Perovskite Solar Cells Consisting of PTAA Modified with Monomolecular Layer and Application to All-Perovskite Tandem Solar Cells with Efficiency over 25%

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This study is on the enhancement of the efficiency of wide bandgap (FA0.8Cs0.2PbI1.8Br1.2) perovskite solar cells (PSCs) used as the top layer of the perovskite/perovskite tandem solar cell. Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA) and the monomolecular layer called SAM layer are effective hole collection layers for APbI₃ PSCs. However, these hole transport layers (HTL) do not give high efficiencies for the wide bandgap FA08Cs02Pbl18Br12 PSCs. It is found that the surface-modified PTAA by monomolecular layer (MNL) improves the efficiency of PSCs. The improved efficiency is explained by the improved FA08Cs02PbI18Br12 film quality, decreased film distortion (low lattice disordering) and low density of the charge recombination site, and improves carrier collection by the surface modified PTAA layer. In addition, the relationship between the length of the alkyl group linking the anchor group and the carbazole group is also discussed. Finally, the wide bandgap lead PSCs ($E_{\sigma} = 1.77 \text{ eV}$) fabricated on the PTAA/monomolecular bilayer give a higher power conversion efficiency of 16.57%. Meanwhile, all-perovskite tandem solar cells with over 25% efficiency are reported by using the PTAA/monomolecular substrate.

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1. Introduction

Organic-inorganic perovskite solar cells (PSCs) have achieved a recorded power conversion efficiency (PCE) of 25.7%.^[1] Thus, PSCs are considered to be the dominant player in the next-generation photovoltaic market.^[2,3] PSCs with bandgaps between 1.2 and 2.3 eV have been reported so far. Although single-junction PSCs with narrow bandgap values have attracted attention since 2014,^[4-7] as a member of perovskite materials, wide-bandgap perovskite (WBG-PVK) also cannot be ignored because it is important for tandem solar cells due to its matchable bandgap.^[8-10] Up to now, the efficiency of the perovskite/ perovskite tandem has reached 28%.[11] In order to enhance the efficiency of the tandem cell, the efficiency of both the top and bottom cell has to be improved. In this report, the enhancement of the effi-

ciency of the top cell with WBG PSCs is discussed.

Monomolecular layers called SAMs have been widely used to improve the PCE of the PSCs.^[12–15] Molecules with phosphonic acid working as the anchoring groups are known to form densely packed, uniform SAMs on the substrate.^[16] Hong et al. achieved a high PCE and stability by designing and synthesizing novel halogenated phenothiazine-based SAMs for the hole transport layers (HTL) in p-i-n solar cells.^[17] Jen et al. reported two carbazole-based SAMs, CbzPh and CbzNaph. Both strategies are capable of increasing the dipole moment and π - π interactions simultaneously. Finally, the PCE of the Pbbased PSCs reached 24.1%^[18] This work proved that the monomolecular layer is effective as the HTL of Pb-based PSCs.^[18,19]

The other representative HTL is poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA). There are various reports on APbI₃ solar cells employing the PTAA.^[20,21] However, the hydrophobicity of the PTAA often leads to poor perovskite film quality. Many strategies have been reported to improve the hydrophobicity of PTAA, such as interface engineering, dopant engineering, etc.^[22–26] It has been reported that the SAM layer and the PTAA are useful for conventional APbI₃ solar cells.



However, these layers did not give high efficiency for wide bandgap $FA_{0.8}Cs_{0.2}PbI_{1.8}Br_{1.2}$ perovskite solar cells.

The interface stress brought by poor interface contact decreases efficiency. Printz and co-workers summarize the origin and the impact of the stress in perovskite devices. They believe that by improving the interface contact, the interface stress can be effectively relieved.^[27] Here, we demonstrate the PTAA layer modified with a series of the monomolecular layer (MNL) with different alkyl chain lengths. It has been reported that the linker group with two carbons gives high efficiency on the transparent conductive oxide layer. In this work, the effect of the chain length on the efficiency was examined when the monomolecular layer is fabricated on the PTAA.^[28,29] Finally. the target device achieves a PCE of 16.57%. Besides, the allperovskite tandem solar cells with the WBG-Pb-PSCs and the narrow bandgap Sn/Pb PSCs gave the PCE of 25.24%. In addition, the improved stability of the unencapsulated tandem cell is discussed.

2. Results and Discussion

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The structure of the PSCs used in the present work is shown in **Figure 1**a, which contains ITO/PTAA/MNL/WBG-PVK/C60/ BCP/Ag.^[19,30–32] Since PTAA did not give high efficiency on FA_{0.8}Cs_{0.2}PbI_{1.8}Br_{1.2} WBG PSCs, we aimed at modifying the PTAA film with various MNL. It has been reported that perovskite film quality, carrier extraction, and carrier transport can be improved by changing the surface of the substrate.^[19,33,34]

The experimental details of the synthesis and the structure of the molecules for the MNL are shown in Figure 1a and Scheme S1 (Supporting Information). They are abbreviated as follows: [3-[3-(carbazol-9-yl)carbazol-9-yl]propyl]phosphonic acid (3,3PrPACz), [4-[3-(carbazol-9-yl)carbazol-9-yl]butyl]phosphonic acid (4,3BuPACz) and [6-[3-(carbazol-9-yl)carbazol-9-yl] hexyl]phosphonic acid (6,3HePACz). The MNL molecules were spin-coated on the PTAA layer, followed by washing the sample substrate with solvent to remove non-bonded additional modified molecules. X-ray photoelectron spectroscopy (XPS) measurement was employed to prove the existence of the MNL after washing. A distinct P 2p signal was observed for the substrate of PTAA/3,3PrPACz, PTAA/4,3BuPACz, and PTAA/6,3HePACz while not on the PTAA (Figure S1a, Supporting Information). In addition, C 1s orbitals of these substrates (PTAA, PTAA/3,3PrPACz, PTAA/4,3BuPACz, and PTAA/6,3HePACz) (Figure S1b, Supporting Information) showed that C with different chain lengths exists on the substrates. These results strongly support the presence of the monomolecular layer on the PTAA. Fourier-transform infrared spectroscopy (FTIR) was used to demonstrate the chemical interaction between 4,3BuPACz and PTAA. As shown in Figure S2 (Supporting Information), PTAA and PTAA/4,3BuPACz prepared on the glass were examined. The peak located at 1232 cm⁻¹ was designated to P-OH stretching vibration. After the 4,3BuPACz was deposited on the PTAA, the P-OH stretching vibration was shifted, which suggests the chemical interaction between PTAA and 4,3BuPACz (probably P-OH and N in the PTAA backbone to make $P-O^{-}...^{+}H-N-$). The N of the PTAA has lone pair



Figure 1. a) Structure of device and molecular structures for surface modification and the chemical structure of [3-[3-(carbazol-9-yl]carbazol-9-yl]propyl] phosphonic acid (3,3PrPACz), [4-[3-(carbazol-9-yl]carbazol-9-yl]butyl]phosphonic acid (4,3BuPACz) and [6-[3-(carbazol-9-yl]carbazol-9-yl]hexyl] phosphonic acid (6,3HePACz). b) Schematic diagram of the chemical interaction between PTAA and 4,3BuPACz. c) Grain size distribution of WBG perovskite grown on PTAA modified with monomolecular layer. The stain was calculated from XRD. e) Urbach energy of WBG perovskite grown on PTAA modified with monomolecular layer.

electrons and shows base properties. The -P-OH of $-PO_3H_2$ has acidic properties. It is well known that acid and the base make ionic products (Figure 1b).

