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A Simple Spiro-Type Hole Transporting Material for Efficient Perovskite Solar Cells

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We developed a cost-effective spiro-type 4,4',4'',4'''-(2H,2'H,4H,4'H-3,3'-spiro-bi[thieno[3,4-b][1,4]dioxepine]-6, 6',8,8'-tetrayl)tetrakis(N,N-bis(4-methoxyphenyl)aniline) hole transporting material (PST1) for perovskite solar cell (PSC) that works efficiently even without cobalt dopant. The PST1 is obtained by employing facile synthetic routes and tend to crystalize in solid state. An X-ray diffraction study of PST1 revealed a unique quasi-spiro molecular configuration and found multiple CH/ π and π - π intermolecular contacts. For the first time, the crystal structure of 2,2',7,7'-tetrakis(N,N'di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) is also studied for comparison. The device based on PST1 exhibited PCE of 13.44%, and a comparable 12.74% PCE was achieved with its undoped form, which paves the way for developing new low cost hole transporting materials and final industrialization of perovskite solar cells.

Solar energy is a gifted source of renewable energy to meet the energy and environmental crisis in the near future. The dye sensitized solar cell (DSSC) is a promising and effective technology to harvest solar energy and convert it into electricity.¹⁻³ In these cells sensitizers are the materials used for harvesting the solar radiation and are the major component in determining the efficiency of the solar cells. The widely used light harvesting materials are organic dyes, inorganic complexes, quantum dots etc.4 Recently, light absorbers based on lead halide perovskite materials exhibit broad absorption in the solar spectrum and excellent charge carrier mobility making them as all-round player in the so called perovskite solar cell (PSCs).⁵⁻⁸ The long term stability of DSSC and PSC focuses on complete solid state device in which the p-type solid state hole transporting materials (HTM) is applied.9-12 PSC devices based on the state-of-the-art spiro-OMeTAD (Figure 1c) as hole transporting materials have shown tremendous advancement in

energy conversion efficiency starting from 3.8 % to reaching 20.1% till date.^{7,13–21} So far improvement of the efficiencies of PSCs mainly relies on employing various device fabricating methods, elaborate engineering of perovskite morphology and composition.^{18,22,23} Recently, to further decrease the cost of the perovskite solar cell and facilitate the large scale application of the new technology, efforts have been made to replace the commonly used spiro-OMeTAD HTM due to its complicated synthesis and purification steps.^{24–26} In this light, several new types of HTM based on small organic molecules, polymers and inorganic salts providing reasonable efficiencies have been reported.^{12,27–39} Among the different types of HTM, small molecules hold advantages over polymer materials due to their easy and convenient synthesis that compatible for large scale manufacturing, high purity with good yield, easy characterisation of molecular structure with definite molecular weight, and ease of infiltration into the nanostructured materials, etc.^{38,40} However, molecular HTM candidates that can compete with commercial Spiro-OMeTAD is rare. Recently Seok et. al. have modified the Spiro-OMeTAD by changing the position of methoxy substituents and achieved a record efficiency of 16.7 %, which infers the potential advantage of spiro-type molecules over other small molecules.⁴¹ In this context, developing new spiro-type molecules with easy and convenient synthetic methods is a great challenge, which will overcome cost factors for large scale applications of solid state solar cells. Based on this premise, in this communication, we report a new class of spiro-type hole transporting material afforded by facile synthetic steps. Photophysical, electrochemical characterizations and X-ray crystallography of **PST1** are running in parallel with that of Spiro-OMeTAD. By employing this new molecule as HTM, the champion PSC device achieved 13.44 % PCE in the presence of ptype dopant. More importantly, the p-type dopant free devices with the new HTM achieved slight lower PCE of 12.7 %, which is commensurate with the performance of spiro-OMeTAD in the presence of dopant.





Figure 1. (a) Chemical structure of **PST1**; (b) ORTEP drawings and perspective views of **PST1** determined by X-ray crystallography with 20% probability thermal ellipsoids. (Hydrogen atoms omitted for clarity); (c) Chemical structure of state-of-the-art HTM spiro-OMeTAD; (d) ORTEP drawings and perspective views of spiro-OMeTAD determined by X-ray crystallography with 50% probability thermal ellipsoids. (Hydrogen atoms omitted for clarity)



Figure 2. (a) View down the b axis of the stacking molecules of **PST1**; (b) Dashed red lines illustrate CH/π hydrogen bonds and $\pi-\pi$ short contacts observed in crystal of **PST1** (ca. 2.8 Å and 3.25 Å). (c) View down the b axis of a unit cell of spiro-OMeTAD; (d) Dashed red lines illustrate $\pi-\pi$ short contacts (ca. 3.39 Å and 3.09 Å).

