A crosslinked polymer as dopant-free hole-transport material for efficient n-i-p type perovskite solar cells

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**Abstract**

A new crosslinked polymer, called P65, with appropriate photo-electrochemical, opto-electronic, and thermal properties, has been designed and synthesized as an efficient, dopant-free, hole-transport material (HTM) for n-i-p type planar perovskite solar cells (PSCs). P65 is obtained from a low-cost and easily synthesized spiro[fluorene-9,9’-xanthene]-3,6’-dial (SFX-OH)-based monomer X65 through a free-radical polymerization reaction. The combination of a three-dimensional (3D) SPX core unit, hole-transport methoxydiphenylamine group, and crosslinked polyvinyl network provides P65 with good solubility and excellent film-forming properties. By employing P65 as a dopant-free hole-transport layer in conventional n-i-p type PSCs, a power conversion efficiency (PCE) of up to 17.7% is achieved. To the best of our knowledge, this is the first time a 3D, crosslinked, polymeric dopant-free HTM has been reported for use in conventional n-i-p type PSCs. This study provides a new strategy for the future development of a 3D crosslinked polymeric dopant-free HTM with a simple synthetic route and low-cost for commercial, large-scale applications in future PSCs.

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1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have been a promising candidate for third-generation photovoltaics (PVs), and the power conversion efficiency (PCE) has surged to 25.2% as of 2019 [1–3]. Meanwhile, studies on PSCs, including fabrication techniques, device architectures, functional components, and new materials, have been systematically and intensively investigated [4–8]. The hole-transport materials (HTMs) play a pivotal role in extracting and transporting holes as well as restraining the charge recombination at the interfaces between the perovskite layer and the hole transport layer [9,10]. Moreover, in conventional n-i-p type PSCs, HTMs act as a protective layer to prevent moisture in the air from permeating and degrading the perovskite materials.

This improves the stability and device performance of the PSCs [11,12]. However, owing to the intrinsically low hole mobility and conductivity, even for the benchmark HTM, \(N^2.N^2.N^2.N^2.N^2.N^7\), \(N^7.N^7.N^7\)-octakis(4-methoxyphenyl)-9,9’-spirobi[9H-fluorene]-2,2’,7,7’-tetramine (Spiro-OMeTAD), the hygroscopic additives, such as bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), and tert-butylpyridine (t-BP), are typically required to improve the charge transport ability to guarantee a significantly better solar cell performance [13–15]. Nevertheless, the application of dopants will inevitably incur offside-effects, for instance, an acceleration of the degradation of the perovskite layer and a poor stability of the solar cells [16,17]. In this regard, a search for potential dopant-free HTM candidates is significant for the practical application of PSCs.

Several novel, dopant-free HTMs aiming to improve the stability of PSCs and achieve excellent PCEs have been designed and synthesized [18–23]. For example, varieties of small organic molecules with different core units, including triphenylamine (TPA) [24,25], tetrafluorovalenole (TTF) [26], tetrahydrolylene (TTE) [27], dibithieno[3,2-b:2’,3’-d]pyrrole (DTP) [28], and triazatruxene [29],
have been extensively investigated. In addition, some metal complexes and inorganic p-type semiconductors have also been considered as dopant-free HTMs, such as copper(II) phthalocyanines (CuPcs) [30], and CuSCN [31]. Such systems typically show a good intrinsic hole mobility, conductivity, and low cost.

In addition to small molecules [32,33], polymer-based HTMs have attracted considerable attention owing to their good thermal stability, tunable functionality, mechanical flexibility, and good film-forming ability, among other benefits [34,35]. One of the common strategies in the design of dopant-free HTMs is the use of donor–acceptor (D–A) conjugation building blocks, which are easy to apply owing to their tunable electrical and optical properties and improved charge-transport characteristics [36–38]. For example, Park et al. combined two polymers, P-OR and P-R, to form a random copolymer RCP as an HTM layer and yielded a PSC PCE of 17.3% [39]. Both polymers displayed a coplanar donor with π-π stacking and a strong electron acceptor, generating a good charge mobility and a suitable HOMO energy level. Undoubtedly, D–A-type, dopant-free HTMs have shown significant potential for use in solar cell devices [40]. Nevertheless, requirements involving noble-metal catalysts and expensive raw materials, complicated synthesis routes and purification procedures, and an intrinsic colored and unsatisfactory solubility limit their further application.