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It is well known that the perovskite precursor solution is difficult to spread on PTAA. As shown in Figure S3 (Supporting Information), the contact angle was decreased in the order of PTAA, 3,3PrPACz/PTAA, 6,3HePACz/PTAA, and 4,3BuPACz/ PTAA. It is expected that a smaller contact angle can lead to better interface contact. As shown in Figure S4 (Supporting Information), some pinholes were observed in the perovskite film on the PTAA, while these pinholes disappeared in the PTAA surface modified with these molecules. Figure 1c shows the crystal size distribution on various substrates. Compared with the perovskite film deposited on the bare PTAA substrate, the perovskite film prepared on the surface-modified PTAA had a larger average grain size.

X-ray diffraction (XRD) of the perovskite fabricated on the PTAA layer with or without MNL modification was measured to gain the effect of the MNL on perovskite film quality. The result shows in Figure S5 (Supporting Information). The characteristic diffraction peaks at 2θ values of 14.7°, 20.7°, 32.7°, and 41.6°, corresponding to the (100), (101), (211), and (212) crystal planes of the perovskite film, respectively.^[35] The results show that the crystal structure of the perovskite film did not change after the NML was introduced. The full width at half maximum (FWHM) of the strongest peak ((101)) is summarized in Figure S6 (Supporting Information). The FWHM of the perovskite layer decreased in the following order: PTAA> 6,3HePACz on PTAA> 3,3PrPACz on PTAA>4,3BuPACz on PTAA. The narrowest FWHM of the perovskite was obtained when the perovskite was deposited on 4,3BuPACz/PTAA, leading to the conclusion that the PTAA/4,3BuPACz gave the best crystal quality. We further evaluated the strain component (lattice disordering) in the perovskite film by using the Williamson-Hall plot (Figure S7, Supporting Information and Figure 1d). The interface strain (lattice disordering) of the perovskite layer deposited on the PTAA (-0.172) was higher than that prepared on the PTAA/ MNL, namely, 3,3PrPACz on PTAA: -0.156, 4,3BuPACz on PTAA: -0.127, and 6,3HePACz on PTAA: -0.150. The released strain mainly comes from the flexibility of the alkyl chain, which can buffer the stress from the PTAA film.[36-38] The crystal quality was improved in the following order of the chain length: 3≦6<4. As shown in Figure S8 (Supporting Information), the absorption intensity of the perovskite film was not varied after depositing on the PTAA with or without MNL modification. The bandgap of the perovskite film deposited on PTAA or PTAA/MNL calculated from the Tauc plot (Figure S9, Supporting Information) showed an E_g of 1.77 eV. In addition, the Urbach energy is summarized in Figure 1e. The perovskite film prepared on PTAA/MNL has a steeper band tail with lower Urbach energy (3,3PrPACz: 28.2 meV, 4,3BuPACz: 24.5 meV, and 6,3HePACz: 29.4 meV) compared with the one on the PTAA (31.5 meV). The lowest was given by the PTAA/4,3BuPACz, which explains the better photovoltaic performances explained later. The dependence of the alkyl chain on the Urbach energy decreased as follows: $6 \ge 3 > 4$, whose order is similar to that of the crystal quality described before.

The photoluminescence (PL) and time-resolved PL (TRPL) were employed to investigate the effect of the PTAA modification

on the defects density and carrier lifetimes of perovskite films. The PL intensity of the perovskite film prepared on glass/MNL is shown in Figure S10 (Supporting Information). The intensity increased in the following order: 6,3HePACz (The number of the alkyl chain:6) <3,3PrPACz (The number of the alkyl chain:3) <4,3BuPACz (The number of the alkyl chain:4). The carrier lifetimes of the perovskite film deposited on a different substrate (PTAA or PTAA/MNL) calculated from TRPL curves are summarized in Figure S11 (Supporting Information). The TRPL dynamics was fitted well through the double-exponential function:^[3,39]

$$I(t) = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + A_2 e^{\left(-\frac{t}{\tau_2}\right)}$$
(1)

$$\tau_{\rm ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{2}$$

where τ_1 and τ_2 correspond to the fast and slow decay lifetime constant, respectively. A_1 and A_2 are the amplitude of the fast and slow decay processes, respectively. The average carrier lifetime (τ_{ave}) can be calculated by Equation (2) and the fitting results are shown in Table S1 (Supporting Information). It was clear that the average carrier lifetime of the perovskite film deposited on the glass was 65.65 ns, while the film deposited on the monomolecular layer showed a longer carrier lifetime in the following order: 6,3HePACz (85.48 ns) < 3,3PrPACz (90.57 ns)< 4,3BuPACz (122.72 ns). The order corresponds to six carbon≦three carbon < four carbon, from the viewpoint of the number of carbon in the linker of the modification molecule. The order is consistent with the results described above. In general, a shorter fluorescence lifetime implies the presence of fewer nonradiative recombination centers.

The photovoltaic performance of these four PSCs was evaluated and these results are shown in Figure S12 (Supporting Information) and Figure 2a. Figure 2b shows the typical J-V curves of the PSCs prepared on PTAA and modified PTAA. The corresponding photovoltaic parameters are summarized in Table S2 (Supporting Information). The champion efficiency of the device fabricated on PTAA was 14.46% (a short circuit current (I_{SC}) of 17.15 mA cm⁻², an open-circuit voltage (V_{OC}) of 1.117 V, and a fill factor (FF) of 75.53%), while the devices fabricated on the PTAA modified with 3,3PrPACz, the PTAA modified with 4,3BuPACz, and the PTAA modified with 6,3HePACz gave PCE of 15.49% (a $J_{\rm SC}$ of 17.59 mA cm⁻², a $V_{\rm OC}$ of 1.141 V and an FF of 77.20%), 16.57% (a JSC of 17.98 mA cm⁻², a $V_{\rm OC}$ of 1.175 V and an FF of 78.44%), and 15.29% (a J_{SC} of 17.53 mA cm⁻², a V_{OC} of 1.146 V and an FF of 76.15%), respectively. In addition, the carbazole without the anchoring group was used to modify the PTAA as a reference, and the results are listed in Table S2 (Supporting Information). The carbazole/PTAA-based PSCs showed a 13.61% (a I_{SC} of 17.98 mA cm⁻², a V_{OC} of 1.175 V, and an FF of 78.44%) championship efficiency. The efficiency was lower than those modified by the molecules with the anchor group. Figure 2c shows the corresponding incident photon-toelectron conversion efficiency (IPCE) spectra of PSCs prepared on the PTAA only and the modified PTAA. The integrated current densities of 16.99 mA cm⁻² for the device prepared on the PTTA, 17.34 mA cm⁻² for the PVK prepared on the PTAA



