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Low-cost synthesis of heterocyclic spiro-type hole transporting materials for perovskite solar cell applications

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Abstract:

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Four Heterocyclic spiro-typed hole transporting materials (HTMs) carrying spiro[fluorene-9,9'-xanthene] (SFX) (SFX-TPAM and SFX-TPA) or spiro[fluorene-9,9 -thioxanthene] (SFT) unit (SFT-TPAM and SFT-TPA) were synthesized through low cost facile route with high yields for perovskite solar cell (PSC) applications. The absorption of these four compounds in film state are all transparent at the wavelength longer than 430 nm, which is beneficial for allowing the visible light to reach the perovskite active layer without being absorbed by hole transporting layer (HTL). The photovoltaic performance of the inverted PSCs based on these small molecular hole transporting materials with the device architecture of glass/ITO/HTL/CH₃NH₃PbI₃/ C₆₀/BCP/Ag was test. Only SFX-TPAM having its highest occupied molecular orbital (HOMO) level matched with the valence band of CH₃NH₃PbI₃. Inverted PSC based on dopant-free SFX-TPAM HTL achieves a power conversion efficiency of 10.23% under the illumination of standard one Sun lighting, which is better than that (8.17%) of the cell based on dopant-free spiro-OMeTAD. The better photovoltaic performance of SFX-TPAM compared to spiro-OMeTAD may be due to the MAPbI₃ film deposited on it has better quality. These results indicate that the facile synthesis, low cost SFX based small molecules can be used as the hole transporting materials for perovskite solar cell.

Keywords: perovskite solar cell, organic hole transporter, Low-cost synthesis.

1. Introduction

Lead halide perovskite based solar cells (PSC) have attracted a great attention in the past 5 years.¹⁻³ To date, the powder conversion efficiency (PCE) of PSC has reached more than 22%.⁴ The inverted (p-i-n) perovskite solar cells exhibiting a PCE of 20% have drown much more attention in recent vears.⁸⁻¹⁰ Inverted PSCs are attractive, due to the advantages of low temperature process, hysteresis-free and simple architecture. The charge transporting materials play an important role in PSC as they match the frontier orbital energy levels of the absorber and transport the free carriers to the corresponding electrodes.⁵⁻⁷ It was known that several polymer based hole transporting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic materials (HTMs), such as acid) (PEDOT:PSS),^{9,10-13} (PTAA),^{14,15} poly-(bis(4-phenyl)(2,4,6-trimethylphenyl) amine) and poly(N,N'-bis(4-butylphenyl)-N, N'-bis(phenyl)benzidine) (poly-TPD)^{5,16} have been used in PSC to achieve high PCE. On the other hand, small molecule based HTMs are also very attractive due to their easy purification, high purity, and no batch-to-batch variations. Spiro-OMeTAD is the mostly used small molecular HTM but it needs a multistep for the synthesis, as a result, high price hindering further progress. Moreover, Spiro-OMeTAD with low hole mobility makes it is necessary to be doped with lithium salt and t-BP. These additives are hydrophilic, which causes the instability of the devices. Furthermore, the doped HTL may lower the device reproducibility due to the inhomogeneous distribution of the dopant. Therefore, new small molecule based HTMs used in the PSCs were developed.¹⁷⁻²¹ Among of them spirobifluorene having a spiro structure with a sp³ carbon connecting two orthogonal π systems together is a good choice because of the rigid spiroconjugation can enhance the hole transporting ability by hopping process.^{22,23} Spiro[fluorene-9,9'xanthene] (SFX) core has received increasing attention due to its competitive facile synthesis by one-pot method.²⁴ The perpendicular spiro structure in the SFX-based building units can effectively inhibit the intermolecular π - π stacking and thus improve the solubility but still keep the good hole mobility. SFX based small molecules thus were widely used in the high performance organic electronics²⁵ and organic light emitting devices.²⁶⁻²⁸ SFX-based HTMs functionalized with an electron-donating bis(4-methoxyphenyl) aniline or bis(4-methoxyphenyl)amine group were used in the regular type perovskite solar cells, showing an impressive PCE over 20%.²⁹⁻³² Thus, the high performance and low-cost synthesis of SFX based HTMs provide as a promising alternative HTM for applying in PSCs. Spiro[fluorene-9,9'-thioxanthene] (SFT) is another interesting building block

with the structure similar to SFX, in which the bridge atom is sulfur instead of oxygen in SFT, is widely used as a hole transporting materials in OPV³³ and OLED.^{34, 35}

