

Tunable Molecular Packing of Dopant-Free Hole-Transport Polymers for Perovskite Solar Cells

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Cite This: *ACS Energy Lett.* 2023, 8, 2878–2885



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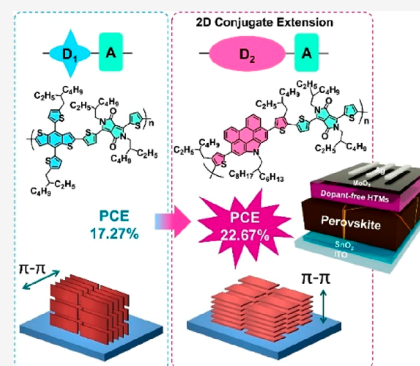


Article Recommendations



Supporting Information

ABSTRACT: Optimizing the molecular packing and orientation of dopant-free hole-transport materials (HTMs) to promote their charge transport is a challenging but effective strategy for achieving high-performance perovskite solar cells (PSCs). Here, we successfully demonstrated tunable molecular packing and orientation of polymers by regulating the donor building blocks by shifting the conjugated side chain to the main chain and using a large core unit. The conjugated polymer we developed, namely PC-DPP, with a thiophene-substituted phenanthrocarbazole (PC-T) as a donor unit and diketopyrrolopyrrole (DPP) as an acceptor unit, shows a preferred face-on orientation. By contrast, the control PBDT-DPP polymer shows a preferred edge-on orientation. As a result, the PC-DPP film shows enlarged hole mobility and strengthened interfacial contact with the perovskite surface. Consequently, in contrast to the PBDT-DPP HTM, the device using dopant-free PC-DPP dramatically improved the efficiency from 17.27% to 22.67%. This work paves a new path for developing dopant-free HTMs.



Perovskite solar cells (PSCs) have emerged as a promising technology for the photovoltaic industry.^{1–8} The hole-transport materials (HTMs) play a crucial role in efficient hole extraction/transport and in keeping water-sensitive perovskite crystals away from the surrounding moisture.^{9–16} Note that the well-known HTM 2,2,7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) has been widely employed to pursue benchmarking efficiency of regular PSCs.^{17–19} Despite the outstanding achievements of Spiro-OMeTAD, the intrinsically large resistivity and low hole mobility caused by the steric hindrance of the spiro core generally make chemical doping essential.^{20,21} Nevertheless, the commonly used dopants exhibit inevitable disadvantages, for example, the *tert*-butylpyridine (TBP) dopant is highly volatile and the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dopant is highly deliquescent.^{22,23} Moreover, lithium ions in LiTFSI dopants can migrate to the perovskite layer, inevitably causing reduced stability of perovskite devices.²⁴ Furthermore, the unfavorable morphology deterioration of HTM layers may also occur due to the migration and relocation of noncovalently bonded dopants.^{21,25,26} All these adverse factors above make the doping strategy inappropriate for industrialization.^{21,27} A large number of research efforts have been made to develop next-

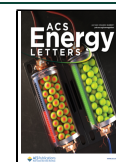
generation dopant-free HTMs, aiming to promote the long-term stability and economic feasibility of PSCs.^{14,23,28–33}

Conjugated polymers are ideal candidates for dopant-free HTMs owing to their advantages, such as tunable energy levels, superb carrier mobility, and excellent hydrophobicity. The polymers with a favorable face-on orientation and compact interaction with the perovskite surface will facilitate an efficient charge transport in HTM layers and promote an interfacial charge transfer between the perovskite and HTMs. Large and planar conjugated blocks containing multiple heteroatoms, such as the benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) unit, have usually been involved in the design of dopant-free HTMs to enhance the interactions between adjacent molecules and the perovskite surface through noncovalent interactions.³⁴ Although more than 22% power conversion efficiencies (PCEs) have been achieved by employing BDT-based PBDB-Cz,³⁵ 2DP-TDB,³⁶ PBQ6,³⁷

Received: April 26, 2023

Accepted: May 31, 2023

Published: June 2, 2023



PM6,³⁸ and PM7,³⁴ the effective routes to tune the molecular packing and orientation of dopant-free polymeric HTMs and further boost PCEs of PSCs are still confronting significant challenges.

