Accepted Manuscript

Title: A new carbazole-based hole-transporting material with low dopant content for perovskite solar cells

Author: Jiang Wang Yu Chen Fusheng Li Xueping Zong Jinlin Guo Zhe Sun Song Xue



PII:	S0013-4686(16)31293-2
DOI:	http://dx.doi.org/doi:10.1016/j.electacta.2016.05.203
Reference:	EA 27427
To appear in:	Electrochimica Acta

 Received date:
 3-3-2016

 Revised date:
 29-5-2016

 Accepted date:
 29-5-2016

Please cite this article as: Jiang Wang, Yu Chen, Fusheng Li, Xueping Zong, Jinlin Guo, Zhe Sun, Song Xue, A new carbazole-based hole-transporting material with low dopant content for perovskite solar cells, Electrochimica Acta http://dx.doi.org/10.1016/j.electacta.2016.05.203

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A new carbazole-based hole-transporting material with low dopant content for perovskite solar cells

Jiang Wang,^{a,b} Yu Chen,^{*,a} Fusheng Li,^a Xueping Zong,^a Jinlin Guo,^a Zhe Sun,^a Song Xue^{*,a}

^a Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P.R. China;

^b Department of Chemistry, School of Science, Tianjin University, Tianjin, 300072, P.R. China Corresponding author: Fax: +86-22-60214252; E-mail address: cy26tj@163.com; xuesong@ustc.edu.cn.

1

Graphical Abstract



Highlights

- A carbazole-based hole-transporting material was synthesized via a facile route.
- This new material with low-content dopant makes device display best performance.
- The optimized doping concentration of 4-tert-butylpyridine was 120mM.

Abstract

A new carbazole-based hole-transporting material incorporating a 3,3'-biphenyl central core has been synthesized via a facile route. A reference compound without carbazole moiety was also prepared. Their geometric structures, thermal stability and photovoltaic properties were investigated. This new carbazole-based material exhibits a high glass transition temperature (167.8 °C) and a suitable highest occupied molecular orbital level well-matched with CH₃NH₃PbI₃ perovskite. A low doping content of 4-tert-butylpyridine (120 mM) is observed for the best performance of perovskite solar cell in conjunction with a carbon counter electrode. The device achieves a power conversion efficiency of 4.53% under illumination of 100 mW·cm⁻². The performance is much better than that of the reference compound (0.19%), and comparable to that of spiro-OMeTAD at the same dopant level (5.10%). The results indicate the carbazole-based material is a promising class of hole-transporting materials for perovskite solar cells.

Keywords: Carbazole; Hole-transporting material; Perovskite solar cells; Dopant; Carbon counter electrode

1. Introduction

Organic-inorganic perovskite solar cells (PSCs) have drawn great attention because of their low cost and high performance in solar to energy conversion [1-4]. The power conversion efficiency (PCE) of PSC has achieved more than 20% by introducing solid-state hole-transport material (HTM) [5-8]. The state-of-the-art HTM is 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene

(spiro-OMeTAD) was used as a solid HTM in dye-sensitized solar cells (DSCs) [9], and it is the most effective and frequently reported HTM for PSCs [10,11]. Recently, alternative low-cost and high-efficiency organic small-molecule HTMs have been developed for PSCs [12-16]. Organic small molecules have superiority of facile synthesis, good infiltration and excellent hydrophobic property. These organic small-molecule HTMs often used by doping lithium are bis(trifluoromethylsulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (TBP)[17]. Occasionally, the dopant of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) bis(trifluoromethylsulfonyl) imide was also used [18]. The frequently reported optimized concentrations of LiTFSI and TBP for spiro-OMeTAD are 30 mM and 200 mM, respectively [1,19].

Carbazoles are a significant class of aromatic heterocyclic compounds. Carbazole-based derivatives have interesting photorefractive, photoconductive, hole-transporting, and light-emitting properties, and they have been widely used as organic photovoltaic materials [20-22]. The carbazole-diphenylamine moiety has currently become an attractive building block of organic small-molecule HTM for PSCs,

owing to their low cost and good reactivity [19,23,24]. Carbazole-based oligomer [25] and organic small molecules have been reported to be used as HTMs for PSCs. In organic small-molecule carbazole-based HTMs, they are bearing two-arm and three-arm type structures. Carbazole-diphenylamines or N-alkyl carbazole can be used for donor groups incorporating with different central core units such as 3,4-ethylenedioxythiophene [26], 1,4-phenyl, 4,4'-biphenyl, triphenyl amine and 1,3,5-trisphenylbenzene [23]. The design of HTM structure has a great influence on their conductivity, molecular aggregation state and solubility in nonpolar solvents [24]. Carbazole-based organic small-molecule HTMs exhibited good thermal stability, film-forming ability and good conductivity by developing reasonable structures. Benefiting from the introduction of carbazole moiety and addition of appropriate dopant, the photovoltaic performances of PSCs fabricated from carbazole-based HTMs were found comparable to that of the device with commercial spiro-OMeTAD [19]. According to previous reports, the dopant content is a key point for enhancing the efficiency of organic HTMs used for PSCs [27]. Reduction of organic HTMs doping content is still a challenging subject in order to prepare both efficient and more economical PSC devices. In the literature, the appropriate amount for LiTFSI that introduce into organic HTMs based on carbazole-diarylamine solution was 30 mM [19]. To the best of our knowledge, the research on organic HTMs based on carbazole-diphenylamine with different doping concentration of TBP has not been involved yet.

