Phenothiazine-Based Hole Transport Materials for Perovskite Solar Cells

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ABSTRACT: The promising photovoltaic solar cells based on the perovskite light-harvesting materials have attracted researchers with their outstanding power conversion efficiencies (over 23% certified). The perovskite work has geared up in just under a decade and is competing with well-established semiconductor technologies such as silicon (Si), copper indium gallium selenide (CIGS), and cadmium telluride (CdTe). To commercialize the perovskite solar cells, their stability is the major concern. To address the stability issue, several factors need to be taken into account, and one of them is developing stable hole transport materials (HTMs), which are the essential building blocks. In this mini-review, we will discuss the important features of the HTMs, such as design and development of phenothiazine-based HTMs. Since phenothiazine is a low cost and stable molecule compared to the spiro-OMeTAD, it can be modified further via molecular engineering.

INTRODUCTION

Due to the growth of the population and the increasing desire for a comfortable life, the demand for energy is very high. The present source of energy is based on fossil fuels. Considering the scarcity of fossil fuels, researchers are working toward renewable energy sources which are clean and green. In this regard, the contingent option for sustainable development of human society is the conversion of sunlight into electricity. The photovoltaic cell is efficient and a good candidate as a renewable energy source. Among the various photovoltaic technologies, dye-sensitized solar cells (DSSCs) have gained more attention from researchers by considering several properties like cost-effectiveness, easy fabrication, eco-friendliness, better stability, flexibility, and high power conversion efficiencies (PCEs). A breakthrough was made by O’Regan and Grätzel in 1991 with the PCE of 7%. Soon after, it reached 13% PCE with a zinc porphyrin photosensitizer and cobalt-based electrolyte system. The DSSC device is facing a stability problem because of the liquid electrolyte system, which does not allow for the commercialization and leads the research toward developing solid-state DSSCs (ssDSSCs). The first ssDSSCs with the heterojunction between the CuSCN and TiO₂ were reported by the Tennakone group. However, all efforts yielded lower PCE; therefore, it is essential to work toward the alternate materials and devices. The PCE of 2.56% was achieved by Bach and Grätzel in 1988 with the spiro-OMeTAD (2,2′-7,7′-tetrakis-(N,N-di-p-methoxy-phenyl-amine) 9,9′-spirobifluorene) as a hole conductor and Ru(II)₂(L₂(SCN))₂ (where L is 4,4′-dicarboxy-2,2′-bipyridyl) as a light harvester in ssDSSCs. However, the hole conductor is suffering from the charge combination rate and pore-filling factor. Some of the research groups address these drawbacks by minimizing the thickness of TiO₂. The PCEs of 3.8% and 6.5% were achieved with the device with CH₃NH₃PbI₃ as the photosensitizer and iodide/triiodide (I/I₃⁻)-based liquid electrolyte by Miyasaka and Park’s group. Using similar perovskite materials and the different hole conductor spiro-OMeTAD, in 2012 Kim’s group reported the PCE of 9.7% with the Jsc of 17 mA/cm², a Voc of 0.888 V, and a FF of 0.62. This was the first time the highest PCE with a spiro-OMeTAD-penetrated mesoscopic TiO₂ film based device was reported. Further, the PCE was shown to reach up to 10.9% by Snaith et al. Then the perovskite solar cells (PSCs) came into existence, where spiro-OMeTAD as a solid hole-transporting material (HTM) and perovskite as the light-harvesting material are used. It is noted that a huge enhancement in PCE is gained within a decade (3.8% to 24.2%), which is competitive with the commercially available silicon solar cells.
The PSCs have unique properties like better molar extinction coefficients, good charge carrier mobility, tunable band gaps, and effective temperature processability. Tremendous research is being conducted for the advancement of perovskite light-harvesting material and fabrication techniques in PSCs. Generally, the PSC device architecture consists of the five components: transparent conductive oxide layer (FTO conductive substrate), an electron-transporting layer (n-type mesoporous semiconductor metal oxide), light-harvesting material (perovskite), hole-transporting layer (spiro-OMe-TAD), and metal electrode (Au). The device architecture, different types of perovskite devices (Figure 1a-d), energy level diagram (e), energy levels of the existing HTMs (f), and crystal structure (g) are shown in Figure 1.

