Three novel carbazole-based molecules have been synthesized and successfully applied as hole-transporting materials (HTMs) of CH$_3$NH$_3$PbI$_3$-based perovskite solar cells. In particular, the perovskite cell with SGT-405, having a three-arm-type structure, exhibited a remarkable photovoltaic conversion efficiency (PCE) of 14.79%.

Methylammonium lead halide based perovskite solar cells have attracted extensive interest as next-generation photovoltaics.\textsuperscript{1-12} Presently, their photovoltaic conversion efficiencies (PCEs) of over 16% are reported\textsuperscript{13-15} and are expected to exceed over 20% in the near future. For further enhancement of their performance as well as for their commercialization, one of the crucial issues will be the development of effective HTMs, mediating the holes from the perovskite light absorber to the metal counter electrode. Conventionally, spiro-OMeTAD has been applied as HTM, but it would be of importance to develop more economical and efficient alternatives. In this perspective, Seok and co-workers reported a PCE of 12.4% using pyrene-core arylamine derivatives PY-C,\textsuperscript{16} and Li et al. reported a PCE of 13.8% using molecular 2,5-bis(4,4'-bis(methoxylamino)phenyl)-3,4-ethylenedioxythiophene.\textsuperscript{17} Above these, several small molecule or polymer-based HTMs have also been synthesized and applied as HTMs of perovskite solar cells,\textsuperscript{18-27} but still more efforts have to be made to develop efficient and economical HTMs for successful commercialization of perovskite solar cells.

Hole-transporting materials based on the carbazole moiety have been often applied as charge mediators for solid state dye-sensitized solar cells.\textsuperscript{28-31} Since their chemical structure has versatile and advantageous features such as the low cost of the starting material (9H-carbazole), good chemical stability, easy functionalization, and facile tuning of electronic and optical properties. Herein, we report the synthesis and characterization of novel carbazole-based HTMs with two-arm and three-arm type structures, which are linked through phenylene, diphenylene or triphenyl amine derived core units, as shown in Fig. 1. Totally four molecular HTMs were synthesized, as described in ESI.\textsuperscript{†} Among them, SGT-404, SGT-405 and SGT-407, showing reasonable solubility in nonpolar solvents, were tested as HTMs of perovskite solar cells.

The UV-visible absorption spectra of several HTMs dissolved in THF solution are shown in Fig. 2a, while the determined molar absorption coefficients (ε) at their absorption maxima are listed in Table S1 in the ESI.\textsuperscript{†} Among the HTMs, SGT-405 showed the lowest absorbance, which would be a favorable property of HTM, because the loss of incident photons by absorption of HTM can be minimized. The oxidation potentials (corresponding to HOMO levels) of the synthesized HTMs were measured by cyclic voltammetry, as shown in Fig. S2 in the ESI.\textsuperscript{†} HOMO energy levels were derived from the first oxidation potential, whereas LUMO levels were determined by subtracting the band gap energies from the corresponding HOMO levels. HOMO levels of the synthesized HTMs (+0.76 V vs. NHE for SGT-404, +0.75 V for SGT-405, and +0.74 V for SGT-407) are very close to that of spiro-OMeTAD (+0.73 V vs. NHE) (see Table S1 in the ESI\textsuperscript{†} and Fig. 3a).

From the TG and DSC analysis, it was found that SGT-405 and 407 showed good thermal stability up to 400 °C, whereas SGT-404 begins to decompose at ~330 °C. Among HTMs, uniquely, SGT-405 showed a sharp endothermic peak at 327.6 °C, indicating its melting temperature ($T_m$). This clearly indicates its intrinsic ability to form a crystalline structure when it is fabricated as a film. However, other HTMs including spiro-OMeTAD showed no $T_m$ suggesting that they are amorphous structures (see Fig. S3-S5 in the ESI\textsuperscript{†}).

Fig. 2b shows the current–voltage characteristics of the in-plane hole-only devices, employing several different HTMs. The conductivities ($σ$) of HTM layers were determined from eqn (1),\textsuperscript{32} where $L$ is the channel length (100 μm), $w$ is the channel...
width (500 μm), t is the film thickness (380 nm), and \( R \) is the resistivity calculated from the gradients of the curves.