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Figure 2. a) Statistical distribution diagram of PCE for PSCs fabricated on PTAA, PTAA modified with 3,3PrPACz, 4,3BuPACz, and 6,3HePACz, respectively. b) J-V curves and c) IPCE curves. d) Steady-state efficiency as a function of time for PSCs fabricated on PTAA, PTAA modified with 3,3PrPACz, 4,3BuPACz, and 6,3HePACz, respectively, measured at the maximum power point. e) N₂ stability of the PSCs fabricated on PTAA and PTAA modified with 4,3BuPACz, stored at room temperature in the nitrogen-filled glovebox (without encapsulation). f) Thermal stability of unencapsulated PSCs fabricated on PTAA and PTAA modified with 4,3BuPACz, kept at 85 °C in a nitrogen-filled glovebox in the dark. From the viewpoint of the number of carbon in the linker group, the efficiency was improved in the following order: six carbons \leq three carbons<four carbons, whose order is consistent with that described before.

modified with 3,3PrPACz 17.72 mA cm⁻² for the PV prepared on the PTAA modified with 4,3BuPACz, and 17.00 mA cm⁻² for the PVK prepared on the PTAA modified with 6,3HePACz, which are in good agreement with the I_{SC} of the I-V characterization. The steady-state PCE for the PSCs on the PTAA with or without this modification was measured at the maximum power point, and these results are shown in Figure 2d. The control device had a stable output PCE of 14.05% while the PVK prepared on the PTAA modified with 3,3PrPACz (15.15%), the PVK prepared on the PTAA modified with 4,3BuPACz (16.38%), and the PVK prepared on the PTAA modified with 6,3HePACz (15.02%) gave higher PCEs. We further evaluated the stability of the PVK prepared on the PTAA modified with 3,3PrPACz and the PVK prepared on the PTAA modified with 4,3BuPACz without encapsulation. The control device was degraded to 75% against the original efficiency after 1000 h in the N₂ glovebox while the PVK prepared on the PTAA modified with 4,3BuPACz kept 81% of their initial PCE (Figure 2e). Furthermore, the thermal stability was measured by placing the unencapsulated PSCs on the hot stage with a temperature of 85 °C in an N2 atmosphere. As shown in Figure 2f, the target device was decreased to 55% of its original PCE while the control device was decreased to 35%.

To further explore the reasons for the improved efficiency, we analyzed the carrier dynamics and interfacial nonradiative recombination in the device. The ideality factor (*n*) was employed to uncover the interfacial nonradiative recombination. The lower *n* supports the less interfacial nonradiative recombination.^[40,41] **Figure 3**a shows the V_{OC} as a function of light intensities for the devices. The n can be calculated by a slope of $k_{\rm B}T/q$ versus light-dependent $V_{\rm OC}$, where $k_{\rm B}$, T, and q are the Boltzmann's constant, Kelvin temperature, and element charge, respectively. Compared with the PSCs prepared on the PTAA (n = 1.89), the devices prepared on the PTAA modified on 3,3PrPACz, the PTAA modified on 4,3BuPACz and the PTAA modified on 6,3HePACz exhibited a lower *n* value of 1.48, 1.24, and 1.52, respectively, which proves that the recombination is suppressed when the PTAA surface modified.^[41] Transient photovoltaic voltage (TPV) dynamics under opencircuit conditions were further employed for insight into carrier recombination. As presented in Figure 3b and Figure S13, Supporting Information, the typical two areas were observed. The area I (lower time) is the intrinsic trap-assisted recombination in the perovskite film, while area II is attributed t the carrier recombination at the interface.^[42,43] After fitting the TPV curves, we got 14.67 µs of the carrier recombination time for the device prepared on PTAA and 59.37 us for the device prepared on the PTAA modified with 4,3BuPACz. These results suggest that the nonradiative charge recombination was suppressed. In conclusion, the recombination is significantly suppressed when the PTAA was modified MNL (supported by TPV and ideality factor), which leads to higher V_{OC} and FF.^[39,41]

PL and TRPL of the perovskite in the structure of ITO/ PTAA/(MNL)/perovskite were carried out to uncover the effect of the MNL on carrier extraction and transport. As shown in Figure S14, Supporting Information, the PL intensity decreased significantly after the surface modification of the PTAA. TRPL www.advancedsciencenews.com

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Figure 3. a) V_{OC} versus light intensity for PSCs fabricated on PTAA, PTAA modified with 3,3PrPACz, 4,3BuPACz, and 6,3HePACz, respectively. b) TPV and c) TPC decay curves of PSCs fabricated on PTAA, PTAA modified with 3,3PrPACz, 4,3BuPACz, and 6,3HePACz, respectively. d) Energy band diagram of all components.

curves were fitted well through the double-exponential function. As exhibited in Figure S15 and Table S3 (Supporting Information), the carrier lifetime was 23 ns for ITO/PTAA/perovskite while the ITO/PTAA modified with 3,3PrPACz/perovskite, the ITO/PTAA modified with 4,3BuPACz/perovskite, and the ITO/ PTAA modified with 6,3HePACz/perovskite showed shorter carrier lifetime of 12, 14.5, and 19 ns, respectively. The shorter lifetime implies the charge transport and extraction were improved after the PTAA was modified by the monomolecular layer.^[40]

Transient photovoltaic current (TPC) of the device with ITO/PTAA/(MNL)/perovskite/C60/BCP/Ag structure was carried out to gain insight into the charge transportation. As shown in Figure 3c, the charge transport was improved after introducing the PTAA modified with a mono-molecular layer. Probably, the three-carbon chain may not give free rotation of the carbazole group, but four carbon chain may make it possible and give packed carbazole groups. Six carbon-chain may disturb the charge transport rate by tunneling because the charge transport rate decrease.^[44,45] It is well known that the built-in potential, as the driving force for carrier transport, is indispensable for evaluating carrier motion. As exhibited in Figure S16, Supporting Information, compared with the device with PTAA (built-in potential, $V_{\rm bi} = 1.01$ V), the device with PATT modified with 3,3PrPACz/PTAA, the device with PATT modified with 4,3BuPACz/PTAA, and the device with PATT modified with 6,3HePACz/PTAA devices show a higher $V_{\rm bi}$ of 1.05 V, 1.12 V, and 1.09 V, consistent with the photovoltaic performance. Figure 3d shows the energy level diagram of these devices (Figure S17, Supporting Information). The valence band of the PTAA, PTAA modified with 3,3PrPACz, PTAA modified with 4,3BuPACz, the PTAA modified with 6,3HePACz were –5.10 eV, –5.27 eV, –5.33 eV, and –5.20 eV, respectively. The difference in the band energy (the difference in valence band level between the HTL and the perovskite) became smaller after the MNL modification. Meanwhile, the PTAA/4,3BuPACz gave the smallest band energy, whose results are consistent with the order giving the best photovoltaic performance. In conclusion, the improved device performance is not only due to fewer defects in the perovskite thin film and suppressed interfacial nonradiative recombination but also to better energy level arrangement.