Another type of attractive dopant-free, polymeric HTM is a non-π-conjugation polymer formed through a free-radical polymerization with a double bond, which has been widely used in electrochromic devices (ECDs) [41], organic light-emitting diodes (OLEDs) [42], and organic photovoltaics (OPVs) [43]. Linear structured polymers with different side chains have also been developed [44]. Huang et al. reported a non-conjugated carbazole-based polymer (PVCz-OMEAD) as a dopant-free HTM for n-i-p-type PSCs, achieving an efficiency of 16.09% [45]. Compared to linear polymers, crosslinked polymers with three-dimensional (3D) network structures provide a higher density of the charge-transport channels, a good solvent/thermal resistance, and mechanical durability [46–48]. Shao et al. employed four diphenylamine derivatives with a fluorene core in inverted p-i-n planar PSCs using in-situ annealing, and achieved a PCE of 18.7% [49]. Some other crosslinked 3D HTMs, e.g., N\textsubscript{4},N\textsubscript{4}-(naphtalen-1-yl)-N\textsubscript{4},N\textsubscript{4}-bis(4-vinylphenyl)biphenyl-4,4'-diamine, termed VNPB, have been applied in semi-transparent PSCs along with an extra deep-work-function transition metal oxide (typically MoO\textsubscript{3}) as an interface doping layer [50,51]. However, little attention has been focused on the development of 3D crosslinked polymers as dopant-free HTMs for use in n-i-p-type PSCs.

Herein, we present a novel spiro[fluorene-9,9'-xanthene]-3,6'-diol (SFX-OH)-based, crosslinked polymer, **P65**, obtained through a mild free-radical polymerization as a dopant-free HTM for n-i-p-type PSCs (Fig. 1). This polymer is characterized by suitable energy levels, adequate charge-transport properties, and good thermal stability and hydrophobicity. An impressive PCE of 17.7% was achieved in PSCs using the newly designed polymer **P65** as an HTM. To the best of our knowledge, this is the first time a 3D, crosslinked-polymeric, dopant-free HTM has been used in a conventional n-i-p-type PSC.

### 2. Experimental

#### 2.1. Materials

All solvents and chemicals used in this study are commercially available and were applied as received unless stated otherwise. The experimental details regarding the synthesis and characterization, as well as the DFT calculations, are provided in the Supporting Information.

#### 2.2. Device fabrication

**Perovskite solar cells**: A fluorine-doped tin oxide (FTO) substrate (TEC 15, Hartford Glass Co.) was patterned using a hydrogen-evolution etching method (zinc powder and a 2 M HCl solution). Pre-patterned FTO was cleaned in soapy water, deionized water, acetone, and ethanol with sonication, and all substrates were then UV-ozone cleaned for 30 min subsequently before further use, followed by deposition with a thin compact TiO\textsubscript{2} layer through spray pyrolysis using 0.2 M Ti(acac)\textsubscript{2}OIP\textsubscript{2} in an isopropanol solution at 450 °C. The sprayed film was annealed at 450 °C for 30 min. Tin oxide was used as an electron transport material. The 15% tin oxide colloid precursor was diluted to 2.67% using deionized water. The solution was spun onto the FTO glass/compact TiO\textsubscript{2} substrate surface at 3000 rpm for 30 s, and then baked on a hotplate in an ambient atmosphere at 120 °C for 20 min. The as-prepared substrates were further cleaned using an UV-ozone cleaner for 20 min before use. The perovskite film was subsequently deposited using the aforementioned spin-coating methods. A hole-transport layer (HTL) was then spin-coated onto the perovskite films. The conventional doped-Spiro-OME-TAD was spun at 4000 rpm for 30 s with an HTL solution consisting of 85.8 mg of Spiro-OME-TAD, 19.3 μL Li-TFSI stock solution (520 mg Li-TFSI in 1 mL acetonitrile), 30 μL t-BP, 10.52 μL FK209 (tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) trifluoroacetate) stock solution (300 mg FK209 in 1 mL of acetonitrile), and 1 mL chlorobenzene solvent. For **P65**, different concentrations (5, 10, and 15 mg/mL) of HTM without dopants were applied. Finally, an 80-nm layer of gold was deposited through thermal evaporation using a shadow mask to pattern the electrodes.