To improve the performance of the devices, we have to enhance the properties of the hole-transporting materials (HTMs). A lot of research is being done on the active layer and hole-transport layer (HTL) to produce stable PSCs for its commercialization. HTMs are crucial components for the PSCs to improve the PCE as well as stability. To become the
champion HTMs, they should possess the following properties: better photochemical and thermal stability, good alignment of the highest occupied molecular orbital (HOMO) for facile hole transfer, and better hole mobility. To date, spiro-OMeTAD is the champion HTM for the PSCs with the PCE over 20%. However, its synthesis is tedious and costly, and hole mobility is low (∼$10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$), which inhibits poor device performance, thereby limiting the scope of commercialization. To make PSCs a commercial product in the market, many research groups are working on the HTMs, which are essential for better stability and high PCE. Until now, various organic HTMs are studied with the spirobi[b]fluorene cores, triphenylamine, tetraphenyl, 3,4-ethylenedioxythiophene, bi[b]fluorene, carbazole, and tetrathiafulvalene.11

Among them, recently, phenothiazine (PTZ)-based HTMs came into the picture for PSCs and were shown to be a good candidate for the PSCs which have also shown good performance in DSSCs. Phenothiazine is a well-known electron-rich heterocyclic compound inbuilt with the heteroatom ‘s nitrogen and sulfur. It can produce a stable radical cation with reversible oxidation and low potential.12 The phenothiazine exists in the butterfly confirmation, which prevents molecular aggregation, and good hole-transport capability encouraged their identity in the DSSCs,13 OLEDs, and OPVs.14 The optical properties are also affected by the degree of disorder in phenothiazine film and molecular aggregation.15,16 In this mini-review, we have discussed the optical, electrochemical, and photovoltaic properties of phenothiazine-based small-molecule HTMs.

In 2018, the Wang group reported three D–A–D HTMs with a dithienopyrrolobenzothiadiazole (DTPBT) core with end group triarylamine, a phenothiazine (PTZ), and alkoxytriarylamine termed as HZ1, HZ2, and HZ3, respectively (Figure 2). Among them, the HZ2 contains the donor group phenothiazine, which shows the highest PCE of 14.2% with the $J_{sc}$ of 20.43 mA cm$^{-2}$, $V_{oc}$ of 1.026 V, and FF of 68%, and better stability (over 280 h at a dehumidification wardrobe with 20% relative humidity without encapsulation) compared to the HZ1 (7.0%), the HZ2 (10.2%), and close to the state-of-the-art spiro-OMeTAD (14.9%). It is a well-known fact that the phenothiazine moiety will be planar in geometry, which is in favor of intermolecular stacking. The large $\pi$-conjugated DTPBT/PTZ made a possible way to get better hole mobility and conductivity. The HTM HZ2 was shown to have a little higher conductivity (3.2 $\times$ $10^{-4}$ S cm$^{-1}$) and hole mobility ($4.80 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) than the spiro-OMeTAD. The fill factor is also responsible for the good photovoltaic performance, which was influenced by the shunt resistance ($R_{sh}$) and series resistance ($R_{s}$). The observed $R_{sh}$ was 2.08 kΩ cm$^2$ for HZ2 which is higher than the HZ1 and HZ3 and resulted in the enhancement of the short-circuit current of the HZ2. The HZ2 showed the $R_{s}$ of 9.6 Ω cm$^2$, which is smaller than other devices HZ1 and HZ3. The nanosecond absorption spectroscopy (ns-TAS) showed a $\tau_{TAS}$ value of 139 ns for the HZ2. These values are a little less than the spiro-OMeTAD ($\tau_{TAS}$ of 148 ns).17

Gritzel et al. developed three HTMs with PTZ moiety attached by the double bonds with the end groups (4,4-dimethyltriphenylamine (Z28), N-ethylcarbazole (Z29), and 4,4-dimethoxytriphenylamine (Z30)) (Figure 3). The HTMs were affordably synthesized in three simple steps including electrophilic substitution followed by the Vilsmeier and Witting reactions. All the HTMs showed intramolecular transitions (ICT) around 400–450 nm. The Z29 showed a blue shift compared to the Z28 and Z30, because of the lower conjugation. The HOMO values of Z28, Z29, and Z30 are $-5.93$ eV, $-5.44$ eV, and $-5.27$ eV, respectively, which are higher than the double cation perovskite ($-5.5$ eV). The LUMO values were found at $-2.83$ eV, $-2.82$ eV, and $-2.73$ eV, respectively, and well-