In this paper, we report the synthesis and characterization of a new organic

small-molecule HTMs containing carbazole, 9,9'- ([1,1'-bi(4-methoxyphenyl)]-3,3'-diyl) bis(N3,N3,N6,N6-tetrakis (4-methoxy-phenyl)-9H-carbazole-3,6-diamine) (**HBZ-70**). A reference HTM, ([1,1'-bi(4-methoxyphenyl)]-3,3'-diyl)-N4,N4'-bis (4-methoxyphenyl)benzenamine (**HBZ-71**), was prepared for a comparative study. Their structures are shown in Fig. 1. Both compounds possess a 3,3'-biphenyl skeleton. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were tested for the thermal stability of **HBZ-70** and **HBZ-71**. Spectral, electrochemical characterizations and theoretical calculations were investigated for their absorption ability, energy level and optimized geometric structures. PSCs based on the two compounds were prepared and measured for studying their photovoltaic performances. The results indicate that **HBZ-70** is a possible candidate for carbazole-based HTMs using low content of dopant.

Fig.1

2. Experimental

2.1. Instrument and materials

All reactions were carried out under an argon condition and solvents were distilled from analytical grade reagents. Benzothiazole, Pd₂(dba)₃, *n*-butyllithium, *t*-BuONa, (*t*-Bu)₃P were purchased from Energy Chemical (China). 4-tert-Pyridine (TBP) and 0.1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Aldrich. The melting points of the samples were measured with a RY-1 melting point apparatus (Tianfen, China), and temperatures were uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were referenced against TMS. High resolution mass spectra (HRMS) were obtained with a

Micromass GCT-TOF mass spectrometer.

2.2. Synthesis

The synthesis routes for **HBZ-70** and **HBZ-71** are shown in Scheme 1. Intermediates from compound **1** to **5** were known compounds, and they were prepared by following synthetic methods reported in the literatures [19,28].

Scheme 1

2.2.1. General procedure for synthesis of HBZ-70, HBZ-71

To a 100 mL two neck round-bottom flask were added compound **5** (5.0 mmol, 1.0 equiv.), bis(4-methoxyphenyl)amine or N3,N3,N6,N6-tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine (2.5 equiv.), $Pd_2(dba)_3$ (0.1 equiv.), *t*-BuONa (3.0 equiv.), $P(t-Bu)_3$ (0.2 equiv.) and 30 mL anhydrous toluene. The reaction mixture was refluxed overnight under argon. After cooling down to room temperature, the mixture was extracted with ethyl acetate and washed with brine (3 × 15 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and concentrated in vacuum to give the crude product, which was purified by column chromatograph packed with silica gel to afford pure compound.

9,9'-([1,1'-bi(4-methoxyphenyl)]-3,3'-diyl)bis(N3,N3,N6,N6-tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine) (**HBZ-70**): A green powder, yield: 59.6%. ¹H NMR (400 MHz, DMSO) δ 7.71 (4H, d, *J* = 1.9 Hz), 7.57 (2H, dd, *J* = 8.7, 2.5 Hz), 7.49 (2H, s), 7.34 (2H, s), 7.32 (4H, d, *J* = 8.8Hz), 7.08 (4H dd, *J* = 8.8, 1.9 Hz), 6.85 (16H, d, *J* = 9.1 Hz), 6.79 (16H, d, *J* = 9.1 Hz), 3.86 (6H, s), 3.68 (24H, s). ¹³C NMR (100 MHz, CDCl₃) δ 155.91, 154.41, 154.08, 141.84, 141.48, 130.70, 129.64, 128.63, 127.63,

122.62, 122.31, 114.32, 114.08, 111.98, 55.84, 55.27. HRMS (ESI) calcd. for $C_{94}H_{80}N_6O_{10}$ (M+H⁺): 1453.5943, found:1453.5936.

([1,1'-bi(4-methoxyphenyl)]-3,3'-diyl)-N4,N4'-bis(4-methoxyphenyl)benzenamine (**HBZ-71**): A light yellow powder, yield: 76%. ¹H NMR (400 MHz, DMSO) δ 6.91 (4H, t, *J* = 2.9 Hz), 6.89 (6H, d, *J* = 3.4 Hz), 6.84 (8H, m), 6.81 (1H, d, *J* = 2.8 Hz), 6.79 (1H, d, *J* = 2.8 Hz), 6.71 (2H, d, *J* = 2.8 Hz), 3.71 (12H, s), 3.63 (6H, s). ¹³C NMR (100 MHz, CDCl₃) δ 154.95, 141.97, 141.46, 130.91, 128.86, 125.03, 123.07, 114.51, 111.94, 56.09, 55.52. HRMS (ESI) calcd. for C₄₂H₄₀N₂O₆ (M+H⁺): 669.2893, found: 669.2886.

The ¹H NMR and ¹³C NMR of **HBZ-70** and **HBZ-71** are given in the supplementary materials.

