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Concise Report

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A Cost-Effective D-A-D Type Hole-Transport Material Enabling 20% Efficiency Inverted Perovskite Solar Cells[†]

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Energy conversion | Donor-acceptor systems | Interfaces | Hole-transport materials | Inverted perovskite solar cells

Main observation and conclusion

High-performance, cost-effective hole-transport materials (HTMs) are greatly desired for the commercialization of perovskite solar cells (PVSCs). Herein, two new HTMs, TPA-FO and TPA-PDO, are devised and synthesized, which have a donor-acceptor-donor (D-A-D) type molecule design featuring carbonyl group-functionalized arenes as the acceptor (A) units. The carbonyl group at the central core of HTMs can not only tune frontier molecular orbital (FMO) energy levels and surface wettability, but also can enable efficient surface passivation effects, resulting in reduced recombination loss. When employed as HTMs in inverted PVSCs without using dopant, TPA-FO with one carbonyl group yields a high power conversion efficiency (PCE) of 20.24%, which is among the highest values reported in the inverted PVSCs with dopant-free HTMs. More importantly, the facile one-step synthetic process enables a low cost of 30 USD g^{-1} for TPA-FO, much cheaper than the most studied HTMs used for high-efficiency dopant-free PVSCs. These results demonstrate the potential of D-A-D type molecules with carbonyl group-functionalized arene core in developing the low-cost dopant-free HTMs toward highly efficient PVSCs.

Comprehensive Graphic Content



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[†] Dedicated to Department of Chemistry, SUSTech, on the Occasion of Her 10th Anniversary.

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Supporting Information

Background and Originality Content

Organic-inorganic metal halide perovskite solar cells (PVSCs) are a promising candidate for next-generation photovoltaic technology.^[1] Benefiting from the continuous effort on improving perovskite composition and film quality,^[2] interfacial optimiza-tion,^[3] and device structures,^[4] the power conversion efficiencies (PCEs) of PVSCs have been boosted up to over 25% recently.^[1b] PVSCs can be divided into conventional (n-i-p) and inverted (p-i-p)*n*) structures. Typically, the n-i-p structures are fabricated with the n-type TiO_2 or SnO_2 as the electron-transporting materials (ETMs) and 2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9spiro-bifluorene (Spiro-OMeTAD) as hole-transport materials (HTMs).^[5] Although most of the high efficiency was achieved by the n-i-p structures, such devices usually suffer from severe hysteresis.^[6] Additionally, Li⁺ dopants for improving the conductivity of Spiro-OMeTAD bring adverse effects on device ambient stability.^[7] By contrast, the p-i-n structures have several distinctive advantages, including reduced hysteresis and low-temperature processing.^[6] The p-i-n structures also offer opportunities for integrating PVSCs on silicon solar cells.^[4a] However, the device performance of inverted PVSCs lags behind those of conventional PVSCs.^[8] In terms of inverted PVSCs, HTMs play an essential role in charge collection or blocking at the interface and can also affect the crystal growth of perovskite.^[9] Therefore, considerable efforts have been devoted to developing dopant-free HTMs for improving the efficiency of inverted PVSCs.



Figure 1 The recent development of D-A-D dopant-free small molecular HTMs utilized in *n-i-p* and *p-i-n* perovskite solar cells.

Compared to inorganic HTMs, organic HTMs have low-temperature solution processability and tunable optoelectrical and morphological properties to match with perovskite.^[10] For example, polymer-based HTMs, poly(3,4-ethylenedioxythiophene): poly-(styrenesulfonate) (PEDOT:PSS) and poly(triarylamine) (PTAA), are the most widely used HTMs for inverted PVSCs.^[11] However, the acidity and hygroscopicity of PEDOT:PSS cause deterioration to device stability. PTAA achieved the highest efficiencies in the state-of-the-art inverted PVSCs, $^{[9,12]}$ but it is synthesized at a high cost of 1980 USD $\rm g^{-1}$ and often needs p-type doping or surface treatments. $^{[6,13\cdot14]}$