The conjugated building blocks with a broad backbone could strengthen the intermolecular packing and promote the face-on orientation of the polymer film.^{39,40} Perylene and its derivatives, featuring a large and rigid 2D plane, have become superior candidates for constructing functional materials.⁴¹ Here, we successfully demonstrated a tunable molecular packing and orientation of polymers by regulating their donor building blocks with different planar sizes. An efficient dopant-free hole-transport polymer (PC-DPP) was established by polymerizing a 2D conjugated thiophene-substituted phenanthrocarbazole (PC-T) unit with a widely used diketopyrrolopyrrole (DPP) unit. Experimental and theoretical computational studies disclosed that the large 2D conjugated PC plane could optimize the self-assembly behavior of the polymer and contribute a dominant face-on orientation successfully, giving rise to enlarged hole mobility and strengthened interfacial contact with perovskite surfaces with respect to those of its control polymer (PBDT-DPP). Importantly, the PC-DPP film exhibits superior charge extraction and transport capability. Time-resolved photoluminescence (TRPL) measurements show that the bulk carrier lifetime of the perovskite film was dramatically decreased from 2095.6 to 211.0 and 2.3 ns, respectively, after capping with PBDT-DPP or PC-DPP films. Consequently, PSCs employing dopant-free PC-DPP as HTMs afforded a champion PCE of 22.67% and dramatically improved stability compared to that of doped Spiro-OMeTAD, ranking it among the best PSCs based on dopant-free HTMs.

The chemical structures of PBDT-DPP and PC-DPP with similar donor–acceptor (D–A) backbones but different donor units are shown in Figure 1a,b. The main difference between these two polymers is their donor building blocks, where the BDT-T unit in the control PBDT-DPP polymer was replaced by a PC-T unit by shifting the thiophene side chain to the main chain and using a conjugate extended PC core unit (Figure 1b). The synthetic routes of the two HTMs are shown in Scheme S1. The number-average molecular weights (M_n) were determined to be 39.8 kDa for PBDT-DPP and 83.3 kDa for PC-DPP by gel permeation chromatography (GPC) (Figures S1 and S2). The corresponding polydispersity indexes (PDI) were 3.50 and 2.62 for PBDT-DPP and PC-DPP, respectively.

Density functional theory (DFT) calculations were performed to investigate the electronic and geometric properties of PBDT-DPP and PC-DPP (Figures S3 and S4). All alkyl chains are substituted with methyl groups to simplify calculations. The dihedral angles in the BDT-T and PC-T units are 54.9 and 50.9°, respectively, which could suppress the excessive aggregation of polymers and tune the self-assembly property of polymers in films, as confirmed by the grazing-incidence wide-angle X-ray scattering (GIWAXS) data discussed below. The electrostatic potential map (ESP) analysis of PBDT-DPP and PC-DPP with one repeating D–A unit was carried out and shown in Figure 1c. The electronegative potential was mainly located at the DPP unit, especially around oxygen, which could facilitate the secondary interaction with undercoordinated and electropositive Pb^{2+} at the perovskite surface,⁴² in agreement with the X-ray photoelectron spectroscopy (XPS) data discussed below.

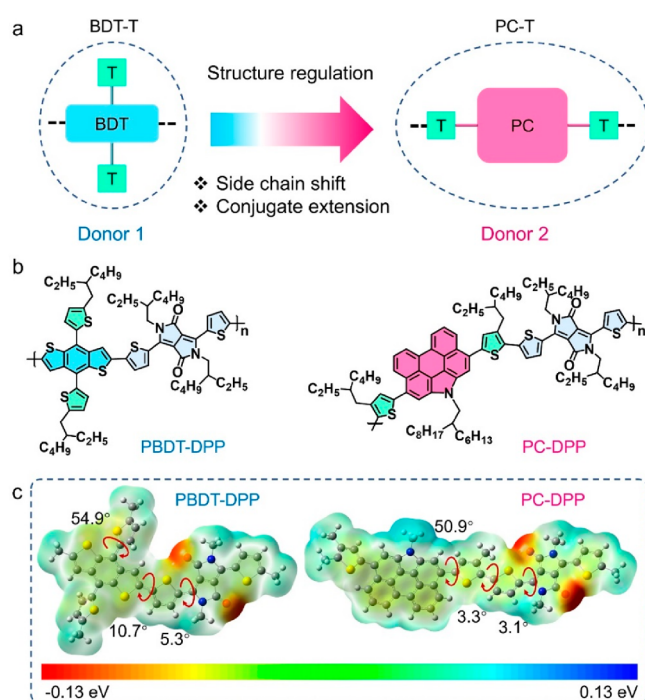


Figure 1. (a) Schematic design strategy of donor building blocks in PBDT-DPP and PC-DPP polymers. (b) Chemical structures of PBDT-DPP and PC-DPP. (c) Molecular geometry and calculated electrostatic potential (ESP) profiles of these two polymers (yellow, sulfur atom; blue, nitrogen atom; red, oxygen atom; gray, carbon atom; white, hydrogen atom).

