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ARTICLE TYPE

Star-shaped hole transporting materials with a triazine unit for efficient perovskite solar cells

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Novel star-shaped hole transporting materials with a triazine unit have been synthesized. When the new Triazine-Th-OMeTPA was used as a hole transporting material in perovskite solar cell, the power conversion efficiency reached 12.51% under AM 1.5G (100 mWcm⁻²) illumination, showing competitive photovoltaic performance with the widely used spiro-OMeTAD based solar cell (13.45%).

Dye-sensitized solar cells (DSSCs) have been considered a promising alternative to the silicon-based solar cells due to their low-cost production and simple device fabrication.¹ DSSCs using liquid electrolytes of Co^{II}/Co^{III} redox couples² have shown efficiencies surpassing 12%. However, the stability issues of the DSSCs devices arise from leakage and evaporation of liquid electrolyte. Many efforts have been made to replace liquid electrolytes with quasi-solid-state electrolytes³ or solid-state hole conductors⁴ to alleviate the stability issues. However, the photovoltaic power conversion efficiency of solid-state DSSCs (ssDSSCs) remains significantly below that of liquid electrolyte-based devices. Recently, the organometal halide perovskites (CH₃NH₃PbX₃, X = Cl, Br, I)⁵ have attracted great attention due to their direct band gap, large optical absorption and high mobility. An impressive photovoltaic performance was achieved over 15% power conversion efficiency using 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) as a hole transporting material (HTM).⁶ The most effective HTM for the hybrid solar cells is spiro-OMeTAD, even though another small molecule HTMs such as 3,4-ethylenedioxythiophene,⁷ pyrene,⁸ linear π -conjugated structure,⁹ butadiene,¹⁰ and swivel-cruciform thiophene¹¹ based HTMs gave high conversion efficiencies of 10–13%. However, the high synthetic cost of spiro-OMeTAD gives another problem for the commercialization. Therefore, the development of cost-effective HTMs with high efficiency and long stability is very important.

Herein, we report new types of hole transporting materials with donor- π -acceptor (D-A) systems by incorporating an electron-deficient 1,3,5-triazine core and an electron-rich diphenylamino unit. The molecular structure of the two HTMs is shown in Figure 1a. Our strategy for choosing a 1,3,5-triazine unit is that the radical anion formed during irradiation is stabilized due to its electron deficiency.¹² Another strategy for introducing the triarylamine derivatives is that the star-shaped

organic materials have been widely used as HTMs in optoelectronic devices.¹³

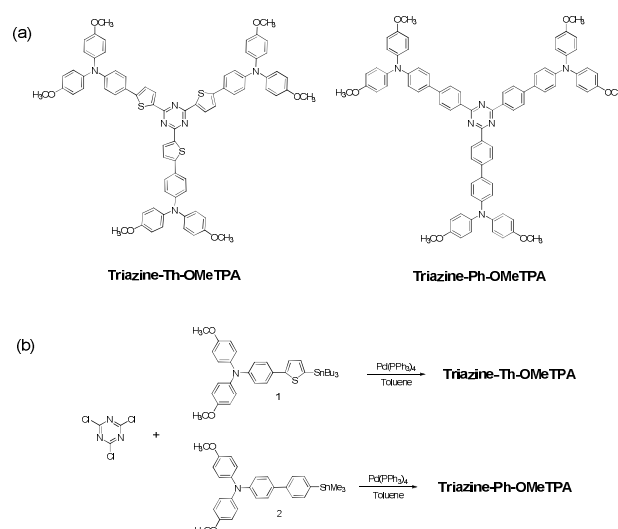


Fig. 1 (a) Chemical structures of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA**. (b) Schematic diagram for the synthesis of the **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA**.