Small molecular HTMs with well-defined molecular structure and good reproductivity show great potential for achieving efficient inverted PVSCs.^[10d,15] Among various design strategies, donor-acceptor-donor (D-A-D) molecular geometry has recently received more attention and been investigated in dopant-free small molecule HTMs (Figure 1).^[16] The D-A-D molecule structure can be ready to modify the frontier molecular orbital energy levels of HTMs to form a suitable energy alignment with perovskite by selecting appropriate D and A units, especially in decreasing the highest occupied molecular orbital (HOMO) energy level. [17] Moreover, the D-A-D molecular backbone is beneficial to construct dopant-free HTMs due to the strong intramolecular charge transfer (ICT) and high dipole moment, which could induce self-doping and built-in potential to promote charge extraction without adding dopants.^[16a,18] On the other hand, it is well desirable to decrease the synthetic cost of the dopant-free HTMs. However, previous D-A-D molecular HTMs in inverted PVSCs were often synthesized via multiple steps, preventing their broad applications.^[16d-16f,19]

Scheme 1 The one-step synthetic routes to TPA-FO and TPA-PDO



In this work, two cost-effective D-A-D type dopant-free molecular HTMs, TPA-FO and TPA-PDO, were designed and synthesized via facile one-step reaction with a decent yield of around 75%. Both HTMs feature carbonyl group-functionalized arene as A unit and 4-(bis(4-methoxyphenyl)amino)phenyl (TPA)^[20] as terminal D unit. Two HTMs show distinct photoelectrical and surface properties due to the different number of carbonyl groups. Moreover, the carbonyl groups can increase the dipole moment and wettability,^[21] and passivate the electron-poor defects of the perovskite as Lewis base groups, resulting in reduced recombination loss.^[22] When used as the dopant-free HTMs in inverted PVSCs, TPA-FO-based PVSCs exhibit a champion PCE of 20.24% with an open-circuit voltage (V_{oc}) of 1.09 V, a short-circuit current density (J_{sc}) of 22.76 mA·cm⁻², and a fill factor (FF) of 81.9%. The device based on TPA-PDO shows an inferior PCE of 17.02% with a $V_{\rm oc}$ of 1.03 V, a $J_{\rm sc}$ of 20.44 mA·cm⁻², and an FF of 80.9%. It is worth mentioning that the synthetic cost of TPA-FO and TPO-PDO can be reduced to 30 and 35 USD g^{-1} . These results demonstrate the potential of our proposed D-A-D molecular design principle with carbonyl group-functionalized arene as A unit for low-cost and efficient dopant-free HTMs.

Results and Discussion

TPA-FO and TPA-PDO in Scheme 1 were synthesized by a one-step Suzuki coupling reaction, and the corresponding route is presented in Scheme S1,^[23] and the synthetic cost was calculated in Table S1. TPA-FO and TPA-PDO consist of TPA as D units, and carbonyl group-functionalized arenes, fluorenone and phenan-threnedione, as the rigid planar A units, respectively. The ultraviolet-visible (UV-vis) absorption spectra of TPA-FO and TPA-PDO in both chlorobenzene solution and films are presented in Figure 2a.

In the solution, both exhibit two characteristic absorption peaks for TPA-FO (383 and 492 nm) and TPA-PDO (387 and 581 nm). The absorption in the visible light can be attributed to the ICT from the HOMO on the TPA donor unit to the lowest unoccupied molecular orbitals (LUMO) on the acceptor unit, while the absorption in the UV region can be ascribed to π – π * transition.^[17b,24] The absorption peak of TPA-PDO is red-shifted compared to TPA-FO due to the stronger ICT effect of more electron-deficient phenanthrenedione core. Compared to their absorption in solution, both TPA-FO and TPA-PDO films show bathochromic shifts of the absorption onsets, with the optical band gap (E_g) of 2.06 and 1.65 eV, respectively. Such phenomena denote increased intermolecular interactions in the solid state.^[17b]



Figure 2 (a) UV-Vis absorption spectra of TPA-FO and TPA-PDO in chlorobenzene solution and thin films. (b) Energy levels of TPA-FO and TPA-PDO derived from the CV curves.