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**Fig. 1.** Chemical structures of HTM **X65** and **P65**.
3. Results and discussion

3.1. Materials synthesis

The synthetic route of the HTM monomer (X65) and polymer (P65) is shown in Scheme S1. The design of the HTMs is based on the spiro[fluorene-9,9'-xanthene] (SFX) unit core, which contains a central tetrahedral sp3 carbon atom and two perpendicular \( \pi \) systems, i.e., xanthene and fluorene [52,53]. This 3D-structural skeleton has been demonstrated to decrease the charge recombination process on the absorption and PL properties of the two compounds [54,55]. In addition, the flexible vinyl groups not only act as reactive sites for radical polymerization, they can also be beneficial for increasing the solubility of the material [56].

The monomer X65 was synthesized through an extremely simple three-step procedure with a high yield. The synthesis was initiated using the construction of a 2,7-dibromospiro[fluorene-9,9'-xanthene]-3,6'-diol (SFX-OH) core through a cyclization reaction, followed by a substitution reaction to anchor the functional group 4-vinylbenzyl; finally, the product X65 was completed through a palladium-catalyzed Buchwald-Hartwig cross-coupling reaction. The polymer HTM P65 was obtained using a free-radical polymerization of the corresponding monomers with 2,2'-azobis(2-methyl propionitrile) (ABN) as an initiator, and the product was purified with different solvents (more detailed information is provided in the Supporting Information) through a Soxhlet extraction according to published procedures [42]. Both the HTM X65 and P65 show good solubility in common organic solvents, such as chloroform, toluene, tetrahydrofuran, and chlorobenzene. The composition and chemical structures of all intermediates were confirmed using \(^1\)H and \(^13\)C NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) (Figs. S1–S6). The size and molecular weight of the polymer were estimated using size exclusion chromatography (SEC) (see the Supporting Information), to render a number-average molecular weight (\( M_n \)) of 153,057 g/mol, a corresponding weight-average molecular weight (\( M_w \)) of 442,495 g/mol, and a relatively low polydispersity (PDI = \( M_w/M_n \)) of 2.89. DFT calculations were conducted to understand the crosslinked structure of P65, as shown in Fig. S14. In addition, a brief cost estimation for the synthesis of 1 g of P65 is given in Scheme S2 and Table S5, and roughly comprises 20% that of Spiro-OMeTAD, as shown in Scheme S3 and Table S6. For low-cost raw materials, a simple synthesis route and a high overall yield show a promising scale-up of P65 for commercial application.

3.2. Optical and electrochemical properties

The normalized UV–visible absorption and photoluminescence (PL) spectra, recorded in a \( 10^{-5} \) M dichloromethane solution, are shown in Fig. 2(a). No apparent influence of the polymerization process on the absorption and PL properties of the two compounds was shown. Both X65 and P65 show a broad shoulder peak at approximately 375–386 nm and no distinct light absorption within visible range. In the PL spectra, X65 and P65 show similar emissions at 427 and 426 nm, respectively. The optical band gaps of the two HTMs are 3.04 and 3.03 eV, respectively, which are close to that of Spiro-OMeTAD (3.05 eV), as estimated from the intersection of the normalized absorption and emission spectra.

The oxidation potentials (\( E_{\text{on}} \)) and highest occupied molecular orbital (HOMO) energy levels of X65 and P65 were obtained from cyclic voltammetry (CV) (Fig. S7) and differential pulsed voltammetry (DPV) (Fig. 2b), as recorded from a \( 10^{-4} \) M dichloromethane solution. The corresponding data are summarized in Table 1. The small molecular substance X65 shows a similar HOMO energy level as Spiro-OMeTAD (−5.09 and −5.08 eV, respectively), whereas P65 displays a marginally deeper HOMO energy level of −5.12 eV.

Despite the matched energy alignment with respect to the perovskite and electrode materials, the deeper HOMO energy level of P65 probably decreases the potential voltage loss, and thus a slightly higher open-circuit voltage in the corresponding solar cell devices can be anticipated. The lowest unoccupied molecular orbital (LUMO) energy levels of the HTMs were calculated using the optical band gap and HOMO energy levels. Both HTMs show suitable LUMO energy levels (−2.05 eV for X65 and −2.09 eV for P65) with respect to the conduction band (CB) energy of the perovskite layer. This may suppress the charge-transfer losses between the perovskite layer and the Au back electrode. The energy level diagrams are shown in Fig. 2(c).