2.2. Device fabrication

FTO glass substrates (Nippon Sheet Glass, Hyogo, Japan, TEC-14) were cleaned in solution of detergent, deionized water, acetone and ethanol, respectively. The compact layer was deposited as reference reported and then sintering at 500 °C for 30 min. Mesoporous TiO₂ films were deposited by spin-coating of a diluted TiO₂ paste at 2000 rmp for 30s. After sintering the film at 500 °C for 30 min and cooling down to room temperature, the film was immersed in 0.04M aqueous TiCl₄ at 70 °C for 40 min. The film was rinsed by deionized water and ethanol, respectively. Then the film was annealed at 500 °C for 30 min. The CH₃NH₃PbI₃ perovskite was obtained in one step by dissolving 0.1 mmol of CH₃NH₃I and 0.1 mmol of PbI₂ (99%, Aldrich) into 2.80 mL of DMF (99.8%, Aldrich). After stirred at 70 °C for 12 h under N₂ protection, the CH₃NH₃PbI₃ solution was obtained. The one-step prepared CH₃NH₃PbI₃ precursory

solution was dropped on the substrate film by spin-coating at 3000 rmp for 30s, and dried on a hot plate at 100 °C for 15 min. The external diameter of the tubular $CH_3NH_3PbI_3$ obtained by one-step deposition is 1 µm [29]. After cooling down to room temperature, the HTM solution (48 mM in chlorobenzene) was spin-coating on top of the $CH_3NH_3PbI_3/TiO_2/FTO$ substrate at 2000 rpm. The thickness of $TiO_2/CH_3NH_3PbI_3$ layer is 360 nm, and that of HTM layer is 310 nm. Finally, the carbon cathode was made by drop coating a carbon paste onto a precleaned FTO substrate with a doctor-blade technique and then annealed at 300°C for 30 min. The carbon paste was prepared by stirring a mixture of commercial conductive carbon powder (800 nm, Chenyang Graphite, Qingdao, China), terpineol and ethanol (1:5:1, wt%) vigorously for 30 min at room temperature. A fixed active area of the carbon cathode placed on the film was 0.09 cm².

2. 3. Spectral, electrochemical and thermal stability measurements

The absorption spectra of HBZ-70 and HBZ-71 in solution and coated on mesoporous TiO_2 and $TiO_2/CH_3NH_3PbI_3$ films were measured by SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer. The morphology and structural properties of the films were analyzed using a ULTRA plus ZEISS field emission scanning electron microscope (SEM).

Cyclic voltammetry (CV) measurements for HBZ-70 and HBZ-71 were performed on a Zennium electrochemical workstation (ZAHNER, Germany) using a three-electrode system. Tetrabutylammoniun hexafluorophosphate ($n-Bu_4NPF_6$) of 0.1

10

M was added into a dichloromethane solution (DCM) as electrolyte. An Ag/0.01 M AgNO₃ electrode (acetonitrile as solvent) was used as the reference electrode. In three-electrode system, a FTO conductive glass was used as the working electrode, and a platinized carbon electrode was used as the counter electrode. The scan rates were 10 mV/s. The measurements were calibrated using ferrocene as standard. The redox potential of ferrocene internal reference is taken as 0.63 V versus NHE.

The thermal stability was determined by thermogravimetry (TG) and differential scanning calorimetry (DSC). TG analyses were performed on TG 209 F3 Tarsus (NETZSCH, Germany) at a heating rate of 10 °C/min under nitrogen atmosphere. DSC analyses were conducted on DSC 200 F3 Maia (NETZSCH, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4. Photovoltaic characterizations

The photocurrent density voltage curves (J-V) characteristics of the PSC devices were carried out using a Keithley 2400 digital source meter controlled by a computer and a standard AM1.5 solar simulator–Oriel 91160–1000 (300W) SOLAR SIMULATOR 2 x 2 BEAM. The light intensity was calibrated by an Oriel reference solar cell. To prevent inflated photocurrents arising from stray light, a black metal mask ($0.09cm^2$) surrounded the active area was placed on a testing cell during all measurements. The action spectra of monochromatic incident photon–to–current conversion efficiency (IPCE) for solar cell were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA). Intensity modulated photovoltage spectroscopes (IMVS) was also measured by the Zennium

electrochemical workstation (ZAHNER, Germany), in which a green light emitting diode (LED, 532 nm) was modulated to yield light frequency ranging from 100 mHz to 10 kHz and illumination intensity from 1 to 40 mW·cm⁻². Electron densities were measured by charge extraction technique as reported [30].

3. Results and discussion

3.1. Spectral characterizations

UV-visible absorption and fluorescence emission spectra of HBZ-70 and HBZ-71 in dichloromethane are given in Fig. 2. The maximum absorption wavelengths (λ_{abs}^{max}) of HBZ-70 and HBZ-71 are 311 nm and 295 nm, respectively. The introduction of carbazole moiety extended conjugation length of HBZ-70, resulting in a red-shifted absorption band compared to HBZ-71. The emission spectra of HBZ-70 and HBZ-71 are measured by fluorescence spectrometer. The maximum emission wavelength (λ_{fl}^{max}) of HBZ-70 and HBZ-71 are 456 nm and 428 nm, respectively. Based on the spectroscopic data [31], the optical band gap (E_g^{opt}) of HBZ-70 and HBZ-71 are calculated to be 2.93 and 3.29 eV, respectively.

