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## Low-cost Carbazole-based Hole Transport Material for

## **Highly Efficient Perovskite Solar Cells**

Zhiliang Chen<sup>[a]</sup>, Hui Li<sup>[b]</sup>, Xiaolu Zheng<sup>[a]</sup>, Qi Zhang<sup>[a]</sup>, Zhanfeng Li<sup>\*[b]</sup>, Yuying Hao<sup>[b]</sup>, Guojia Fang<sup>\*[a]</sup>

[a] Dr. Z. Chen, Dr. X. Zheng, Dr. Q. Zhang, Prof. Dr. G. Fang

Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education of China, School of Physics and Technology, Wuhan University, Wuhan 430072, People's Republic of China.

E-mail: gjfang@whu.edu.cn

[b] Dr. H. Li, Prof. Dr. Z. Li, Prof. Dr. Y. Hao

Key Laboratory of Advanced Transducers and Intelligent Control System, Ministry of Education and Shanxi Province, College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, People's Republic of China.

E-mail: lizhanfeng@tyut.edu.cn

Zhiliang Chen and Hui Li contribute equally to this work.

А low carbazole based small molecule material cost 1,3,6,8-tetra(N,N-p-dimethoxyphenylamino)-9-ethyl-carbazole was designed and synthesized using a facile three-step synthetic route. The novel material was fully characterized and further applied as hole transport material (HTM) for low temperature processed planar perovskite solar cells (PSCs). Devices based on this new HTM exhibit a high power conversion efficiency (PCE) of 17.8%, which is comparable that (PCE of 18.6%) of the costly to 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene

(Spiro-OMeTAD) based PSCs.

#### Introduction

In the last few years, organic-inorganic metal halide perovskite materials (ABX<sub>3</sub>, A=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, HC-(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>, B=Pb, Sn, X=Cl, Br, I) have attracted considerable attention as light absorber for third generation solar cells. Due to their excellent opto-electronic properties, such as high absorption coefficient,<sup>[1]</sup> ambipolar charge transportation,<sup>[2]</sup> and long carrier diffusion length,<sup>[3, 4]</sup> the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has been improved from 3.8% to 22.1% in just 8 years (2009-2017).<sup>[5-10]</sup> In efficient PSCs, the perovskite layer is generally sandwiched between electron transport material (ETM) and hole transport material (HTM), which play a crucial role in transporting photo-generated charges from perovskite absorber to electrodes. The most common HTM used in high performance **PSCs** 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene is (Spiro-OMeTAD), which was first introduced in PSCs by Kim five years ago<sup>[6]</sup> and is still indispensable for PSCs to achieve high efficiencies.<sup>[11-13]</sup> To date, the record PCEs of >20% was achieved using this organic HTM combined with state-of-the-art perovskite materials as light absorber.<sup>[14]</sup> However, during the period of its wide application in laboratory research, Spiro-OMeTAD still has some weakness, such as complex synthetic route and the high cost it causes, as well as humidity instability, leading to a setback for the commercial process of PSCs. Given this, plenty of efforts were made to explore substitutes for this imperfect HTM.<sup>[15-18]</sup> Liu and co-workers

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reported Spiro[fluorene-9,9'-xanthene]-based HTMs for PSCs, in which not only high PCE but also better stability were achieved.<sup>[19]</sup> And Xu and Bi et al. achieved high PCEs of over 19% based on similar structure small molecule material (X59 and X60).<sup>[20, 21]</sup> However, the materials reported above and Spiro-OMeTAD all comprise fluorine group, which is expensive and responsible for a large proportion of the final cost of ultimate product. Replacing fluorine with a cheaper substitute seems to be an effective way to cut the cost of the HTMs. Carbazole is commercially available material and the price is temptingly low. Because of its special rigid structure and large conjugated system, carbazole has excellent photoelectrical property.<sup>[22]</sup> Since 1, 3, 6, 8 reactive sites of carbazole can be easily substituted with functional groups to meet a variety of requirements, carbazole-based derivatives are widely used in electroluminescence and photovoltaic devices. Recently, carbazole derivatives with various molecular structures have been designed for HTMs in PSCs.<sup>[23-32]</sup> In the molecular structure of many HTMs, carbazole together with some atypical hole transport groups form the core of the molecular, with phenylamine structure outside.<sup>[23, 24, 26-29]</sup> These atypical hole transport groups such as benzene and biphenyl can transport both holes and electrons, which may impair the hole-mobility of these HTMs. Taking away these moieties and using a single carbazole group as a molecular core may be an effective way to produce high mobility HTM. In the present work, we report on the synthesis of a structure-simple carbazole based small molecule material 1,3,6,8-tetra(N,N-p-dimethoxyphenylamino)-9-ethyl-carbazole (Cz-OMeTAD) as HTM for PSCs. The Cz-OMeTAD compound was synthesized using a facile