Besides, the optical transmission of HTMs deposited on ITO was also measured because HTMs are the front layers before the active layer and sufficient transmittance of HTM is the prerequisite for high J_{sc} of the inverted PVSCs. The results in Figure S5 manifest that the transmittance of both TPA-FO and TPA-PDO in the visible range is reduced only slightly compared with the pristine ITO substrate due to the absorption of TPA-FO and TPA-PDO, while TPA-FO is lightly more transparent than TPA-PDO.

 Table 1
 Optical and electrochemical properties of TPA-FO and TPA-PDO

 HTMs

Name	$\lambda_{\text{onset,film}}^a/\text{nm}$	$E_{g}^{opt b}/eV$	HOMO ^c /eV	LUMO ^d /eV	$\mu_{\rm h}/({\rm cm}^2 \cdot {\rm V}^{-1} \cdot {\rm s}^{-1})$
TPA-FO	602	2.06	-5.33	-3.27	4.19×10^{-5}
TPA-PDO	751	1.65	-5.37	-3.72	9.34×10^{-6}
^a Films we	ere snin-coate	d using 10) mg·ml ⁻¹ so	lution with	a speed of 2000

r/min. ^b Estimated from the film absorption edge using the equation: E_g^{opt} = 1243/ λ_{onset} (eV). ^c E_{HOMO} = -5.1–(E_{OX} – $E_{1/2}$ (Fc/Fc⁺)) (eV). ^d E_{LUMO} = E_{HOMO} + E_g^{opt} (eV).

It is well recognized that the HTM/perovskite interfacial band alignment is decisive in the interfacial hole transport and determining the final PVSC performances. As shown in Table 1, the HOMO energy levels of TPA-FO and TPA-PDO were derived from the onset oxidation potentials by cyclic voltammetry (CV) measurements (Figure S6) and found to be -5.33 and -5.37 eV, respectively. The LUMO energy levels were determined to be -3.27 and -3.72 eV for TPA-FO and TPA-PDO by $E_{LUMO} = E_{HOMO} + E_{g}$. Hence, increasing from one carbonyl group in TPA-FO to two carbonyl groups in TPA-PDO downshifts both the HOMO and LUMO energy levels simultaneously but shows a more significant impact on LUMO level. Ultraviolet photoelectron spectroscopy measurement (Figure S7) also demonstrated a similar trend. Based on the space-charge-limited current (SCLC) measurement method, the hole mobility of neat TPA-FO film is determined to be 4.19×10^{-5} $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (Table 1 and Figure S8), which is higher than that (9.34 $\times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) of neat TPA-PDO film and comparable to that of widely used PTAA ($\sim 10^{-5} - 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).^[10d] The relatively low charge mobility of TPA-PDO can be explained as the sacrifice of the excessive dipole moment of TPA-PDO, according to the

Bässler's model.^[25] Thus, neat TPA-FO film shows sufficient hole mobility, implying it as a potential dopant-free HTM in inverted PVSCs.



Figure 3 AFM height images of the HTM films for (a) TPA-FO and (b) TPA-PDO; Water contact angle images for the (c) TPA-FO and (d) TPA-PDO HTMs on ITO substrates; Top-view SEM images of the prepared perovskite films on (e) TPA-FO and (f) TPA-PDO.

