

Reconfiguring the band-edge states of photovoltaic perovskites by conjugated organic cations

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Abstract:

The band edges of metal-halide perovskites with a general chemical structure of ABX_3 are constructed mainly of the orbitals from B and X sites. Hence, the structural and compositional varieties of the inorganic B-X framework are mainly responsible for regulating their electronic properties, whereas A-site cations are thought to only help stabilize the lattice and do not directly contribute to near-edge states. We report a π -conjugation-induced extension of electronic states of A-site cations that impacts perovskite frontier orbitals. The π -conjugated pyrene-containing A-site cations electronically contribute to the surface band edges and impact the carrier dynamics with a properly tailored intercalation distance between the inorganic framework. The ethylammonium pyrene increased hole mobilities, improved power conversion efficiencies relative to a reference perovskite, and also improved device stability.

The band-edge electronic structure of hybrid metal-halide perovskites (ABX_3 , where A is usually a monovalent organic cation, B is a divalent cation, and X is a halide anion) develops from the orbitals of B and X sites (1) and can be tuned through the compositional and structural flexibility of the B-X framework (2–12). In contrast, the A-site cations are generally not thought to affect electronic structure directly near the band edges because their electronic states lie far from the inorganic band edges (13), but different A-site cation sizes can induce indirect effects on the inorganic B-X framework, such as the unit volume variation, octahedral distortion, and dimensional reduction (14–17). We now show that the electronic states of the A-site cations can be extended and directly contribute to the frontier orbitals of the hybrid perovskite through a combination of a large π -conjugated structure and a tailored intercalation distance with the inorganic framework, which adds additional degrees of electronic tunability to near-edge electronic configuration. The carrier dynamics could be rationally tuned in accordance to the device architecture by modifying the A-site organic structure.

We designed a polycyclic aromatic tail with large π -conjugation that was attached to an ammonium A-site cation. The chemical structures of the as-synthesized organic cations featured different lengths of the tethering alkylammonium group, namely PRA, PRMA, and PREA for the pyrene-based ammonium, methylammonium, and ethylammonium, respectively (**Fig. 1A**; see synthesis details in **Supplementary Text S1**). When these organic cations were assembled with the inorganic framework, the extent to which the positively charged ammonium head group intercalated into the octahedral cavity depended on the length of the bridging alkyl chain. Electron delocalization in the large conjugated pyrene structure lowered the frontier orbital separation of the organic molecule and enabled orbital overlap with the inorganic moiety (18).

The alkyl chain length affected the electronic interaction between the two moieties. Ultraviolet photoemission spectroscopy (UPS) of PRMA and PREA cations assembled onto the surface of the Pb-I framework of formamidinium (FA)-based perovskite thin film (**Fig. 1B**) revealed additional electronic states near the tail of the valence band (the Fermi energy has been aligned for better comparison). However, a perovskite thin film with the PRA moieties attached exhibited similar band tail characteristics to that of the reference, indicating a lack of electronic contribution from PRA to the surface band edges.

First-principle calculations of the partial density of states revealed electronic states near the surface band edges (**Fig. 1C**). As the alkyl chain of the ammonium group became longer, the electronic states from the organic components at the valence band were pushed to a higher energy level. The electronic states from PRA were as far as 0.34 eV below the valence band maximum (VBM) but

PRMA and PREA had electronic states near the VBM. The distribution of the electronic states of the organic ammonium cations with respect to the inorganic band structure (Fig. 1D) showed that the orbitals of PRMA and PREA greatly overlapped with the inorganic VBM with the highest unoccupied orbital just 0.02 eV below the VBM, and 0.01 eV above the VBM, respectively. Thus, the band structure of PRA resembled that of the reference film with the VBM consisting of I 5p and Pb 6s orbitals, but for PRMA and PREA, the VBM had contributions from the orbitals of both inorganic and organic components. The participation of PRMA and PREA in the surface band edge construction was also observed in all-inorganic CsPbI₂Br perovskite (**Supplementary text S2**), indicating the generality of this concept.