The chemical structure of PST1 is displayed in Figure 2a and the synthetic route is given in the supporting information (ESI). Synthesis of PST1 starts with the reaction of 3,4-dimethoxythiophene with pentaerythritol to form spirobipropylenedioxythiophene as the spiro-type core, which undergoes

bromination reaction with NBS to form the tetrabrominated intermediate (BTS). Following a four-fold Suzuki reaction between BTS and boronic acid pinacol ester of bis(4-methoxyphenyl)aniline (OMT-BPin), the final product PST1 is received with 60 % yield.

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amorphous solid.

As shown in Figure 1b, X-ray diffraction analysis unambiguously clarified the structure of PST1. The tetrahedral sp3 hybridized carbon in between the two propylenedioxythiophenes adopts a spiro conformation. However, the two seven-membered alkylenedioxy rings are large enough to smooth away the distortion. Therefore, although the four carbon atoms directly connecting to the spiro carbon do not lie in a plane, the two thiophene rings and four oxygen atoms are almost coplanar. This is completely different from the spiro-OMeTAD, which shows an absolutely non-coplanar spiro structure due to the two orthogonally interconnected fluorenes. (Figure 1d) At the four ends of both molecules, the propeller-shaped MeO-triphenylamine (MeO-TPA) derivatives give the same types of distortion. The measured dihedral angle between the two thiophene rings in the core of PST1 is merely 7° compared to 89.94° between the two fluorenes planes in spiro-OMeTAD. (Figure S1) The quasiplanar core of **PST1** will induce stronger intermolecular interaction

PST1 was found to crystallize in the monoclinic space group Cc. In the crystal lattice, the PST1 molecules forms alternately inter-embedded columns along the b axis, with four OMe-TPA moieties as redox centre's from one molecule overlapped with another eight OMe-TPA counterparts from four molecules of two adjacent columns. (Figure 2a) When observing the crystal perpendicular to the bc plane, CH/ π hydrogen bonds and π - π short contacts were observed between the OMe-TPA moieties and with thiophene rings of nearby molecules. Mean interaction distances of 2.8 Å and 3.25 Å are measured for CH/ π interaction and π - π interaction respectively (Figure 2b). In contrast, spiro-OMeTAD

than that of spiro-OMeTAD, which normally presents as an

crystallize in the triclinic space groups P1, of which the crystal packing's are also shown in Figure 2. There are two independent molecules in one unit cell. Due to the highly non-coplanar molecular geometry, the two molecules are well separated and no direct short contacts is measured between them. To fill the space, solvent molecules are therefore inserted which bind them together via CH/π hydrogen bonds. (Figure 2c) Although there are no contacts between the two molecules in one unit cell, each of the two molecules has multiple short contacts with molecules from surrounding unit cells including CH/ π hydrogen bonds, oxygen-carbon and π - π short contacts. (Figure S2) The shortest π - π contact between two fluorene planes is measured to be 3.09 Å, which is exceptionally close given the fact that there is almost no π overlap between the two fluorene structures. (Figure 2d) To the best of our knowledge, this is the first report on the crystal structure and packing of spiro-OMeTAD, which is nowadays the star molecule in perovskite photovoltaic community. In both HTM crystals, the abundance of short contacts provides ample channels for charge transport among the HTM molecules.

The UV-Vis absorption spectrum of PST1 in dichloromethane (DCM) is depicted in Figure 3a. PST1 shows two absorption bands in the UV region at 300 and 396 nm, which is red shifted by 25 nm compared to the absorption band edge of spiro-OMeTAD. In Figure 1a, the absorption spectrum of PST1 in thin film state is also displayed, the maximum absorption of which is red shifted by 38 nm compared to the solution state due to the presence of intermolecular π - π stacking. However there is no change in the absorbance of spiro-OMeTAD in the solid state compared to that of its solvated state as observed in the literature indicating the complete amorphous characteristic of spiro-OMeTAD.²⁶



Figure 3. (a) Normalised absorption spectra of PST1, Spiro OMeTAD in DCM and PST1 in solid state. (b). Absorption spectra of PST1 in the presence of various doping ratio (5%, 10%, 15%, 20% and 25%) of FK209.

