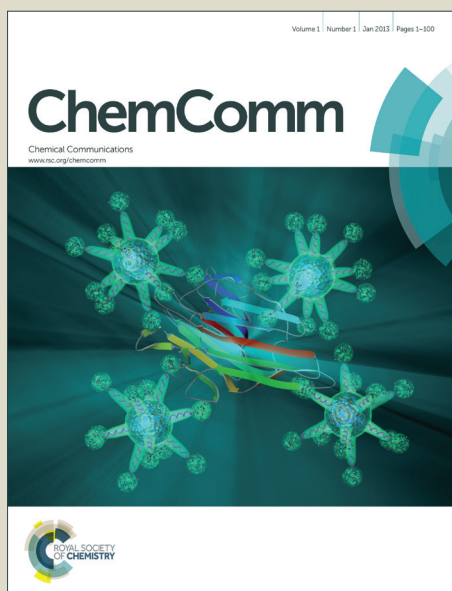


ChemComm

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: S. D. Sung, M. S. Kang, I. T. Choi, H. M. Kim, H. Kim, M. Hong, H. K. Kim and W. I. Lee, *Chem. Commun.*, 2014, DOI: 10.1039/C4CC06716A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

14.8% Perovskite Solar Cells Employing Carbazole Derivatives as Hole Transporting Materials

Cite this: DOI: 10.1039/x0xx00000x

Sang Do Sung,^{†a} Min Soo Kang,^{†b} In Taek Choi,^{†b} Hong Mo Kim,^b Hyoungjin Kim,^c MunPyo Hong,^c Hwan Kyu Kim^{*b} and Wan In Lee^{*a}Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Three novel carbazole-based molecules have been synthesized and successfully applied as hole-transporting material (HTM) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cells. In particular, the perovskite cell with SGT-405, in a three-arm-typed structure, exhibited a remarkable photovoltaic conversion efficiency (PCE) of 14.79%.

Methylammonium lead halide based perovskite solar cells have attracted extensive interest as a next-generation photovoltaics.^{1–12} Presently, their photovoltaic conversion efficiencies (PCEs) over 16% have been reported,^{13–15} and its efficiency is expected to exceed over 20% in the near future. For the further enhancement of device performance as well as for its commercialization, one of the crucial issues will be development of effective HTM, 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 PCE of 12.4% with pyrene-cored arylamine derivatives PY-C,¹⁶ and Li et al. reported PCE of 13.8% with molecular 2,5-bis(4,4'-bis(methoxyphenyl)aminophen-4''-yl)-3,4-ethylenedioxythiophene.¹⁷ Above these, several small molecule or polymer-based HTMs have also been synthesized and applied for

perovskite solar cells,^{18–27} but still more efforts have to be exerted to develop efficient and economical HTMs for successful commercialization of perovskite solar cell.

Hole-transporting materials based on the carbazole moiety have been often applied as charge mediator for solid state dye-sensitized solar cells,^{28–31} since its chemical structure has versatile and advantageous features such as low cost of the starting material (9H-carbazole), good chemical stability, easy functionalization, and facile tuning of electronic and optical properties. Herein, we report synthesis and characterization of novel carbazole-based HTMs retaining two-arm and three-arm typed 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 electronic supplementary information (ESI†). Among them, three HTMs, SGT-404, SGT-405 and SGT-407, showing reasonable solubility to nonpolar solvents, were tested as HTM for perovskite solar cell.

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 ESI†. Among the HTMs, SGT-405 showed the lowest absorbance, which would be a favorable property for HTM, because the loss of incident photons by absorption of HTM can be minimized. The oxidation potentials (corresponding to HOMO levels) of the

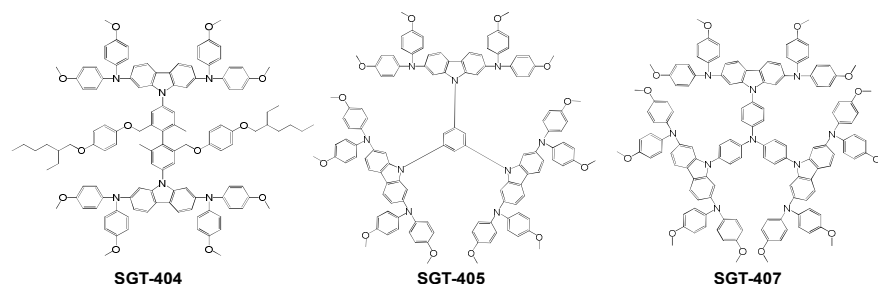


Fig. 1 Chemical structures of the synthesized carbazole-based molecular HTMs.