The optical bandgaps (E_g) for PBDT-DPP and PC-DPP were calculated to be 1.51 and 1.62 eV, respectively (Figure S5). The temperature-dependent absorption spectra in Figure 2a,b show that the PC-DPP solution exhibits a larger blue-shifted absorption band from 0 to 100 °C compared to PBDT-DPP, suggesting its strong aggregation behavior.⁴³ The highest occupied molecular orbital (HOMO) levels of PBDT-DPP and PC-DPP were calculated to be −5.29 and −5.35 eV, respectively, from cyclic voltammetry (CV) measurements (Figure 2c,d). The lowest unoccupied molecular orbital (LUMO) levels were calculated to be −3.78 eV for PBDT-DPP and −3.73 eV for PC-DPP by subtracting the optical band gaps from the corresponding HOMO levels. The results indicated that the PC-T unit with a more twisted skeleton could effectively lower the HOMO energy levels, facilitating energy level alignment at perovskite/HTM interfaces in n-i-p structured PSCs.⁴⁴ The valence band (VB) of the perovskite film was estimated to be −5.94 eV, which was obtained through ultraviolet photoelectron spectroscopy (UPS).⁴⁵ The hole mobility (μ_h) estimated by the space-charge-limited current (SCLC) method (Figure 2e and Figure S6) was $1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PC-DPP and $9.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PBDT-DPP. The higher mobility of the PC-DPP film could be attributed to its larger 2D conjugated skeleton with dominant face-on orientation as discussed below, consistent with the higher conductivity of PC-DPP ($\sigma = 4.6 \times 10^{-4} \text{ S cm}^{-1}$) in comparison with PBDT-DPP ($\sigma = 3.2 \times 10^{-4} \text{ S cm}^{-1}$) (Figure S7).

The molecular stacking and crystallinity of polymer films were assessed by GIWAXS measurements (Figure S8) and the corresponding line-cut profiles (Figure 3a,b). A strong peak at $q_z \approx 1.63 \text{ \AA}^{-1}$ was observed in the in-plane direction, which

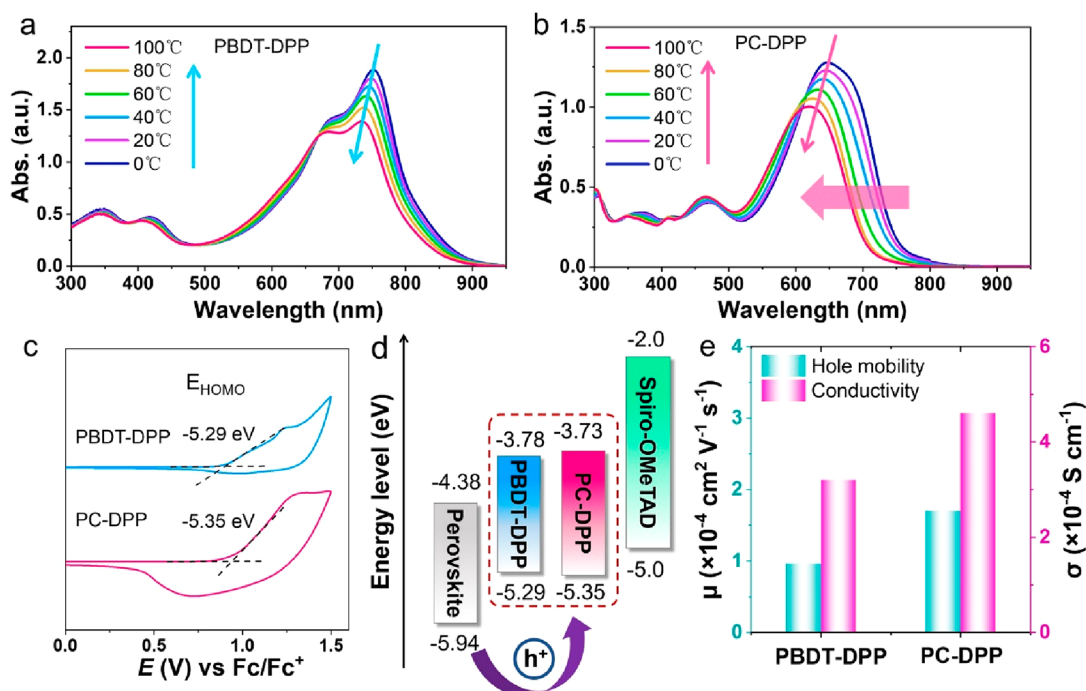


Figure 2. (a, b) Absorption spectra of PBDT-DPP (a) and PC-DPP (b) solution in chlorobenzene at different temperatures. (c) Cyclic voltammetry (CV) of the two polymers measured in films. (d) Schematic diagram of energy level arrangement. (e) Hole mobility and conductivity of PBDT-DPP and PC-DPP films.