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three-step synthetic route and shows high solubility in organic solvents (e.g. chlorobenzene, toluene), which is applicable for fabricating thin film devices via solution processing. Photoelectrical measurements (UV/Vis, cyclic voltammetry (CV), thin-film conductivity and mobility) suggest that Cz-OMeTAD exhibits excellent properties, such as suitable energy levels, high mobility and conductivity, making it an ideal candidate for HTM in efficient PSCs. We prepared planar PSCs with a device structure of FTO/SnO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/HTM/Au. The Cz-OMeTAD based PSCs achieve a high PCE of 17.81% with open circuit voltage ( $V_{OC}$ ) of 1.14 V, short circuit current density ( $J_{SC}$ ) of 22.26 mA cm<sup>-2</sup>, and fill factor (FF) of 0.71, which is comparable to that of devices using the costly Spiro-OMeTAD as HTM, suggesting that the novel material we synthesize is very promising for replacing the costly Spiro-OMeTAD in commercial application of PSCs in the future.

#### **Results and Discussion**

The synthetic route towards Cz-OMeTAD is illustrated in Scheme 1 and the detailed information can be found in the experimental section. As shown, the synthesis of Cz-OMeTAD requires only three-step reaction process and is much simple than that of Spiro-OMeTAD, which typically need five steps to obtain the ultimate product.<sup>[33]</sup> Firstly, commercially available material carbazole was used as the starting material to synthetize 1,3,6,8-TetrabroMocarbazole via a bromine substitute reaction in a 91% yield, which was in preparation for the final cross-coupling reaction to add diphenylamine group on the carbazole core. The second reaction process (yield 98%) of substituting the active hydrogen on N-H with ethyl aimed at improving the stability

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of the final product. On the other hand, the ethyl-substituent was believed to be beneficial for the solubility of the material. The synthesis of Cz-OMeTAD was cross-coupling finished palladium-catalyzed C-N reaction with by а 4,4'-dimethoxydiphenylamine and 9-ethyl-1,3,6,8-tetrabromocarbazole (vield 80%). The overall yield of this synthetic route is >70%, and no air sensitive, corrosive or toxic reagents were used during the synthesis process. Most importantly, the synthesis cost of Cz-OMeTAD is much lower than that of Spiro-OMeTAD. We compared the synthesis cost of these two compounds using the cost model described by Pablo et al.<sup>[33]</sup> and Osedach et al.<sup>[34]</sup> The quotes for the necessary raw material were mainly collected from the official websites (China Mainland region) of Sigma-Aldrich and Alfa. Since the only difference in molecule structure between Cz-OMeTAD and Spiro-OMeTAD is the center part (9-ethyl-carbazole for Cz-OMeTAD and spirobifluorene for Spiro-OMeTAD, Figure 1), we estimated the synthesis costs of 1 9-ethyl-1,3,6,8-tetrabromocarbazole gram and 2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] to compare the cost of these two materials. As presented in Figure S4 and Table 1, the synthesis cost of 1 gram

9-ethyl-1,3,6,8-tetrabromocarbazole is estimated to be 21.94  $g^{-1}$ , which is almost 20 times lower than that of its counterpart (Figure S3 and Table S1).



Scheme 1. The synthetic route of Cz-OMeTAD.

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Cz-OMeTAD Molecular Weight: 1103

Figure 1. Molecular structure of the Cz-OMeTAD synthesized in this work. The molecular weight is given in  $g \mod^{-1}$ .

Table	1.	Materials	quantities	and	cost	for	the	synthesis	of
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Chemical name	Weight	Weight	Weight	Price of Chemical	Material cost	Cost per step
	reagent	solvent	workup	( <b>\$/kg</b> )	(\$/g product)	(\$/step)
	( <b>g</b> )	(g)	(g)			
Carbazole	1.57			476.54	0.75	8.71
N,N-DiMethylfor		4.47		170.46	0.76	
MaMide						
N-Bromosuccinimi	6.70			197.18	1.32	
de						
N,N-DiMethylfor		29.78		170.46	5.08	

9-ethyl-1,3,6,8-tetrabromocarbazole.