Finally, all-perovskite tandem solar cells were fabricated. The structure of the solar cell was shown in **Figure 4a**. IZO was used as the charge recombination layer. Figure S18 (Supporting Information) shows the statistical results of the tandem solar cells deposited on the PTAA modified with 4,3BuPACz. Figure 4b presents the *J*–V curves of the cells prepared on the PTAA modified with 4,3BuPACz. A high PCE of 25.24% was obtained (a J_{SC} of 17.115 mA cm⁻², a V_{OC} of 1.814 V, and an FF of 81.3%) with forward scan and 24.50% with reverse scan (a J_{SC} of 17.161 mA cm², a V_{OC} of 1.800 V and an FF of 79.3%). Figure 4c shows the IPCE curves of the tandem solar cell, which corresponds with the J_{SC} of the *J*–V curve.

3. Conclusions

In conclusion, several new MNL molecules (named 3,3PrPACz, 4,3BuPACz, and 6,3HePACz) were synthesized and were evaluated as the mono-molecular layer of the PTAA. The MNL



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Figure 4. a) Structure of all-perovskite tandem solar cell. b) J–V curves and c) IPCE curves of tandem solar cells.

molecules with four carbons as the spacer group gave the best results. The experimental results show that after the introduction of 4,3BuPACz, the quality of the perovskite thin film (grain size and pinhole density) has significantly improved. The introduction of the MNL reduced the non-radiative recombination of the device and decreased the valence band offset between the perovskite and HTL, promoting charge collection by the HTL. Finally, 4,3BuPACz/PTAA-based PSCs achieved a high PCE of 16.57% with a bandgap of 1.77 eV. The target tandem solar cells gave a PCE of 25.24%. This work reveals that PTAA modified with an MNL can improve the Pb PSCs with a wide bandgap.

4. Experimental Section

Materials: All chemical reagents were used as received without further purification. Xi'an Polymer Light Technology Corp. supplied PTAA. PCBM, FAI, CsI, PbBr₂, and PbI₂ were purchased from Advanced Election Technology CO., Ltd. FABr, MAI, and MABr were obtained from Tokyo Chemical Industry Co., Ltd. Sigma Aldrich provided EDA, CsBr, SnI₂, SnF₂, GuASCN, BCP, and C60. All solvents were purchased from Sigma Aldrich. PEDOT-PSS aqueous solution (Al 4083) was purchased from Heraeus Clevios. [3-[3-(Carbazol-9-yl]carbazol-9-yl]propyl]phosphonic acid, [4-[3-(carbazol-9-yl)carbazol-9-yl]butyl]phosphonic acid, and [6-[3-(carbazol-9-yl)carbazol-9-yl]butyl]phosphonic acid were synthesized as new derivatives according to the description presented in Scheme S1 (Supporting Information).

Experimental Details of the Synthesis: 9H-carbazole (1), 18-crown-6, acetic acid, 1,3-dibromopropane, 1,4-dibromobutane, 1,6-dibromohexane, triethyl phosphite, KOH, KI, K₂CO₃, KIO₃, Cu, CuI, Na₂SO₄, 1,4-dioxane, bromotrimethylsilane, acetone, tetrahydrofuran (THF) and dimethylformamide (DMF) were purchased from Aldrich and used as received.

3-Iodo-9*H*-carbazole (2) was synthesized from commercially available 9*H*-carbazole by Tucker iodination with KI/KIO_3 in acetic acid according to the described procedure.^[46]

9-(3-Bromopropyl)-3-iodo-9*H*-carbazole (3): 3 g (10.24 mmol) of compound **2** was dissolved in acetone (50 mL). 6.2 g (30.71 mmol) of 1,3-dibromopropane and 1.72 g (30.7 mmol) of KOH were added into the solution. The resulting mixture was stirred at 80 °C for 2 h, then cooled and filtered. The solvent was evaporated, and the crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:30) as an eluent. Yield: 2.5 g of white product (84%). MS (APCI+, 20 V): 413.53 ([M+H], 100%). ¹H NMR (400 MHz, CDCl₃, ∂): 8.42 (s, 1H, Ar), 8.06 (d, 1H, J = 7.6 Hz, Ar), 7.74 (d, 1H, J = 8.8 Hz, Ar), 7.56-7.46 (m, 2H, Ar), 7.34–7.24 (m, 2H, Ar), 4.49 (t, 2H, J = 7.2 Hz, NCH₂), 3.38 (t, 2H, J = 7.4 Hz, BrCH₂), 2.51–2.36 (m, 2H, CH₂).

9-(4-Bromobutyl)-3-iodo-9*H*-carbazole (4): 3 g (10.24 mmol) of compound 1 was dissolved in acetone (50 mL). 6.63 g (30.71 mmol) of 1,3-dibromobutane and 1,72 g (30,7.18 mmol) of KOH were added into the solution. The resulting mixture was stirred at 80 °C for 2 h, then cooled and filtered. The solvent was evaporated, and the crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:30) as an eluent. Yield: 2.3 g of white product (80%). MS (APCI+, 20 V): 427.33 ([M+H], 100%). ¹H NMR (400 MHz, CDCl₃, ∂): 8.32 (s, 1H, Ar), 7.95 (d, 1H, J = 7.2 Hz, Ar), 7.62 (d, 1H, J = 8.6 Hz, Ar), 7.45–7.27 (m, 2H, Ar), 7.21-7.07 (m, 2H, Ar), 4.23 (t, 2H, J = 7.6 Hz, NCH₂), 3.29 (t, 2H, J = 7.6 Hz, BrCH₂), 2.02–1.90 (m, 2H, CH₂), 1.86-1.74 (m, 2H, CH₂).

9-(6-Bromohexyl)-3-iodo-9*H*-carbazole (5): 3 g (10.24 mmol) of compound **2** was dissolved in acetone (50 mL). 6.63 g (30.71 mmol) of 1,3-dibromobutane, and 1,72 g (30.18 mmol) of KOH were added into the solution. The resulting mixture was stirred at 80 °C for 2 h, then cooled and filtered. The solvent was evaporated, and the crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:30) as an eluent. Yield: 2.6 g of white product (90%). MS (APCI+, 20 V): 456.13 ([M+H], 100%). ¹H NMR (400 MHz, CDCl₃, ∂): 8.45 (s, 1H, Ar), 8.06 (d, 1H, J = 7.6 Hz, Ar), 7.75 (d, 1H, J = 8.6 Hz, Ar), 7.60–7.45 (m, 1H, Ar), 7.43–7.26 (m, 2H, Ar), 7.15 (d, 1H, J = 7.6 Hz, Ar), 4.19 (t, 2H, J = 6.8 Hz, NCH₂), 3.38 (t, 2H, J = 7.8 Hz, BrCH₂), 1.87–1.74 (m, 4H, 2×CH₂), 1.48-1.30 (m, 4H, 2×CH₂).