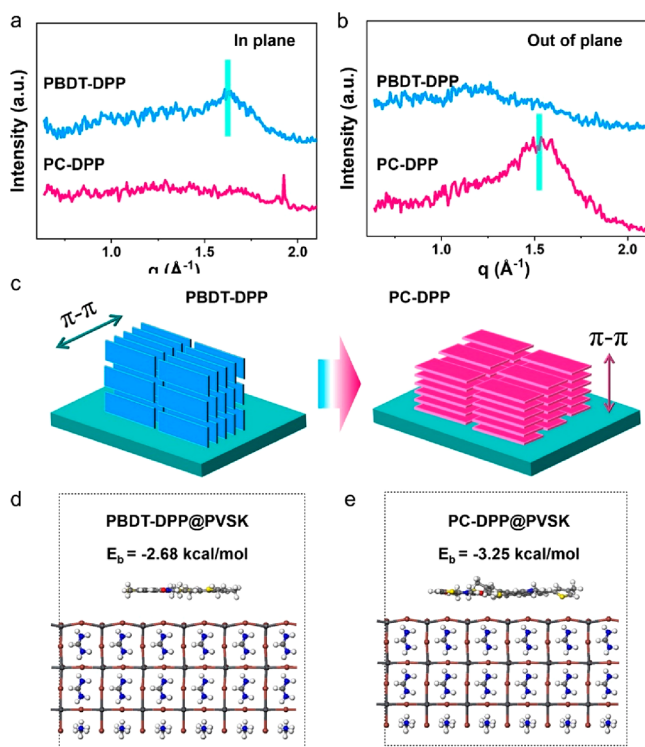


Figure 3. (a, b) GIWAXS integrated line files of PBDT-DPP and PC-DPP films on the silicon wafer. (c) The proposed packing modes of two polymers based on GIWAXS data. (d, e) Theoretically modeled PBDT-DPP and PC-DPP stacking patterns on top of a perovskite (PVSK) surface.

suggested that the PBDT-DPP film preferred to grow with a typical edge-on orientation (Figure 3c). A stacking model transition from an edge-on orientation to a more favorable

face-on orientation can be observed in the PC-DPP film, which showed a dominant peak at $q_z \approx 1.53 \text{ \AA}^{-1}$ in the out-of-plane direction for the PC-DPP film.⁴⁶ Therefore, considering that both polymers had the same DPP unit, this preferential face-on orientation of the PC-DPP film could be attributed to the larger PC-T donor unit. So, the size of the building unit with extended conjugation in two dimensions (2D) should play a vital role in the dominant face-on stacking orientation of the PC-DPP polymer in the film. The calculated π - π stacking distance of PBDT-DPP was $3.85 \text{ \AA}$, which was smaller than that of PC-DPP ($d = 4.10 \text{ \AA}$) with a twisted polymer backbone. The X-ray diffraction (XRD) patterns in Figure S9 show that the PBDT-DPP and PC-DPP films exhibited prominent characteristic peaks at 4.5 and 5.1° , respectively, which could be assigned to the (100) plane of the crystalline polymers. The stronger (100) diffraction peak and smaller full width at half-maximum (fwhm) of the PBDT-DPP film than those of the PC-DPP film indicated that PBDT-DPP had a higher crystallinity due to its more planar polymer conjugate backbone and stronger π - π stacking, consistent with the shortened π - π stacking distance calculated from GIWAXS data discussed above.

DFT calculations were further implemented to study the secondary interaction at perovskite/HTM interfaces. One repeating unit of each polymer was chosen and positioned on the top of the perovskite crystal model and optimized under subsequent constraints. As shown in Figure 3d,e and Figure S10, the larger binding energy of $-3.25 \text{ kcal mol}^{-1}$ for PC-DPP@PVSK than that of $-2.68 \text{ kcal mol}^{-1}$ for PBDT-DPP@PVSK indicated that PC-DPP stacked with the perovskite surface more tightly, which could be attributed to the large PC-T donor unit used in the PC-DPP polymer. These results suggested that conjugated backbones with larger and broader conjugation, such as PC-T units, could effectively enhance the interactions between the perovskite and polymer.