The topographic morphology of the HTMs films was investigated via atomic force microscopy (AFM). The AFM image of a TPA-FO film in Figure 3a reveals that TPA-FO film shows a smoother surface than the TPA-PDO one in Figure 3b, with rootmean-square (RMS) roughness: 1.15 nm versus 2.4 nm. Furthermore, the surface wettability of two HTMs was investigated because a moderately hydrophobic surface is supposed to facilitate the growth of larger high-quality perovskite crystals along with impending water penetration for enhancing ambient device stability, while sufficient wettability is the prerequisite for the attachment of the polar perovskite precursor solution on substrates.^[14a] The contact angle measurements (Figures 3c and 3d) demonstrate that TPA-FO has a modest contact angle of 40.3° to water, which is much higher than that of TPA-PDO (16.6°). The decrease in contact angle may originate from more carbonyl groups on TPA-PDO with a higher dipole moment and thus stronger wettability.^[21] Consequently, the perovskite grown on TPA-FO shows larger grain sizes compared to that grown on TPA-PDO, as revealed by the scanning electron microscopy (SEM) images in Figures 3e and 3f. Besides, a higher intensity of X-ray diffraction (XRD) pattern was observed from perovskite films grown on TPA-FO, indicating its better film crystallinity (Figure S9). We have calculated crystal size using Scherrer's equation based on XRD analysis and the corresponding results are listed in Table S2. Average crystalline size of perovskites grown on TPA-FO is determined to be 47.11 nm compared to that (45.49 nm) of TPA-PDO. The higher value for that on TPA-FO may be ascribed to the relatively more hydrophobic surface for TPA-FO film, which also agrees with the larger grain sizes based on SEM results (Figures 3e, f).

XPS measurements were conducted to confirm the possible

interactions between carbonyl groups as Lewis base groups in HTMs and undercoordinated Pb^{2+} in perovskite (Figure 4a). The signals of the Pb²⁺ in pristine perovskite exhibit two main single peaks from the excited electrons of the 4f orbitals accompanied by two small peaks that can be ascribed to the defects of unsaturated Pb²⁺.^[26] As shown in Figures 4a and 4b, after coating a thin layer of TPA-FO or TPA-PDO on the top of perovskite, the small peaks of Pb 4f disappeared, and shifts of Pb 4f peaks and O 1s peaks to lower binding energy can be detected in both TPA-FO/ perovskite and TPA-PDO/perovskite film, which can be ascribed to the interactions between carbonyl groups and Pb²⁺ in both films. Moreover, Fourier transform infrared (FTIR) spectroscopy (Figure 5) was utilized to further verify the interaction between HTM and perovskite.^[3c] The peaks of 1717 and 1678 cm^{-1} are appointed to the symmetric stretching vibrations of C=O bonds (v(C=O)) of the pristine TPA-FO and TPA-PDO, respectively. To distinguish differences between HTM and HTM/perovskite, maximum peak at 1505 cm⁻¹ was normalized as the reference, which is allocated to stretching vibrations of aromatic C=C bonds and is not sensitive to Pb²⁺. The FTIR spectroscopy of both HTM/perovskite blends shows similar weakened vibration strength for v(C=O) by 53%, further validating the interaction between perovskite and the carbonyl groups of HTMs. However, it should be noted that a slightly smaller Pb 4f shift was observed in TPA-PDO/perovskite compared to that of TPA-FO/perovskite films. This phenomenon indicates that although both HTMs can interact with perovskite, TPA-FO exhibits stronger interaction with Pb²⁺ ions than TPA-PDO. The slightly weaker interaction between TPA-PDO and Pb²⁺ ions may be that Pb²⁺ and 9,10-phenanthrenedione can only form a semiquinonate structure, that is to say, only one carbonyl group can interact with Pb2+ ion without chelation effect of two carbonyl groups, which is supported by a previous report.^[27]



Figure 4 XPS spectra of the (a) Pb 4f and in the perovskite films without or with coating TPA-FO or TPA-PDO. The black dash lines indicate the unsaturated Pb^{2*} signals. (b) O 1s signal in TPA-FO and TPA-PDO on the perovskite or the ITO.



Figure 5 FTIR spectra of TPA-FO and TPA-PDO with perovskite together with pristine TPA-FO and TPA-PDO as the control.

