View Article Online View Journal

# Journal of Materials Chemistry C

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Liu, F. Zhang, Z. Liu, Y. Xiao, S. Wang and X. Li, *J. Mater. Chem. C*, 2017, DOI: 10.1039/C7TC03931J.



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 **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, 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.



rsc.li/materials-c

Published on 12 October 2017. Downloaded by Freie Universitaet Berlin on 12/10/2017 20:43:26.

# COYAL SOCIETY OF CHEMISTRY

### Journal of Materials Chemistry C

## ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx Materials for Efficient and Stable Perovskite Solar Cells<sup>†</sup> Xicheng Liu<sup>a,+</sup>, Fei Zhang<sup>b,c,+</sup>, Zhe Liu<sup>a</sup>, Yin Xiao<sup>b,c</sup>, Shirong Wang<sup>b,c</sup>, Xianggao Li<sup>b,c</sup>\*

Dopant-Free and Low-cost molecular "Bee" Hole-Transporting

DOI: 10.1039/x0xx00000x

www.rsc.org/

With the dramatic development of the power conversion efficiency (PCE) of perovskite solar cells (PSCs), device lifetime has become one of the extensive research interests and concerns. To enhance the device durability, developing dopant-free hole-transporting materials (HTMs) with high performance is a promising strategy. Herein, three new HTMs with *N*,*N'*-diphenyl-*N*,*N'*-di(*m*-tolyl)benzidine (TPD) core: TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz are designed and synthesized, showing suitable energy levels and excellent film-formation property. PCEs of 15.28% was achieved based on pristine TPD-4MeOTPA as HTM, which is a little lower than p-doped 2,2',7,7'-tetrakis-(*N*,*N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (*spiro*-OMeTAD)-based device (17.26%). Importantly, the devices based on new HTMs show relatively improved stability compared to devices based on *spiro*-OMeTAD when aged under ambient air with 30% relative humidity in the dark.

#### 1. Introduction

Recently, a new class of solid-state heterojunction solar cells based on solution-processable organometal halide perovskite absorbers have caused the extensive concern.<sup>1-8</sup> Owing to the unique characteristics, such as high charge carrier mobility, large absorption coefficient, broad spectral absorption range, and long diffusion length,<sup>9-11</sup> the power conversion efficiency (PCE) of solid-state perovskite solar cells (PSCs) quickly increased to over 20%.<sup>12-14</sup>

Due to the advantages of promoting hole migration, preventing internal charge recombination and enhancing the stability of cells, hole-transporting materials (HTMs) play a key role in PSCs.<sup>15-18</sup> Many kinds of HTMs have been applied in PSCs, such as inorganic p-type semiconductors, conducting polymers, and small molecule hole conductors.<sup>19-30</sup> Owing to the advantage of convenient purification, controllable molecular structures and relatively high efficiency,<sup>31-33</sup> small molecular HTMs were widely used in PSCs. Among these, 2,2',7,7'-tetrakis-(*N*,*N*-di-4-methoxyphenylamino)-9,9'-spirobifluore-ne (*spiro*-OMeTAD) was the most studied. Due to the relatively tedious synthesis and fancy price, numerous alternative HTMs have been explored to replace *spiro*-OMeTAD.<sup>34-37</sup> However, the PCE of dopant-free PSCs based on which are consistently lying between 10% and 13%, few are over 15%.<sup>38-42</sup>

N,N'-diphenyl-N,N'-di(m-tolyl)benzidine (TPD) is a promising hole-transporting material for application in organic photoelectric

# G (100 mW cm<sup>-2</sup>) illumination. This result is a little lower than the well-known p-doped *spiro*-OMeTAD (17.26%) obtained under the same conditions. Moreover, the devices based on the assynthesized HTMs present improved stability compared with the device based on *spiro*-OMeTAD under ambient air with 30% relative humidity without encapsulation after 600 h in the dark.

field. However, unbefitting energy level, poor solubility and thermal

stability limit its application.<sup>31-33</sup> In this paper, we designeed and

synthesized three novel TPD-based HTMs as shown in Fig. 1. The

energy levels of the HTMs was tuned by substituting the TPD-core

with different electron-donating groups through olefinic bonds.