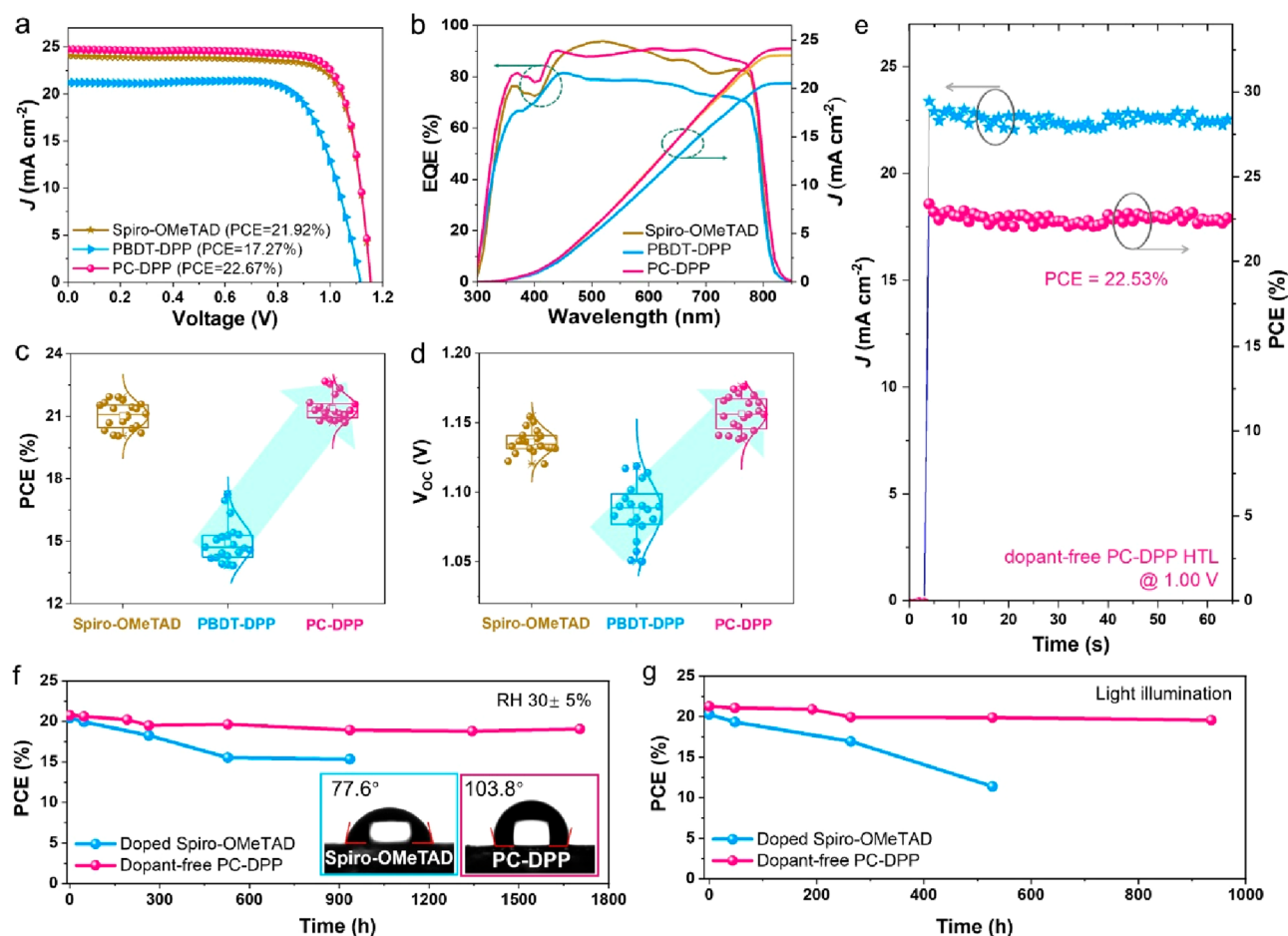


Figure 4. (a) J - V curves of the PSCs based on different HTMs. (b) EQE spectra of the corresponding photovoltaic devices. (c) Statistical PCE data of the corresponding devices. (d) Statistical V_{oc} data of the corresponding devices. (e) The steady-state power output of the champion PC-DPP-based device at the maximum power point. (f) PCE as a function of time for unencapsulated devices stored in air (RH, 30 ± 5%) at room temperature. Insets are images of water droplet contact angles on surfaces of Spiro-OMeTAD and PC-DPP with glass/ITO/SnO₂/perovskite as the substrate. (g) PCE as a function of time for unencapsulated devices stored in N_2 at 40 °C under continuous light illumination (white-light-emitting diode (LED), 100 mW cm^{-2}).