Diethyl [3-(3-iodo-9*H*-carbazol-9-yl)-propyl]phosphonate (**6**): 2 g (4.84 mmol) of compound **3** were dissolved in 4.14 mL of triethyl phosphite (24.16 mmol). The resulting mixture was stirred at 165 °C for 48 h. The crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 1:2) as an eluent. Yield: 1.5 g of yellow product (75%). MS (APCI+, 20 V): 486.05 ([M+H], 100%. ¹H NMR (400 MHz, DMSO-d6, ∂): 8.31 (s, 1H, Ar), 7.95 (d, 1H, J = 7.4 Hz, Ar), 7.61 (d, 1H, J = 8.4 Hz, Ar), 7.45–7.28 (m, 2H, Ar), 7.21–7.07 (m, 2H, Ar), 4.21 (t, 2H, J = 7.8 Hz, NCH₂), 4.09–3.89 (m, 4H, 2×OCH₃), 1.94–1.84 (m, 2H, CH₂), 1.62–1.52 (m, 2H, CH₂), 1.28–1.15 (m, 6H, 2×OCH₃).

Diethyl [4-(3-iodo-9/H-carbazol-9-yl)-butyl]phosphonate (7): 2 g (4.69 mmol) of compound 4 were dissolved in 3.77 mL of triethyl phosphite (22 mmol). The resulting mixture was stirred at 165 °C for 48 h. The crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 1:2) as an eluent. Yield: 1.7 g of yellow product (82%). MS (APCI+, 20 V): 472.26 ([M+H], 100%). ¹H NMR (400 MHz, DMSO-d6, δ): 8.41 (s, 1H, Ar), 8.05 (d, 1H, *J* = 7.4 Hz, Ar), 7.76 (d, 1H, *J* = 8.8 Hz, Ar), 7.53–7.45 (m, 2H, Ar), 7.32–7.26 (m, 2H, Ar), 4.47 (t, 2H, *J* = 7.6 Hz, NCH₂), 4.00–3.86 (m, 4H, 2×OCH₃).

Diethyl [6-(3-iodo-9H-carbazol-9-yl)-hexyl]phosphonate (8): 2 g (4.39 mmol) of compound 5 were dissolved in 3.76 mL of triethyl phosphite (21.98 mol). The resulting mixture was stirred at 165 $^{\circ}$ C for 48 h. The crude product was purified by silica gel column

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chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 1:2) as an eluent. Yield: 1.5 g of yellow product (73%). MS (APCI+, 20 V): 513,35 ([M+H], 100%. ¹H NMR (400 MHz, DMSO-d6, δ): 8.31 (s, 1H, Ar), 7.95 (d, 1H, J = 7.4 Hz, Ar), 7.61 (d, 1H, J = 8.4 Hz, Ar), 7.48–7.26 (m, 2H, Ar), 7.22–7.09 (m, 2H, Ar), 4.18 (t, 2H, J = 7.8 Hz, NCH₂), 4.05–3.93 (m, 4H, 2×OCH₃), 1.83–1.73 (m, 2H, CH₂), 1.69–1.58 (m, 2H, CH₂), 1.52–1.41 (m, 2H, CH₂), 1.27–1.21 (m, 6H, 2×OCH₃), 1.15–1.03 (m, 4H, 2×CH₂).

Diethyl [3-[3-(9H-carbazol-9-yl)-9H-carbazol-9-yl]-propyl] phosphonate (9): 0.50 g (1.06 mmol) of compound 6, 0.27 g (1.62 mmol) of 9H-carbazole (1) and 0.05 g (0.20 mmol) of 18-crown-6 were stirred in 10 mL of DMF at reflux under nitrogen. Then potassium carbonate (0.37 g, 2.68 mmol), Cu (0.08 g, 1.25 mmol), and CuI (0.28 g, 1.47 mmol) were added stepwise. The mixture was left to react at reflux for 24 h. After TLC control, the inorganic materials were filtered off and the product was extracted by chloroform. The combined extract was dried over anhydrous Na2SO4, and the solvent was evaporated. The crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 2:1) as an eluent. Yield: 0.25 g of yellow powder (45%). MS (APCI+, 20 V): 511.15 ([M+H], 100%). ¹H NMR (400 MHz, DMSO-d6, δ): 8.32 (s, 1H, Ar), 8.22–8.10 (m, 3H, Ar), 7.62 (d, 1H, / = 7.4 Hz, Ar), 7.57–7.40 (m, 5H, Ar), 7.30–7.06 (m, 5H, Ar), 4.41 (t, 2H, / = 7.8 Hz, NCH₂), 4.04–3.76 (m, 4H, 2×OCH₃), 2.10–1.98 (m, 2H, CH₂), 1.86–1.60 (m, 4H, 2×CH₂), 1.28–1.14 (m, 6H, 2×CH₃).

Diethyl [4-[3-(9H-carbazol-9-yl)-9H-carbazol-9-yl]-butyl] phosphonate (10): 0.50 g (1.03 mmol) of compound 7, 0.26 g (1.56 mmol) of 9H-carbazole (1) and 0.05 g (0.20 mmol) of 18-crown-6 were stirred in 10 mL DMF at reflux under nitrogen. Then potassium carbonate (0.36 g, 2.61 mmol), Cu (0.08 g, 1.25 mmol), and CuI (0.28 g, 1.47 mmol) were added stepwise. The mixture was left to react for 24 h at reflux. After TLC control, the inorganic materials were filtered off and the product was extracted by chloroform. The combined extract was dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 2:1) as an eluent. Yield: 0.4 g of yellow powder (65%). MS (APCI+, 20 V): 525.23 ([M+H], 100%). ¹H NMR (400 MHz, DMSO-d6, δ): 8.42 (s, 1H, Ar), 8.32–8.17 (m, 3H, Ar), 7.82 (d, 1H, J = 7.4 Hz, Ar), 7.77–7.37 (m, 5H, Ar), 7.35–7.15 (m, 5H, Ar), 4.53 (t, 2H, J = 7.6 Hz, NCH₂), 3.98–3.86 (m, 4H, 2×OCH₃), 2.00–1.88 (m, 2H, CH₂), 1.86–1.72 (m, 2H, CH₂), 1.67-1.52 (m, 2H, CH₂), 1.20–1.09 (m, 6H, 2×CH₃).