In this work, we report the synthesis and photovoltaic performance of two SFX and two SFT based small molecules in which the SFX or SFT unit was functionalized with 4-methyl-N-phenyl-N-(p-tolyl)aniline (TPAM) or triphenylamine (TPA), respectively. The chemical structure of these (4,4',4",4"'-(spiro[fluorene-9,9'-xanthene]-2,2',7,7'four small molecular HTMs: new tetrayl)tetrakis(N,N-di-p-tolylaniline) (SFX-TPAM), 4,4', 4",4"'-(spiro[fluorene-9,9'-xanthene]-2,2',7,7'-tetrayl)tetrakis (N,N-diphenylaniline) (SFX-TPA), 4,4',4",4"'-(spiro[fluorene-9,9'-thioxanthene]-2,2',7,7'-tetrayl) tetrakis(N,N-di-p-tolylaniline) (SFT-TPAM) and 4,4',4",4"'-(spiro-[fluorene-9,9'-thioxanthene]-2,2',7,7'-tetrayl)tetrakis(N,N-diphenylaniline) (SFT-TPA) are displayed in Figure 1.



Figure 1: The chemical structures of four new spiro-based HTMs

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These four new HTMs were designed to increase the mobility of the spiro-based HTM to avoid the side-effect of the dopants used in Spiro-OMeTAD and to tune the surface properties for depositing high quality perovskite film. The propeller-like triphenylamine (TPA) serves as a building block to construct the molecules with high hole mobility.³⁶ The electron donating TPAM and TPA on the central core unit were used to promote the π - π stacking for efficient charge

transporting and increase the surface hydrophobility. The non-planar spiro-based architecture makes the molecule soluble in common organic solvents, which is compatible to the fabrication of the devices using the wet chemical process such as spin-coating. Moreover, the cost effective and easy synthesis are the merits for these spiro-based small molecules to be used as the HTM in PSCs to reach the low cost devices.

2. Experimental section

2.1 Materials and physicochemical studies

All chemicals, unless otherwise specified, were purchased from the commercial resources and used as received. PbI₂ (99.999% from Aldrich), CH₃NH_{2(aq)} (40% from TCI), HI_(aq) (57% from Aldrich), BCP (Aldrich) and C₆₀ (Solenne B. V., Netherlands) were used in this study. CH₃NH₃I was synthesized from CH₃NH_{2(aq)} and HI_(aq) with the method similar to that reported in the literature.³⁷ ¹H NMR and ¹³C NMR spectra were recorded with a Bruker 300 MHz NMR spectrometer using CDCl₃ as a solvent. FAB-MS spectra were obtained using JMS-700 HR-MS. UV/Vis absorption spectra were measured using a Cary 300 Bio spectrometer. Emission spectra were measured using FluoroMax-4 spectrofluorometer (HORIBA JOBIN YVON) at an exciting wavelength of 500 nm. HPLC grade CH₂Cl₂ was purchased from ACROS Co. and was distilled over CaH₂ under an argon (Ar) atmosphere for electrochemical study. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆) was recrystallized from ethanol twice and then stored in a desiccator to be an electrolyte. The glassy carbon working electrode was polished with 0.05 mm alumina on Buehler felt pads and was ultrasonicated for 2 min to remove the residue contamination. A platinum wire is used as the auxiliary electrode and a home-made Ag/AgCl, KCl (sat'd) is the reference electrode. The supporting electrolyte is 0.1 M tetrabutylhexafluorophosphate (TBAPF₆) dissolved in CH₂Cl₂ and the amount of the HTMs is ca. 5 mg. The cyclic and square-wave voltammograms (frequency: 25 Hz; step potential: 0.0051 V; amplitude: 0.01995 V) were recorded using a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands) and ferrocene was used as a calibration standard (0.54 V versus Ag/AgCl reference electrode). Scanning electron microscopy (SEM) images were obtained from a Hitachi S-800 microscope at 10 kV. Samples for SEM imaging were mounted on a metal stub with a piece of conducting tape and then

