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

Kwangseok Do,^a Hyeju Choi,^a Kimin Lim,^a Hyunjun Jo,^a Jin Woo Cho,^b
Mohammad K. Nazeeruddin^c and Jaeyung Ko^{*a}

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 cells, the power conversion efficiency reached 12.51% under AM 1.5 G (100 mW cm⁻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 DSSC devices arise from leakage and evaporation of liquid electrolytes. Much 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 other 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 Fig. 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 opto-electronic devices.¹³

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

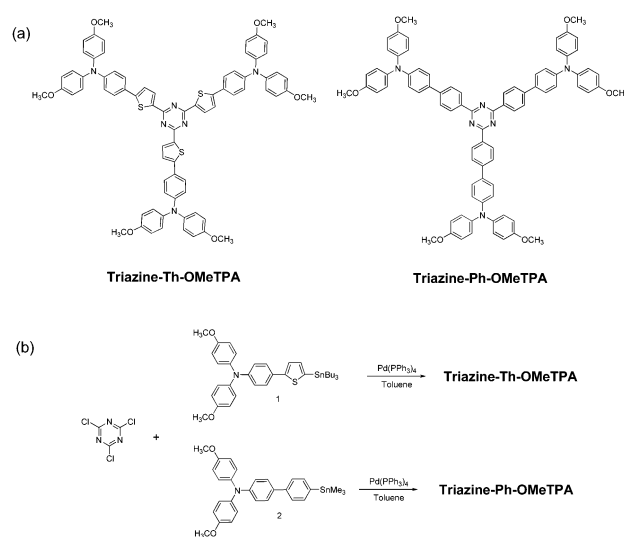


Fig. 1 (a) Chemical structures of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA**. (b) Schematic diagram for the synthesis of the **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA**.

^a Department of Advanced Materials Chemistry, Korea University Sejong Campus, Sejong-ro 2511, Sejong City 339-700, Republic of Korea. E-mail: jko@korea.ac.kr; Fax: +82-44-860-1331; Tel: +82-44-860-1337

^b Advanced Analysis Center, Korea Institute of Science and Technology(KIST), Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

^c Laboratory of Photonics and Interfaces, Department of Chemistry and Chemical Engineering, Swiss Federal Institute of Technology, Station 6, CH-1015 Lausanne, Switzerland

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(**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 Fig. 1b.¹⁴ Detailed synthetic procedures are provided in the ESI.[†] 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 inset of Fig. 2a. The absorption spectrum of **Triazine-Ph-OMeTPA** exhibits an intense peak at 412 nm. 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 of **Triazine-Th-OMeTPA**, which possesses a 11.4° twist between the 1,3,5-triazine and the thienyl unit, as compared with the more twist one (25.7°) between the 1,3,5-triazine and the 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 triazine and the thiophenyl unit.¹⁶ Fig. 2a shows the absorption spectra of three HTMs processed on the perovskite-coated TiO₂ films. Two new HTMs-coated films exhibit a broad and enhanced absorption band from 380 to 520 nm due to the superposed absorption characteristics of their constituents.

Fig. 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 CH₃NH₃PbI₃ (-5.43 eV). Fig. 2c shows the device structure of the hybrid solar cells. The cross-sectional scanning electron

microscopy (SEM) images shown in the Fig. 2d show the formation of a well-defined hybrid structure with clear interfaces. The thickness of TiO₂, perovskite and the HTM layer is ~320, 200 and 180 nm, respectively.

Fig. 3a shows photocurrent density-voltage (*J*-*V*) curves of 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 a **Triazine-Th-OMeTPA** or a **Triazine-Ph-OMeTPA** hole conductor. The **Triazine-Ph-OMeTPA** based device gave $J_{\text{sc}} = 19.14 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.93 \text{ V}$ and FF = 0.61, affording 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 mA cm⁻², a V_{oc} of 0.92 and 0.94 V and a FF of 0.66 and 0.67, corresponding to a η of 12.51 and 13.45%, respectively. The photocurrent action spectra of the three devices are presented in Fig. 3b. The integrated photocurrent density of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA** is 20.12 and 18.62 mA cm⁻², respectively, which is in good agreement with the measured photocurrent density of 20.74 and 19.14 mA cm⁻².

From the photovoltaic performances (Table 1), we have observed that the η value (12.51%) of **Triazine-Th-OMeTPA** based

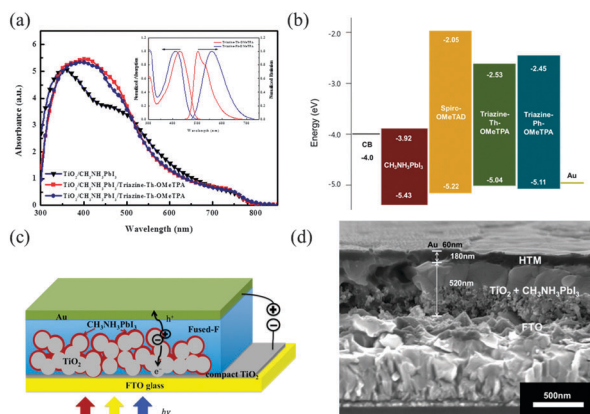


Fig. 2 (a) UV-vis absorption spectra of HTMs coated on *mp*-TiO₂ and *mp*-TiO₂/MAPbI₃ films. Inset: absorption and emission spectra of the HTMs in chlorobenzene. (b) Energy level diagram of each component. (c) Schematics of the whole device. (d) Scanning electron microscopy (SEM) picture of the cross section of the *mp*-TiO₂/MAPbI₃/HTMs/Au.