3.3. Thermal properties

The thermal properties of the HTMs X65 and P65 and Spiro-OMeTAD were investigated through a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 2d, 2e, 2f, and Fig. S8). The TGA traces in Fig. 2(d) show an outstanding thermal stability for both HTMs, and the decomposition temperatures (\( T_d \)) of X65 and P65, defined as the 2% weight loss temperature, are 317 °C and 381 °C, respectively. It is also worth noting that X65 from −200 °C displays a weight loss, which could be attributed to an exothermic process caused by a heat-induced self-polymerization. Similar phenomena can be observed in the DSC results shown in Fig. 2(e). The DSC analysis reveals a stable amorphous state of the HTM P65 based on a higher glass transition temperature (\( T_g \)) of 266 °C (Fig. 2f) than that of its corresponding monomeric material X65 (\( T_g \) of 90 °C before polymerization, thermally crosslinked at 199 °C, as indicated in Fig. 2e) and Spiro-OMeTAD (\( T_g \) of 120 °C, as shown in Fig. S8), most likely owing to the higher molecular weight of its building blocks [56].

3.4. Charge-carrier mobility

The \( J-V \) curve models of the conductivity and hole mobility for the two HTMs X65 and P65 are shown in Fig. 3(a) and 3(b), respectively, whereas the corresponding extracted data are given in Table S1. Both investigations were executed for the dopant-free materials, and the concentrations of the HTM precursor solutions were the same as those used for the solar cell device manufacturing. Clearly, P65 demonstrates a higher hole mobility, i.e., \( 4.30 \times 10^{-6} \) cm²/(V·s), than that of X65 at 2.77 \( \times 10^{-5} \) cm²/(V·s), which may be attributed to a closer stacking interaction between the monomer fragments after polymerization (Fig. S11). In addition, a polymerized, extended, and conjugated P65 system requires fewer hopping steps in the conduction channels than the monomeric X65. It should also be noted that P65 exhibits an improved conductivity of \( 1.20 \times 10^{-5} \) S/cm as compared to that of X65 (8.80 \( \times 10^{-6} \) S/cm). One further possible reason for the slight difference between the two HTMs could be the similar film-forming properties of P65. The polymeric 3D-network can also be beneficial for an efficient charge transport [57,58].

To probe the charge transfer properties at the interfaces between the perovskite and HTM layers, steady-state photoluminescence (PL) and time-resolved photoluminescence decay (TR-PL) were conducted (Fig. 3c and 3d). As shown in Fig. 3(c), both non-doped X65- and P65-based films efficiently quench the PL emission of the perovskite layer, suggesting a good hole-extraction capability. Among these films, the P65-based film displayed a more efficient PL quenching, indicating a better hole-extraction capability as compared to those of X65 and Spiro-OMeTAD. These results are further supported by TR-PL traces, as shown in Fig. 3(d). After capping the perovskite layer with
dopant-free P65 as a hole-transport layer, the perovskite film exhibits the strongest quenching effect along with the shortest lifetime (Table S2), thus minimizing the recombination losses within the bulk. This could contribute to the higher \( V_{OC} \) observed in solar cell devices, suggesting an effective hole transfer at the perovskite/HTM interface.

![Fig. 2. (a) Normalized UV–visible light absorption and photoluminescence spectra, (b) differential pulsed voltammograms (DPVs) of X65 and P65 in dichloromethane, (c) energy level diagram, and (d) thermogravimetric analysis (TGA) traces and differential scanning calorimetry (DSC) scans of X65 (e) and P65 (f), respectively.](image)

**Table 1** Summary of optical and electrochemical properties of X65, P65, and Spiro-OMeTAD.

| HTMs     | \( \lambda_{abs} \) (nm) | \( \lambda_{em} \) (nm) | \( E_{ox}^0 \) (V) | \( E_{0-0}^0 \) (eV) | HOMO (eV) | LUMO (eV) |
|----------|--------------------------|--------------------------|-------------------|---------------------|-----------|-----------|
| X65      | 295                      | 386                      | 0.62              | 3.04                | -5.09     | -2.05     |
| P65      | 295                      | 375                      | 0.65              | 3.03                | -5.12     | -2.09     |
| Spiro-OMeTAD | 306                  | 386                      | 0.62              | 3.05                | -5.08     | -2.03     |

*a 0.1 M of tetrabutylammonium hexafluorophosphate (n-Bu4NPF6) in dichloromethane as an electrolyte, Ag/0.01 M AgNO3 electrode (acetonitrile as a solvent) as a reference electrode, a glassy carbon disk (3-mm diameter) as the working electrode, and a platinum wire as the counter electrode. Scan rate = 100 mV/s. All redox potentials were calibrated versus the normal hydrogen electrode (NHE) by the addition of ferrocene. The conversion factor \( E_{1/2}(Fc/Fc^+) = 630 \) mV versus NHE was used.