The discrepancy in the surface band-edge configuration originated from different chemical interaction modes between the inorganic framework and the ammonium cations with different alkyl chain lengths; theoretical modeling of the assembly of these organic ammoniums on the surface of the Pb-I framework is shown in **Fig. 2A**. We used time-of-flight secondary-ion mass spectrometry and grazing-angle polarization-dependent infrared reflection-absorption spectroscopy to verify the vertical assembly of the ammonium cations on the surface (**Supplementary Text S2 and S3**). Both PRMA and PREA could anchor into the octahedral cavity through electrostatic interactions between the ammonium cations and the PbI₆²⁻ octahedra. However, PRMA, which has a shorter alkyl chain length between the ammonium head and pyrene tail, exhibited a distorted intercalation configuration because of the structural rigidity and large steric hindrance induced by the pyrene ring.

The elongated alkyl chain in PREA enabled more flexibility with less steric hindrance and displayed almost vertical intercalation of PREA into the inorganic layers. The conjugated tails of the PREA were stacked almost perpendicular to the plane of the inorganic layer. With a reduction in the length of the tethering alkylammonium group, the orientation of PRMA tilted away from the vertical direction by ~30°, which disrupted the π - π stacking and reduced the electronic delocalization. In contrast, PRA, which lacked a flexible alkyl chain, failed to relieve the steric hindrance of the pyrene group when anchoring into the Pb-I framework and its binding mode to the inorganic surface would be better described as adsorption than anchoring motif, as also evidenced by the vertically oriented pyrene tail in PRA stacking. With a shallow interaction depth, the steric hindrance from the large pyrene tail no longer takes a role in affecting the intercalation configuration, enabling a molecular orientation driven by the surface energy and π - π stacking.

We used attenuated total reflection Fourier-transform infrared (ATR-FTIR) to investigate the chemical binding between the organic cations and the Pb-I framework. The difference ATR-FTIR spectra of perovskite films with PRA, PRMA, and PREA with respect to the reference film, are shown in **Fig. 2B**. Distinct vibration features from the reference and PRA samples were observed in PRMA and PREA samples between 900 to 1100 cm⁻¹. Both PRMA and PREA showed remarkably reduced absorption near 930 cm⁻¹ and increased absorption near 1060 cm⁻¹, which we attributed to the change of the out-of-plane N-H wagging and C-N stretching modes, respectively. The absence of distinct vibration features in PRA samples indicated a different binding mode with a weak interaction. High-resolution x-ray photoemission spectroscopy (XPS) of the Pb 4f for the perovskite film with different ammonium cations (**Fig. 2C**) showed two main peaks located at ~138 and ~143 eV, corresponding to the Pb 4f_{7/2} and Pb 4f_{5/2}, respectively (19). The peaks from Pb 4f shifted to higher binding energies in the film with PRMA and PREA, whereas the spectra of PRA samples remained almost identical to the reference sample. This difference suggested a

stronger interaction between PRMA/PREA and the Pb as well as a more profound influence on the bonding character of Pb in the inorganic framework compared to that in the case of PRA.

The dense and periodic insertion of the pyrene-based ammoniums into the Pb-I framework was further evaluated by grazing-incident wide-angle x-ray scattering (GIWAXS) and the growth of two-dimensional (2D) perovskite single crystals. The GIWAXS patterns of perovskite thin films formed by stoichiometrically mixing PbI₂ and PRA, PRMA, PREA salt in order to form a 2D perovskite phase, are shown in **Fig. 3, A to C**, respectively. Both PRMA and PREA-based perovskite samples exhibited out-of-plane diffraction patterns of {100} planes, indicating the formation of 2D perovskite phases, but this diffraction feature was absent for PRA, confirming that it failed to anchor into the Pb-I framework. The PREA-based 2D perovskite showed much higher crystallinity and preferred out-of-plane crystallographic orientation compared to PRMA ones (**Fig. 3D**), which further verified the distorted intercalation configuration of PRMA. Single crystals of PREA-based 2D perovskite showed periodic stacking mode of the pyrene-based ammonium cations, and the pyrene rings had an edge-on packing with the Pb-I framework (**Fig. 3E**, see details of the crystal structures and the growth of single crystals in **Supplementary Text S4**)