Fig.2

Fig.3

Fig. 3 displays the absorption spectra of HTMs (**HBZ-70/HBZ-71**)/TiO₂ and HTMs (**HBZ-70/HBZ-71**)/perovskite(CH₃NH₃PbI₃)/TiO₂ films. The HTMs(**HBZ-70/HBZ-71**) /TiO₂ films mainly exhibit a UV absorption, and the UV absorption of **HBZ-70**/TiO₂ film is obviously stronger than that of **HBZ-71**/TiO₂. Perovskite (CH₃NH₃PbI₃) acts as a light absorber, the perovskite /TiO₂ film shows long wavelength absorption extending to

800 nm. The presence of HTMs(HBZ-70/HBZ-71) coated on perovskite /TiO₂ films enhances the absorption in the UV region of perovskite/TiO₂ film. The HTMs(HBZ-70/HBZ-71) coated on CH₃NH₃PbI₃/TiO₂ films show obvious absorption in the whole visible range from 400 to 750 nm, which facilitates the use of the whole light range of sunlight source. The spectroscopic data of HBZ-70 and HBZ-71 employed in solution and in thin films are summarized in Table 1.

Table 1

3.2. Quantum chemical calculations

To gain insight into the electronic properties and geometries of **HBZ-70** and **HBZ-71**, quantum chemical calculations were performed. Their geometric structures were optimized on the basis of DFT at the B3LYP/6-31G level. All structural optimization and energy calculations were performed using the GAUSSIAN 09 program. The optimized structures of **HBZ-70** and **HBZ-71** are shown in Fig.4, and their representative dihedral angles are marked. The introduction of a carbazole fragment decreases the dihedral angle between two phenyl of the 3,3'-biphenyl skeleton ranging from 51.6° to -46.2°, and also decreases the dihedral angle between two methoxyphenyl of the diarylamine group from 42.8° to -41.7°. **HBZ-70** exhibits a more planar 3,3'-biphenyl skeleton than that of **HBZ-71**. The 3,3'-biphenyl skeleton has a C-C linkage, and this C-C bond length of **HBZ-70** (1.489 Å) is shorter than that of **HBZ-71** are presented in Table S1 and Fig.S1 of the supplementary materials.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied

molecular orbital (LUMO) of **HBZ-70** and **HBZ-71** were simulated using Gaussian 09 program. Fig. 5 shows the frontier orbitals of molecules. The HOMO of **HBZ-70** is localized in the carbazole-diarylamine part, and the LUMO is localized in the 3,3'-biphenyl central core. The HOMO of **HBZ-71** is mainly localized in the diarylamine group, and the LUMO of **HBZ-71** is almost delocalized over the whole molecule. The results indicate both of compounds have a capability of photoinduced electron transfer by the HOMO-LUMO excitation. The HOMO-LUMO energy gap obtained from quantum chemical calculations decrease as the conjugated length increases, a finding consistent with that obtained from UV-vis absorption measurement.

Fig.4

Fig.5

3.3. Electrochemical measurements

We further carried out cyclic voltammograms to determine the accurate HOMO level of **HBZ-70** and **HBZ-71** (Fig. 6), and the values are presented in Table 2. The HOMO levels of **HBZ-70** and **HBZ-71** calculated from CV are -5.26 and -5.42 eV, respectively [32]. The HOMO levels of the two compounds are between that of CH₃NH₃PbI₃ (-5.43 eV) [33] and the carbon counter electrode (-5.0 eV) [34]. **HBZ-70** has a more appropriate HOMO level in mediating holes from the CH₃NH₃PbI₃ to the carbon counter electrode. In addition, the higher LUMO levels of **HBZ-70** (-2.33 eV) and **HBZ-71** (-2.13 eV) than the conduction band edge of CH₃NH₃PbI₃ (-3.93 eV) can block electron transportation from CH₃NH₃PbI₃ to the carbon counter electrode [35].

Table 2

3.4. Thermal properties

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to test the thermal stability of **HBZ-70** as compared with **HBZ-71**. The measured DSC and TG results were plotted in Fig. 7(a) and (b), respectively. Both **HBZ-70** and **HBZ-71** can form amorphous in solid states. TG data show **HBZ-70** exhibits better thermochemical stability. **HBZ-70** has a higher decomposition temperature (T_d , 418.4 °C) than that of **HBZ-71** (T_d , 368.4 °C). DSC data show **HBZ-70** has a high glass transition temperature (T_g) of 167.6 °C, while **HBZ-71** has a T_g of 71.8 °C. The T_g of **HBZ-70** is also higher than that of spiro-OMeTAD (125 °C) [36].

Fig.7

3.5. Device performance

To evaluate the potential of studied HTMs, PSC devices based on **HBZ-70** and **HBZ-71** were fabricated. Note that, a carbon counter electrode prepared by a low-temperature-process was used to replace noble metallic materials. The photovoltaic performance of PSCs with one-step deposition of CH₃NH₃PbI₃ was investigated. Tubular CH₃NH₃PbI₃ was obtained by the one-step deposition method according to our previous report [29, 37]. Thin films of HTMs were obtained by spin coating, and the morphology of **HBZ-70** on perovskite surface was measured by SEM technology (Fig. S2 of the supplementary material). Fig.S2 (a) and (b) displays the top view SEM images of the perovskite before and after **HBZ-70** deposition coated on perovskite layer, respectively. Fig. S2 (c) gives the cross-sectional image of a representative device. In

Fig.S2, HBZ-70 shows a good and stable amorphous state without aggregation.