The synthetic scheme for the preparation of 2,4,6-tris[*N,N*-bis(4-methoxyphenyl)amino-*N*-phenylthiophen-2-yl]-1,3,5-triazine (**Triazine-Th-OMeTPA**) and 2,4,6-tris[*N,N*-bis(4-methoxyphenyl)amino-*N*-diphenyl]-1,3,5-triazine (**Triazine-Ph-OMeTPA**) is shown in Figure 1b.¹⁴ Detailed synthetic procedures are provided in the Supporting information (SI). The key step for their syntheses is the Stille coupling reaction¹⁵ of 2,4,6-trichloro-1,3,5-triazine with *N,N*-bis(4-methoxyphenyl)-*N*-[(5-(tributylstannyl)thiophen-2-yl)phenyl]amine and *N,N*-bis(4-methoxyphenyl)-*N*-[(trimethylstannyl)biphenyl]amine. The target compounds **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA** were obtained in ~50% yield.

The UV-vis spectra of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA** measured in chlorobenzene are shown in the insert of Figure 2a. The absorption spectrum of **Triazine-Ph-OMeTPA** exhibits an intense peak at 412 nm. The λ_{max} of **Triazine-Th-OMeTPA** (429 nm) was red-shifted by 17 nm relative to that of **Triazine-Ph-OMeTPA**. This bathochromic shift was attributed to the more planar configuration in **Triazine-Th-OMeTPA**, which possesses a 11.4° twist between the 1,3,5-triazine and thienyl unit, as compared with the more twist one (25.7°) between

the 1,3,5-triazine and phenyl unit in **Triazine-Ph-OMeTPA**. The fluorescence spectrum of **Triazine-Th-OMeTPA** exhibits a maximum emission at 502 nm with a small Stoke's shift of 73 nm compared to a large Stoke's shift of 146 nm in **Triazine-Ph-OMeTPA**, demonstrating that a small structural change in the excited state occurs in **Triazine-Th-OMeTPA** due to a slight interaction between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and thiophenyl unit.¹⁶ Figure 2a shows the absorption spectra of three HTMs processed on the perovskite-coated TiO_2 films. Two new HTMs-coated films exhibit a broad and enhanced absorption band from 380 to 520 nm due to the superposed absorption characteristic of their constituents.

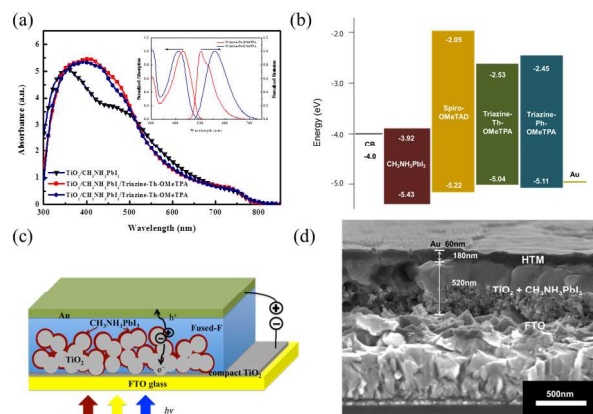


Fig. 2 (a) UV-vis absorption spectra of HTMs coated on $mp\text{-TiO}_2$ and $mp\text{-TiO}_2/\text{MAPbI}_3$ films. Insert : absorption and emission spectra of the HTMs in chlorobenzene. (b) Energy level diagram of each components. (c) Schematics of the whole device. (d) Scanning electron microscopy (SEM) picture of the cross section of the $mp\text{-TiO}_2/\text{MAPbI}_3/\text{HTMs}/\text{Au}$.

Figure 2b shows the energy level diagram of the corresponding components in the device. The energy levels of HTMs were characterized by cyclic voltammetry. The HOMO levels of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA** are measured to be -5.04 and -5.11 eV respectively, which could match with the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (-5.43 eV). Figure 2c shows the device structure of the hybrid solar cells. The cross-sectional scanning electron microscopy (SEM) images shown in the Figure 2d show the formation of a well-defined hybrid structure with clear interfaces. The thickness of TiO_2 , perovskite and HTM layer is ~320, 200 and 180 nm, respectively.