To evaluate the device performance of two D-A-D type small molecules as dopant-free HTMs in inverted PVSCs, we fabricated PVSCs with device architecture of ITO/HTM/perovskite/LiF/C₆₀/

BCP/Ag (Figure 6b) and tested the photovoltaic performance. Figure 6a illustrates the *J*-*V* curves of the best-performing PVSCs in both reverse and forward scan directions under the AM 1.5G solar illumination, while the corresponding photovoltaic parameters are summarized in Table 2.



Figure 6 (a) J-V curves of the best performing TPA-FO- and TPA-PDObased PVSCs. (b) Statistical analysis of the device performance (20 devices) with the device architecture of inverted PVSCs insides. (c) EQE spectra and integrated J_{sc} curves. (d) Stabilized power output at the maximum power point.

The TPA-FO-based device shows a high PCE of 20.24% in the reverse scan with a V_{oc} of 1.09 V, a J_{sc} of 22.76 mA·cm⁻² and an FF of 81.85%, and a PCE of 19.85% was achieved in the forward scan. In comparison, a moderate PCE of 17.02% with a V_{oc} of 1.03 V, a J_{sc} of 20.44 mA·cm⁻², and an FF of 80.91% was obtained for the TPA-PDO based devices in the reverse scan, while a PCE of 16.46% in the forward scan. The hysteresis of the devices can be described by the hysteresis index (HI) of the followed equation:^[6c]

$$HI = \frac{PCE_{reverse} - PCE_{forward}}{PCE_{reverse}}$$

The HIs of TPA-FO- and TPA-PDO-based devices were calculated to be 1.9% and 3.2%, respectively.

 Table 2
 Photovoltaic performance of the best inverted PVSCs based on

 TPA-FO and TPA-PDO as the HTMs (with average performance of 20 devices in paranthesis)

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HTM	Scan di- rection	V _{oc} /eV	J _{sc} /(mA·cm ^{−2})	FF/%	PCE/%		
TPA-	Forward	1.09	22.83	79.93	19.85		
FO	Reverse	1.09	22.76	81.85	20.24		
		(1.08±0.004)(22.30±0.31)	(81.91±0.78)	(19.80±0.20)		
TPA-	Forward	1.02	20.34	79.30	16.46		
PDO	Reverse	1.03	20.44	80.91	17.02		
		(1.02±0.015) (20.24±0.28)	(79.35±1.11)	(16.39±0.35)		

Additionally, external quantum efficiency (EQE) spectra (Figure 6c) were recorded, and the TPA-FO-based devices show higher EQE response over the whole absorption spectrum of the perovskite active layer when compared with the TPA-PDO-based devices. The integrated J_{sc} s of TPA-FO (22.10 mA·cm⁻²) and TPA-PDO (20.17 mA·cm⁻²) based devices matched well with the J_{sc} s obtained from *J-V* measurements.

To further verify the reliability of device performance, we measured current densities as a function of time at the maximum power point and the stabilized PCE through 180-second tracing.

As shown in Figure 6d, the stabilized PCE of 19.60% at 0.94 V for the TPA-FO-based device and 16.76% at 0.88 V for the TPA-PDbased devices, respectively, are in agreement with J-V scan results. Besides, the statistical distribution of the photovoltaic parameters of TPA-FO-based devices is narrower than that of TPA-PDO, suggesting better reproducibility of PVSCs on TPA-FO (Figures 6b and S10).



Figure 7 (a) PL and (b) TRPL spectra of the perovskite films deposited on ITO, ITO/TPA-FO, and ITO/TPA-PDO.