Fig.8

Table 3

J-V characterizations of PSC devices based on HBZ-70 with five different concentrations of LiTFSI and TBP as dopant were conducted under illumination of 100 $mW \cdot cm^{-2}$. The performances of these devices are shown in Fig. 8. The proportions of LiTFSI/TBP including 30 mM/200 mM, 30 mM/120 mM, 30 mM/60 mM, 15 mM/200 mM and 15 mM/120 mM were investigated. The corresponding performance parameters are listed in Table 3. The dopant content had an obvious influence on the photovoltaic performances of these devices. The optimized concentration of LiTFSI and TBP for the device fabricated from HBZ-70 is 30 mM and 120 mM, respectively. Under the optimized doping conditions, the device shows a short-circuit current density (J_{sc}) of 8.47 mA·cm⁻², an open-circuit voltage (V_{oc}) of 1.03 V, and a fill factor (FF) of 0.50, leading to a PCE of 4.53%. This result is comparable to that of spiro-OMeTAD obtained by our test at the same doping level (5.10%). In addition, the PCE of device decreased when keeping the concentration of LiTFSI constant and increasing that of TBP from 120 mM to 200 mM (Conditions "1 and 2", Conditions "4 and 5", Table 3). This new carbzaole-based HTM can exhibit the best performance with low content of TBP. In addition, J-V measurements of PSCs based on HBZ-70 (48 mM) as well as that based on spiro-OMeTAD (48 mM) doped by LiTFSI/TBP with the proportion of 30 mM/120 mM were repeated more than three times. Their performance displayed replicability, possibly benefiting from the stability of the solid-state HTM films. The corresponding

photovoltaic results of these cells are listed in the supplementary material (Table S2 and Table S3).

As shown in Fig 8, the dark current measurements were correspondingly carried out [29]. As the concentration of TBP increased from 60 mM to 120 mM, the dark current was greatly decreased. However, when the concentration was up to 200 mM, the dark current was increased. This phenomenon suggests that charge recombination was greatly reduced under the condition of **HBZ-70** doped with LiTFSI of 30 mM and TBP of 120 mM [38]. From curve "5" and "5 dark" in Fig. 8, it was indicated that the dropped V_{oc} value may caused by the increase of charge recombination [39]. Therefore, it is very important to screen an appropriate proportion of additives for HTM, so as to obtain highly efficient PSCs.

Fig.9

The device based on **HBZ-71** was also fabricated under the same doping condition, which gave a PCE of 0.19% (Table 3). The corresponding J-V characteristics of PSCs based on **HBZ-70** and **HBZ-71** are shown in Fig.9 (a). In addition, the incident photon-to-current conversion efficiency (IPCE) spectra of devices using the HTMs(**HBZ-70/HBZ-71**) were recorded in Fig. 9(b). The device fabricated from **HBZ-70** shows obvious enhancement of the photocurrent in the whole visible region from 400 to 750 nm than that of **HBZ-71**. The much deeper HOMO level of **HBZ-71** (-5.42 eV) is too close to the valence band of CH₃NH₃PbI₃ peroskite (-5.43 eV), which may greatly accelerate charge recombination process at the CH₃NH₃PbI₃/HTM interface. Therefore, Time constant of electron recombination (τ_n) was measured from the

characteristic frequency at the minimum imaginary component of intensity modulated photovoltage spectroscopy (IMVS) [40, 41]. As shown in Fig. S3 of the supplementary materials, the recombination time constant τ_n for device based on **HBZ-70** is obviously larger than that based on **HBZ-71**. PSC based on **HBZ-70** shows a higher electron density, suggesting the electron recombination rate was decreased accordingly. Therefore, the device based on **HBZ-70** performed much better than **HBZ-71**. The introduction of carbazole moiety plays an important role in developing high-efficiency PSC devices.

4. Conclusion

A new carbazole-based HTM (HBZ-70) and a reference (HBZ-71) were prepared. Both compounds 3,3'-biphenyl skeleton possess central a as core. Carbazole-diarylamine groups were linked at the central core in the structure of HBZ-70, which exhibits a more planar skeleton than that of HBZ-71 with diarylamines linked at the central core. **HBZ-70** shows higher thermal stability and more suitable HOMO energy level by the introduction of carbazole moiety. The research on this new carbazole-diphenylamine based HTM with different doping concentration of TBP has been investigated. The best performance of device was obtained by doping with a lower concentration of 4-tert-butylpyridine (120 mM) than the frequent reported concentration (200 mM). The device fabricated from HBZ-70 achieved its best performance with a power conversion efficiency of 4.53% under illumination of 100 mW \cdot cm⁻², which is comparable to the performance of spiro-OMeTAD at the same dopant level (5.10%). HBZ-71 displayed much poorer performance with a power conversion efficiency of

0.19%, as a result of the increasing electron recombination at the $CH_3NH_3PbI_3/HTM$ interface according to the dark current measurements. Therefore, the new carbazole-based material (**HBZ-70**) is effective for developing highly efficient perovskite solar cells.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21376179, 21506164).