MaMida

Ivialvilue						
Water			62.88	-	-	
$CH_2Cl_2$			15.71	50.89	0.80	
NaH	0.96			3696.11	3.55	13.23
N,N-DiMethylfor		7.57		170.46	1.29	
MaMide						
Bromoethane	0.80			2110.92	1.69	
water		150		-	-	
$CH_2Cl_2$			125.88	50.89	6.41	
$Na_2SO_4$			1	165.88	0.17	
Methanol			3.96	31.07	0.12	
Total				_	-	21.94

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were then carried out to measure the thermal stability of the product obtained above. As presented in Figure 2a, the decomposition temperature corresponding to a 5% weight loss (T<sub>d</sub>) is about 423 °C, indicating good thermal stability of Cz-OMeTAD. The concave point at around 262 °C (Figure 2b) represents the melting point of Cz-OMeTAD, and the glass transition temperature (T<sub>g</sub>) of Cz-OMeTAD is evaluated to be 114.9 °C.



Figure 2. TGA (a) and DSC (b) curves of Cz-OMeTAD with a scan rate of 10  $\,^{\circ}$ C

min<sup>-1</sup> under a nitrogen atmosphere.

To evaluate the value of the novel material we synthesize for application in photovoltaic devices, we conducted a series of measurements to characterize the photoelectrical properties of Cz-OMeTAD, with the commonly used Spiro-OMeTAD as a reference. Figure 3a shows the UV-vis absorption spectra of Cz-OMeTAD and Spiro-OMeTAD in CH<sub>2</sub>Cl<sub>2</sub>. Similar to other work reported,<sup>[35]</sup> Spiro-OMeTAD exhibits characteristic absorption peaks at about 310 nm and 390 nm, which were attributed to the aromatic ring and conjugated system composed of triarylamine, respectively. Compared to Spiro-OMeTAD, one more absorption peak was observed at 420 nm for Cz-OMeTAD, this weaker characteristic peak may be ascribed to the ethyl substituent on carbazole. Figure 3b depicts the corresponding Tauc plot of the absorption spectra, from which the optical band gap (Eg) can be evaluated by extending the linear portion of the plots to the binding energy axis. As labeled in Figure 3b, the obtained  $E_g$  values are 3.02 eV for Spiro-OMeTAD and 2.75 eV for Cz-OMeTAD, respectively.



**Figure 3.** (a) UV-vis absorption spectra of Cz-OMeTAD and Spiro-OMeTAD tested in CH<sub>2</sub>Cl<sub>2</sub> and (b) the corresponding Tauc plot of the absorption spectra. (c) Cyclic voltammogram of Cz-OMeTAD in acetonitrile with ferrocene/ferrocenium as an internal standard. (d) Energy level diagram of the corresponding materials applied in PSCs in this work.

For HTMs used in photovoltaic devices, suitable energy levels can facilitate the transporting of photoexcited holes from light absorber layer to the anode. Here we conducted CV characterization to determine the highest occupied molecular orbital (HOMO) energy level of Cz-OMeTAD, in which ferrocene/ferrocenium were used as an internal standard reference. Figure 3c shows the CV curves of Cz-OMeTAD.

According to the method reported,<sup>[36]</sup> the HOMO energy levels is obtained at -5.27 eV for Cz-OMeTAD, which is well-aligned with the valence band of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (-5.43 eV). And the HOMO energy level of Cz-OMeTAD is slightly lower than that of Spiro-OMeTAD (5.22 eV),<sup>[8]</sup> which allows photoexcited holes cascade into the HTM with less energy loss and this will further increase the  $V_{OC}$  value of devices. Combined with the band gaps obtained from the Tauc plot of the absorption spectrum, the lowest unoccupied molecular orbital (LUMO) energy levels of Spiro-OMeTAD and Cz-OMeTAD were determined to be at -2.20 eV and -2.52 eV, respectively (Table 2). The energy barrier (1.41 eV) existing between the LUMO of Cz-OMeTAD and the conduction band edge of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> would effectively block electron carrier transporting (Figure 3d), which should avoid charge recombination.



**Figure 4.** (a) Current density-voltage and (b) current-voltage characteristics of the doped Cz-OMeTAD and Spiro-OMeTAD films.