coated with a thin layer of platinum film to avoid charging. The thickness of the films was measured from the cross section SEM images. Hole mobility was measured according to a method based on the space charge–limited current (SCLC) model described in the literature,^{38,39} using a diode configuration of ITO/PEDOT:PSS/HTL/Au The I-V curve was measured under dark conditions using a Keithley Model 2400 unit. The slope of the logJ *vs* logV curve was used to evaluate the SCLC region and the mobility of the HTL was calculated according to the Mott-Gurney's law. The detailed analysis method can be found in the supporting information (SI).

2.2 Synthesis of the four new HTMs

The detailed synthetic procedures and structural analysis of the four new small molecular HTMs can be found in the supporting information (SI).

2.3 Device fabrication and characterization

Prior to the fabrication, the ITO coated glass substrates were cleaned in an ultrasonic bath with DI water, followed by acetone and isopropanol. Subsequently the substrates were dried and UV-Ozone treating for 10 min. The substrates were then transferred into the glove box. The HTM solution (5 mg mL⁻¹ in chlorobenzene) was spin coated onto the ITO and annealed at different temperature for 5 min. The perovskite precursor solution (1.25 M) was prepared by mixing CH₃NH₃I and PbI₂ (molar ratio 1:1) in dimethylsulfoxide (DMSO)/ γ -butyrolactone (GBL) mixed solvent (volume ratio 3:7). The perovskite precursor solution was then spin-coated on the hole transporting layer (HTL) using one-step spin-coating combined with the anti-solvent washing method (1000 rpm for 35s, 5000 rpm for 15s and toluene was dropped on the film at the last 5 seconds of the spinning) to form a full coverage perovskite film. The substrate was thermally annealed at 100°C for 5 min and subsequently the electron transporting layer (50 nm of C₆₀), buffer layer (5 nm of BCP) and Ag electrode (100 nm) were deposited by high-vacuum thermal evaporation. The current density-voltage (J-V) curves of the cells were measured using a Keithley 2400 source-measurement unit under the AM1.5G solar simulator light (Oriel, 91 150 V, using Xenon lamp) calibrated to 100 mW cm⁻² with a KG-5 silicon reference cell. The external quantum

efficiency (EQE) or incident photo-to-current conversion efficiency (IPCE) was measured in air after sealing the device with a silica sealant and measuring immediately. A chopper and lock-in amplifier were used for the phase sensitive detection with the QE-R3011 measurement system designed by Enlitech Inc., Taiwan.

3. Results and discussion

3.1 Synthesis

The spiro[fluorene-9,9'-xanthene] (SFX) core was prepared by one-pot, non-solvent synthetic method⁴⁰ using ready available starting materials such as phenol, methane sulfonic acid with the yield of 75%. Brominated SFX (SFX-Br₄) was prepared by reacting SFX with Br₂ at room temperature to get a yield of 78%. The SFX-TPAM and SFX-TPA were synthesized by Stille coupling using Pd(PPh₃)₄ as a catalyst and toluene as the solvent as illustrated in Figure 2.