Figure 3. Molecular structures of Z28, Z29, and Z30 (reproduced with permission from ref 18).
The hole mobility was measured using the space charge limited current (SCLC). The hole mobility of the Z28, Z29, and Z30 was found to be $6.18 \times 10^{-5}$, $6.82 \times 10^{-6}$, and $6.70 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The highest PCE of 19.17% with the $J_{sc}$ of 23.53 mA cm$^{-2}$, $V_{oc}$ of 1.114 V, and FF of 0.73% was observed in Z30 compared to the Z28 PCE of 17.77% (J$sc$ of 23.01 mA cm$^{-2}$, V$oc$ of 1.087 V, and FF of 0.60%) and Z29 (J$sc$ of 22.35 mA cm$^{-2}$, V$oc$ of 1.114 V, and FF of 0.73%) (Figure 4). The Z28 showed lower PCE because of the HOMO energy level, which was because the double cation perovskite leads the insufficient driving force of hole injection and less hole mobility. The overall conclusion was that the PCE was affected by the conjugation of the molecular structures. The HTM Z30 containing the highly conjugated 4,4-dimethoxytriphenylamine showed better PCE, and Z28 consists of the less conjugated peripheral group (N-ethylcarbazole), leading to lower PCE. The same strategy was followed in the stability studies also.

The research group of Roberto Grisorio synthesized two HTMs with the PTZ core attached by the donor group’s diarylamine (PTZ1) and triarylamine (PTZ2) (Figure 5). They concluded that the optical and photovoltaic properties of the PSCs are mostly affected by the small variation in the molecular design. The molecules were synthesized by the well-known synthetic steps such as Buchwald–Hartwig and Suzuki–Miyaura cross-couplings with the synthesis cost of PTZ1 ($111.90 \$/g) and PTZ2 ($156.76 \$/g), which are much less than that of spiro-OMeTAD ($\sim 600 \$/g).

The absorption maxima were found for PTZ1 at 282 nm with a shoulder peak at the longer wavelength, and for PTZ2 it was observed at 308 and 332 nm. For PTZ1 and PTZ2, HOMO values were found at $-4.77$ and $-5.15$ eV, respectively, following the same conditions as the spiro-OMeTAD, showing $-5.02$ eV.
PTZ2 showed higher $V_{oc}$ due to the favorable oxidation potential. The stability studies revealed that PTZ2 (359 °C) is more stable compared to PTZ1 (416 °C) with the $T_g$ of 74 and 135 °C (Figure 6). The PSC device of the double cation mixed halide perovskite with PTZ1, PTZ2, and spiro-OMeTAD showed the $J_{sc}$ of 4.2, 21.1, and 21.6 mA/cm$^2$, a $V_{oc}$ of 0.82, 1.11, and 1.15 V, and FF of 0.61, 0.75, and 0.71 along with a PCE of 2.1%, 17.6%, and 17.7%, respectively.\textsuperscript{19}

Salunke’s group developed a similar molecular design of PTZ2 and Z30 using low-cost two-phenothiazine-based HTMs (AZO-I and AZO-II) functionalized with azomethine moieties (Figure 7). These HTMs are synthesized via Schiff base chemistry which is an eco-friendly, simple Pd-free synthetic route. The AZO-I and AZO-II are the least costly phenothiazine-based HTMs to date (9 and 12 $$/\text{gram})$. The PTZ2 and Z30 were prepared by the Pd-catalyzed Suzuki coupling and yielded 24.9% and 27.7%. In case of the AZO-I and AZO-II, they are synthesized by the Pd-free synthetic route with 51% and 40% yield, respectively. Due to the length of conjugation, $\lambda_{\text{max}}$ was red-shifted in the DCM solvent (AZO-II: 453 nm, AZO-I: 422 nm). The HOMO values of the AZO-I, AZO-II, and spiro-OMeTAD were $-4.97$, $-4.94$, and $-4.80$ eV, respectively, which are well aligned with the mixed cation perovskite. The stability studies revealed that the AZO-II is stable up to 405 °C with the $T_g$ at 120 °C, and AZO-I was up to 392 °C with the $T_g$ at 85 °C. The higher $T_g$ was found in the AZO-II because of the high molecular weight and stiffness. The HTM AZO-II showed higher hole mobility ($2 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$) compared to the AZO-I ($2 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) due to the two-electron-donating triarylamine groups on the phenothiazine core.\textsuperscript{20}