Subsequently, The hole mobility of Cz-OMeTAD and Spiro-OMeTAD films were measured using space-chargelimited currents model,<sup>[37, 38]</sup> in which a hole-only device

10.1002/cssc.201700678

with a structure of FTO/PEDOT:PSS/HTMs/Au was used. By fitting the current density-voltage (J-V) curves (Figure S5), the mobility values were obtained according to the modified Mott-Gurney equation.<sup>[39]</sup>

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$
(1)

where *J* is the current density,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity,  $\mu$  is the zero-field mobility, *V* is the applied voltage and *d* is the thickness of active layer. As listed in Table 2, the doped Cz-OMeTAD film exhibits a mobility of  $1.82 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which is at the same order of magnitude and slightly lower than that of Spiro-OMeTAD based film  $(3.08 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ . We also tested the conductivities of the two HTMs with a two-contact electrical conductivity set-up as literature.<sup>[23]</sup> The conductivities of these HTMs were determined from equation (2),<sup>[37]</sup> where  $\sigma$  is the conductivity, *L* is the channel length, *w* is the channel width, *t* is the film thickness, and *R* is the resistivity calculated from the gradients of the curves (Figure 4b). The obtained conductivity of Spiro-OMeTAD is also a little higher than that of Cz-OMeTAD (Table 2).

$$\sigma = \frac{L}{Rw}$$
(2)

 Table 2. Summary of optical, electrochemical and electrical data of Cz-OMeTAD and
 Spiro-OMeTAD.

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HTM	$\lambda_{abs}^{[a]}$ [nm]	E <sub>gap</sub> [eV]	HOMO [eV]	LUMO [eV]	Hole mobility $[cm^2 V^{-1} s^{-1}]$	Conductivity [S cm <sup>-1</sup> ]
Cz-OMeTAD	450.9	2.75	-5.27	-2.52	$1.82 \times 10^{-3}$	$1.20 \times 10^{-4}$
Spiro-OMeTAD	410.6	3.02	-5.22	-2.20	$3.08 \times 10^{-3}$	$4.41 \mathrm{x10}^{-4}$

[a] Absorption onset determined at UV-vis spectra.

The excellent photoelectrical properties of Cz-OMeTAD, such as suitable energy levels and high hole mobility (after Li-doping), make it promising for HTM in PSCs. We prepared PSCs applying Cz-OMeTAD as HTM with Spiro-OMeTAD as a reference. The schematic view in Figure 5a shows of the device structure used in this work, wherein a thin layer (ca.40 nm) of SnO<sub>2</sub> nanocrystals was used as ETM on fluorine-doped SnO<sub>2</sub> (FTO) glass, a thickness of 360 nm CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film as light absorber, and ~50 nm gold as electrode. The thickness of HTMs layer here is about 150 nm. All the thickness data were obtained from the cross-section scanning electron microscopy (SEM) image shown in Figure S6. The photovoltaic performance of the best-performing device was presented in Figure 5b. The champion PCE obtained is 17.81% with a  $V_{\rm OC}$  of 1.14 V, a  $J_{\rm SC}$  of 22.26 mA cm<sup>-2</sup>, and a FF of 0.71 for Cz-OMeTAD based devices, which is comparable to that of Spiro-OMeTAD based PSCs. Devices based on these two HTMs both exhibit good long-term stability, the average PCE of Li-TFSI doped Cz-OMeTAD and Spiro-OMeTAD based PSCs retains around 90% of the initial PCEs after 1000 h storage at 30  $\pm$  5% RH and room temperature (Figure S7). However, PSCs based on Cz-OMeTAD and Spiro-OMeTAD exhibit J-V hysteresis (Figure S8), which may originate from the ferroelectric nature of the perovskite material or accumulation of charges in defects at its surface/interfaces.<sup>[40]</sup> Further work on preparing hysteresis free Cz-OMeTAD based PSCs is on the way in our laboratory. Figure 5c displays the corresponding Incident photon-to-current conversion efficiency (IPCE) spectrum, the value of  $J_{SC}$  integrated from its IPCE spectrum is 20.54 mA cm<sup>-2</sup>, which closely agree with the value obtained from the J-V curve. The IPCE spectrum exhibits a broad plateau from 400 to 800 nm, suggesting a high photon-charge conversion efficiency of the PSC. The statistics data of the PCEs are presented with histogram in Figure 5d. The average PCE of the 40 devices is 16.22±0.80%, and 60% of the fabricated devices exhibit a PCE over 16%. These results indicate that Cz-OMeTAD is an excellent HTM and very promising for replacing Spiro-OMeTAD in commercially application of PSCs.