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Figure 2: The synthetic scheme of the four new spiro-based HTMs

Stille coupling between SFX-Br4 and stannated TPAM afforded SFX-TPAM with the yield of 85%. Similar method was used for reacting SFX-Br4 with stannated TPA to obtain SFX-TPA with yield of 78%. The spiro[fluorene-9,9[']-thioxanthene] (SFT) core was synthesized by one-step from dibenzo- [b,d]thiophene 5,5-dioxide and 9H-thioxanthene in the presences of KHMDS with the yield of 76% using the method reported in literature.⁴¹ SFT was brominated with Br₂ at room temperature to form SFT-Br4 (73% yield). The Stille coupling reactions similar to that used for preparing SFX-TPAM and SFX-TPA mentioned above were used to obtain the final products SFT-TPAM and SFT-TPA with the yields of 71% and 73%, respectively. All new compounds were characterized by ¹H NMR, ¹³C NMR and HR-MS as described in SI. These four compounds have

good solubility in common organic solvents such as dichloromethane, ethyl acetate, toluene, chloroform and chlorobenzene.

3.2 Optical properties

The UV-Vis absorption spectra of these new spiro-based molecules in dichloromethane and solid film form are shown in the Figure 3(a) and (b). The absorption peak at 350 nm ~ 420 nm was assigned to the π - π * transition of the entire molecules. Substitution of a sulfur atom by oxygen atom on the spiro-core, the absorption profile has no significant change. In dichloromethane, the λ_{max} values of SFT-TPAM (399 nm) and SFT-TPA (395 nm) are slightly longer than those of SFX-TPAM (385 nm) and SFX-TPA (391 nm), respectively. The absorption spectra of the films are quite similar to those of the corresponding solutions except the bands are broader due to the molecular aggregation in the solid state films. All new HTMs show very low absorption at the wavelength longer than 430 nm in the film state, which is beneficial for using as a HTL in the inverted PSC. The optical band gaps of the HTMs were calculated from the onset of the absorption spectra (in CH₂Cl₂) and the optical properties of the new HTMs as well as spiro-OMeTAD are summarized in Table 1.



Figure 3: UV/Vis spectra of the four new HTMs (a) in CH₂Cl₂. (b) in film state. (c) PL spectra of the four new HTMs in CH₂Cl₂. (concentration 1 x 10⁻⁵ M)

HTMs	SFX- TPAM	SFX- TPA	SFT- TPAM	SFX- TPA	Spiro- OMeTAD
λ_{max} in CH_2Cl_2 (nm)	385	391	399	395	385
λ_{Em} in CH_2Cl_2 (nm) ^a	452	441	456	442	429
Stoke shift (cm ⁻¹) ^b	3850	2900	3130	2690	2660
E _{1/2} (V vs Ag/AgCl) ^c	0.51	0.87	0.99	1.01	-0.06
HOMO (eV) ^d	-5.21	-5-57	-5.69	-5.71	-5.0
$E_{0-0} (eV)^{e}$	2.92	2.94	2.88	2.93	2.95
LUMO (eV) ^f	-2.29	-2.63	-2.81	-2.78	-2.05

Table 1: The optical and electrochemical data of the four new HTMs

. Excitation wavelength: the absorption maxima (λ_{max}).

b. The difference between the maximum of absorption and maximum of emission spectra.

c. FeCp2^{+/0} = +0.50 V (vs Ag/AgCl) in CH₂Cl₂/TBAPF₆

d. The HOMO energy level was calculated from the half –wave potential of oxidation according to the empirical $E_{HOMO} = -(E_{1/2}+4.5)$ V by assuming the energy level of ferrocene to be -4.5 eV below vacuum level. ($E_{1/2}(V)$ vs. NHE)

e. The energy gap level ($E_{0.0}$) was calculated from the onset wavelength of UV-Vis spectrum according to the empirical $E_{gap} = 1240/\lambda_{onset}$