COMMUNICATION

synthesized HTMs were measured by cyclic voltammetry, as shown in Fig. S2 in ESI†. 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 ESI† and Fig. 3a).

From the TG and DSC analysis, it was found that SGT-405 and 407 showed a 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 property to form a crystallized 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 ESI†).

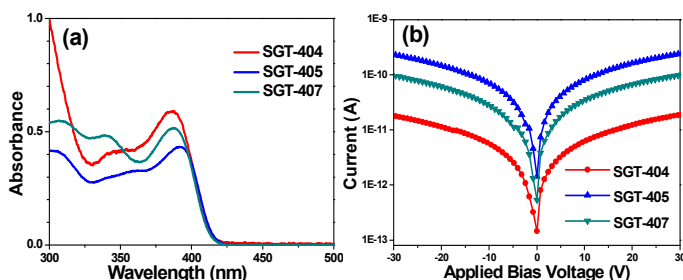


Fig. 2 (a) UV-visible absorption spectra of several HTMs dissolved in THF; (b) I-V characteristics for the in-plane devices employing several HTMs, spin-coated by the 5 wt% toluene solution.

Fig. 2b shows the current-voltage characteristics for the in-plane hole-only devices, employing several different HTMs. The conductivities (σ) of HTM layers were determined from the equation $1,^{34}$ where L is channel length (100 μm), w is channel width (500 μm), t is film thickness (380 nm), and R is resistivity calculated from the gradients of the curves.

$$\sigma = L/Rwt \quad (1)$$

The obtained σ of SGT-404, SGT-405, and SGT-407 were 3.3×10^{-9} , 4.2×10^{-8} , and $1.6 \times 10^{-8} \text{ S} \cdot \text{cm}^{-1}$, respectively. SGT-405 and SGT-407, belonging to the three-arm typed structure, exhibited relatively higher σ than that of the two-arm typed SGT-404. Thus, the three-arm typed structure is expected to be more promising scaffold in designing efficient HTMs. Relatively higher conductivity of SGT-405 seems to originate from its unique property to form a crystallized structure.

The synthesized SGT series were then applied as HTM 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 $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ layer and Au electrode were ~200 nm and ~60 nm, respectively, whereas those of the HTM layers were varied in the range of 230–300 nm to obtain the optimum device performances (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 J_{SC} of 20.28 mA/cm^2 , V_{OC} of 1.023 V, and 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 value among the devices with small-molecular HTMs except *spiro*-OMeTAD. Their V_{OC} values were decreased in order of SGT-405,

SGT-407, and SGT-404, whereas J_{SC} values were not significantly varied. The obtained result suggests that the V_{OC} is closely related to σ of the employed HTMs. As σ of the HTM decreases, the hole-transport rate will slow down, and thereby the recombination rate of photo-excited electron-hole pairs in $\text{CH}_3\text{NH}_3\text{PbI}_3$ will be increased, leading to decrease of V_{OC} .

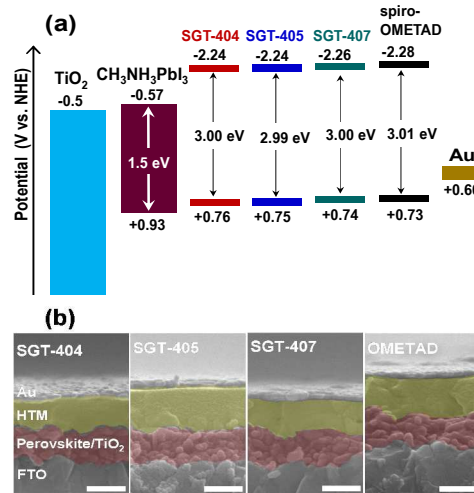


Fig. 3 Energy level diagram (a) and cross-sectional SEM images (b) of the perovskite solar cells employing several HTMs. All scale bars in b indicate 250 nm.

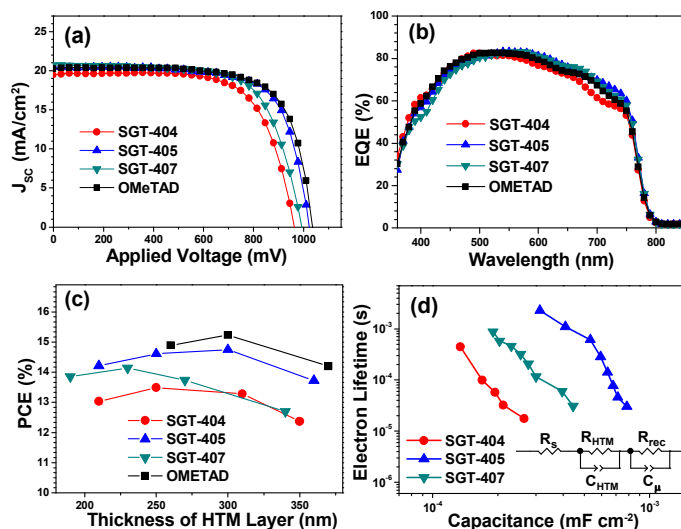


Fig. 4 J-V curves (a) and IPCE spectra (b) of the perovskite solar cells employing several HTMs; (c) Variation of PCE according to the thickness of HTM layers; (d) Plots of electron lifetime vs. capacitance for the perovskite solar cells employing several HTMs.