Based on the excellent material properties discussed above, we fabricated PSCs with the n-i-p structure of ITO/SnO₂/perovskite/HTMs/MoO₃/Ag (Figure S11). The optimized thickness of the PC-DPP layer was ~31.6 nm as measured by atomic force microscopy (AFM) (Figure S12), in agreement with the cross-sectional SEM results (Figure S13). As shown in Figure 4a, the device based on dopant-free PBDT-DPP exhibits a V_{oc} of 1.117 V, a J_{sc} of 21.18 mA cm^{-2} , and a FF of 78.89%, achieving a PCE of 17.27%. The efficiency was improved to 22.67% for the device using PC-DPP as the HTM, coupled with a high V_{oc} of 1.156 V, a J_{sc} of 24.74 mA cm^{-2} , and a FF of 79.28%. The enlarged V_{oc} of the device based on PC-DPP compared to PBDT-DPP was consistent with the downshifted HOMO level. The significantly improved FF and J_{sc} of PC-DPP-based devices could be attributed to their improved hole mobility and enhanced hole extraction capability discussed below. Notably, the PSCs using doped Spiro-OMeTAD as the HTM (Figure 4a and Table S1) showed a PCE of 21.92%, lower than that of the PC-DPP-based devices.

The integrated J_{sc} values from the EQE spectra for devices based on Spiro-OMeTAD, PBDT-DPP and PC-DPP HTMs (Figure 4b) were 23.41, 20.52, and 24.10 mA cm^{-2} , respectively, in good agreement with the J - V results (<3%

difference). Note that the EQE of the PC-DPP-based PSC is significantly improved compared with the Spiro-OMeTAD-based device in the 600–800 nm range, which could be attributed to the better hole extraction capability of the PC-DPP. Note that the best performance of the dopant-free PC-DPP-based PSC was achieved at a low concentration of 8 mg/mL for PC-DPP in chloroform/*o*-xylene (*v/v* = 1/1) solution, much lower than that of ~80 mg/mL typically used for doped Spiro-OMeTAD, indicating its great potential to improve the economic viability of PSCs as well. Furthermore, the PC-DPP-based devices (Figure 4c,d and Figure S14 and Table S1) showed superior reproducibility with an average PCE of 21.39% for the 20 individual devices, which was higher than that of doped Spiro-OMeTAD-based devices (PCE_{average} = 21.03%). After device optimization with different concentrations of HTM, the optimal thickness of PC-DPP was achieved with a low concentration of 8 mg mL^{-1} (Table S2). The dopant-free PC-DPP-based PSCs exhibited less hysteresis than the PBDT-DPP-based devices (Figure S15 and Table S3), which could be attributed to the better charge collection and surface passivation capabilities of PC-DPP polymers as discussed below.⁴⁷ The optimal PC-DPP-based PSC exhibited a steady-state PCE of 22.53% measured at the maximum power point (MPP), in agreement with the J - V results (Figure 4e).