The PSC devices (ITO/SnO$_2$/C$_{0.8}$MA$_{1-x}$FA$_x$PbI$_{3-}\gamma$Cl$_{\gamma}$/HTM/Au) with the HTMs AZO-I and AZO-II exhibited a PCE of 14.3% and 15.6%, with the $J_{sc}$ of 20.1 mA cm$^{-2}$ and 21.6 mA cm$^{-2}$, $V_{oc}$ of 1.00 and 0.95 V, and FF of 0.66 and 0.71, respectively. In AZO-I, the interaction with the perovskite was
poor because the high hysteresis resulted in a low PCE. In similar conditions, the champion HTM spiro-OMeTAD showed a PCE of 19.3% with the $J_{sc}$ of 23.4 mA cm$^{-2}$, $V_{oc}$ of 1.04 V, and FF of 0.74 (Figure 8).

Recently, Cheng et al. developed two novel phenothiazine 5,5-dioxide (PDO) based low-cost ($62.1791$ $/$ g and $61.2761$ $/$ g) HTMs. In PDO1, the PDO N-position with anisole and the PDO2 N-position with 4,4$'$-dimethoxytriphenylamine and 4,4$'$-dimethoxydiphenylamine are the end groups (Figure 9). These are synthesized by the Buchwald–Hartwig reaction followed by the radical substitution and oxidation. The conversion of PTZ to PDO has resulted in a better charge affinity of the moiety. The $\lambda_{max}$ was observed at around 350 nm, and HOMO energy levels were calculated as $-5.25$ and $-5.24$ eV vs vacuum, for the PDO1 and PDO2, respectively, revealing that the substitution at the N-site of the PDO moiety will not be affected more on the optical properties.21

The PDO moiety was found as a twisted butterfly and planar conformation with the monoclinic space group $C2/c$ and $I2/a$ in PDO1 and PDO2, respectively. The device was fabricated with the mixed cation and halide perovskite (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ as the light-harvesting material and PDO1 and PDO2 as the HTMs under simulated AM 1.5 G (100 MW cm$^{-2}$). The observed $J_{sc}$ of 22.6 mA cm$^{-2}$ and 23.9 mA cm$^{-2}$, $V_{oc}$ of 1.08 and 1.15 V, and FF of 68.3 and 73.6 with a PCE of 16.7% and 20.2% for the PDO1 and PDO2, respectively.

Figure 8. (a) Current density–voltage ($J$–$V$) curves for perovskite solar cells (reverse scans) measured with a scan rate of 10 mV/s under AM 1.5G simulated solar light illumination by using spiro-OMeTAD, AZO-I, and AZO-II as HTMs. PCE (b), $J_{sc}$ (c), FF (d), and $V_{oc}$ (e) distributions of PSC devices based on different HTMs (figure adapted from ref 20).

Figure 9. Molecular structures of the PDO1 and PDO2 (reproduced with permission from ref 21).
Figure 10. $J$–$V$ characteristic curves of the PSCs contain (a) PDO1, (b) PDO2, and (c) spiro-OMeTAD as HTMs, (d) IPCE spectra of PSCs containing PDO1, PDO2, and spiro-OMeTAD as HTMs, (e) steady-state power outputs at the maximum point, and (f) statistics of PCE for PSCs containing PDO1 and PDO2 as HTMs (figure adapted from ref 21).

Figure 11. Molecular structures of the HTMs (reproduced with permission from ref 22).
The hysteresis index values were 0.025 and 0.016% observed from the scan of open circuit (OC) to short circuit (SC) (Figure 10). Under the similar conditions the spiro-OMeTAD resulted in a PCE of 19.8% with the $J_{sc}$ of 24.2 mA cm$^{-2}$, $V_{oc}$ of 1.14, and FF of 71.1 and hysteresis index of 0.020%. The best efficiency was observed for the PDO2, which has a planar structure of the PDO core and good molecular stacking behavior. The successful molecular engineering of the HTMs with the conversion of the PDO core and good molecular stacking behavior. The successful FF of 71.1 and hysteresis index of 0.020%. The best electron mobilities of 2.1 cm$^2$ V$^{-1}$ s$^{-1}$ for BDT-POZ, BDT-PTZ, and PTAA showed hole mobility respectively. The MAPbI$_3$/BDT-POZ showed less PL, due to suggesting the best hole extraction efficiency, $\lambda_{max}$ was noted at around 440 nm, and BDT-POZ was red-shifted compared to the BDT-PTZ in the case of the solution and solid phase. The HOMO and LUMO values were calculated as $-5.42$ eV, $-5.35$ eV and $-2.81$, $-2.78$ eV for BDT-PTZ and BDT-POZ, respectively, which are well-matched with the MAPbI$_3$ energy level.