Table 1 J-V characteristics of perovskite solar cells employing several HTMs.

HTM	PCE (%)	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF
SGT-404	13.28	19.76	0.963	0.698
SGT-405	14.79	20.28	1.023	0.713
SGT-407	13.86	20.35	0.993	0.686
OMeTAD	15.23	20.31	1.036	0.723

IPCE spectra of the 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 the SGT-405, the optimum thicknesses were determined to be ~300 nm, whereas those of the SGT-404 and SGT-407 were 250 and 230 nm, respectively.

The electron lifetime ($\tau_n = C_{\mu} \times R_{rec}$, where R_{rec} is the recombination resistance) versus the chemical capacitance (C_{μ}) is plotted for all the perovskite solar cells to compare the differences in the electron recombination processes of the devices employing the individual HTMs, as shown in Fig. 4d.³⁵⁻³⁷ The equivalent circuit applied to the electron impedance spectroscopy (EIS) analysis is shown in its inset. SGT-405 with higher σ exhibited significantly longer electron lifetime, suggesting its lower recombination rate caused by more efficient hole transport. The achieved result is consistent with the trends of σ of the HTMs.

Conclusions

Three novel carbazole-based HTMs have been synthesized and applied as HTM of the perovskite solar cells. Among them, SGT-405 exhibited the highest σ , which seems to be due to its intrinsic property to form a crystallized structure when it is coated as a film, and the perovskite solar cells employing SGT-405 exhibited the highest PCE of 14.79%, comparable to that of the device from the commercial *spiro*-OMeTAD (15.23%). It is deduced that the conductivity of HTM is one of the major factors in determining the cell performance. In this regard, SGT-405, belonging to a three-arm typed 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

^a Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, Korea. E-mail: wanin@inha.ac.kr

^b Global GET-Future Lab. & Department of Advanced Materials Chemistry, Korea University, Sejong 339-700, Korea. E-mail: hkk777@korea.ac.kr

^c Department of Display & Semiconductor Physics, Korea University, Sejong 339-700, Korea.

[†] Electronic Supplementary Information (ESI) available: [Preparation and characterization of HTMs, solar cell fabrication, device characterizations, cyclic voltammograms and DSC/TGA analysis of HTMs are included]. See DOI: 10.1039/c000000x/