Earlier reports emphasized that in the presence of p-type dopant such as Co (III) complex, spiro-OMeTAD reduces the Co (III) to Co (II) and itself is simultaneously oxidized to form spiro-OMeTAD[•]⁺, which can be detected by the formation of new absorption peaks in the visible region.⁴² In a similar way, we analysed the absorption changes of PST1 in the presence of p-type dopant (tris[2-(1H-pyrazol-1-yl)-4-tert-butylpyridine]cobalt (III) tris(bis(trifluoromethylsulfonyl) imide) FK209. Figure 3b shows the UV/vis absorption of PST1 in the absence and presence of various concentrations of dopant. On increasing the percentage of dopant, the absorption band of PST1 at 396 nm is decreasing with the formation of two new absorption bands around 590 and 640 nm in the visible region, which correspond to the mono-cation radical of PST1. The formation of cation radical reveals the effective doping of PST1 by FK209, which is believed to create additional charge carriers (holes) leading to an increased charge carrier density.



Figure 4. Cyclic voltammogram of PST1 and spiro-OMeTAD in dichloromethane solvent.

Cyclic voltammetric measurements were carried out to analyse and compare the energy levels of the new HTM with spiro-OMeTAD for the favourable hole injection process from the perovskite layer. For better comparison of energy levels of PST1 with spiro-OMeTAD, we have measured the cyclic voltammogram of both the HTMs under the same condition with ferrocene as internal standard and displayed in Figure 4. PST1 exhibits two

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reversible oxidation peaks indicating their electrochemical stability. The HOMO value of PST1 is calculated to be -5.15 eV, which is slightly lower than that of spiro-OMeTAD (-5.07 eV)⁴³ and more positive than the perovskite revealing the favourable hole transfer from the perovskite to the PST1 (Figure 5). It is worth noting that the HOMO of PST1 is 80 mV lower than that of spiro-OMeTAD, which may assist in gaining higher open circuit potential of the devices. Figure S3 displays the thermal behaviour of the PST1 measured by differential scanning calorimetry (DSC). The DSC trace shows that replacing the spiro-bifluorene linkage of spiro-OMeTAD⁴³ with spiro-bipropylenedioxythiophene groups (PST1) substantially increase the Tg and Tm to 175 °C and 280 °C, respectively (Table 1). This is in agreement with the crystallography study, which disclosed a partial coplanar structure and multiple close interactions between the molecules of PST1.



Figure 5. Energy level diagram of the perovskite and hole transporting materials

Table 1. Summary of the electrochemical, photophysical, and thermal properties of the HTMs used in this study

HTM	HOMO (eV) ^a	LUMO (eV) ^b	$E_{opt. gap}$ (eV) ^c	UV (nm)	Tg $(^{o}C)^{d}$	Тт (°С) ^d
Spiro- OMeTAD	-5.07	-2.09	2.98	309, 389	125 ^e	248 ^e
PSTI	-5.15	-2.40	2.75	300, 396	175	280

^{*a*} Determined by solution-based cyclic voltammetry (CV). ^{*b*} LUMO = HOMO + $E_{opt. Gap.}$ ^{*c*} Determined at the UV absorption onset. ^{*d*} Determined by DSC. ^{*e*} see ref.41.

Photovoltaic performance of the perovskite solar cell by employing PST1 as HTM is analysed by J-V and IPCE measurements. The solar cells were fabricated comprising FTO/TiO₂/CH₃NH₃PbI₃/PST1/Au in the presence of LiTFSI and *t*BP as additives and with FK209 as dopant in the HTM layer. Figure 6 displays the cross section image of a typical perovskite solar cell analysed through high resolution scanning electron microscope (HRSEM). The optimized device can be seen to be clearly composed of a 450 nm thick dense and mesoporous TiO₂ layer infiltrated with perovskite on FTO, a 210 nm PST1 layer, and an 80 nm thermally evaporated Au layer as the back contact. Page 4 of 7



Figure 6. SEM cross sectional image of the perovskite solar cell made with PST1 as HTM.

For comparison, photovoltaic measurement of perovskite solar cells fabricated with the commercial spiro-OMeTAD as HTM was also performed under similar conditions. Figure 7a displays the current-voltage curves of perovskite solar cells utilizing PST1 as HTM and the average photovoltaic parameters measured under simulated AM 1.5 G illumination at an intensity of $\sim 100 \text{ mW cm}^{-2}$ are summarized in table 2. The device with PST1 shows J_{SC} of 17.63 mA/cm² with open circuit potential (V_{OC}) of 1.02 V and a fill factor (FF) of 0.73 and results in an overall power conversion efficiency of 13.44 %. Under similar conditions, the device with spiro-OMeTAD as HTM produces a comparable PCE of 12.16%. A higher V_{OC} with PST1 based device is responsible for the slightly higher PCE than that of Spiro-OMeTAD based device, which can be related to the difference in their HOMO energy levels and proves again the possibility of Voc modulation by choosing HTMs with appropriate HOMO level. Figure S4 shows the incident to photocurrent conversion efficiency (IPCE) of the perovskite device employing PST1 as hole transporting material. It can be seen clearly that the device with PST1 has excellent PCE above 60% from the UV region to 800 nm. These results suggest that this new spiro-type molecule can be potential substituents for commercial Spiro-OMeTAD in high performance PSCs.