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\sigma = \frac{L}{RwT}
\]  

The obtained \( \sigma \) values of SGT-404, SGT-405, and SGT-407 were \( 3.3 \times 10^{-9}, 4.2 \times 10^{-8}, \) and \( 1.6 \times 10^{-8} \) S cm\(^{-1} \), respectively. SGT-405 and SGT-407, belonging to the three-arm type structure, exhibited a relatively higher \( \sigma \) than that of the two-arm type SGT-404. Thus, the three-arm type structure is expected to be a more promising scaffold in designing efficient HTMs. The relatively high conductivity of SGT-405 seems to originate from its unique ability to form a crystalline structure.

The synthesized SGT series were then applied as HTMs of the \( \text{CH}_3\text{NH}_3\text{PbI}_3 \)-based perovskite solar cells. As shown in Fig. 3a, all HTMs have appropriate HOMO levels in mediating holes from the \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) VB to the Au Fermi level. The thicknesses of the \( \text{CH}_3\text{NH}_3\text{PbI}_3/TiO_2 \) layer and the Au electrode was \( \sim 200 \) nm and \( \sim 60 \) nm, respectively, whereas those of the HTM layers were varied in the range of 230–300 nm to obtain the optimum device performance (see Fig. 3b). \( J-V \) curves of the perovskite solar cells, applying SGT-404 (Cell-404), SGT-405 (Cell-405), SGT-407 (Cell-407), and spiro-OMeTAD (Cell-S), respectively, are shown in Fig. 4a, while the detailed photovoltaic parameters are listed in Table 1. Among the three perovskite cells, Cell-405 exhibited the highest PCE of 14.79% with a \( J_{SC} \) of 20.28 mA cm\(^{-2}\), a \( V_{OC} \) of 1.023 V, and an FF of 0.713, which is comparable to that of Cell-S (15.23%) employing spiro-OMeTAD. To the best of our knowledge, the achieved PCE is the highest among the devices with small-molecular HTMs except spiro-OMeTAD. Their \( V_{OC} \) values decreased in the order of SGT-405, SGT-407, and SGT-404, whereas \( J_{SC} \) values did not vary significantly. The obtained results suggest that \( V_{OC} \) is closely related to \( \sigma \) of the employed HTMs. As \( \sigma \) of the HTM decreases, the hole-transport rate will slow down, and therefore the recombination
rate of photo-excited electron–hole pairs in CH$_3$NH$_3$PbI$_3$ will be increased, leading to a decrease of $V_{OC}$.

IPCE spectra of several perovskite solar cells are shown in Fig. 4b. The integrated current densities estimated from the IPCE spectra were in good agreement with the $J_{SC}$ values acquired from the J–V curves. Fig. 4c shows the variation of PCEs as a function of HTM layer thickness for the SGT series. For SGT-405, the optimum thickness was determined to be ~300 nm, whereas those of SGT-404 and SGT-407 were 250 and 230 nm, respectively.

Electron lifetime ($\tau_e = C_m \times R_{\text{rec}}$, where $R_{\text{rec}}$ is the recombination resistance) versus chemical capacitance ($C_m$) is plotted for all the perovskite solar cells to compare the differences in the electron recombination processes of the devices employing individual HTMs, as shown in Fig. 4d. The equivalent circuit applied in the electron impedance spectroscopy (EIS) analysis is shown in the inset of Fig. 4d. SGT-405 with a higher $\tau_e$ exhibited a significantly longer electron lifetime, suggesting its lower recombination rate caused by a more efficient hole transport. The achieved result is consistent with the trends of $\sigma$ of the HTMs.

Three novel carbazole-based molecules have been synthesized and applied as HTMs of perovskite solar cells. Among them, SGT-405 exhibited the highest $\tau_e$, which seems to be due to its intrinsic ability to form a crystalline structure when it is coated as a film, and the perovskite solar cells employing SGT-405 exhibited the highest PCE of 15.23%. It is deduced that the conductivity of HTM is one of the major factors determining the cell performance. In this regard, SGT-405, having a three-arm type carbazole-based structure, is considered to be a highly promising candidate as HTM. This work was supported by the Converging Research Center Program through the Ministry of Science, ICT and Future Planning (MSIP) (Project No. 2013K000203) and the Korea Center for Artificial Photosynthesis funded by MSIP through the National Research Foundation of Korea (Project No. 2009-0093883).

### Notes and references