Figure 3a shows photocurrent density-voltage (J - V) curves for three devices. For reference, the device with spiro-OMeTAD as HTM is fabricated. As the solid-state sensitized cells have exhibited an impressive enhancement in photovoltaic conversion efficiency (PCE) by increasing the conductivity of HTMs via doping the additives such as 4-*tert*-butylpyridine (*t*-Bp), lithium bis(trifluoromethane-sulfonyl)imide (Li-TFSI) and tris(2-(1*H*-pyrazol-1-yl)pyridine)cobalt(III) into the HTM,¹⁷ we attempted to fabricate the device by doping the three additives into **Triazine-Th-OMeTPA** or **Triazine-Ph-OMeTPA** hole conductor. The **Triazine-Ph-OMeTPA** based device gave a $J_{sc} = 19.14 \text{ mAcm}^{-2}$, a $V_{oc} = 0.93 \text{ V}$ and a $FF = 0.61$, affording a PCE = 10.90%. Under the similar condition, the **Triazine-Th-OMeTPA** and **spiro-OMeTAD** based cells gave a J_{sc} of 20.74 and 21.37 mAcm^{-2} , a V_{oc} of 0.92 and 0.94 V and FF of 0.66 and 0.67, corresponding to η of 12.51 and 13.45%, respectively. The

photocurrent action spectra of the three devices are presented in Figure 3b. The integrated photocurrent density of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA** is 20.12 and 18.62 mAcm^{-2} , respectively, which is in good agreement with the measured photocurrent density of 20.74 and 19.14 mAcm^{-2} .

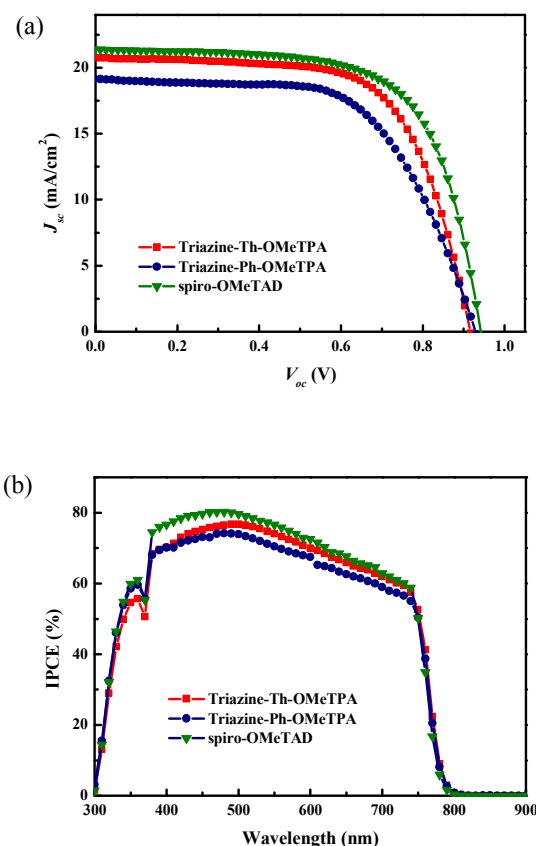


Fig. 3 (a) Photocurrent-voltage (J - V) characteristics of the solar cells with **Triazine-Th-OMeTPA** (■), **Triazine-Ph-OMeTPA** (●), and **spiro-OMeTAD** (▼) as the HTM. (b) corresponding IPCE spectra.

Table 1 Summary of photovoltaic parameters derived from J - V measurements of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based devices.

HTM	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF	η (%)
Spiro-OMeTAD	21.37	0.94	0.67	13.45
Triazine-Th-OMeTPA	20.74	0.92	0.66	12.51
Triazine-Ph-OMeTPA	19.14	0.93	0.61	10.90

Performances of DSSCs were measured with 0.16 cm^2 working area.

From the photovoltaic performances (Table 1), we have observed that the η value (12.51%) of **Triazine-Th-OMeTPA** based device is higher than that (10.90%) of **Triazine-Ph-OMeTPA** based one due to a high photocurrent and fill factor. The V_{oc} in **Triazine-Ph-OMeTPA** based cell is slightly higher than that of **Triazine-Th-OMeTPA** based one, which is in good agreement with the relative difference in the HOMO levels of two HTMs. The high photo-current density of **Triazine-Th-OMeTPA** based cell relative to **Triazine-Ph-OMeTPA** based one is responsible for the broad and red-shifted absorption of $mp\text{-TiO}_2/\text{MAPbI}_3$.