By using the SCLC method, the hole-based device (indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS)/HTM/MoO$_3$/Ag) and the HTMs BDT-PTZ, BDT-POZ, and PTAA showed hole mobilities of $2.1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, $9.8 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, and $4.1 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, and the BDT-POZ showed nearly two-times higher hole mobility compared to the BDT-PTZ and five times more than the PTAA because of the smaller N−N distance between redox centers and proper molecule packing. To know the hole extraction behaviors, steady-state and transient photoluminescence (PL) spectra were recorded for perovskites, BDT-POZ, BDT-PTZ, and bare glass. The strong steady PL peak of MAPbI$_3$ is clearly observed in the MAPbI$_3$/glass, and when coming to the MAPbI$_3$/BDT-PTZ, the peak intensity was decreased compared to the MAPbI$_3$/BDT-POZ, suggesting the best hole extraction efficiency compared to the MAPbI$_3$/BDT-PTZ. This is further confirmed by TRPL, and the average PL lifetimes of 114.9, 42.1, and 25.8 ns were found from MAPbI$_3$/glass, MAPbI$_3$/BDT-PTZ, and MAPbI$_3$/BDT-POZ, respectively. The MAPbI$_3$/BDT-POZ showed less PL, due to the better charge carrier ability (Table 1). In order to know the suitability of the HTM, the device architecture with the ITO/HTM(BDT-PTZ) and BDT-POZ as dopant-free HTMs/MAPbI$_3$/[6,6]-phenyl-C(61)-butyric acid methyl ester/bathocuproine/Ag was fabricated. The inverted device with 4 mg mL$^{-1}$ of BDT-POZ resulted in $J_{sc}$ of 22.46 mA cm$^{-2}$, $V_{oc}$ of 0.96 V, FF of 84.4%, and overall PCE of 18.20%, and a concentration increase of up to 8 mg mL$^{-1}$, the small increment of the $J_{sc}$ from 22.46 to 22.56 mA cm$^{-2}$, $V_{oc}$ from 0.96 to 1.04 V, and a slight decrease in FF from 84.4% to 81.7% were observed. The p-i-n device with the optimized concentration and dopant-free BDT-PTZ, BDT-POZ, and PTAA resulted in the $J_{sc}$ of 22.43, 22.56, and 22.26 mA cm$^{-2}$, $V_{oc}$ of 1.02, 1.04, and 1.08 V, FF of 79.8, 81.7, and 74.2%, and the overall PCE of 18.26, 19.16, and 17.85%, respectively, under AM 1.5 G illumination with the small hysteresis (Figure 12).

Robertson et al. reported triphenylbenzene (TPB) core based HTMs, 1,3,5-tris(2’-(N,N-di(4-methoxyphenyl)amino)-phenyl)benzene (TPB(2-MeOTAD)) and 1,3,5-tris(2’-(N-phenothiazoyl)phenyl)benzene (TPB(2-TPTZ)) (Figure 13). First, they replaced the 4,4’-dimethoxydiphenylamine with the PTZ unit. The synthesis involved a low cost two-step starting material,1,3,5-tris(2-bromophenyl)-benzene that was prepared using the aldol condensation and Buchwald−Hartwig coupling, resulting in the final HTMs with notable yields (73% and 50%) and with the cost of 12.98 $ g$^{-1}$ and 3.09 $ g$^{-1}$, respectively. The manufacturing cost is less than the standard spiro-OMeTAD (100 to 400 $ g$^{-1}$). The absorption spectra were recorded in the DCM solvent. The absorption maxima of the TPB(2-TPTZ) were shifted 23 nm toward the red region (323 nm) compared to the 4,4’-dimethoxydiphenylamine-substituted TPB(2-MeOTAD). The calculated HOMO values were −5.29 eV and −5.34 eV, respectively, which are lower than the −5.44 eV (spiro-OMeTAD) and matched with a perovskite (MAPbI$_3$) valence bond for smooth hole injection. The HTMs are stable up to around 120 °C, and $T_d$ values of TPB(2-MeOTAD) and TPB(2-TPTZ) were observed at 89 and 110 °C, respectively, and at 122 °C for spiro-OMeTAD. In order to investigate the performance of SFX-MeOTAD as a hole transport material in perovskite solar cells, the FTO/ZnO-Mg-EA(NH$_3$)$_2$)/m-TiO$_2$/MAPbI$_3$/HTM were fabricated and compared with spiro-OMeTAD.