 Table 3
 Fitted parameters of photoluminescence decay curves of TPA-FO/perovskite and TPA-PDO/perovskite films with pristine perovskite film on ITO as control

Sample	A ₁ /%	τ ₁ /ns	A ₂ /%	τ₂/ns	τ_{avg}^{a}/ns
ITO/perovskite	9.3	20.0	90.7	100.9	99.3
ITO/TPA-FO/perovskite	25.7	13.12	74.3	78.9	75.3
ITO/TPA-PDO/perovskite	17.4	16.7	80.0	82.0	79.2
a					

^a τ_{avg} refers to the average lifetime, which is calculated as follows: $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

To investigate possible reasons for the enhanced J_{sc} , V_{oc} , and FF of the devices, we conducted photoluminescence (PL) measurement of the perovskite films deposited on TPA-FO and TPA-PDO to study the hole extraction and charge recombination in the perovskite and at HTM/perovskite interfaces. The PL and TRPL results are plotted in Figure 7. All the PL emission peaks are located at 774 nm, and efficient PL quenching occurs in both TPA-FO/perovskite film and TPA-PDO/perovskite film compared to the perovskite film on ITO (Figure 7a). To be specific, TPA-FO HTM can quench PL of perovskite film more efficiently than TPA-PDO HTM, which may result from either charge transfer between perovskite and HTM or more severe recombination at interfacial trap/defects in the perovskite/HTMs interfaces. [14b,28] We obtained time-resolved photoluminescence (TRPL) of the above three perovskite films to further analyze the charge carrier lifetimes. As shown in Figure 7b, TRPL spectra for all three samples are fitted by the bi-exponential decay model, and the corresponding fitting parameters are summarized in Table 3. The fast lifetime (τ_1) refers to charge transfer quenching of PL or defectdriven recombination rate, while the slower lifetime (τ_2) comes from the non-radiative charge recombination quenching of PL.^[29] TPA-FO/perovskite exhibits the shortest τ_1 of 13.1 ns compared to those τ_1 of 16.7 ns and 20.0 ns for TPA-PDO/perovskite and ITO/perovskite, respectively. In addition, the portion of τ_1 moderately increases from 17.4% in TPA-PDO/perovskite to 25.7% in TPA-FO/perovskite. Besides, the averaged PL lifetime of the ITO/perovskite was calculated to be 99.3 ns. The average lifetimes for the perovskite films spun on TPA-PDO decreased to 79.2 ns, while the further reduced average lifetime is 75.3 ns for the perovskite on TPA-FO. TRPL results suggest that charge recombination of perovskite on both D-A-D HTMs are suppressed, and hole transfer is more efficient at the interface between perovskite and TPA-FO.

The long-term stability of PVSCs is essential for practical



Figure 8 Devices ambient stability measurement for the unencapsulated PSVCs based on TPA-FO and TPA-PDO HTMs with a relative humidity of (40 \pm 5)%, 25 °C.

application. We evaluated the device stability of TPA-FO- and TPA-PDO-based PVSCs in the ambient environment (Figure 8) and inert N₂ atmosphere (Figure S13). Although both unencapsulated devices degraded in a high-humidity environment due to the airand water-sensitive nature of perovskite, it is clear that TPA-FO-based devices degraded much slower than TPA-DPO based devices. As shown in Figure S12, the V_{oc} of both remained stable over the duration time, but the FF of both declined similarly from ~80% to 55%. Different degrading behaviors occurred in J_{sc} ; 88% of original J_{sc} was kept for TPA-FO based device in comparison to only 55% left for that of TPA-PDO. TPA-FO based PVSCs can maintain over 55% of the initial PCE after storage for 100 h, while only 34% for that of TPA-DPO based devices (relative humidity 45%-55%, 25 °C), which can be attributed to the more hydrophobic surface and thus better film quality mentioned above, for protecting films from water permeation. Also, better intrinsic stability of TPA-FO based devices is achieved with a PCE above 19% after the storage of 70 d, while relatively low stability of TPA-PDO based devices is observed with the decline of PCE to only 80% of its initial value (Figure S13).