Reference

- [1] M. Grätzel, The light and shade of perovskite solar cells, Nature Mater. 13 (2014)838.
- [2] P. Gao, M. Grätzel, M.K. Nazeeruddin, A simple spiro-type hole transporting material for efficient perovskite solar cells, Energy Environ. Sci. 7 (2014) 2448.
- [3] S. Bai, N. Cheng, Z. Yu, P. Liu, C. Wang, X.Z. Zhao, Cubic: Column composite structure (NH₂CH=NH₂)_x(CH3NH3)_{1-x}PbI₃ for efficient hole-transport material-free and insulation layer free perovskite solar cells with high stability, Electrochimica Acta 190 (2016) 775.
- [4] X.C. Bao, Y.J. Wang, Q.Q. Zhu, N. Wang, D.Q. Zhu, J.Y. Wang, A.L. Yang, Renqiang Yang, Efficient planar perovskite solar cells with large fill factor and excellent stability, J. Power Sources 297 (2015) 53.
- [5] J.H. Heo, S.H. Im, J.H. Noh, T.N. Mandal, C.S. Lim, J.A. Chang, Y. H. Lee, H. Kim, A. Sarkar, M.K. Nazeeruddin, M. Grätzel, S.I. Seok, Efficient inorganic–organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors, Nat. Photonics 7 (2013) 486.
- [6] Y.M. Xiao, G.Y. Han, J.H. Wu, J.Y. Lin, Efficient bifacial perovskite solar cell based on a highly transparent poly(3,4-ethylenedioxythiophene) as the p-type hole-transporting material, J. Power Sources 306 (2016) 171.
- [7] G. Murugadoss, H. Kanda, S. Tanaka, H. Nishino, S. Ito, H. Imahoric, T. Umeyama, An efficient electron transport material of tin oxide for planar structure perovskite

solar cells, J. Power Sources 307 (2016) 891.

- [8] S. Lv, Y. Song, J. Xiao, L. Zhu, J. Shi, H. Wei, Y. Xu, J. Dong, X. Xu, S. Wang, Y. Xiao, Y. Luo, D.i Li, X. Li, Q. Meng, Simple triphenylamine-based hole-transporting materials for perovskite solar cells, Electrochimica Acta 182 (2015) 733.
- [9] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätze, Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies, Nature 395 (1998) 583.
- [10] D. Liu, T.L. Kelly, Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques, Nat. Photonics 8 (2014) 133.
- [11] N.J. Jeon, H.G. Lee, Y.C. Kim, J. Seo, J.H. Noh, J. Lee, S.I. Seok, *o*-Methoxy substituents in spiro-OMeTAD for efficient inorganic–organic hybrid perovskite solar cells, J. Am. Soc. Chem. 136 (2014) 7837.
- [12] H. Choi, S. Park, M.S. Kang, J. Ko, Efficient, symmetric oligomer hole transporting materials with different cores for high performance perovskite solar cells, Chem. Commun. 51 (2015) 15506.
- [13] K. Rakstys, A. Abate, M.I. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel, M.K. Nazeeruddin, Triazatruxene-based hole transporting materials for highly efficient perovskite solar cells, J. Am. Chem. Soc. 137 (2015) 16172.
- [14] H. Nishimura, N. Ishida, A. Shimazaki, A. Wakamiya, A. Saeki, L.T. Scott, Y.

Murata, Hole-transporting materials with a two-dimensionally expanded π -system around an azulene core for efficient perovskite solar cells, J. Am. Chem. Soc. 137 (2015) 15656.

- [15] J. Cao, Y.M. Liu, X. Jing, J. Yin, J. Li, B. Xu, Y.Z. Tan, N. Zheng, Well-defined thiolated nanographene as hole-transporting material for efficient and stable perovskite solar cells, J. Am. Chem. Soc. 137 (2015) 10914.
- [16] A. Krishna, D. Sabba, J. Yin, A. Bruno, P.P. Boix, Y. Gao, H.A. Dewi, G.G. Gurzadyan, C. Soci, S.G. Mhaisalkar, A.C. Grimsdale, Facile synthesis of a furan–arylamine hole-transporting material for high-efficiency, mesoscopic perovskite solar cells, Chem. Eur. J. 21 (2015) 15113.
- [17] S. Park, J.H. Heo, C.H. Cheon, H. Kim, S.H. Im, H.J. Son, A [2,2]paracyclophane triarylamine-based holetransporting material for high performance perovskite solar cells, J. Mater. Chem. A 3 (2015) 24215.
- [18] J. Burschka1, N. Pellet, S.J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin,M. Grätzel, Sequential deposition as a route to high-performance perovskite-sensitized solar cells, Nature 499 (2013) 316.
- [19] B. Xu, E. Sheibani, P. Liu, J. Zhang, H. Tian, N. Vlachopoulos, G. Boschloo, L. Kloo, A. Hagfeldt, L. Sun, Carbazole-based hole-transport materials for efficient solid-state dye-sensitized solar cells and perovskite solar cells, Adv. Mater. 26 (2014) 6629.
- [20] Y. Chen, D.D. Han, T. Wang, X.Y. Li, Efficient synthesis of arylated carbazole from cyclopentadienyliron complexes, Ind. Eng. Chem. Res. 52 (2013) 3646.