Owing to structure readjustment and increasing molecular weight,

solubility and thermal stability were effective improved. The devices

based on  $[(FAI)_{0.85}(PbI_2)_{0.85}(MABr)_{0.15}(PbBr_2)_{0.15}]$ , fabricated with

doped-free HTMs, achieve the highest PCE of 15.28 % under AM 1.5



#### 2. Results and Discussions

TPD-4MeTPA: R=CH<sub>3</sub> TPD-4MeOTPA: R=OCH<sub>3</sub>

#### 2.1 Normal Information

HTMs were obtained by Wittig reaction with cheap starting materials and simple synthesis process. These three new HTMs were fully characterized by  ${}^{1}$ H NMR spectroscopy and mass spectrum. All the analytical data are consistent with the proposed

TPD-4EtCz



<sup>&</sup>lt;sup>a.</sup> Qufu Normal University, School of Chemistry and Chemical Engineering.

<sup>&</sup>lt;sup>b.</sup> School of Chemical Engineering and Technology, Tianjin University.

<sup>&</sup>lt;sup>c</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin).
\*Corresponding author: E-mail: lixianggao@tju.edu.cn (Xianggao Li). Tel: +86 22
27404208

<sup>+</sup> X. C. L. and F. Z. have equivalent contribution

 $<sup>^{+}</sup>$  Electronic supplementary information (ESI) available. See DOI:\ 10.1039/ x0xx00000x

DOI: 10.1039/C7TC03931J

Journal Name

#### ARTICLE

Published on 12 October 2017. Downloaded by Freie Universitaet Berlin on 12/10/2017 20:43:26

structures (ESI **Fig. S1**). We roughly estimated the synthetic cost of 1 **S1, S2** and **S3**). The g as-synthesized HTMs according to previous report<sup>43-45</sup> (ESI **Table** 

Table 1 The optical, electrochemical, thermal properties and energy levels of HTMs.

	λ <sub>onset</sub> [nm]ª	λ <sub>abs</sub> [nm <sup>b</sup> a	E <sub>g</sub> [eV] <sup>b</sup>	HOMO [eV] <sup>c</sup>	LUMO [eV] <sup>d</sup>	T <sub>g</sub> [°C] <sup>e</sup>	Τ <sub>d</sub> [°C] <sup>f</sup>
TPD-4MeTPA	454	305, 407 / 309, 408 <sup>#</sup>	2.68	-5.33	-2.65	145	432
TPD-4MeOTPA	459	299, 408 / 303, 423 <sup>#</sup>	2.59	-5.28	-2.69	150	416
TPD-4EtCz	442	301, 394 / 304, 397 <sup>#</sup>	2.76	-5.34	-2.58	138	452

<sup>a</sup> Absorption spectra in the 1.0×10<sup>-5</sup> mol L<sup>-1</sup> THF solution. <sup>b</sup> Optical energy gaps calculated by the absorption thresholds ( $\lambda_{onset}$ ) from UV-Vis absorption spectra of films. <sup>c</sup> Measured by photoelectron yield spectroscopy (PYS, ESI **Fig. S3**). <sup>d</sup> |LUMO|=|HOMO|-|*E*<sub>g</sub>|. <sup>e</sup> Decomposition temperatures, measured by TGA at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>. <sup>f</sup> Measured by DSC at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> according to the heat-cool-heat procedure. <sup>#</sup> Absorption peaks of solid films.

estimated synthesis cost are 83.4 \$ g<sup>-1</sup>, 96.7 \$ g<sup>-1</sup> and 44.5 \$ g<sup>-1</sup> for TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz, respectively, which were much cheaper than that of *spiro*-OMeTAD (581.52 \$ g<sup>-1</sup>).<sup>46</sup> The glass transition temperatures ( $T_g$ ) and decomposition temperatures ( $T_d$ ) of HTMs were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively (ESI **Fig. S2**). As shown in **Tabel 1**, outstanding thermal stability of assynthesized HTMs were confirmed by high  $T_a$  and  $T_d$ .