The reconfiguration of the surface electronic band-edge electronic structures involving A-site organic cations and the alkylammonium-controlled intercalation distance were also reflected in the change of surface carrier dynamics, which were probed by transient reflection spectroscopy (TRS) and time-resolved terahertz (THz) spectroscopy (TRTS) (20, 21). By modeling the measured surface carrier kinetics with a surface interaction distance defined (see the modeling details in **Supplementary Text S5**), we could determine the binding configuration because the electronic interaction distance was related to the binding character between the organic ammonium cations and the inorganic moieties (**Fig. 4A**). The surface carrier kinetics probed by transient optical reflection for the cases of reference, PRA, PRMA, and PREA (**Fig. 4B**) revealed a ~33% increase in the interaction distance for PRMA or PREA compared to PRA (the absolute values may be longer than expected in the model because of the effects of film roughness). This increase in the interaction distance was consistent with the interaction mode between the organic ammonium cations and perovskite lattice, where PRMA and PREA inserted into the lattice unlike PRA.

The photoinduced electron and hole carrier mobilities are extracted by combining TRS and TRTS results. The surface photogenerated carrier transport was measured with the reflected optical probe (22) and provided information on the ambipolar diffusion coefficient (D_{ab}) (23, 24), whereas the terahertz probe pulse was sensitive to the sum of the electron and hole mobilities $\sum\mu = \mu_e + \mu_h$. (33) By using the Einstein relation to determine the ambipolar mobility (μ_{ab}) from D_{ab} and combining it with $\sum\mu$, the individual mobilities of electrons μ_e and holes μ_h can be derived, because $1/\mu_{ab} = (1/\mu_e) + (1/\mu_h)$. The sum of DC mobility (μ_{dc}) was extracted by using a Drude-Smith model from transient THz spectra at 5 ps delay for reference, PRA, PRMA and PREA (**Fig. 4C**; see modeling details in **Supplementary Text S5**). The best-fit parameters and the calculated carrier mobilities are summarized in **Table S1**. Because the orbitals of the organic ammonium cations mainly interacted with the valence band of the inorganic lattice, the hole mobility was most affected. The largest increase in the hole mobility was observed for PREA; electron mobilities remained almost invariant across all samples.

The enhancement in the hole mobility benefitted the carrier collection in perovskite photovoltaic devices, as reflected by an increase in the short-circuit current (J_{sc}) and fill factor (FF). The power conversion efficiency (PCE) of the as-fabricated perovskite solar cells with PREA exhibit the

largest enhancement from 20.1 % to 23.0% (**Fig. 4D**). A smaller enhancement of hole mobility and thus J_{sc} and FF was observed for PRMA, which we attributed to the distorted intercalation of the ammonium cations generating energy disordering in the lattice. However, PRA actually led to a decrease in PCE because of a reduced open circuit voltage that resulted from an unmatched energy level with the hole-transporting layer (**Supplementary Text S3**). Thus, rational control of the intercalation distance regulated by the tethering alkyl ammonium enabled electronic contribution of A-site cation to the near-edge band structure, and in turn modified the carrier kinetics within devices. The insertion of the ammonium head into the framework, and thus the exposure of the hydrophobic polycyclic aromatic tail, further increased the stability of the devices. After 2000 hours exposure to continuous light under open-circuit condition, the device with PREA maintained over 85% of its original PCE, whereas the reference device degraded to only 60% of its initial PCE. (**Supplementary Text S6**).

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Data and materials availability: All data are available in the main text or the supplementary materials. Crystallographic parameters for the structure of $\text{PREA}_2\text{PbI}_4$ are archived at the Cambridge Crystallographic Data Centre ([https:// www.ccdc.cam.ac.uk/](https://www.ccdc.cam.ac.uk/)) under reference number CCDC 2045757.