- 1 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050.
- 2 H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel and N.-G. Park, *Sci. Rep.*, 2012, **2**, 591.
- 3 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643.
- 4 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, *Nano Lett.*, 2013, **13**, 1764.
- 5 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.
- 6 M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395.
- 7 S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum and Y. M. Lam, *Energy Environ. Sci.*, 2014, **7**, 399.
- 8 M. H. Kumar, N. Yantara, S. Dharani, M. Grätzel, S. Mhaisalkar, P. P. Boix and N. Mathews, *Chem. Comm.*, 2013, **49**, 11089.
- 9 N.-G. Park, *J. Phys. Chem. Lett.*, 2013, **4**, 2423.
- 10 G. E. Eperon, V. M. Burlakov, A. Goriely and H. J. Snaith, *ACS Nano*, 2014, **8**, 591.
- 11 F. J. Ramos, M. C. López-Santos, E. Guillén, M. K. Nazeeruddin, M. Grätzel, A. R. Gonzalez-Elipe and S. Ahmad, *ChemPhysChem*, 2014, **15**, 1148.
- 12 J. H. Rhee, C.-C. Chung and E. W.-G. Diau, *NPG Asia Mater.*, 2013, **5**, e68.
- 13 N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seok, *Nat. Mater.*, doi:10.1038/nmat4014
- 14 J.-W. Lee, D.-J. Seol, A.-N. Cho and N.-G. Park, *Adv. Mater.*, 2014, **26**, 4991.
- 15 H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, **345**, 542.
- 16 N. J. Jeon, J. Lee, J. H. Noh, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, *J. Am. Chem. Soc.*, 2013, **135**, 19087.
- 17 H. Li, K. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar and A. C. Grimsdale, *Angew. Chem. Int. Ed.*, 2014, **53**, 4085.
- 18 P. Qin, S. Paek, M. I. Dar, N. Pellet, J. Ko, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2014, **136**, 8516.
- 19 S. Lv, L. Han, J. Xiao, L. Zhu, J. Shi, H. Wei, Y. Xu, J. Dong, X. Xu, D. Li, S. Wang, Y. Luo, Q. Meng and X. Li, *Chem. Commun.*, 2014, **50**, 6931.
- 20 J. Wang, S. Wang, X. Li, L. Zhu, Q. Meng, Y. Xiao and D. Li, *Chem. Commun.*, 2014, **50**, 5829.
- 21 A. Krishna, D. Sabba, H. Li, J. Yin, P. P. Boix, C. Soci, S. G. Mhaisalkar and A. C. Grimsdale, *Chem. Sci.*, 2014, **5**, 2702.
- 22 H. Zhang, Y. Shi, F. Yan, L. Wang, K. Wang, Y. Xing, Q. Dong and T. Ma, *Chem. Commun.*, 2014, **50**, 5020.
- 23 Y. S. Kwon, J. Lim, H.-J. Yun, Y.-H. Kim and T. Park, *Energy Environ. Sci.*, 2014, **7**, 1454.
- 24 J. Liu, Y. Wu, C. Qin, X. Yang, T. Yasuda, A. Islam, K. Zhang, W. Peng, W. Chen and L. Han, *Energy Environ. Sci.*, 2014, **7**, 2963.
- 25 B. Cai, Y. Xing, Z. Yang, W.-H. Zhang and J. Qiu, *Energy Environ. Sci.*, 2013, **6**, 1480.
- 26 T. Krishnamoorthy, F. Kunwu, P. P. Boix, H. Li, T. M. Koh, W. L. Leong, S. Powar, A. Grimsdale, M. Grätzel, N. Mathews and S. G. Mhaisalkar, *J. Mater. Chem. A*, 2014, **2**, 6305.
- 27 Y. Xiao, G. Han, Y. Chang, H. Zhou, M. Li and Y. Li, *J. Power Source*, 2014, **267**, 1.
- 28 T. Leijtens, I.-K. Ding, T. Giovannina, J. T. Bloking, M. D. McGehee and A. Sellinger, *ACS Nano*, 2012, **6**, 1455.
- 29 G. Pucklyte, B. Schmaltz, A. Tomkeviciene, M. Degbia, J. V. Grazulevicius, H. Melhem, J. Bouclé and F. Tran-Van, *J. Power Sources*, 2013, **233**, 86.
- 30 B. J. Song, H. M. Song, S. K. Kim, M. S. Kang, K. D. Seo, I. T. Choi, D. Cho, M. J. Ju and H. K. Kim, *Chem. Eur. J.*, 2011, **17**, 11115.
- 31 I. T. Choi, M. J. Ju, S. H. Song, S. G. Kim, D. W. Cho, C. Im and H. K. Kim, *Chem. Eur. J.*, 2013, **19**, 15545.
- 32 M. J. Ju, I. T. Choi, S. G. Kim, K. M. Lim, J. Ko, J. C. Kim, S. Saker, J. J. Lee, I.-Y. Jeon, H.-J. Choi, J.-B. Baek and H. K. Kim, *ACS Nano*, 2013, **7**, 5243.
- 33 M. J. Ju, I.-Y. Jeon, J. C. Kim, K. M. Lim, H.-J. Choi, S. M. Jung, I. T. Choi, Y. K. Eom, Y. J. Kwon, J. Ko, J. J. Lee, H. K. Kim and J.-B. Baek, *Adv. Mater.*, 2014, **26**, 3055.
- 34 H. J. Snaith and M. Grätzel, *Appl. Phys. Lett.*, **89**, 262114.
- 35 J.-H. Yum, T. W. Holcombe, Y. Kim, J. Yoon, K. Rakstys, M. K. Nazeeruddin and M. Grätzel, *Chem. Commun.*, 2012, **48**, 10727.
- 36 W. Ying, J. Yang, M. Wielopolski, T. Moehl, J.-E. Moser, P. Comte, J. Hua, S. M. Zakeeruddin, H. Tian and M. Grätzel, *Chem. Sci.*, 2014, **5**, 206.

COMMUNICATION

View Article Online
DOI: 10.1039/C4CC06716A

- 37 A. Abate, T. Leijters, S. Pathak, J. Teuscher, R. Avolio, M. E. Errico, J. Kirkpatrick, J. M. Ball, P. Docampo, I. McPherson and H. J. Snaith, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2572.