The overall PCEs of TPB(2-MeOTAD) and TPB(2-TPTZ) were 12.14% and 4.32% with the $J_{sc}$ of 19.32 and 8.89 mA cm$^{-2}$, $V_{oc}$ of 0.97 and 0.88 V, and the FF of 64.54% and 55.30%, respectively. The state-of-the-art spiro-OMeTAD yielded a PCE of 18.04%. The TPB(2-TPTZ) showed lower efficiency with higher stability. The stability studies were performed using a dry and dark box, at 25 °C, and the relative humidity was 30%. The initial PCEs of 85% (TPB(2-TPTZ)), 75% (TPB(2-MeOTAD)), and 72% (spiro-OMeTAD) were retained over 300 h, respectively. The faster degradation was observed in TPB(2-TPTZ) (85%), which consisted of hydrophilic dimethoxy diphenylamine as a side chain and better stability observed due to the hydrophobic nature of the phenothiazine.

To reduce the cost of the HTMs, Robertson developed a series of spiro[fluorene-9,9’-xanthene] SFX-based HTMs, SFX-TAD, SFX-TCz, SFX-TPTZ, and SFX-MeOTAD (Figure 14). These HTMs were synthesized using the Buchwald−Hartwig amination reaction between 2,2’,7,7’-tetrabromo-spiro-fluorene-9,9’-xanthene) in very good yields of 71%, 56%, 35%, and 83%, respectively. The UV−visible spectra were measured in the presence of the DCM solution. There were two absorption bands observed at 307, 367, 307, 379, 291, and 340 nm, for the SFX-MeOTAD, SFX-TAD, and SFXTCz, while SFX-TPTZ showed one broad absorption peak at $\lambda_{max}$ = 310 nm. From the cyclic voltammetry studies, the HOMO value was determined as −5.34, −5.70, and −5.39 eV for SFX-TAD, SFX-TCz, and SFX-TPTZ and as −5.1 eV for SFX-MeOTAD, which was similar to the spiro-OMeTAD (Figure 15). The lower HOMO of the SFX-TAD and SFX-TPTZ resulted in the high $V_{oc}$.

### Table 1. Parameters of Lifetimes ($\tau$) and Weight Fractions (A) Derived from TRPL Decay Studies

| HTM          | $\tau_1$ (ns) | $A_1$ (%) | $\tau_2$ (ns) | $A_2$ (%) | $\tau_{avg}$ (ns) |
|--------------|--------------|-----------|--------------|-----------|------------------|
| no HTM       | 114.9        | 100       | -            | -         | 114.9            |
| BDT-PTZ      | 46.4         | 32.3      | 2.37         | 67.7      | 42.1             |
| BDT-POZ      | 31.2         | 24.4      | 2.31         | 75.6      | 25.8             |

https://doi.org/10.1021/acsomega.0c00065
ACS Omega 2020, 5, 5608−5619
The XRD study reveals that all HTMs were well crystallized in monoclinic C2/c (SFX-TPTZ), triclinic space group P1 (SFX-MeOTAD), and orthorhombic Pbca (SFX-TCz). The three hydrogen bonds are formed in the SFX-MeOTAD with lengths of 2.549 Å and 2.572 Å for OMe−OMe and 2.522 Å for CHO (xanthenes). The dihedral angles 87.54°, 88.89°, and 87.57° were found between xanthenes and fluorene moieties for SFX-MeOTAD, SFX-TPTZ, and SFX-TCz, which are similar to spiro-OMeTAD (89.94°). The thermal study (differential scanning calorimetry) data revealed that the Tg value was observed at 270°C for SFX-TPTZ and SFX-TCz and at 122°C, 118°C, and 108°C for spiro-OMeTAD, SFX-TAD, and SFX-MeOTAD, respectively.