Figure 5. (a) Schematic view of the structure of device used in this work. (b) J-V curves of PSCs based on Cz-OMeTAD and Spiro-OMeTAD, with a table of

10.1002/cssc.201700678

performance data inserted. (c) IPCE spectrum of the champion Cz-OMeTAD based PSCs. (d) Histogram of efficiency of PSCs with a structure of FTO/SnO<sub>2</sub>/ Perovskite/Cz-OMeTAD/Au.

#### Conclusions

In developed small molecule summary, we have a novel 1,3,6,8-tetra(N,N-p-dimethoxyphenylamino)-9-ethyl-carbazole (termed Cz-OMeTAD) as HTM for efficient PSCs. The Cz-OMeTAD was synthesized via a simple three-step synthetic route using inexpensive starting material without air sensitive, corrosive or toxic reagents in the synthetic process, making it cost effective and environmental friendly for photovoltaic devices. PSCs based on Cz-OMeTAD HTM exhibited high performance (PCE of 17.81%,  $V_{OC}$  of 1.14 V,  $J_{SC}$  of 22.26 mA cm<sup>-2</sup>, and FF of 0.71), which is competitive with the costly Spiro-OMeTAD based PSCs. These results suggest that this novel HTM is very promising for commercial application in photovoltaic devices in the future.

During revision of the manuscript upon editorial request, we synthesized a series of 9-ethyl-carbazole core based HTMs, with only the outside part different from the Cz-OMeTAD (Figure S9). But devices based on these HTMs exhibit poor performance (PCE of nearly 0), this result suggests the important role of OMeTAD groups outside the carbazoles core to achieve high performance as HTM in PSCs.

#### **Experimental Section**

#### Materials

Tin oxide (SnO<sub>2</sub>) nanocrystals were prepared as reported and used with a mole concentration of 0.1M. 617.1 mg of lead iodide (PbI<sub>2</sub>) (Aladdin reagent, 99.99%), 219.5 mg methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I) (Aladdin reagent, 99.99%) and were dissolved in 1 mL solution of 800µL N,N-dimethylformamide (DMF) (Alfa-aesar) and 200µL dimethyl sulfoxide (DMSO) (Alfa-aesar). The obtained mixture was stirred at 60 °C overnight. 68 mM Spiro-OMeTAD (Shenzhen Feiming Science and Technology Co., Ltd., 99.0%), 55 mM TBP (Aladdin reagent), and 26 mg of Li-TFSI (Aladdin reagent) were dissolved in acetonitrile and chlorobenzene (1:10 in volume ratio). Cz-OMeTAD powder was synthesized as detailed below and used to prepare precursor. The doping concentrations of Cz-OMeTAD were the same as those in Spiro-OMeTAD.

#### **Synthesis**

**Synthesis of 1,3,6,8-Tetrabromocarbazole.** Carbazole (5g, 29.94mM) and 15mL DMF were mixed in a three-necked flask and stirred in the ice bath under nitrogen atmosphere for 1h to prepared solution A. N-Bromosuccinimide (21.317g, 119.76mM) and 100mL DMF were mixed and stirred to form solution B. Then solution B was added dropwise into the cooling solution A. Then the reaction mixture was kept at room temperature. After 10h, 200mL deionized water was added in to the mixture and a precipitate was appeared. Preliminary product was obtained by filtering, washing and drying the precipitate. Then highly purified 1,3,6,8-Tetrabromocarbazole was

recrystallization by dichloromethane to afford a final product in 91% yield (13.04g).

Synthesis of 9-ethyl-1,3,6,8-tetrabromocarbazole. 1,3,6,8-Tetrabromocarbazole (11.95g, 25.0mM) and NaH (12g, 50.0mM) ) were dissolved in 100mL DMF, then the solution was added dropwise into bromoethane (10g, 50mM). The obtained mixture was stirred at 40 °C under a nitrogen atmosphere for 4h. When the reaction stopped, the mixture was extracted with  $CH_2Cl_2$ . The organic phases were washed with deionized water and dried with anhydrous MgSO<sub>4</sub>. After the solvent was evaporated, the residue was recrystallization by  $CH_2Cl_2$  and  $CH_3OH$  to afford a white solid in 98% yield (12.51g).