f. LUMO = HOMO + E_{0-0}

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The emission of the HTMs in dichloromethane at room temperature is shown in Figure 3(c). All HTMs have a broad photo luminescence band in the range of 400-600 nm which comes from the $\pi^*-\pi$ transition. The λ_{Em} is in the order of: SFX-TPA (441 nm) = SFT-TPA (442 nm) < SFX-TPAM (452 nm) = SFT-TPAM (456 nm). The SFX-TPAM and SFT-TPAM have a red-shift in the PL peaks compared to SFX-TPA and SFT-TPA, respectively. These could be attributed to that 4-methyl-N-phenyl-N-(p-tolyl) aniline (TPAM) has stronger electron-donating ability than triphenylamine (TPA), similar tendency was observed in the absorption spectra. Stokes shifts (the difference between the λ max of the absorption and emission peaks) of SFX-TPAM (3850 and 3130 cm⁻¹ respectively), which is due to the latter couple have larger geometry differences between the ground and excited states arising from the increasing number of nonhindered inter-ring torsional angles.²²

3.3 Electrochemical properties

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The electrochemical behaviors of the HTMs were investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV) studies. All four molecules show quasi-reversible in the first oxidation/reduction couple at the potential of $0.5 \sim 1.1$ V (*vs* Ag/AgCl), similar potentials were observed in SWV curves as the CV and SWV diagrams displayed in Figure 4.



Figure 4: The cyclic voltammograms (CV) and square wave voltammograms of the four new HTMs.

SFX-TPAM containing the electron rich 4-methyl-N-phenyl-N-(p-tolyl)aniline shows the lowest first oxidation potential of 0.51 eV. On the other hand, triphenylamine attached SFX-TPA is oxidized at more positive oxidation of 0.87 eV. The spiro[fluorene-9,9[']-thioxanthene] based SFT-TPAM, SFT-TPA are oxidized at even more positive potential of 0.99 and 1.01 eV, respectively. The presence of a sulfur atom (instead of an oxygen atom) on the heterocyclic spiro core makes the significant change in the oxidation potential, although their absorption profiles are close with each other. This is due to the interaction between the 3P orbital of S and the π orbitals of carbons is weaker than that between 2P orbital of O and the π orbitals of carbons. The same characteristic has been observed in the spiro[fluorene-9,9'-thioxanthene] core based small molecules.²⁶

The HOMO energy levels of SFX-TPAM and SFX-TPA calculated from the oxidation potentials are -5.21 and -5.57 eV, respectively whereas SFT-TPAM and SFT-TPA have the HOMO energy levels of -5.69 and -5.71 eV, respectively. The optical band gaps estimated from the onset of the absorption spectra (in CH_2Cl_2 solution) are 2.29 eV (SFX-TPAM), 2.94 eV (SFX-TPA), 2.88 eV (SFT-TPAM) and 2.93 eV (SFT-TPA). The LUMO energy levels were calculated from the optical band gap and HOMO levels, all data are also summarized in Table 1 and Figure 5. Figure 5 reveals clearly that only SFX-TPAM having its HOMO energy level matches with the HOMO of $CH_3NH_3PbI_3$ (-5.4 eV) used in this paper for providing sufficient hole extraction capabilities although all new HTMs can block the electrons transferred from the $CH_3NH_3PbI_3$ photoactive layer to ITO electrode within the PSC.



Figure 5: The frontier orbital energy levels of the four new HTMs and spiro-OMeTAD as well as the components used in the fabrication of the inverted perovskite solar cell

3.4 Photovoltaic performance

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The photovoltaic performance of all four new HTMs used in the inverted perovskite solar cells was verified even the HOMO levels of three of them do not match the HOMO energy of MAPbI₃. The structure of the cell is ITO/HTL/CH₃NH₃PbI₃/C₆₀/BCP/Ag (see Figure S1, SI)) and the corresponding photovoltaic parameters are summarized in Table 2. The data clearly reveal that cell