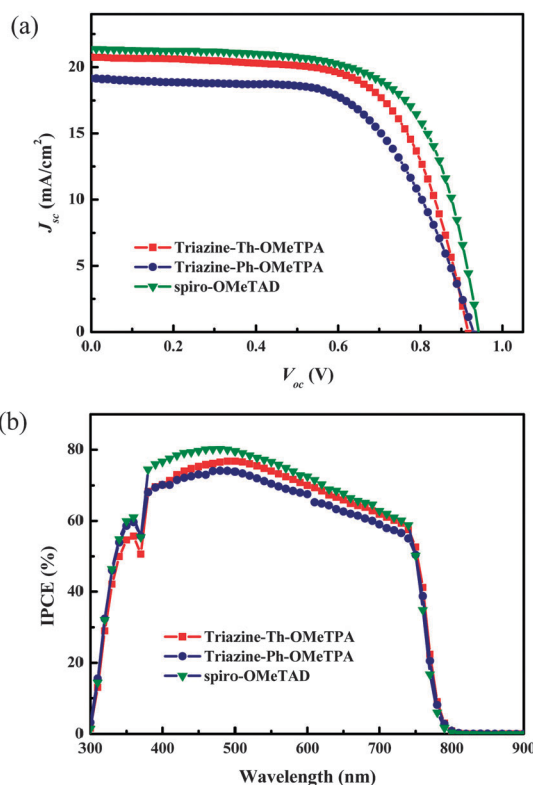


Fig. 3 (a) Photocurrent-voltage (*J*-*V*) characteristics of the solar cells with **Triazine-Th-OMeTPA** (■), **Triazine-Ph-OMeTPA** (●), and **spiro-OMeTAD** (▼) as the HTM. (b) Corresponding IPCE spectra.

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

HTM	J_{sc} (mA cm^{-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

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

device is higher than that (10.90%) of **Triazine-Ph-OMeTPA** based one due to a high photocurrent and fill factor. V_{oc} of the **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 photocurrent density of the **Triazine-Th-OMeTPA** based cell relative to **Triazine-Ph-OMeTPA** based one is responsible for the broad and red-shifted absorption of the $mp\text{-TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Triazine-Th-OMeTPA}$ device. In addition, the high fill factor of the **Triazine-Th-OMeTPA** based cell can be interpreted as its low series resistance (R_s) and high mobility. From the slope of the J - V curve around V_{oc} , the R_s values of **Triazine-Th-OMeTPA** and **Triazine-Ph-OMeTPA** based cells are calculated to be 21.4 and $32.6 \Omega \text{ cm}^{-2}$, respectively, in which the lower value of R_s in the former 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 values 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 $4.43 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The high hole mobility of **Triazine-Th-OMeTPA** relative to the **Triazine-Ph-OMeTPA** based cell led to an improved fill factor.

Fig. 4 show the photovoltaic performance during the long-term aging test of three devices. After 250 h of aging, the initial efficiency of 12.08% of 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% of 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 Pb of perovskite and S of the thiophenyl unit of HTM.¹⁶

In summary, we have designed and synthesized two novel star-shaped HTMs with a 1,3,5-triazine core. Although the photo-physical properties of the two HTMs are 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 250 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 to this goal are now in progress.

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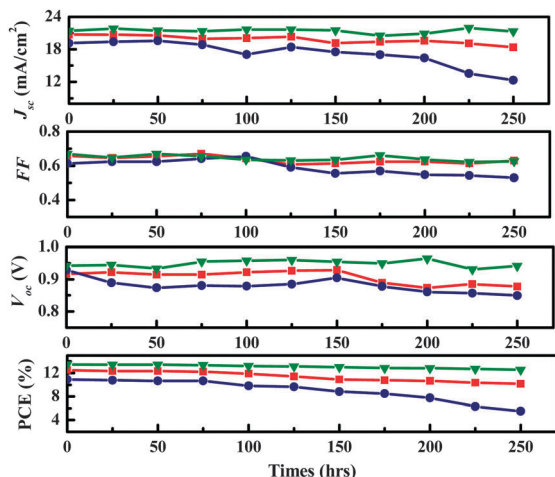


Fig. 4 Evolution of solar-cell parameters with **Triazine-Th-OMeTPA** (■), **Triazine-Ph-OMeTPA** (●) and **spiro-OMeTAD** (▼)-based cells stored in air at room temperature under one sun illumination.

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