*b Estimated from the intersection of the normalized absorption and emission spectra.

*c HOMO = -5.1 eV = \( E_{1/2}^F - E_{1/2}^F \).

*d LUMO = HOMO + \( E_{0-0} \).
3.5. Photovoltaic performance of devices

To evaluate the device performance of the synthesized X65 and P65, we fabricated PSCs by employing them as HTMs without any additives. The device architecture was as follows: FTO/compact TiO2/SnO2/MAPbI3/HTM/Au [59], which is clearly illustrated by the cross-sectional SEM image shown in Fig. 4(d). All details regarding the fabrication procedure and characterization can be found in the Supporting Information.

Fig. 4(e) shows the photocurrent density versus voltage (J–V characteristics) with synthesized small molecular HTM X65, polymeric P65, and the well-known Spiro-OMeTAD, respectively, when implemented as dopant-free solar cell devices. The corresponding photovoltaic parameters determined from the J–V data are analyzed in Table 2. Unexpectedly, the X65-based PSC shows a low efficiency of 8.42%. The low photovoltaic performance can be linked to the low conductivity and hole mobility of the material, rendering a higher interface recombination loss. Moreover, in the SEM images of the perovskite layer covered by X65, as shown in Fig. 4(b), pinholes can be identified in the film, indicating a poor film-forming ability and further contributing to the reduced solar cell performance. Under the same conditions, the PSC based on the dopant-free P65 provides an efficiency of 17.7% (reverse scan), whereas the reference of the dopant-free Spiro-OMeTAD-based PSC offers a PCE of 10.6%. The highest open-circuit voltage (VOC) of a P65-based device obtained (1.09 V) can probably be ascribed to a combination of a more negative HOMO energy level and less recombination loss compared to devices containing X65 and Spiro-OMeTAD. The remarkable fill factor (FF) recorded for devices based on P65 (75%) (Table 2) contributes significantly to the device performance (Fig. 4c and 4d). The reduced hysteresis behavior achieved by a dopant-free P65-based device can be attributed to the efficient hole extraction and enhanced charge transport between the perovskite layer and the HTM layer [60,61]. The incident photon-to-current-conversion efficiency (IPCE) spectra of P65-based PSC devices are shown in Fig. 4(f) and illustrate a wide photoelectric response with respect to the solar spectrum ranging from 400 to 750 nm with a maximum IPCE of greater than 75%. The corresponding integrated short-circuit current density (JSC) calculated from the IPCE spectra is 20.1 mA/cm², which is in good agreement with the experimental JSC. A stabilized photocurrent density of 19.1 mA/cm² for the P65-based PSC devices was determined by applying a constant bias voltage taken from the maximum power point at 0.90 V, as shown in Fig. 4(g), corresponding to a stabilized efficiency of 17.3%. These results demonstrate that a P65-based device exhibits a highly stable power output, as well as an extremely fast photo-response, thus further suggesting the reliability of the above device performance and indicating the efficient charge extraction and low charge recombination losses in P65-based devices. In addition, Fig. S10 summarizes the statistical data of P65-based cells from the synthesis of three individual batches, which demonstrates the good reproducibility of the materials and the solar cell devices.

There is no doubt that P65-based PSCs offer the best photovoltaic performance among the three HTMs under dopant-free conditions. We may also compare the champion dopant-free HTM-based PSCs under regular doping conditions, the results of which are shown in Fig. S11 and Table S4. It is not surprising that the monomeric X65-based PSC devices showed a similar photovoltaic performance as cells based on the standard Spiro-OMeTAD after doping because both molecular materials have similar intrinsic properties. This also illustrates that the monomeric material X65 can be considered a replacement for traditional Spiro-OMeTAD when applied in devices and when dopants/additives are used. It is notable that the P65-based dopant-free PSC devices exhibit a comparable efficiency as compared to the other two types of devices based on doped HTMs. In addition, the estimated cost of P65 used in solar cell devices is only 2.68% as
compared to the standard material Spiro-OMeTAD (Table S7), which is mainly due to the easy synthesis procedure of P65 and the small amount of material required in such devices. This result indicates that P65 has potential for large-scale industrial application in PSCs.