Diethyl [6-[3-(9H-carbazol-9-yl)-9H-carbazol-9-yl]hexyl] phosphonate (11): 0.50 g (0.97 mmol) of compound 8, 0.24 g (1.44 mmol) of 9H-carbazole (1), and 0.05 g (0.20 mmol) of 18-crown-6 were stirred in 10 mL DMF at reflux under nitrogen. Then potassium carbonate (0.34 g, 2.46 mmol), Cu (0.08 g, 1.25 mmol), and CuI (0.28 g, 1.47 mmol) were added stepwise. The mixture was left to react for 24 h at reflux. After TLC control, the inorganic materials were filtered off and the product was extracted by chloroform. The combined extract was dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography using the mixture of tetrahydrofuran and hexane (vol. ratio 2:1) as an eluent. Yield: 0.3 g of yellow powder (50%). MS (APCI+, 20 V): 553.18 ([M+H], 100%). ¹H NMR (400 MHz, DMSO-d6, δ): 8.14 (s, 1H, Ar), 8.09 (d, 2H, / = 7.6 Hz, Ar), 7.99–7.94 (m, 1H, Ar), 7.52–7.30 (m, 7H, Ar), 7.25–7.09 (m, 4H, Ar), 4.29 (t, 2H, J = 7.6 Hz, NCH₂), 4.06–3.94 (m, 4H, 2×OCH₃), 1.93–1.82 (m, 2H, CH₂), 1.68–1.53 (m, 2H, CH₂), 1.57– 1.45 (m, 2H, CH₂), 1.24–1.19 (m, 6H, 2×CH₃), 1.15–0.97 (m, 4H, 2×CH₂).

[3-[3-(carbazol-9-yl]carbazol-9-yl]propyl]phosphonic acid (3,3PrPACz): 0.5 g (1.10 mmol) of compound **9** was dissolved in 1,4-dioxane (15 mL). Then 2.7 g (17.63 mmol) of bromotrimethylsilane was added to the solution. The resulting mixture was stirred at room temperature for 24 h. The crude product was poured into a mixture of water and methanol. The resulting precipitate was filtered. Yield: 0.2 g of black product (40%). MS (APCI+, 20 V): 455.17 ([M+H], 100%). ¹H NMR (400 MHz, DMSO-d6, δ): 8.47 (s, 1H, Ar), 8.34–8.25 (m, 3H, Ar), 7.97 (d, 1H, J = 7.6 Hz, Ar), 7.82–7.65 (m, 2H, Ar), 7.61–7.44 (m, 3H, Ar), 7.42–7.25 (m, 5H, Ar), 5.06–4.76 (m, 2H, 2×OH), 4.65 (t, 2H, J = 8.2 Hz, NCH₂), 2.17–2.06 (m, 2H, CH₂), 1.77–1.65 (m, 2H, CH₂). ¹³C NMR (400 MHz, DMSO-d6, δ): 141.73, 141.21, 139.61, 139.68, 128.55, 126.92, 126.61, 125.39, 125.34,

123.60, 122.86, 122.31, 121.48, 120.91, 120.09, 119.86, 119.62, 110.06, 110.17, 43.34, 34.86, 30.90.

[4-[3-(Carbazol-9-yl]carbazol-9-yl]butyl]phosphonic acid (4,3BuPACz): 0.5 g (1.05 mmol) of compound **10** was dissolved in 1,4-dioxane (15 mL). Then 2.61 g (17.05 mmol) of bromotrimethylsilane was added into the solution. The resulting mixture was stirred at room temperature for 24 h. The crude product was poured into a mixture of water and methanol. The resulting precipitate was filtered. Yield: 0.3 g of black product (50%). MS (APCI+, 20 V): 469-58 ([M+H], 100%). ¹H NMR (400 MHz, DMSO-d6, δ): 8.42 (s, 1H, Ar), 8.32–8.11 (m, 3H, Ar), 7.91 (d, 1H, *J* = 7.6 Hz, Ar), 7.75–7.59 (m, 2H, Ar), 7.55–7.41 (m, 3H, Ar), 7.34–7.14 (m, 5H, Ar), 5.21–4.80 (m, 2H, 2×OH), 4.52 (t, 2H, *J* = 7.6 Hz, NCH₂), 2.02–1.89 (m, 2H, CH₂), 1.67–1.49 (m, 4H, 2×CH₂). ¹³C NMR (400 MHz, DMSO-d6, δ): 14.74, 141.19, 139.58, 128.44, 126.87, 126.60, 125.27, 123.57, 123.57, 122.28, 121.43, 120.92, 120.09, 119.79, 119.52, 111.09, 110.16, 42.82, 28.54, 27.18, 20.99.

[6-[3-(Carbazol-9-yl]carbazol-9-yl]hexyl]phosphonic acid (6,3HePACz): 0.5 g (1.00 mmol) of compound **11** was dissolved in 1,4-dioxane (15 mL). Then 2.70 g (16.13 mmol) of bromotrimethylsilane was added into the solution. The resulting mixture was stirred at room temperature for 24 h. The crude product was poured into a mixture of water and methanol. The resulting precipitate was filtered. Yield: 0.25 g of black product (45%). MS (APCI+, 20 V): 497,23 ([M+H], 100%). ¹H NMR (400 MHz, DMSOd6, ϑ): 8.41 (s, 1H, Ar), 8.31–8.19 (m, 3H, Ar), 7.87 (d, 1H, J = 7.4 Hz, Ar), 7.73–7.56 (m, 2H, Ar), 7.55–7.39 (m, 3H, Ar), 7.87–7.17 (m, 5H, Ar), 5.23–4.20 (m, 2H, 2×OH), 4.49 (t, 2H, J = 7.6 Hz, NCH₂), 1.89–1.79 (m, 2H, CH₂), 1.53–1.35 (m, 8H, 4×CH₂). ¹³C NMR (400 MHz, DMSOd6, ϑ): 141.73, 141.19, 139.58, 128.42, 126.86, 126.60, 125.28, 123.55, 122.86, 122.27, 121.45, 120.91, 120.09, 119.81, 119.50, 111.01, 110.16, 110.06, 42.96, 30.30, 28.93, 27.31, 26.65, 23.18.

Device Fabrication: ITO glasses were ultrasonically cleaned for 20 min in sequence with detergent water and isopropyl alcohol. Then the ITO was treated for 5 min with plasma. Then the glasses were transformed into the glove box. 1.5 mg PTAA was dissolved in 1 mL toluene and stirring 3 h at room temperature. Then the PTAA was spin-coated on the ITO with the speed of 2000 rpm for the 30 s, followed by annealing at 100 °C for 10 min. 1 mg of 3,3PrPACz, 1 mg of 4,3BuPACz, and 1 mg of 6,3HePACz were dissolved in 1 mL DMF and this solution was spin-coated on the PTAA at a speed of 5000 rpm for the 30 s. Then the substrate was put on the hot stage at a temperature of 100 °C for 5 min. In order to form the monolayer, the surface was washed with 50 µL DMF by using the spinning coated with a speed of 5000 rpm for the 30s. The perovskite precursor solution was prepared by dissolving FAI (99.05 mg), CsI (37.41 mg), FABr (47.98 mg), PbI₂ (331.93 mg), PbBr₂ (176.16 mg), and CsBr (20.43 mg) in 1 mL of DMSO/DMF (1/4, v/v) mixture. The perovskite film was deposited using the two-step spin-coating method at 2000 rpm for 10 seconds and 6000 rpm for the 40s, with 150 μ L of CB antisolvent dripped over perovskite films for 30 s before the program was terminated, and the film was subsequently annealed at 100 °C for 10 min. After cooling to room temperature, the substrates were transferred to the evaporation system. Finally, C60 (20 nm), BCP (7 nm), and Ag (100 nm) were sequentially deposited on top of the perovskite by thermal evaporation under a vacuum of 10^{-5} Pa through using a shadow mask.