Conclusions

In summary, we reported two new dopant-free D-A-D type small molecular HTMs with carbonyl group-functionalized arenes as the acceptor units and TPA groups as the donor co-unit, which can be synthesized via a facile one-step Suzuki coupling reaction, showing distinct photophysical and electrochemical properties depending on the number of carbonyl groups. Benefiting from suitable FMO energy level alignment, moderate wettability, passivation effect, and good crystallinity of perovskite films on HTM substrates, the device based on one-carbonyl-group-functionalized TPA-FO yielded an optimal PCE of 20.24% with a negligible hysteresis, which is among the highest values reported for inverted PVSCs based on dopant-free HTMs. Our results demonstrate that the molecule design of D-A-D type HTMs with carbonyl group-functionalized arene cores can pave the way to develop the cost-effective dopant-free HTMs toward highly efficient PVSCs.

Experimental

Materials

Anhydrous *N*,*N*-dimethylformamide (DMF, 99.8%), anhydrous dimethyl sulfoxide (DMSO, 99.8%), anhydrous ethanol (99.8%), anhydrous chlorobenzene (CB, 99.8%), and all other solvents were purchased from Sigma-Aldrich. Lead (II) iodide (PbI₂) and lead (II) chloride (PbCI₂), methylammonium iodide (MAI), formamidinium iodide (FAI), and C₆₀ were purchased from *p*-OLED. BCP (99%) was obtained from TCI. All the materials were used as received. The

synthesis details are shown in Supporting Information.

Characterization and measurements

The ¹H NMR and ¹³C NMR spectra were tested on the Bruker Ascend 400 MHz spectrometer. High-resolution mass spectra were measured by ThermoScientificTM Q-Exactive. UV-Vis optical absorption spectra were tested on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Atomic force microscopy (AFM) measurements were tested using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone). Cyclic voltammetry measurements were conducted under an argon atmosphere using the CHI760E voltametric workstation with an argon-saturated supporting electrolyte solution of 0.1 mol/L *tetra-n*-butyl ammonium hexafluorophosphate (Bu₄NPF₆) in CH₃CN, using a platinum working electrode, a platinum wire counter electrode, and a silver wire reference electrode. And the ferrocene/ferrocenium redox couple (Fc/Fc⁺) was used as the external standard for all the measurements with a scanning rate of 50 mV·s⁻¹.

Device fabrication

PVSCs were fabricated with an architecture of ITO/HTMs/ perovskite/LiF/C₆₀/BCP/Ag. ITO glass was cleaned by sequentially washing with detergent, deionized water, acetone, and isopropanol. The substrates were dried by the dry air and treated by UV ozone for 15 min. (FA_{0.17}MA_{0.94}PbI_{3.11})_{0.95}(PbCl₂)_{0.05} precursor solution was prepared by mixing (1.17 mol/L) PbI₂, (0.13 mol/L) PbCI₂, (0.2 mol/L) FAI and (1.1 mol/L) MAI in DMF/DMSO (V/V = 9/1). The solution was stirred for 2 h at 60 °C and then cooled down to room temperature. TPA-FO or TPA-PDO HTMs were prepared by dropping the CB or toluene solution (2 $mg \cdot mL^{-1}$ for the optimized devices) on the substrates and then spin-coated at a rate of 4500 r/min for 30 s, followed by thermal annealing at 120 °C for 15 min. Before the perovskite spin-coating process, the precursor solution was filtered by a 0.45-µm Teflon-filter. Perovskite films formed by spin coating the precursor solution with a two-step spin-coating program (500 r/min for 3 s, 5000 r/min for 27 s). In the last 20 s of the procedure, 125 µL antisolvent (CB) was dropped on the perovskite films quickly and annealed at 60 °C for 1 min plus 100 °C for 10 min. A thin layer of LiF (1 nm) and 30 nm of a layer of C_{60} was deposited on the perovskite active layer by thermal evaporation at a high vacuum ($\sim 3 \times 10^{-5}$ Pa). Then a thin layer of BCP (0.6 mg/mL in ethanol) was spin-coated as cathode buffer layers at a rate of 2500 r/min. Finally, ~100 nm Ag back electrode with an area of 0.037 cm^2 was deposited by thermal evaporation at a high vacuum (~ 3×10^{-5} Pa).

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202100022.

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