To calculate the efficiency, the device with glass/FTO/compact TiO2/mesoporous Al2O3/CH3NH3PbI3−xClx/HTM/Au and SFX-MeOTAD exhibited the PCE of 12.4%, near the spiro-OMeTAD PCE of 13.0%, and showed higher Voc and less Jsc and FF compared to others. The hole mobility of SFX-MeOTAD (1.6 × 10−5 m2 V−1 s−1) was also similar to the spiro-OMeTAD (1.4 × 10−5 m2 V−1 s−1), respectively.

Zhao’s group designed and developed the SFX core-based HTMs termed as SFX-PT1 and SFX-PT2 along with the spiro-PT. The HTMs SFX-PT1 and SFX-PT2 were prepared by the Buchwald−Hartwig amination in good to excellent yield (Figure 16). The λmax was found at around 321 nm for both SFX-PT1 and SFX-PT2, while spiro-PT showed 313 nm (Figure 17). The cyclic and differential pulse voltammetry studies were recorded to know the HOMO level of HTMs. The HOMO values were observed as −5.08 eV, −5.20 eV, and −5.33 eV for SFX-PT1 and SFX-PT2, while spiro-PT showed 313 nm (Figure 17). The cyclic and differential pulse voltammetry studies were recorded to know the HOMO level of HTMs. The HOMO values were observed as −5.08 eV, −5.20 eV, and −5.33 eV for SFX-PT1, SFX-PT2, and spiro-PT, respectively. Spiro-PT, SFX-PT1, and SFX-PT2 possess higher decomposition temperatures (Td) and...
$T_g$ of 324 °C, 435 °C, 421 °C, 110 °C, 153 °C, and 148 °C, respectively. The hole mobilities of the SFX-PT1, SFX-PT2, and spiro-PT are calculated as $2.08 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, $2.76 \times 10^{-4}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, and $1.29 \times 10^{-4}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The hole mobility of SFX-PT1, SFX-PT2, and spiro-PT can be calculated as

$$\mu = \frac{q}{e} \frac{L}{W} \frac{1}{V} \frac{I}{V}$$

where $q$ is the charge, $e$ is the electron charge, $L$ is the channel length, $W$ is the channel width, $V$ is the applied voltage, $I$ is the current, and $\mu$ is the hole mobility.