5 **Supplementary Materials:**

Materials and Methods

Supplementary Text S1-S6

Figs. S1-S22

Tables S1-S3

10 References (25-32)

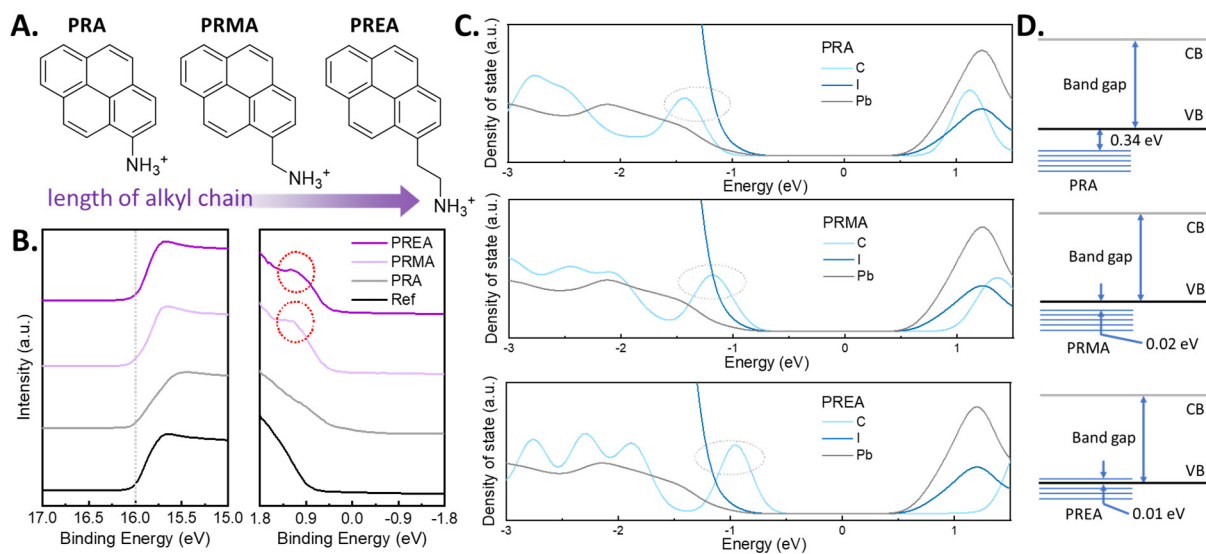


Fig. 1. Surface band-edge structures with the electronic contribution from conjugated A-site cations. (A) Chemical structures of three different organic ammoniums featuring different length of tethering alkylammonium. (B) Ultraviolet photoelectron spectroscopy. (C and D) Calculated partial density of state (C) and band diagram (D) of perovskites with PRA, PRMA, and PREA.