Ultraviolet-Visible (UV-Vis) absorption spectra of assynthesized HTMs in dilute tetrahydrofuran (THF) solutions (1.0×10<sup>-5</sup> mol L<sup>-1</sup>) and solid films are shown in Fig. 2. The peaks at short wavelength (~300 nm) can be assign to  $n-\pi^*$  transition of the TPA moiety, while peaks at longer wavelength (~400 nm) are intramolecular charge transfer (ICT) of  $\pi - \pi^{*}$ .<sup>47</sup> These three compounds showed similar  $n-\pi^*$  transition peaks, while the ICT peaks showed an bathochromic shift from TPD-4EtCz to TPD-4MeTPA and TPD-4MeOTPA due to extend of  $\pi$ - $\pi$  conjugation.<sup>48,49</sup> No obvious change in absorption spectra for thin films indicate the amorphous structure of spin-coated films, which were further identified by XRD measurements (ESI Fig. S4).<sup>50</sup> A slight bathochromic shift (1 nm, 15 nm and 3 nm for TPD-4MeTPA TPD-4MeOTPA and TPD-4EtCz, respectively) and broadening of ICT bands in the solid films can be observed which indicate the existing of slight intermolecular interactions in the solid state.<sup>51</sup>



**Fig. 2** Normalized UV-Vis absorption spectra of the new HTMs (a) THF solution ( $c = 1.0 \times 10^{-5}$  mol L<sup>-1</sup>); (b) solid films.

The optimized molecular structures and frontier molecular orbital distribution of the new HTMs were studied by DFT calculation.<sup>31</sup> The highest occupied molecular orbital (HOMO) levels, lowest unoccupied molecular orbital (LUMO) energy levels and the energy gap ( $E_g$ ) are shown in **Fig. 3**. From **Fig. 3**, we found that the HOMO distribute on the whole molecular skeleton. The LUMO

mainly distribute on the TPD branches. As shown in Fig. 3, similar to spiro-OMeTAD, the TPD center of as-synthesized HTMs adopt a spiro conformation because of the larger terminal branches. The measured angles between two terminal branches are 62.72°, 64.87° and 61.77° for TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz, respectively. Compared to 89.94° between the two fluorine rings in spiro-OMeTAD,<sup>50</sup> the spiro conformation of as-synthesized HTMs will prevent stronger intermolecular stacking and form an amorphous solid film. The energy levels agreed well with the tendency determined by photoelectron yield spectroscopy (PYS, ESI Fig. S3) and optical measurements (Table 1). The HOMO levels of assynthesized HTMs matched well with the valence band level of organometal halide perovskite (-5.5 eV) to favor the hole migration. The LUMO levels are much higher than the conduction band level (-3.9 eV) to block the electron back-transfer from perovskite to Au electrode (Fig. 4a).15-18



**Fig. 3** Distributions of HOMO and LUMO and optimized molecular structures of the new HTMs.

The time-of-flight (TOF, ESI **Fig. S5**) transient hole-current measurement was applied to measure the hole mobilities of HTMs.<sup>52</sup> At room temperature, the hole mobilities are  $2.14 \times 10^{-4}$ ,  $4.92 \times 10^{-4}$  and  $1.27 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz, respectively, compared to  $1.42 \times 10^{-4}$ 

Published on 12 October 2017. Downloaded by Freie Universitaet Berlin on 12/10/2017 20:43:26

#### Journal Name

 $\text{cm}^2$  V<sup>-1</sup> s<sup>-1</sup> for *spiro*-OMeTAD at applied electric fields of  $1.5 \times 10^5$  V cm<sup>-1</sup>, respectively.

#### 2.2 Application in the mesoporous structured PSCs

The HOMO levels of as-synthesized HTMs (-5.28~-5.34 ev) matched well with the valence band level of organometal halide perovskite (-5.5 eV) to favour the hole migration. The LUMO levels (-2.69~-2.58 ev) are much higher than the conduction band level (-3.9 eV) to block the electron back-transfer from perovskite to Au electrode (**Fig. 4a**).<sup>15-18</sup> The perovskite layer was obtained by using the anti-solvent method as described in literature.<sup>53</sup> The device structure can be clearly seen from a high-resolution cross-sectional scanning electron microscopy (SEM) image (**Fig. 4b**). As can be seen from the image, the perovskite penetrates into the mp-TiO<sub>2</sub> and forms an overlayer. Similarly, the HTMs blend into the pores in the TiO<sub>2</sub>/perovskite layer and form a thin capping layer on the top.