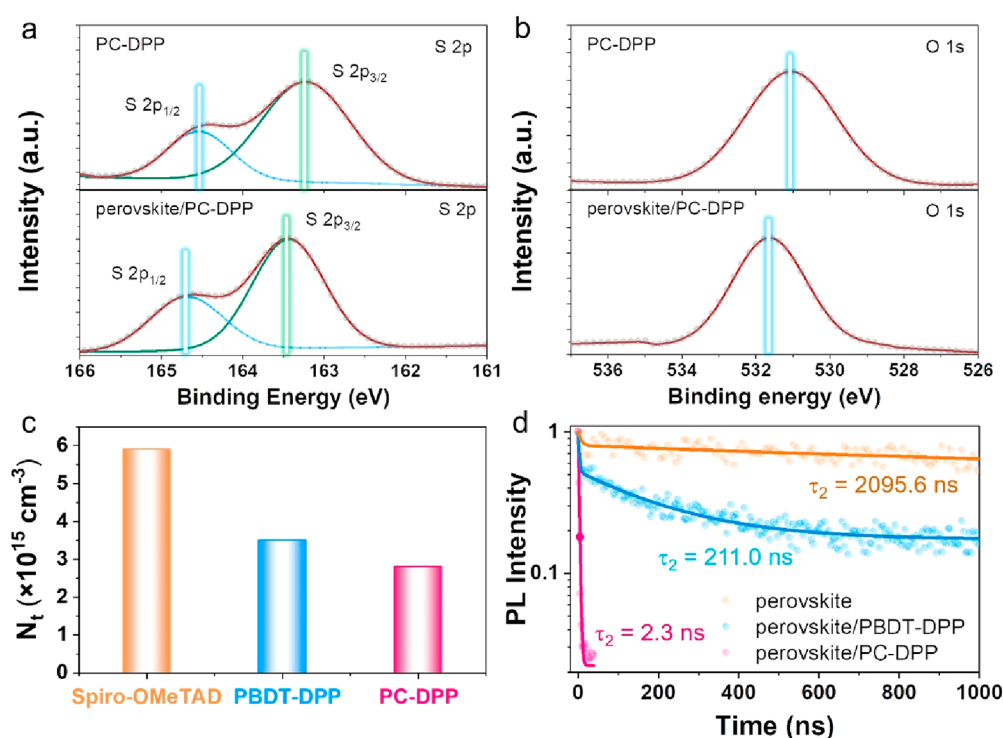


Figure 5. (a) XPS of S 2p peaks of the pristine PC-DPP film and PC-DPP capped perovskite film. (b) XPS of O 1s peaks of the pristine PC-DPP film and PC-DPP capped perovskite film. (c) The trap-state density N_t of perovskite films capped with different HTMs. (d) TRPL spectra of the pristine perovskite film and perovskite capped with PBDT-DPP and PC-DPP films.

The large-area (1.01 cm^2) device showed a high PCE of 20.82%, coupled with a J_{SC} of 24.25 mA cm^{-2} , a V_{OC} of 1.173 V, and a FF of 73.89% (Figures S16 and S17 and Table S4), benefiting from the preferred face-on orientation, excellent morphology (Figure S18), and hole mobility of the PC-DPP film.

The water contact angle of the perovskite films covered by PBDT-DPP or PC-DPP is $\sim 104^\circ$, much larger than that of the doped Spiro-OMeTAD capped film ($\sim 78^\circ$) (Figure 4f and Figure S19). The results suggested that these polymeric HTMs exhibit increased water resistance. The humidity stability of unencapsulated devices stored under ambient conditions (RH = $30 \pm 5\%$) was also evaluated (Figure 4f and Figure S20). The PCE of the control device using the doped Spiro-OMeTAD HTM dropped to 75% of its original value after 936 h, while the device utilizing dopant-free PC-DPP as the HTM could maintain more than 92% of its initial PCE after 1704 h. The aging test under continuous 1 sun irradiation (white LED, 100 mW cm^{-2} , 40°C , N_2) (Figure 4g and Figure S21) showed that the PSC utilizing dopant-free PC-DPP as the HTM retained over 92% of its original efficiency after 936 h. By contrast, the PCE of the doped Spiro-OMeTAD-based PSC had significantly decreased to 56% of the initial value after 528 h. Note that the operational stability measured by tracking the maximum power point (MPP) also showed that the PC-DPP-based device has much better stability than that of the control device (Figure S22). These results indicated that the dopant-free PC-DPP HTM could substantially improve the device stability under different storage conditions in comparison with the PSCs based on doped Spiro-OMeTAD.

The X-ray photoelectron spectroscopy (XPS) characterization in Figure S23 shows two major peaks at 142.6 and 137.8 eV for the pristine perovskite films, corresponding to Pb