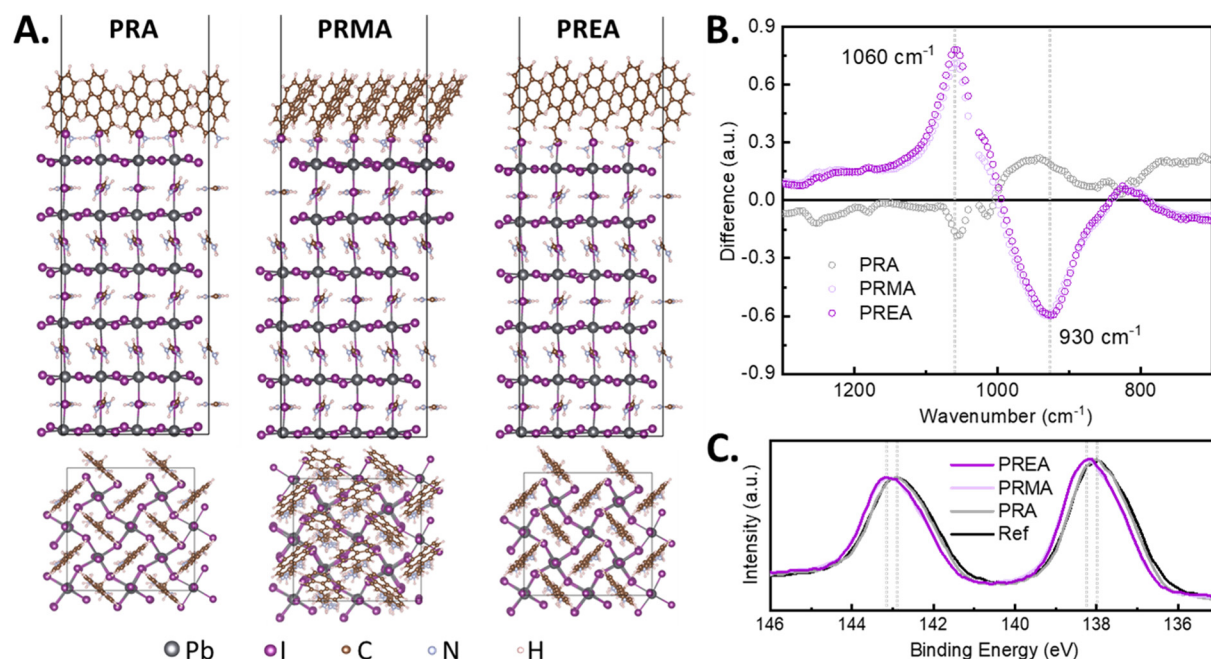


Fig. 2. The interaction mode between the conjugated ammoniums and perovskite framework. (A) The side view (top) and top view (bottom) of intercalation configuration modeled by DFT for PRA, PRMA, and PREA. (B) Difference ATR spectra of perovskite with PRA, PRMA and PREA with respect to reference. (C) XPS data for Pb 4f 7/2 and Pb 4f 5/2 core level spectra for perovskite with PRA, PRMA and PREA.

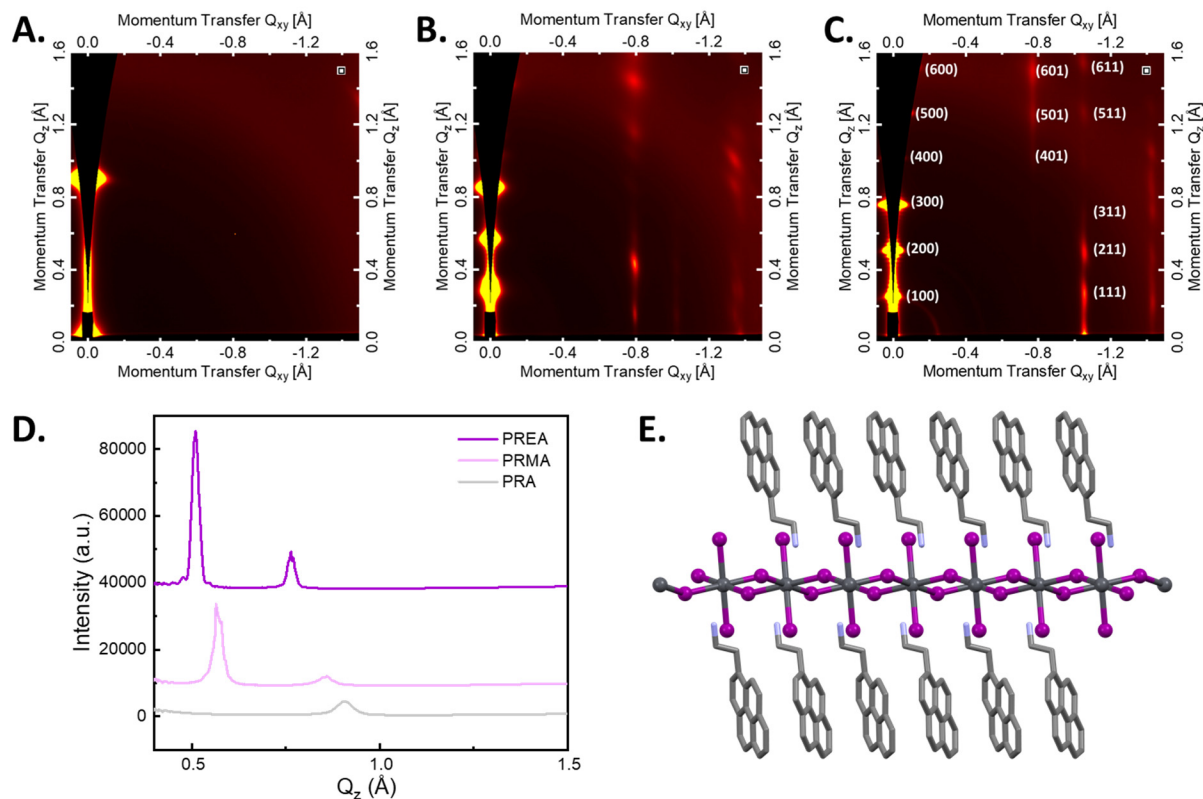


Fig. 3. The intercalation configuration of the conjugated ammoniums. (A to C) Grazing incident wide angle X-ray scattering (GIWAXS) patterns of perovskite thin films when stoichiometrically mixing PbI₂ and (A) PRA, (B) PRMA, and (C) PREA salt, respectively, in order to form a two-dimensional (2D) perovskite phase. (D) Out-of-plane GIWAXS profiles for PRA, PRMA, PREA-based samples. (E) Crystal structure of 2D PREA₂PbI₄ perovskite single crystal.

