of metallic Pb⁰ and potentially under-coordinated Pb^{(2-δ)+} species [Fig. 8(a)]. Pb⁰ acts as a trap state that induces non-radiative recombination and reduces the PL intensity [Fig. 8(c)]. However, the deposition of F6-TCNNQ significantly eliminates the Pb⁰ state by withdrawing electrons from it [Figs. 8(b) and 8(d)]. Moreover, F6-TCNNQ effectively covers the terrace edges of PEA₂PbI₄, where the imperfect crystal structure forms Pb⁰ and Pb^{(2-δ)+}. The F6-TCNNQ LUMO lies between the Pb⁰ states and PEA₂PbI₄ VBM, ensuring that electrons are transferred only from the Pb⁰ states to the F6-TCNNQ while preserving intact PEA₂PbI₄ [Fig. 8(d)]. As a result, the reduced PL intensity recovers to a level comparable to that of pristine PEA₂PbI₄ [Fig. 8(e)]. Our findings allow us to answer the two questions raised in the introduction. (1) Yes, molecular surface passivation can effectively enhance the photostability of 2D RP perovskites. (2) The Pb⁰ passivation mechanism in 2D RP perovskites is fundamentally different from that of 3D perovskites because the organic spacer hinders orbital overlap and the deep-lying VBM induces selective electron transfer to the LUMO level of acceptor molecules.

III. CONCLUSION

We successfully showed that passivation of 2D RP perovskite PEA₂PbI₄ with a strong molecular acceptor effectively eliminates the Pb⁰ states produced during photodegradation. XPS and PL measurements confirmed that F6-TCNNQ passivation led to the recovery of the PL intensity and elimination of the Pb⁰ state in photodegraded PEA₂PbI₄. Additionally, PEA₂PbI₄ covered with F6-TCNNQ displayed significantly better photostability compared to the pristine PEA₂PbI₄. This improved photostability can be attributed to the inhibition of the initial Pb⁰ defects that are primarily generated at terrace edges. The UPS results show that the passivation mechanism involves selective electron transfer from the Pb⁰ states in PEA₂PbI₄ to the F6-TCNNQ LUMO. This selective electron transfer is facilitated by energy level alignment of the Pb⁰ states close to the E_F, PEA₂PbI₄ VBM, and deep-lying F6-TCNNQ LUMO. Our findings provide new insights into defect passivation in 2D RP perovskites and offer a way to develop high-stability perovskite optoelectronic devices.

SUPPLEMENTARY MATERIAL

See the supplementary material for experimental details, which are given in Sec. 1.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Kitae Kim: Conceptualization (lead); Data curation (equal); Formal analysis (lead); Investigation (lead); Writing – original draft (lead). **Donghee Kang:** Data curation (equal); Formal analysis (equal); Investigation (equal). **Sylke Blumstengel:** Data curation (equal); Formal analysis (equal); Investigation (equal). **Nicolas Zorn-Morales:** Data curation (equal); Formal analysis (equal); Investigation (equal). **Emil J. W. List-Kratochvil:** Formal analysis (equal); Funding acquisition (equal); Investigation (equal). **Sang Wan Cho:** Data curation (equal); Formal analysis (equal); Investigation (equal). **Hyunbok Lee:** Funding acquisition (equal); Supervision (equal); Writing – review & editing (equal). **Soohyung Park:** Funding acquisition (lead); Investigation (lead); Resources (lead); Supervision (lead); Writing – review & editing (lead). **Yeonjin Yi:** Funding acquisition (lead); Investigation (lead); Resources (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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