**Fig. 4** (a) Energy level diagram of the perovskite solar cells based on different HTMs; (b) Cross-sectional SEM image of the PSC with configuration of FTO/compact TiO<sub>2</sub> (40 nm)/mesoporous TiO<sub>2</sub> (200 nm)/perovskite (480 nm)/HTM (160 nm)/Au (80 nm), the scale bar is 200 nm; (c) J-V hysteresis curves of PSCs comprising champion devices with HTMs measured starting with backward scan and continuing with forward scan, and (d) IPCE spectra of the devices based on the new HTMs without additives/dopants and *spiro*-OMeTAD with additives/ dopants.

We evaluated the photovoltaic performance of PSCs based on the three new HTMs and *spiro*-OMeTAD with or without additives and dopants. The photocurrent densitiy–voltage (*J*–*V*) curves under AM 1.5 G irradiation of 100 mW cm<sup>-2</sup> are presented in **Fig. 4c**, and the photovoltaic parameters are summarized in **Table 2**. The lower performance by TPD-4EtCz is mainly related to the lower FF caused by the poor film-forming ability shown in ESI **Fig. S6**.<sup>54</sup> As expected, TPD-4MeTPA and TPD-4MeOTPA give higher open-circuit voltage than *spiro*-OMeTAD for the device, which are correspond with their lower HOMO levels. The best device based on TPD-4MeOTPA affords a *V<sub>oc</sub>* of 1.099 V, a short-circuit current density (*J<sub>sc</sub>*) of 20.84 mA cm<sup>-2</sup>, and a fill factor (FF) of 0.667, leading to a PCE of 15.28% under AM 1.5 G (100 mW cm<sup>-2</sup>) illumination. This result is a little lower than *spiro*-OMeTAD (17.26%) doped with Lithium bis(trifluoromethyl-sulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (tBP). However, devices based the new HTMs doped with LiTFSI and tBP exhibit lower photovoltaic performance, especially in terms of FF and J<sub>sc</sub> (ESI Table S4). This is partly because the additives and dopants which work well with spiro-OMeTAD may not be suitable for the new HTMs.55,56 Moreover, the dopants seem to have a negative impact on film morphology, which are further confirmed by the SEM image in ESI Fig. S6. Similar behaviour was observed in other reports.<sup>42,54,57-60</sup> In the absence of additives and dopants, spiro-MeOTAD-based devices generated a PCE of only 5.43% owing to significant lowering of the  $V_{OC}$  and FF compared to the doped devices.<sup>61,62</sup> Only small hysteresis was observed in the J-V curves. The measured PCE differences [(PCE<sub>backward</sub> - PCE<sub>forward</sub>) / PCE<sub>average</sub> × 100%] are 1%, 9%, 3% and 1% and the stabilized power outputs are 14.31%, 15.02%, 11.28% and 17.09% for devices based on TPD-4MeTPA, TPD-4MeOTPA, TPD-4EtCz and spiro-OMeTAD, respectively (ESI Fig. S7), consistent with the obtained PCE.<sup>54</sup>

The incident photon-to-electron conversion efficiency (IPCE) spectrums of the cell with the four different HTMs are presented in **Fig. 4d**. The integrated current densities estimated from the IPCE spectra (19.90 mA cm<sup>-2</sup>, 20.30 mA cm<sup>-2</sup>, 19.45 mA cm<sup>-2</sup>, and 20.83 mA cm<sup>-2</sup> for TPD-4MeTPA, TPD-4MeOTPA, TPD-4EtCz, and *spiro*-OMeTAD,

respectively) are in good agreement with the  $J_{SC}$  values obtained from the *J*–*V* curves. We fabricated batches of 10 cells each using different HTMs and demonstrate in **Fig. 5** excellent reproducibility by the narrow statistical distribution of the photovoltaic metrics.



**Fig. 5** Statistical deviation of the photovoltaic parameters for 10 different solar cells using different HTM: (a) *Voc*, (b) *Jsc*, (c) FF, and (d) PCE.