- [21] H.P. Shi, W.X. Zhang, X.Q. Dong, X.H. Wu, Y.Wua, L. Fang, Y.Q. Miao, H. Wang, A novel carbazole derivative containing dimesitylboron units: Synthesis, photophysical, aggregation induced emission and electroluminescent properties, Dyes Pigments 104 (2014) 34.
- [22] P. Zhou, Z. Wan, Y. Liu, C. Jia, X. Weng, J. Xie, L. Deng, Synthesis and electrochromic properties of a novel conducting polymer film based on dithiafulvenyl-triphenylamine-di(N-carbazole), Electrochimica Acta 190 (2016) 1015.
- [23] M.S. Kang, S.D. Sung, I.T. Choi, H. Kim, M.P. Hong, J. Kim, W.I. Lee, H.K. Kim, Novel carbazole-based hole-transporting materials with star shaped chemical structures for perovskite-sensitized solar cells, ACS Appl. Mater. Interfaces 7 (2015) 22213.
- [24] D. Sung, M.S. Kang, I.T. Choi, H.M. Kim, H. Kim, M.P. Hong, H.K. Kim, W.I. Lee, 14.8% perovskite solar cells employing carbazole derivatives as hole transporting materials, Chem. Commun. 50 (2014) 14161.
- [25] P. Qin, N. Tetreault, M.I. Dar, P. Gao, K.L. McCall, S. R. Rutter, S. D. Ogier, N. D. Forrest, J. S. Bissett, M.J. Simms, A.J. Page, R. Fisher, M. Grätzel, M.K. Nazeeruddin, A novel oligomer as a hole transporting material for efficient perovskite solar cells, Adv. Energy Mater. 5 (2015) 1400980.
- [26] H. Wang, A.D. Sheikh, Q.Y. Feng, F. Li, Y. Chen, W.L. Yu, E. Alarousu, C. Ma, M. A. Haque, D. Shi, Z.S. Wang, O.F. Mohammed, O.M. Bakr, T. Wu, Facile synthesis and high performance of a new carbazole-based hole-transporting material for

hybrid perovskite solar cells, ACS Photonics, 2 (2015) 849.

- [27] B. Xu, H. Tian, D. Bi, E. Gabrielsson, E. M. J. Johansson, G. Boschloo, A. Hagfeldt,L. Sun, Efficient solid state dye-sensitized solar cells based on an oligomer hole transport material and an organic dye, J. Mater. Chem. A. 1 (2013) 14467.
- [28] M. Kesselgruber, M. Lotz, P. Martin, G. Melone, M. Müller, B. Pugin, F. Naud, F. Spindler, M. Thommen, P. Zbinden, H.U. Blaser, Solphos: A new family of efficient biaryl diphosphine ligands, Chem. Asian J. 3 (2008) 1384.
- [29] X.P. Zong, Z. Sun, H. Wang, J. Wang, M. Liang, S. Xue, A tubular perovskite solar cell: improvement of charge separation at the perovskite/HTM interface, Chem. Commun. 51 (2015) 14076.
- [30] P.R.F. Barnes, K. Miettunen, X. Li, A.Y. Anderson, T. Bessho, M. Grätzel, B.C. O'Regan, Interpretation of optoelectronic transient and charge extraction measurements in dye-sensitized solar cells, Adv. Mater. 25 (2013) 1881.
- [31] Y.L. Tan, M. Liang, Z.Y. Lu, Y.Q. Zheng, X.L. Tong, Z. Sun, S. Xue, Novel triphenylamine donors with carbazole moieties for organic sensitizers toward cobalt(II/III) redox mediators, Org. Lett. 16 (2014) 3978.
- [32] Z.S. Huang, H.L. Feng, X.F. Zang, Z. Iqbal, H.P. Zeng, D.B. Kuang, L.Y. Wang, H. Meierd, D.R. Cao, Dithienopyrrolobenzothiadiazole-based organic dyes for efficient dye-sensitized solar cells, J. Mater. Chem. A 2 (2014) 15365.
- [33] H. Choi, S. Park, S. Paek, Efficient star-shaped hole transporting materials with diphenylethenyl side arms for an efficient perovskite solar cell, J. Mater. Chem. A 2 (2014)19136.