based on dopant-free SFX-TPAM HTL has much higher power conversion efficiency (PCE) compared to those used the other three HTMs. For the comparison, cells without HTL or using dopant-free spiro-OMeTAD HTL were also tested and the best PCE of 5.87% and 8.17%, respectively were achieved (see Table 2). The frontier orbitals energy levels of the new HTMs and MAPbI₃ illustrated in Figure 5 reveal that besides sprio-OMeTAD, only SFX-TPAM has a suitable HOMO (-5.21 eV) level for MAPbI₃ (HOMO: -5.4 eV) to transport its photo excited holes. That is the reason that SFX-TPAM has the best photovoltaic performance. After optimizing the spin rate for depositing perovskite film and film post thermal annealing temperature the highest PCE of 10.23% was achieved for cell based on SFX-TPAM HTL. Cells based on SFX-TPA, SFT-TPAM and SFT-TPA HTLs, which having HOMO levels lower than that of MAPbI₃, show the PCE even lower than the cell without HTL, due to the hole blocking HOMO level and insulating nature of the organic molecules. Moreover, the inverted PSC based on SFX-TPAM HTL exhibits higher efficiency compared to that used dopant-free spiro-OMeTAD HTL under the same devices fabrication processes.

The I-V and IPCE curves of the cells based on dopant-free SFX-TPAM and spiro-OMeTAD HTLs displayed in Figure 6 clear disclose that the inverted PSC based on the former HTL has larger Jsc (the Jsc integrated from IPCE spectra is consistent with that obtained from the I-V measurements). Interesting, Figure 6 (b) reveal that PSC based on SFX-TPAM HTL has lower IPCE value at short wavelength but higher at the wavelength longer than 635 nm compared to the cell based on spiro-OMeTAD HTL. This may due to the difference in perovskite film quality which will be discussed in more detail later. SFX-TPAM and spiro-OMeTAD have the right HOMO level to transport hole from MAPbI₃ to the electrode but show differentiated photovoltaic performance. It is valuable to know some properties, such as the surface hydrophobicity, hole mobility and charge extraction ability, of these two HTMs to learn how to design the small HTMs for inverted PSC by.

Table 2: The photovoltaic parameter of the inverted perovskite based on various HTLs and no HTL.

НТМ	J _{sc} (mA/cm ²)	V _{oc} (V)	Fill Factor	Efficiency (%)
SFX-TPAM	19.12	1.01	0.53	10.23

SFX-TPA	15.35	0.64	0.39	3.83
SFT-TPAM	12.17	1.04	0.25	3.16
SFT-TPA	11.32	0.68	0.37	2.85
none	15.20	0.99	0.39	5.87
spiro-OMeTAD	17.02	1.00	0.48	8.17



Figure 6: (a) I-V and (b) IPCE curves of the PSC based on SFX-TPAM and spiro-OMeTAD HTLs.

3.5 Surface hydrophilicity, hole mobility and charge extraction ability of SFX-TPAM and spiro-OMeTAD HTLs and the quality of the perovskite films deposited on the two HTLs.

The surface wetting capability of HTLs is an important factor that affects the morphology of the perovskite films deposited on them and therefore the photovoltaic performance of the corresponding PSC. The water contacting angles of SFX-TPAM and sipro-OMeTAD are 97° and 85°, respectively (the H₂O wetting pictures are shown in the Figure S2, SI). SFX-TPAM has a slightly hydrophobic surfaces⁴² but the surface of sipro-OMeTAD is weakly hydrophilic according to the definition by Quere⁴² although the hydrophobicity has no significant difference. Recent study⁴³ suggests that a higher hydrophobic surface will facilitate the formation of the perovskite films with larger grains although inverted PSC based on very hydrophilic PEDOT:PSS HTL exhibits the highest efficiency of 20 % was proved.⁹ We found that the provskite films deposited on more hydrophobic SFX-TPAM HTL has much larger grains compared to that coated on sipro-

OMeTAD surface as the SEM images displayed in Figure 7. Therefore the superior photovoltaic performance of SFX-TPAM HTL may due to MAPbI₃ film deposited on SFX-TPAM has larger grains. However, there are so many holes on the large perovskite grains. As a result PSC based on SFX-TPAM HTL exhibits only 10% efficiency. Uv/Vis absorption spectra of the provskite films on both HTLs are illustrated in Figure S3, SI. It was shown that MAPbI₃ deposited on SFX-TPAM has weaker absorption at short wavelength but stronger at long wavelength compared to that coated on spiro-OMeTAD HTL.This is due to the difference in the light scattering of the perovskite films which have different morphology. Nevertheless, the absorption spectra are consistent with the IPCE curves displayed in Figure 6 (b).