Synthesis of 1,3,6,8-tetra(N,N-p-dimethoxyphenylamino)-9-ethyl-carbazole. The synthesis of 1,3,6,8-tetra(N,N-p-dimethoxyphenylamino)-9-ethyl-carbazole powder was achieved by Buchwald–Hartwig reaction in which 9-ethyl-1,3,6,8-tetrabromocarbazole (0.51g, 1.0mM), 4,4'-dimethoxydiphenylamine (1.15g, 5.0mM), Nat-Bu (0.57g, 6.0mM), tris(dibenzylideneacetone)dipalladium (0.037g, 0.04mM) and tritertbutylphosphine (0.012g, 0.06mM) were added to 20mL of dry toluene under nitrogen atmosphere. The mixture solution was heated to 110°C and refluxed overnight. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and the organic phases were dried with anhydrous MgSO<sub>4</sub>. After the solvent was evaporated, the residue was purified by column chromatography (petroleum ether/ethyl acetate =10/1) to afford 0.88g (yield 80%) of Cz-OMeTAD. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.21-6.55 (m, 32H), 3.92-3.62 (m, 24H), 1.26 (d, J = 3.1 Hz, 3H), 1.20 (s, 2H), 1.18 (d, J = 1.6 Hz, 2H), 1.16 (s, 2H). <sup>13</sup>C

10.1002/cssc.201700678

NMR (101 MHz, CDCl<sub>3</sub>) δ: 154.6, 154.4, 142.0, 141.6, 134.2, 133.2, 127.4, 126.2, 124.2, 122.6, 114.4, 114.2, 113.0, 80.4, 55.4, 55.4, 28.5, 15.4. HR-MS (ESI) m/z: [M+1]<sup>+</sup> calcd for 1103.4827; found, 1104.4874. Corresponding spectrums can be found in Figure S1 and Figure S2.

#### **Solar Cell Fabrication**

FTO substrates (OPVtech, 13 Ohm/square) were sequentially rinsed by sonication in detergent, deionized water, acetone, and ethanol and finally dried in air. The SnO<sub>2</sub> nanoparticles were spin-coated on the cleaned FTO substrates at 3000 rpm for 30 s, followed by an annealing process at 200°C for 30 mins. Perovskite absorber layer was then deposited on the samples using a solvent-engineering technique reported as literature. The perovskite solution was deposited on the SnO<sub>2</sub> films by spin-coating first at 1000 for 10 s and then at 4000 rpm for 40 s. During the spin-coating process, 400µL chlorobenzene was dripped on the substrate 10 s prior to the end of the step, the as-deposited films were then annealed at 100°C for 10 mins to achieve a uniform perovskite film. The Cz-OMeTAD and Spiro-OMeTAD films were spin-coated on perovskite film at 3000 rpm for 30 s. The devices were completed by thermal evaporation of a thin layer of gold as back contact.

#### Characterization

<sup>1</sup>H NMR was recorded on a Bruker 400 MHz NMR spectrometer. TGA and DSC were carried on a STA 409 PC instrument at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Absorption spectra were recorded by a Unico UV-2600 PCS

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spectrophotometer. CV was performed using a CHI 660E electrochemical workstation at a scan rate of 100 mV s<sup>-1</sup>. All experiments were carried out in a three-electrode compartment cell with a Pt-sheet counter electrode, a glassy carbon working electrode, and a Pt-wire reference electrode. The supporting electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) solution in dry acetonitrile. The cell containing the solution of the sample (1 mM) and the supporting electrolyte was purged with a nitrogen gas thoroughly before scanning for its oxidation and reduction properties. Ferrocene was used for potential calibration in each measurement. All the potentials were reported relative to ferrocene-ferrocenium couple, whose oxidation potential was +0.13 V relative to the reference electrode. Density functional theory (DFT) calculations (B3LYP) were performed for the target compound with the 6-31G (d,p) basis set by using the Gaussian 09 program. The cross section image of the PSCs was observed by a high-resolution field emission SEM (JSM 6700F, Japan). J-V characteristics of devices were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua Instruments, China) with a standard ABET Sun 2000 Solar Simulator. The area of the Au electrode was 0.09 cm<sup>2</sup>. IPCE was measured by a QE/IPCE system (Enli Technology Co. Ltd.) in 300-800 nm wavelength range.

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Keywords: carbazole • small molecule • hole transport material • perovskite solar

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