- [34] F.G. Zhang, X.C. Yang, H.X. Wang, M. Cheng, J.H. Zhao, L.C. Sun, Structure engineering of hole-conductor free perovskite-based solar cells with low-temperature-processed commercial carbon paste as cathode, ACS Appl. Mater. Interfaces 6 (2014) 16140.
- [35] Y.K. Song, S.T. Lv, X.C. Liu, X.G. Li, S.R. Wang, H.Y. Wei, D. Li, Yin Xiao, Q. Meng, Energy level tuning of TPB-based hole-transporting materials for high efficient perovskite solar cells, Chem. Commun. 50 (2014) 15239.
- [36] S.Y. Ma, H. Zhang, N. Zhao, Y.B. Cheng, M.K. Wang, Y. Shena, G. Tu, Spiro-thiophene derivatives as hole-transport materials for perovskite solar cells, J. Mater. Chem. A 3 (2015) 12139.
- [37] J. Wang, Y. Chen, M. Liang, G.Y. Ge, R.Y. Zhou, Z. Sun, S. Xue, A new thermal-stable truxene-based hole-transporting material for perovskite solar cells, Dyes and Pigments 125 (2016) 399.
- [38] N. Li, H.P. Dong, H. Dong, J.L. Li, W.Z. Li, G.D. Niu, X.D. Guo, Z.X. Wu, L.D. Wang, Multifunctional perovskite capping layers in hybrid solar cells, J. Mater. Chem. A 2 (2014) 14973.
- [39] S.T. Lv, L.Y. Han, J.Y. Xiao, L.F. Zhu, J.J. Shi, H.Y. Wei, Y.Z. Xu, J. Dong, X. Xu, D.M. Li, S.R. Wang, Y.H. Luo, Q.B. Meng, X.G. Li, Mesoscopic TiO₂/CH₃NH₃PbI₃ perovskite solar cells with new hole-transporting materials containing butadiene derivatives, Chem. Commun. 50 (2014) 6931.
- [40] G.D. Niu, W.Z. Li, F.Q. Meng, L.D. Wang, H.P. Dong, Y. Qiu, Study on the stability of CH₃NH₃PbI₃ films and the effect of post-modification by aluminum oxide in

all-solid-state hybrid solar cells, J. Mater. Chem. A 2 (2014) 705.

[41] Y. Zhao, K. Zhu, Charge transport and recombination in perovskite (CH₃NH₃)PbI₃ sensitized TiO₂ solar cells, J. Phys. Chem. Lett. 4 (2013) 2880.

Figure Captions

Fig. 1. Structures of HBZ-70 and HBZ-71.

Scheme 1. Synthesis route for HBZ-70 and HBZ-71.

Fig. 2. Normalized absorption and fluorescence emission spectra of HBZ-70 and HBZ-71 in dichloromethane solution.

Fig. 3. UV-vis spectra of thin films including **HBZ-70** coated on TiO₂ film (**HBZ-70**/TiO₂), **HBZ-71** coated on TiO₂ film (**HBZ-71**/TiO₂), perovskite (CH₃NH₃PbI₃) coated on TiO₂ film (perovskite/TiO₂) and HTMs(**HBZ-70**/**HBZ-71**) coated on perovskite/TiO₂ film (**HBZ-70**/perovskite/TiO₂ and **HBZ-71**/perovskite /TiO₂).

Fig. 4. Representative dihedral angles of HBZ-70 and HBZ-71.

Fig. 5. Frontier molecular orbitals of HBZ-70 and HBZ-71.

Fig. 6. Cyclic voltammograms of **HBZ-70** and **HBZ-71**. The experimentally determined HOMO-LUMO energy gap values for **HBZ-70** and **HBZ-71** are 2.93 and 3.29 eV, respectively. The theoretical calculated HOMO-LUMO energy gap values for **HBZ-70** and **HBZ-71** are 3.36 and 3.94 eV, respectively.

Fig. 7. (a) TG and (b)DSC curves of HBZ-70 and HBZ-71.

Fig. 8. *J*–*V* characteristics of PSCs based on **HBZ-70** doping with different proportions of LiTFSi/TBP. 1: 30 mM/200 mM; 2: 30 mM/120 mM; 3: 30 mM/60 mM; 4: 15 mM/200 mM; 5: 15 mM/120 mM.

Fig. 9. (a) *J–V* characteristics and (b) IPCE spectra of PSC devices based on HTMs(HBZ-70/HBZ-71).

Scheme 1



Fig.1



Fig.2



Fig.3



Fig.4.







Fig.6



Fig.7



(a)



(b)

Fig.8



Fig.9



(a)



(b)

Tables

Table 1. The spectroscopic data of compound HBZ-70 and HBZ-71 employed in

solution and in solid-state films.

Compound	$\lambda_{abs}^{max}(nm)$ film	$\lambda_{abs}^{max}(nm)$ soln.	$\lambda_{fl}^{max}(nm)$ soln.	$E_g^{opt}(eV)$
HBZ-70	326	311	456	2.93
HBZ-71	327	295	428	3.29

Compound	$E_{\rm pc}({ m V})$	$E_{\mathrm{pa}}\left(\mathrm{V}\right)$	$E_{\mathrm{ox},1/2}\left(\mathrm{V}\right)$	$E_{\rm HOMO}(\rm V)$	$E_{\rm LUMO}(\rm V)$
HBZ-70	0.648	0.412	0.53	-5.26	-2.33
HBZ-71	0.881	0.501	0.69	-5.42	-2.13

 Table 2. The electrochemical data of HBZ-70 and HBZ-71.

Condition	LiTFSI/mM	TBP/mM	$Jsc/mA^{-}cm^{-2}$	Voc/V	FF	η %
1	30	200	6.24	1.02	0.64	4.08
2	30	120	8.47	1.03	0.52	4.53
3	30	60	6.61	0.966	0.41	2.62
4	15	200	4.61	0.948	0.46	2.01
5	15	120	8.83	0.793	0.34	2.38
HBZ-71	30	120	0.8	0.595	0.40	0.19
Spiro-OMeTAD	30	120	11.42	0.876	0.51	5.10

Table 3. J–V characteristics of photovoltaic measurements.