The Tandem perovskite solar cell was prepared in the following way. After depositing the C60 on the wide bandgap perovskite film, the substrates were then transferred to the ALD system to deposit 20 nm SnO₂ at 100 °C. Tetrakis(dimethylamino) tin(iv) and deionized water were employed as the precursor. After ALD-SnO₂ deposition, the substrates were transferred to the magnetron sputtering system to deposit 100 nm IZO on the ALD-SnO2. The PEDOT-PSS layer was spincast on IZO and annealed at 120 °C for 20 min. Then the narrow bandgap perovskite was prepared on the PEDOT:PSS. The previous preparation technology was adopted: Cs_{0.025}FA_{0.475}MA_{0.5}Sn_{0.5}Pb_{0.5}I_{2.925}Br_{0.075} was obtained by mixing Cs_{0.05}FA_{0.95}SnI₃ (1.4 м) (228.72 mg of FAI, 521.52 mg of SnI_2 , and CsI of 18.2 mg in 1 mL of DMF: DMSO (4:1, v/v) solution), MAPbI₃ (1.4 м) (222.56 mg of MAI, 645.41 mg of PbI₂, and 13.23 mg of GuASCN in 1 mL of DMF: DMSO (9:1, v/v) solution)



and MAPbBr₃ (1.4 m) (156.76 mg of MABr and 513.82 mg of PbBr₂ in 1 mL of DMF: DMSO (9:1, v/v) solution) in a certain volume ratio.^[16] The perovskite precursor was then dropped onto the PEDOT:PSS and spin-coated at 1000 rpm for 10 s, followed by 5000 rpm for 50 s. 750 μ L toluene was dropped at 20 s from the beginning, followed by heating at 100 °C for 5 min. The perovskite layer was then modified by EDA (0.1 × 10⁻³ M in toluene) molecules by employing a spin coater. Next, PCBM (7.5 mg mL⁻¹ in CB) was coated at 5000 rpm for 50 s, followed by heating at 75 °C for 5 min. Finally, C60 (20 nm), BCP (7 nm), and Ag (100 nm) were deposited under high vacuum conditions by thermal evaporation to give the tandem perovskite solar cell.

Characterization: XRD patterns were obtained by a Rigaku Smartlab X-ray diffractometer. The solar cell performances were measured using a Keithley 4200 source meter and a solar simulator under 100mW cm⁻² AM 1.5G in the air condition (Bunkouki CEP-2000SRR). The effective active area of the device is defined to be 0.1 cm^2 by using a black metal mask. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a monochromatic Xenon lamp (Bunkouki CEP-2000SRR). Mott-Schottky (MS). Electrochemical impedance spectroscopy (EIS), Transient photovoltaic voltage (TPV), and Transient photovoltaic current (TPC) were carried out via PAIOS software with LED light. HOMO and valence band energy levels were obtained from a photoelectron yield measurement system (PYS, BUNKOKEIKI, KV-205 HK) under high vacuum ($\approx 10^{-4}$ Pa) conditions. Scanning electron microscopy (SEM, FE-SEM, JEOL JSM-6340) was employed to observe the surface morphology of the perovskite thin film. The photoluminescence (PL) and time-resolved photoluminescence (TRPL) were measured with Jasco FP6500 Spectrofluorometer. XPS spectra were measured by Shimadzu Kratos Axis-Nova spectrometer.

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 from the corresponding author upon reasonable request.

Keywords

all perovskite tandem solar cells, inverse structures, monomolecular layers, nonradiative recombination, wide bandgap perovskite solar cells