The time-resolved photoluminescence (PL) spectra are shown in **Fig. 6**, which are obtained by fitting the data with a bi-exponential decay function (ESI **Table S5**). For the TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> film without a HTM layer, the pristine perovskite film gave short-lived lifetime  $\tau_1$  = 22.14 ns and long-lived lifetime  $\tau_2$  = 171.70 ns. When coated with a thin HTM layer on the surface of perovskite, the lifetime significantly decreases to ( $\tau_1$  = 8.50 ns,  $\tau_2$  = 74.53 ns), ( $\tau_1$  = 7.55 ns,  $\tau_2$  = 63.70 ns), ( $\tau_1$  = 12.26 ns,  $\tau_2$  = 92.58 ns) and ( $\tau_1$  = 3.59 ns ,  $\tau_2$  = 30.26 ns) for TPD-4MeTPA, TPD-4MeOTPA, TPD-4EtCz and *signo* 

DOI: 10.1039/C7TC03931J Journal Name

#### ARTICLE

OMeTAD based film, respectively. The PL decay lifetime for new efficiently. HTMs are somewhat longer compared with doped *spiro*-OMeTAD, but significantly shorter than the HTM-free device, which means that the new HTMs can extract the holes from the perovskite

Table 2 J-V curves of HTMs and spiro-OMeTAD based device under different scan directions [a]

HTMs <sup>[b]</sup>		J <sub>sc</sub> (mA cm <sup>-2</sup> )	$V_{oc}(V)$	FF	PCE (%)
	backward	20.601	1.089	0.637	14.33
TPD-4IMETPA	forward	20.502	1.099	0.625	14.13
	backward	20.835	1.099	0.667	15.28
TPD-4MEOTPA	forward	20.800	1.118	0.599	13.94
	backward	20.310	1.104	0.523	11.73
TPD-4EIC2	forward	20.271	1.134	0.493	11.34
chira OMATAD LL	backward	21.612	1.074	0.714	17.26
spiro-Olvie IAD ++	forward	21.593	1.089	0.696	17.04

[a] Bias step of 5 mV. [b]+ + = samples include LiTFSI and tBP additives



**Fig. 6** Normalized time-resolved PL spectra of the devices based on as-synthesized without additives/dopants and *spiro*-OMeTAD with additives/dopants.

#### 2.3. Stability and lifetime of PSCs

The stability of PSCs is a difficulty for application, especially in arbitrary environment. We compared the stability of the PSCs with as-synthesized HTMs and *spiro*-OMeTAD by exposing them to ambient air at 30% relative humidity without encapsulation. The operation stability was investigated in following way: The *J*-*V* curves were measured after storage under atmospheric environment per 24 hours. The time evolution of the photovoltaic metrics is shown in **Fig. 7**.

The PCE based on three HTMs only decreased < 8% after 600 h storage in ambient air without encapsulation. (**Fig. 7**). In the first 300 h, a slight increase of *Voc* can be observed in non-doped PSCs with as-synthesized HTMs. For the long storage time (300-600 h), the decreased of  $J_{sc}$  in PSCs based on doped *spiro*-OMeTAD are more obvious. This indicated the non-doped PSCs based on as-synthesized HTMs have promising long-term stability at room temperature. Which was mainly attributed to their lack of doping additives and less pinholes in the HTM layer.<sup>12,63</sup> The contact angles (ESI **Fig. S8**) of TPD-4MeTPA (89.4°), TPD-4MeOTPA (94.8°), and TPD-4EtCz (89.1°) are larger than for doped *spiro*-OMeTAD (66.9°) reported by our recent paper.<sup>60</sup> Larger contact angles indicate higher hydrophobicity of the film. The more hydrophobic nature of as-synthesized HTMs help to expel moisture away from the perovskite film, which could also lead to enhanced device stability.

#### 3. Experimental Section



**Fig. 7** The stability of the new HTMs and *spiro*-OMeTAD-based PSCs in ambient air without encapsulation (■ TPD-4MeTPA; ● TPD-4MeOTPA; ▲ TPD-4EtCAZ; ▼ *spiro*-OMeTAD).

#### 3.1 Materials

*N*,*N*<sup>'</sup>-Diphenyl-*N*,*N*<sup>'</sup>-di(m-tolyl)benzidine (TPD) was purchased from Heowns Biochemical Technology CO., LTD., Tianjin, China. Pbl<sub>2</sub> and PbBr<sub>2</sub>was purchased from Tokyo Chemical Industry CO., LTD, *N*,*N*<sup>'</sup>dimethylformide (DMF) from Alfar Aesar, hydroiodic acid (AR, 45 wt.% in water) and methylamine (AR, 27% in methanol) from Sinopharm Chemical Reagent Co. Ltd. 2,2',7,7'-tetrakis (*N*,*N*-di-*p*methoxy-phenylamine)-9,9'-spirobifluorene (*spiro*-OMeTAD) was from Luminescence Technology Corp., Taiwan, China. Tetrahydrofuran was distilled before using, all the other agents were directly used without further purification. Substrates were FTO conducting glass (Pilkington, thickness: 2.2 mm, sheet resistance: 14  $\Omega$ /square). Patterned FTO glass was first cleaned with mild detergent, rinsed several times with distilled water and subsequently with ethanol in an ultrasonic bath, finally dried under air stream.