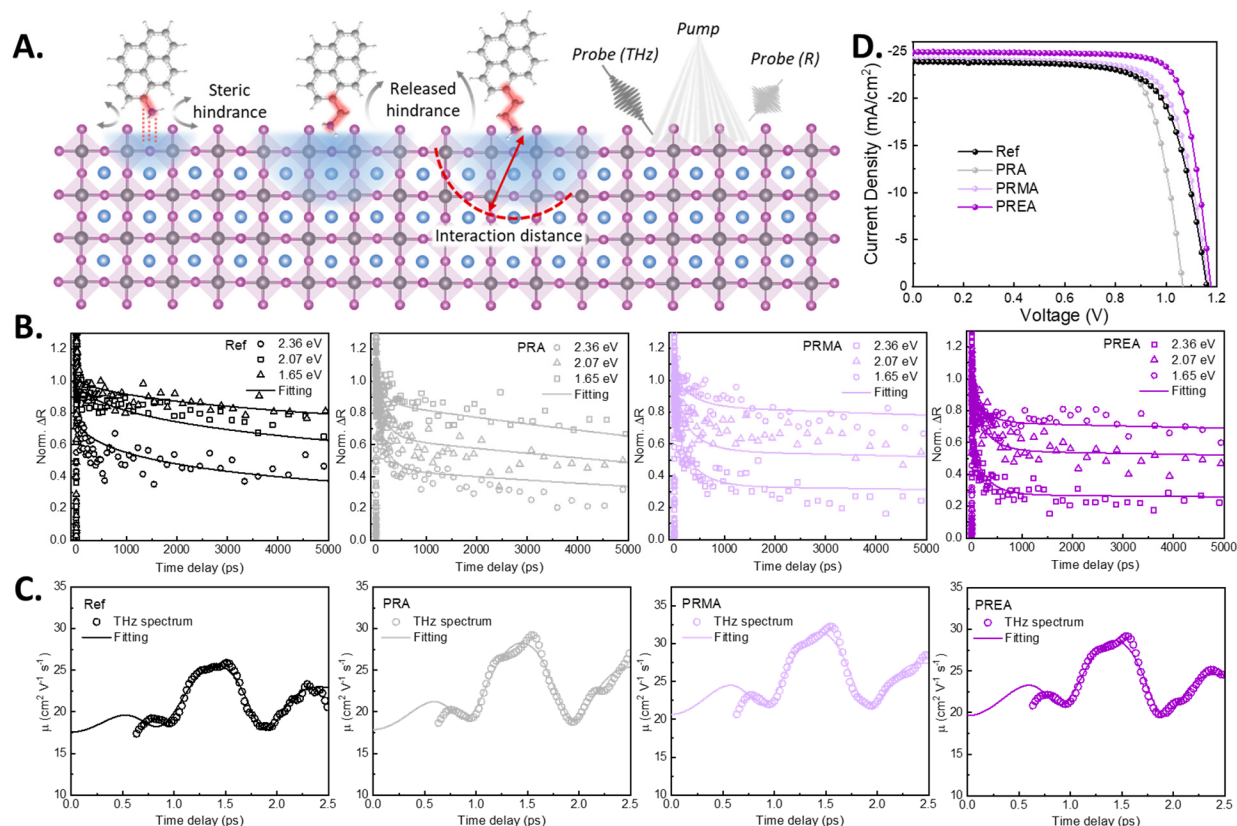


Fig. 4. Investigations on the change of carrier dynamics and photovoltaic response. (A) Schematic illustration of the influence of intercalation configuration and the interaction distance revealed by the combination of transient reflection spectroscopy (TRS) and transient THz spectroscopy (TRTS). (B) Surface-carrier kinetics pumped at 2.36, 2.07, and 1.65 eV probed by TRS and fitted with diffusion model and (C) TRTS spectrum at 5-ps time delay and fitted with Drude-Smith model for reference and perovskite with PRA, PRMA, and PREA. (D) Current density-voltage curves of the as-fabricated perovskite solar cells showing the influence of the changed band edge configurations and thus the carrier dynamics on photovoltaic performance.