Motivated by the idea of further reducing the fabrication cost, we continued to fabricate the devices by removing the p-type dopant from both PST1 and spiro-OMeTAD based HTM layers. The corresponding J-V curves were displayed in Figure 7b and the photovoltaic parameters were summarized in table 2. Interestingly, after removing the dopant from PST1, the J_{SC} increased by 1.6 mA, while the V_{OC} dropped by 87 mV with a FF of 0.695 leading to a comparable overall efficiency of 12.74 % to the undoped devices. Under similar conditions, however for spiro-OMeTAD based devices, Voc and FF dropped significantly and resulted in a PCE of 9.7%. This observation is in line with our earlier reports indicating the poor performance of spiro-OMeTAD in the absence of a p-type dopant.²⁷ It is worth noting that from the same batch of devices, the loss in the FF of dopant free PST1 based devices is much less and giving an comparable FF to that of doped spiro-OMeTAD. This result demonstrate that an effective molecular stacking is essential to facilitate the transport of the charges as seen from the crystal data of both HTM and reduce the dependence on various dopants. The stability of device performance was investigated when the devices (with two different types of HTM layer) were stored under ambient conditions without any type of encapsulation. Both sets of devices

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started to degrade after four days under these conditions, the average performance of the PST-based cells was slightly higher than that of the Spiro-OMeTAD-based devices within the period of evaluation. (Figure S8) The more compact crystalline nature of PST1 is supposed to be able to protect the perovskite layer better than spiro-OMeTAD



Figure 7. Current-voltage characteristics of the PST1 and Spiro-OMeTAD in the absence and presence of cobalt dopant FK209.

Table 2: Photovoltaic parameters from J-V measurements of perovskite devices with PST1 and Spiro-OMeTAD as HTM in the presence and absence of cobalt dopant FK209.

Condition	НТМ	Light Intensity (mW/cm ²)	Jsc (mA/cm^2)	Voc (mV)	FF	PCE (%)
With	PST1	98.1	17.63	1024	0.73	13.44
FK209	Spiro-OMeTAD	97.9	18.6	910	0.70	12.16
Without	PST1	98.2	19.21	937	0.695	12.74
FK209	Spiro-OMeTAD	99.6	19.43	798	0.615	9.57

In summary, we have designed and successfully prepared a spiro-type hole transporting material 4,4',4",4"'new (2H,2'H,4H,4'H-3,3'-spiro-bi[thieno[3,4-b][1,4]dioxepine]-6,6', 8,8'-tetrayl)tetrakis(N,N-bis(4-methoxyphenyl)aniline) (PST1) via facile synthetic route. Then the titled new compound was fully characterized and tested as hole transporting materials for perovskite based solar cells. Parallel X-ray crystallography study on single crystals of PST1 and Spiro-OMeTAD indicated completely different types of spiro configuration and found multiple CH/ π , O–C and π – π intermolecular short contacts. This is the first report on the crystal structure of Spiro-OMeTAD to show that dopant is essential due to lack of $\pi - \pi$ intermolecular stacking. The perovskite solar cell employing PST1 as HTM layer exhibited overall conversion efficiency of 13.44 %, which is comparable with that obtained using the spiro-OMeTAD under the same fabrication conditions. This can be partially attributed to the increased V_{OC} with PST1 as HTM layer, which has a lower HOMO level than that of spiro-OMeTAD. Only a marginal decrease in PCE was observed when cobalt dopant is removed from PST1 leading to a PCE of 12.7 %. This is remarkably in contrast to the performance drop to 9.57 % in the device made with spiro-OMeTAD under the same condition. To the best of our knowledge, this is the first report on a new spiro-type molecule for efficient perovskite solar cells. An evaluation of device stability with PST1 based perovskite solar cells signifies that this material will emerge as

potential HTM candidates for solid state photovoltaic applications. Molecular engineering of this spiro core to further improve energy conversion efficiencies is currently under investigation in our laboratory.

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Notes and references

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