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- NREL https://www.nrel.gov/pv/cell-efficiency.html (accessed: April 2023).
- [2] H. Bi, X. Zuo, B. Liu, D. He, L.e Bai, W. Wang, X. Li, Z. Xiao, K. Sun, Q. Song, Z. Zang, J. Chen, J. Mater. Chem. A 2021, 9, 3940.
- [3] H. Bi, Y. Guo, M. Guo, C. Ding, S. Hayase, T. Mou, Q. Shen, G. Han, W. Hou, *Chem. Eng. J.* **2022**, 439, 135671.
- [4] R. Zhao, L. Xie, R. Zhuang, T. Wu, R. Zhao, L. Wang, L. Sun, Y. Hua, ACS Energy Lett. 2021, 6, 4209.
- [5] Z. Guo, A. K. Jena, G. M. Kim, T. Miyasaka, Energy Environ. Sci. 2022, 15, 3171.
- [6] S. Ma, G. Yuan, Y. Zhang, N. Yang, Y. Li, Q.i Chen, Energy Environ. Sci. 2022, 15, 13.
- [7] F. Hao, C. C. Stoumpos, R. P. H. Chang, M. G. Kanatzidis, J. Am. Chem. Soc. 2014, 136, 8094.
- [8] K.e Xiao, R. Lin, Q. Han, Y.i Hou, Z. Qin, H. T. Nguyen, J. Wen, M. Wei, V. Yeddu, M. I. Saidaminov, Y. Gao, X. Luo, Y. Wang, H. Gao, C. Zhang, J. Xu, J. Zhu, E. H. Sargent, H. Tan, *Nat. Energy* 2020, 5, 870.
- [9] J. Wen, H. Tan, Sci. China Mater. 2022, 65, 3353.
- [10] Y. Gao, R. Lin, K. Xiao, X. Luo, J. Wen, X. Yue, H. Ta, *Joule* 2022, 6, 1944.
- [11] M. A. Green, E. D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, K. Bothe, D. Hinken, M. Rauer, X. Hao, Prog. Photovoltaics 2022, 30, 687.
- [12] S. Y. Kim, S. J. Cho, S. E. Byeon, X. He, H. J. Yoon, Adv. Energy Mater. 2020, 10, 2002606.
- [13] F. Ali, C. Roldán-Carmona, M. Sohail, M. K. Nazeeruddin, Adv. Energy Mater. 2020, 10, 2002989.
- [14] K. Choi, H. Choi, J. Min, T. Kim, D. Kim, S. Y. Son, G.-W. Kim, J. Choi, T. Park, Sol. RRL 2020, 4, 1900251.
- [15] S. Y. Kim, H. Kang, K. Chang, H. J. Yoon, ACS Appl. Mater. Interfaces 2021, 13, 31236.
- [16] G. Kapil, T. Bessho, Y. Sanehira, S. R. Sahamir, M. Chen, A. K. Baranwal, D. Liu, Y. Sono, D. Hirotani, D. Nomura, K. Nishimura, M. A. Kamarudin, Q. Shen, H. Segawa, S. Hayase, ACS Energy Lett. 2022, 7, 966.
- [17] A. Ullah, K. H. Park, H. D. Nguyen, Y. Siddique, S. F. A. Shah, H. Tran, S. Park, S. I. Lee, K.-K. Lee, C.-H. Han, K. Kim, S. Ahn, I. Jeong, Y. S. Park, S. Hong, *Adv. Energy Mater.* **2022**, *12*, 2103175.
- [18] W. Jiang, F. Li, M. Li, F. Qi, F. R. Lin, A. K. Jen, Angew. Chem., Int. Ed. 2022, 51, 202213560.
- [19] X. Deng, F. Qi, F. Li, S. Wu, F. R. Lin, Z. Zhang, Z. Guan, Z. Yang, C.-S. Lee, A. K.-Y. Jen, Angew. Chem., Int. Ed. 2022, 61, 202203088.
- [20] Y. Wang, L. Duan, M. Zhang, Z. Hameiri, X.u Liu, Y. Bai, X. Hao, Sol. RRL 2022, 6, 2200234.
- [21] Y. Li, J.-F. Liao, H. Pan, G. Xing, Sol. RRL 2022, 6, 2200647.
- [22] Y. Li, B. Wang, T. Liu, Q. Zeng, D. Cao, H. Pan, G. Xing, ACS Appl. Mater. Interfaces 2022, 14, 3284.
- [23] J. Xu, J. Dai, H. Dong, P. Li, J. Chen, X. Zhu, Z. Wang, B.o Jiao, X. Hou, J. Li, Z. Wu, Org. Electron. 2022, 100, 106378.
- [24] C.-H. Kuan, G.-S. Luo, S. Narra, S. Maity, H. Hiramatsu, Y.-W. Tsai, J.-M. Lin, C.-H. Hou, J.-J. Shyue, E. Wei-Guang Diau, *Chem. Eng. J.* 2022, 450, 138037.
- [25] W. Dong, S. Xiong, J. Yang, W. Qiao, Q.i Zeng, X. Wang, Y. Yao, Q. Bao, Org. Electron. 2021, 89, 106052.
- [26] L. Xu, Y. Liu, W. Qiu, Y. Li, H. Wang, M. Li, L. Xian, C. Zheng, Y. Chen, R. Chen, J. Power Sources 2021, 506, 230120.
- [27] M. Dailey, Y. Li, A. D. Printz, ACS Omega 2021, 6, 30214.
- [28] Z. Sun, Z. Liu, J. Zhang, C. Zhou, Z. Chen, L. Chen, S. Zhang, X. Jia, J. Zhang, Y.i Zhou, B.o Song, N. Yuan, J. Ding, ACS Appl. Energy Mater. 2022, 5, 7988.
- [29] B. Tu, Y. Wang, W. Chen, B. Liu, X. Feng, Y. Zhu, K. Yang, Z. Zhang, Y. Shi, X. Guo, H.-F. Li, Z. Tang, A. B. Djurisic, Z. He, ACS Appl. Mater. Interfaces 2019, 11, 48556.
- [30] X. Deng, F. Qi, F. Li, S. Wu, F. R. Lin, Z. Zhang, Z. Guan, Z. Yang, C.-S. Lee, A. K.-Y. Jen, Angew. Chem., Int. Ed. 2022, 61, e202203088.

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- [31] I. Levine, A. Al-Ashouri, A. Musiienko, H. Hempel, A. Magomedov, A. Drevilkauskaite, V. Getautis, D. Menzel, K. Hinrichs, T. Unold, S. Albrecht, T. Dittrich, *Joule* **2021**, *5*, 2915.
- [32] D. Song, S. Narra, M.-Y. Li, J.-S. Lin, E. W.-G. Diau, ACS Energy Lett. 2021, 6, 4179.
- [33] J. A. Hong, M. Jeong, S. Park, A.-Y. Lee, H. S. Kim, S. Jeong, D. W. Kim, S. Cho, C. Yang, M. H. Song, *Adv. Sci.* **2023**, *10*, 2205127.
- [34] S. Zhang, R. Wu, C. Mu, Y. Wang, L. Han, Y. Wu, W.-H. Zhu, ACS Mater. Lett. 2022, 4, 1976.
- [35] J. Liang, C. Chen, X. Hu, Z. Chen, X. Zheng, J. Li, H. Wang, F. Ye, M. Xiao, Z. Lu, Y. Xu, S. Zhang, R. Yu, C. Tao, G. Fang, ACS Appl. Mater. Interfaces 2020, 12, 48458.
- [36] N. Yang, C. Zhu, Y. Chen, H. Zai, C. Wang, X.i Wang, H. Wang, S. Ma, Z. Gao, X. Wang, J. Hong, Y. Bai, H. Zhou, B.-B. Cui, Q.i Chen, *Energy Environ. Sci.* **2020**, *13*, 4344.
- [37] Q. Zhou, J. Duan, X. Yang, Y. Duan, Q. Tang, Angew. Chem., Int. Ed. 2020, 59, 21997.

- [38] C.-C. Zhang, S. Yuan, Y.-H. Lou, Q.-W. Liu, M. Li, H. Okada, Z.-K. Wang, Adv. Mater. 2020, 32, 2001479.
- [39] H. Bi, B. Liu, D. He, L.e Bai, W. Wang, Z. Zang, J. Chen, Chem. Eng. J. 2021, 418, 129375.
- [40] M. Kim, G.-H. Kim, T. K. Lee, I. W. Choi, H. W. Choi, Y. Jo, Y. J. Yoon, J. W. Kim, J. Lee, D. Huh, H. Lee, S. K. Kwak, J. Y. Kim, D. S. Kim, *Joule* **2019**, *3*, 2179.
- [41] J. Chen, N.-G. Park, Adv. Mater. 2019, 31, 1803019.
- [42] C. Ding, D. Wang, D. Liu, H. Li, Y. Li, S. Hayase, T. Sogabe, T. Masuda, Y. Zhou, Y. Yao, Z. Zou, R. Wang, Q. Shen, *Adv. Energy Mater.* **2022**, *12*, 2201676.
- [43] S. Bi, H. Wang, J. Zhou, S. You, Y. Zhang, X. Shi, Z. Tang, H. Zhou, J. Mater. Chem. A 2019, 7, 6840.
- [44] F. C. Simeone, H. J. Yoon, M. M. Thuo, J. R. Barber, B. Smith, G. M. Whitesides, J. Am. Chem. Soc. 2013, 135, 18131.
- [45] N. Cho, S. Kang, H. Lee, H. Kang, G. D. Kong, H. J. Yoon, Nano Lett. 2021, 21, 360.
- [46] S. H. Tucker, J. Chem. Soc. 1926, 129, 546.