TiO₂/CH₃NH₃PbI₃/Triazine-Th-OMeTPA device. In addition, the high fill factor of Triazine-Th-OMeTPA based cell can be interpreted as its low series resistance (R_s) and high mobility. From the slope of *J-V* curve around the V_{oc}, the R_s value of Triazine-Th-OMeTPA and Triazine-Ph-OMeTPA based cell are calculated to be 21.4 and 32.6 Ω cm⁻² respectively, in which the lower value of R_s in the former's cell results in the enhanced photocurrent density. To check the effect of hole mobility on the fill factor, we measured the hole mobility of HTMs from the space charge limitation of current (SCLC) *J-V* characteristics. The hole mobility of Triazine-Th-OMeTPA, Triazine-Ph-OMeTPA and spiro-OMeTAD evaluated using the Mott-Gurney law¹⁸ are calculated to be 1.74 × 10⁻⁴, 1.50 × 10⁻⁴, and 4.43 × 10⁻⁴ cm²V⁻¹S⁻¹, respectively. The high hole mobility of Triazine-Th-OMeTPA relative to Triazine-Ph-OMeTPA based cell led to an improved fill factor.

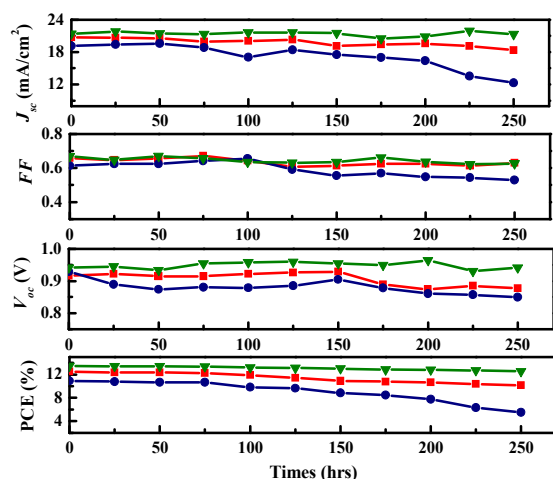


Fig. 4 Evolution of solar-cell parameters with Triazine-Th-OMeTPA (■), Triazine-Ph-OMeTPA (●) and spiro-OMeTAD (▼)-based cell stored in air at room temperature under one sun illumination.

Figure 4 show the photovoltaic performance during long-term aging test of three devices. After 500 h of aging, the initial efficiency of 12.08% in the Triazine-Th-OMeTPA based cell decreased to 10.10%, giving a 16.4% reduction, which is comparable to that (12.4%) of spiro-OMeTAD based one. On the other hand, the initial efficiency of 10.42% in the Triazine-Ph-OMeTPA based cell sharply decreased to 6.08%, giving a 41.7% reduction. The stability of the Triazine-Th-OMeTPA based cell compared with the Triazine-Ph-OMeTPA based one may be attributable to a tight packing through an interfacial interaction between the Pb in perovskite and S of thiophenyl unit in HTM.¹⁶

In summary, we have designed and synthesized two novel star-shaped HTMs with 1,3,5-triazine core. Although the photo-physical properties of the two HTMs is quite similar, the photovoltaic performance is quite sensitive to the structural modification of peripheral substituents. The perovskite based cell using Triazine-Th-OMeTPA as a HTM affords an overall conversion efficiency of 12.51%, showing a competitive photovoltaic performance to the spiro-OMeTAD based cell (13.45%). Moreover, the Triazine-Th-OMeTPA based cell showed a good stability for 500 h. We believe that the development of highly efficient hole transporting materials

comparable to the state-of-the-art HTM spiro-OMeTAD is possible through meticulous molecular design, and studies directed this goal are now in progress.

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