$4f_{5/2}$ and Pb $4f_{7/2}$, respectively, while after capping the polymer films on perovskites, these two Pb $4f$ peaks were shifted to lower binding energies at 142.0 and 137.1 eV for PBDT-DPP and 142.2 and 137.4 eV for PC-DPP, respectively. The shifts of the Pb $4f$ peaks of PBDT-DPP- and PC-DPP-capped perovskite films could be attributed to the $\text{C}=\text{O}\cdots\text{Pb}^{2+}$ interactions between the HTM and undercoordinated Pb^{2+} , indicating that these polymers could passivate the Pb^{2+} defects on the perovskite surface. Furthermore, the shifts of S 2p and O 1s peaks of a polymer-capped perovskite compared with the pristine perovskite film further indicated the direct interactions between the perovskite and the perovskite film (Figure 5a,b). Overall, the shifts of the O, S, and Pb signals confirmed the existence of $\text{C}=\text{O}\cdots\text{Pb}^{2+}$ or $\text{S}\cdots\text{Pb}$ interactions at the perovskite/perovskite interfaces, leading to reduced surface defects and suppressed carrier nonradiative recombination loss. The trap state densities (N_t) of PBDT-DPP- and PC-DPP-coated perovskite films were estimated by the SCLC method (Figure 5c and Figure S24). The device structure of the hole-only device was ITO/PEDOT:PSS/perovskite/HTMs/Ag. Compared to doped Spiro-OMeTAD ($N_t = 5.9 \times 10^{15} \text{ cm}^{-3}$), the polymer-capped perovskite film showed a significantly decreased trap density of $3.5 \times 10^{15} \text{ cm}^{-3}$ for PBDT-DPP and $2.8 \times 10^{15} \text{ cm}^{-3}$ for PC-DPP, indicating the excellent defect passivation capability of polymeric HTMs. The reduced trap density was consistent with the decreased charge transport resistance of the devices measured by impedance spectroscopy (Figure S25). Note that the SCLC method may have some limitations, although it has been widely used to measure the trap density of perovskite films.^{48,49}

To verify the defect passivation and hole extraction capability of polymer HTMs on the perovskite surface, we performed thickness-dependent steady-state PL measurements

(Figures S26 and S27). When the solution concentration exceeded 0.01 mg/mL for depositing the PC-DPP film, the PL intensity of the PC-DPP-capped perovskite film decreased rapidly with increasing thickness, suggesting that only a very thin PC-DPP layer is needed for surface defect passivation and the thicker PC-DPP film could not only play the role of hole extraction and transport but also surface defect passivation.⁵⁰ To investigate the charge transfer dynamic between perovskite and HTM films, time-resolved photoluminescence (TRPL) measurements were carried out. As shown in Figure Sd, the pristine perovskite film exhibited a long bulk charge carrier lifetime ($\tau_2 = 2096$ ns) as calculated by the empirical biexponential equation.⁵¹ In contrast, the PBDT-DPP- or PC-DPP-capped perovskite films showed much-decreased bulk carrier lifetimes of 211.0 and 2.3 ns, respectively, indicating the superior charge extraction capability of the PC-DPP film, which could be attributed to its preferred face-on orientation and large binding energy with the perovskite surface as discussed above. All these unique properties contribute to the improved photovoltaic performance of PSCs using PC-DPP as a dopant-free HTM. Based on the excellent device performance of PC-DPP, we summarize and show the design strategy and structure–function relationship of polymer HTMs in Figure S28

In summary, we have successfully demonstrated tunable molecular packing and orientation of polymers by regulating their donor building blocks by shifting the side chain to the main chain and using a large PC core unit. It is found that the PC-DPP shows a self-assembly behavior and contributes to a dominant face-on orientation, whereas the PBDT-DPP polymer shows a preferred edge-on orientation. As a result, the PC-DPP film with preferred face-on orientation shows enlarged hole mobility and strengthened interfacial contact with the perovskite surface, resulting in a superior charge extraction capability. The PC-DPP and PBDT-DPP films could decrease the bulk carrier lifetime of the perovskite film from >2000 to 211.0 and 2.3 ns, respectively. The rich Lewis base groups in the DPP skeleton also play an essential role by passivating surface defects of perovskite through $C=O \cdots Pb^{2+}$ and $S \cdots Pb^{2+}$ interactions. As a result, PSCs employing dopant-free PC-DPP as the HTM afford an excellent PCE of 22.67% along with significantly improved stability in comparison to doped Spiro-OMeTAD, ranking it among the best PSCs based on dopant-free HTMs. The results of this work will promote the understanding of the structure–properties relationship of dopant-free polymers for developing more efficient HTMs toward high-performance PSCs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.3c00855>.

Materials synthesis, GPC, device characterization and stability measurements, charge mobility, theoretical calculations, and 1H NMR and ^{13}C NMR data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the National Key Research and Development Program of China (No. 2019YFA0705900), the National Natural Science Foundation of China (Grant Nos. 52273182 and 21935007), the Fundamental Research Funds for the Central Universities (020-92220002), the starting grant from Nankai University (020-ZB22000110), the Natural Science Foundation of Hebei Province (Grant No. B2022408005), China Postdoctoral Science Foundation (2022M711696), and the Haihe Laboratory of Sustainable Chemical Transformations.

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