To further explore the charge recombination properties, electrochemical impedance spectroscopy (EIS) was conducted by applying a bias voltage of 0 V to 0.8 V under the illumination of simulated one sun light intensity. An equivalent circuit model was used to evaluate the EIS response, and the extracted charge recombination resistance ($R_{\text{rc}}$) at the interfaces is as shown in Fig. S13(a). Clearly, the $R_{\text{rc}}$ of the P65-based device is higher than that of the other two HTM-based devices at different bias voltages. The larger $R_{\text{rc}}$ value indicates a retarded charge recombination loss between interfaces, which is in good accordance with the higher $J_{\text{SC}}$ and FF obtained by the P65-based devices. In addition, Fig. S13(b) shows the transient photovoltage decay in the PSCs under open-circuit conditions. In principle, a longer decay time implies a slower charge recombination. Hence, the P65-based hole transport layer can more efficiently suppress the surface charge recombination in solar cell devices.

Table 2
Photovoltaic parameters of the devices based on the dopant-free HTMs X65, P65, and Spiro-OMeTAD.

| HTMs      | Scan direction | $J_{\text{SC}}$ (mA/cm²) | $V_{\text{OC}}$ (V) | FF (%) | $\eta$ (%) |
|-----------|----------------|--------------------------|---------------------|--------|------------|
| X65       | Reverse        | 18.4                     | 0.98                | 46.8   | 8.4        |
|           | Forward        | 18.1                     | 0.91                | 39.7   | 6.5        |
| P65       | Reverse        | 21.7                     | 1.09                | 75.0   | 17.7       |
|           | Forward        | 21.7                     | 1.08                | 72.3   | 16.9       |
| Spiro-OMeTAD | Reverse      | 20.1                     | 1.04                | 51.0   | 10.6       |
|           | Forward        | 20.0                     | 1.01                | 47.7   | 9.7        |
The long-term stability of the unencapsulated devices was stored in an ambient atmosphere with a humidity of 40%–65% (Fig. 5a). After 30 days, the dopant-free P65-based PSC devices maintain 84% of the original PCE, whereas the doped Spiro-OMeTAD-based devices only retain 12% of the initial efficiency. The hydrophobicity of the hole transport layer is extremely important for the stability of a PSC because it can protect the perovskite layer against moisture. We further determined the hydrophobicity of P65, X65, and Spiro-OMeTAD layers through a contact angle measurement with water droplets, as shown in Fig. 5(b)–5(e). The P65-based hole transport layer exhibited the largest contact angle of close to 95° among all three materials, which indicates a good hydrophobic ability. This is also in good agreement with the device stability testing shown in Fig. 5(a). The much better stability of a dopant-free P65-based device can be attributed to its intrinsic hydrophobic property and the absence of hydrophilic additives. Consequently, a remarkable long-term stability along with a high PCE highlight the potential application of P65 as an efficient dopant-free HTM for use in future PSCs.

4. Conclusions

We successfully designed and synthesized a novel crosslinked polymer P65 through a mild free-radical polymerization with low-cost raw materials for application in conventional n-i-p type PSCs. The corresponding dopant-free PSCs based on P65 exhibit a maximum efficiency of 17.7%, which transcend the standard Spiro-OMeTAD-based devices (10.6%). The photo-electrochemical, opto-electronic, and thermal properties of the newly designed polymer were systematically investigated. Our study highlights the potential application of low-cost, polymeric, crosslinked, SFX-skeleton-based molecules as dopant-free HTMs for efficient and stable PSCs. This study also describes a new design strategy of SFX-based molecules and polymers for application in some other opto-electronic devices, such as OLEDs, perovskite-LEDs, and perovskite tandem solar cells. Future work will focus on the development of co-polymers by introducing another functionalized monomer into the X65 to further control the opto-electronic properties of the materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2020.06.062.

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Fig. 5. (a) Stability of unsealed PSCs based on dopant-free P65 and standard Spiro-OMeTAD with dopants, recorded in an ambient atmosphere with a humidity of 40%–65% under 100 mW/cm² AM 1.5G illumination for 30 day, and contact angle measurements of water droplets on a perovskite layer covered by HTM layers of (b) doped Spiro-OMeTAD, (c) dopant-free Spiro-OMeTAD, (d) dopant-free X65, and (e) dopant-free P65 samples, respectively.