Table 2. Optical and Photovoltaic Properties of the HTMs

| HTM            | HOMO (eV) | LUMO (eV) | $E_{opt}$ (eV) | hole mobility (cm$^2$ V$^{-1}$ s$^{-1}$) | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) | ref |
|----------------|----------|----------|---------------|----------------------------------------|-------------------------|--------------|----|---------|-----|
| HZ1            | −5.29    | −3.00    | 2.29          | $3.49 \times 10^{-4}$                  | 18.30                   | 0.82         | 46 | 7.0     | 17  |
| HZ2            | −5.30    | −3.04    | 2.26          | $4.06 \times 10^{-4}$                  | 20.43                   | 1.02         | 68 | 14.2    | 17  |
| HZ3            | −5.22    | −2.94    | 2.28          | $6.18 \times 10^{-3}$                  | 19.44                   | 0.92         | 57 | 10.2    | 17  |
| Z28            | −5.39    | −2.83    | 2.56          | $6.82 \times 10^{-3}$                  | 23.01                   | 1.12         | 69 | 17.7    | 18  |
| Z29            | −5.44    | −2.82    | 2.62          | $6.70 \times 10^{-3}$                  | 23.53                   | 1.11         | 73 | 19.1    | 18  |
| Z30            | −5.27    | −2.73    | 2.54          | $7.00 \times 10^{-3}$                  | 23.53                   | 1.11         | 73 | 19.1    | 18  |
| PTZ1           | −4.77    | −1.74    | 3.03          |                                        | 4.2                     | 0.82         | 61 | 2.1     | 19  |
| PTZ2           | −5.15    | −2.39    | 2.76          |                                        | 21.1                    | 1.11         | 75 | 17.6    | 19  |
| AZO-I          | −4.97    | −2.67    | 2.30          | $2 \times 10^{-5}$                     | 20.1                    | 1.00         | 66 | 14.3    | 20  |
| AZO-II         | −4.94    | −2.74    | 2.20          | $2 \times 10^{-5}$                     | 21.6                    | 0.95         | 71 | 15.6    | 20  |
| PDO1           | −5.25    | −2.35    | 2.90          | $1.76 \times 10^{-4}$                  | 22.0                    | 1.08         | 68 | 16.7    | 20  |
| PDO2           | −5.24    | −2.67    | 2.57          | $5.93 \times 10^{-4}$                  | 23.9                    | 1.15         | 73 | 20.2    | 21  |
| BDT-PTZ        | −5.42    | −2.81    | 2.62          | $9.8 \times 10^{-3}$                   | 22.43                   | 1.03         | 79 | 18.2    | 22  |
| BDT-POZ        | −5.35    | −2.78    | 2.57          | $2.10 \times 10^{-4}$                  | 22.56                   | 1.04         | 81 | 19.1    | 22  |
| TPB(2-MeOTAD)  | −5.29    | −1.75    | 3.54          |                                        | 19.32                   | 0.97         | 64 | 12.1    | 23  |
| TPB(2-TPTZ)    | −5.34    | −2.02    | 3.32          |                                        | 8.89                    | 0.88         | 55 | 4.32    | 23  |
| SFX-MeOTAD     | −5.16    | −2.20    | 2.96          | $1.60 \times 10^{-5}$                  | 21.38                   | 0.98         | 59 | 12.4    | 24  |
| SFX-TAD        | −5.34    | −2.27    | 3.07          |                                        | -                       | -            | -  | -       | -   |
| SFX-TCz        | −5.70    | −2.31    | 3.39          |                                        | -                       | -            | -  | -       | -   |
| SFX-TPTZ       | −5.39    | −2.14    | 3.25          |                                        | -                       | -            | -  | -       | -   |
| SFX-PT1        | −5.08    | −1.93    | 3.15          | $2.08 \times 10^{-3}$                  | -                       | -            | -  | -       | -   |
| SFX-PT2        | −5.20    | −2.04    | 3.16          | $2.76 \times 10^{-4}$                  | -                       | -            | -  | -       | -   |
| spiro-PT       | −5.33    | −2.18    | 3.15          | $1.29 \times 10^{-4}$                  | -                       | -            | -  | -       | -   |

Figure 16. Molecular structures of SFX-PT1, SFX-PT2, and spiro-PT (reproduced with permission from ref 25).

Figure 17. (a) Absorption and photoluminescence spectra. (b) Cyclic voltammograms of SFX-PT1, SFX-PT2, and spiro-PT (figure adapted from ref 25).
mobility of SFX-PT1 is more than the spiro-OMeTAD (2.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}).^{25} \text{ Optical and photovoltaic parameters of mentioned HTMs are shown in Table 2.}

**SUMMARY AND OUTLOOK**

In this mini-review, we have summarized the research progress on the PTZ-based HTMs. The HTMs are the crucial components to enhance the PCE along with the stability. This review provided the basic idea about the PSC device architecture and information about phenothiazine-based HTMs. There is rapid growth happening in the perovskite solar cells; therefore, there is a need to develop a highly stable device that consists of a better perovskite layer and an efficient and cost-effective electron/hole transport layers. Until now, the champion spiro-OMeTAD is used as the HTM layer, which includes tedious synthesis and an expensive process. Hence, researchers are looking toward the development of less expensive new transport materials to promote the PSCs into the commercial market. Simultaneously, the novel HTMs should be stable and synthesized from sustainable sources of materials; tunable energy levels with high mobility will provide efficient and stable PSCs. In this scenario, PTZ-based HTMs came into existence because of the favorable optoelectronic properties, cheap synthetic route, suitable electron-donating nature, and better hole mobility. The PTZ is an electron-rich hetero aromatic core, which leads to the production of various HTMs with low-cost production. In this mini-review, we conclude the importance of the PTZ moiety to improve the efficiency as well as stability of the perovskite solar cell devices.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

T.S. acknowledges support from the Department of Science and Technology, SERB, for a National Postdoc Fellowship (ref. no. PDF/2018/000880). S.P.S. acknowledges financial support from DST-SERB (ref. no. EMR/2017/001506), CSIR-IICT Communication number IICT/Pubs./2019/442.

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