Figure 7: SEM images of MAPbI3 films spin-coated on SFX-TPAM and spiro-OMeTAD films.

The Space-Charge-Limited Current (SCLC) was widely used to estimate the carrier mobility of thin semiconductor film without knowing the conductivity (or carrier intensity)⁴⁴ of the smaple. The hole mobility of these new HTMs were also investigated by SCLC according to the Mott-Gurney's law.⁴⁵ The hole only device with the structure of ITO/ PEDOT:PSS/HTL/Au was fabricated and its *I-V* curve under dark was measured. The interception of the log V vs log J curve (at the slope of 2) was used to calculate the hole mobility as reported previously.⁴⁶ The *I-V* curves of the hole-only devices based on SFX-TPAM and spiro-OMeTAD are displayed in Figure S4, SI

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and the corresponding hole mobility data are also displayed in the insert of the Figure (the principle of SCLC theory used to calculate the charge mobility is also described under Figure S4, SI). SFX-TPAM film has the hole mobility of 2.0×10^{-4} cm²V⁻¹S⁻¹ which is lower than that $(5.2 \times 10^{-4} \text{cm}^2 \text{V}^{-1}\text{S}^{-1})$ of spiro-OMeTAD film. Therefore the difference in the photovoltaic performance is not due to the hole mobility of the HTLs, mainly due to the quality of the provskite films coated on them. PL spectra can provide the information regarding to the quality of the perovskite film and the charge extraction capability at the CH₃NH₃PbI₃/HTL interface. The PL intensity (shown in Figure 8) of CH₃NH₃PbI₃/SFX-TPAM is weaker than that of CH₃NH₃PbI₃/spiro-OMeTAD, and both are lower than CH₃NH₃PbI₃/ITO which has no HTL indicating that both SFX-TPAM has weaker PL peak but lower hole mobility than CH₃NH₃PbI₃/spiro-OMeTAD, suggesting that the hole extraction is not totally determined by the hole mobility, probably because of the two HTLs have same order of magnitude in mobility. PSC based on SFX-TPAM HTL has higher Jsc value (19.12 mA cm⁻²) than that used sprio-OMeTAD HTL (17.02 mA cm⁻²) is due to MAPbI₃ film with bigger grains was formed on SFX-TPAM HTL as revealed by the SEM images displayed in Figure 7.



Figure 8: PL spectra of MAPbI₃ films deposited on SFX-TPAM film or spiro-OMeTAD film or ITO/glass

4. Conclusion:

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In conclusion, four heterocyclic spiro-types HTMs, namely SFX-TPAM, SFX-TPA, SFT-TPAM and SFT-TPA were synthesized by few synthetic steps with cost effective upscale. The structure-physicochemical property relationship of these four molecules were well-studied and their application as HTLs in the inverted PSC was investigated. It was found that when sulfur was introduced onto spiro-core (replaced oxygen) will lower the HOMO and LUMO energy levels of the molecules due to the weak interaction between the 3p orbital of sulfur atom and π -orbital of the phenyl ring. On the other hand adding electron-donating alkyl groups will raise the HOMO level (such as SFX-TPAM/SFT-TPAM pair). As a result only SFX-TPAM with the HOMO level compatible to that of MAPbI₃ perovskite to perform good photovoltaic properties. Inverted PSC based on dopant-free SFX-TPAM HTL achieves a high PCE of 10.23% which is higher than that (8.17%) of the cell using dopant-free spiro-OMeTAD as a HTL. The better performance of the SFX-TPAM HTL is due to that it has high mobility, therefore have extract hole more efficiently compared to dopant-free spiro-OMeTAD.

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