#### 3.2 Measurements

The as-synthesized compounds were identified by nuclear magnetic resonance (NMR) spectrum and high-resolution mass spectroscopy (HRMS). The NMR was obtained on a Bruker AVANCE III 400 MHz spectrometer, with the chemical shifts reported in ppm using

#### Journal Name

tetramethylsilane (TMS) as an internal standard. HRMS was recorded on a SolariX maldi-FTMS mass spectrometer. Ultraviolet-Visible absorption (UV-Vis) spectroscopy was obtained by the Thermo Evolution 300 UV-Visible spectrometer. Decomposition temperature ( $T_d$ ) and glass transition temperature ( $T_g$ ) were determined by the thermo gravimetric analysis (TGA) and differential scanning calorimeter (DSC) on a TA Q500 thermo gravimetric analysis and TA Q20 thermal analysis under a nitrogen atmosphere. The photoelectron yield spectroscopy (PYS) was carried out on the Sumitomo PYS-202 ionization energy detection system. X-ray diffraction (XRD) was measured with a Rigaku Miniflex 600 X-Ray diffraction. Scanning electron microscope (SEM) was measured with Hitachi S-4800.

Current-voltage characteristics (*J–V*) were measured on a Keithley 2602 SourceMeter under AM 1.5 irradiation (100 mW cm<sup>-2</sup>) from an Oriel Solar Simulator 91192. A mask with a window of 0.16 cm<sup>2</sup> was clipped on the TiO<sub>2</sub> side to define the photoactive area of the cells. Incident-photon-to-current conversion efficiency (IPCE) was measured by the direct current (DC) method using a lab-made IPCE setup under 0.3-0.9 mW cm<sup>-2</sup> monochromic light illumination without bias illumination. Time resolved PL spectra was recorded on PL spectrometer, Edinburgh Instruments, FLS 900, excited with a picosecond pulsed diode laser (EPL-445), and measured at 775 nm after excitation at 445 nm. The time-of-flight (TOF) measurement was record on a TOF401 measurement system, Sumitomo Heavy Industries. Ltd. Samples were prepared through spin-coated with a structure of ITO/as-synthesized compounds (~1  $\mu$ m)/Al (100 nm) with a working area of 3×3 mm<sup>2</sup>.

#### 3.3 Synthesis

The designed synthetic routes for as-synthesized compounds are depicted in **Scheme 1**, which were synthesized by Wittig reaction using formyl replaced TPD (**2**) and Wittig reagents (**3**) in three steps from commercially available and relatively inexpensive starting reagents. The structure of as-synthesized compounds were confirmed *via* <sup>1</sup>H NMR and MS, which agreed well with the proposed molecular structure (See ESI **Fig. S1**).



Scheme 1 Synthetic route for the three new HTMs.

#### 4,4'-([1,1'-biphenyl]-4,4'-diylbis((4-formylphenyl) azanediyl))bis(2methylbenzaldehyde) (2)

TPD (5.0 g, 9.7 mmol), imidazole (5.1 g, 61.5 mmol) were added into

a two neck 250 mL round bottom flask, followed by 90 mL of acetonitrile. Trifluoroacetic anhydride (17.3 mL, 123.0 mmol) was droped under nitrogen atmosphere (N<sub>2</sub>). Then above mixture refluxed until TPD consumed completely (monitored by thin-layer chromatography). The reaction solution was poured into 1 L water to dissolve out yellow powder. The filter cake washed with water until the filtrate became colorless, compound (1) obtained: yellow solid (15.0 g, 99.1%): mp 243-245°C,<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 2.63 (s, 6H), 6.89 (s, 4H), 7.04-7.24 (m, 14H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.38 (d, *J* = 8.5 Hz, 4H), 6.74 (d, *J* = 10.1 Hz, 8H), 7.27 (s, 4H); ESI-MS (*m/z*): [M<sup>-</sup>] Calcd for C<sub>66</sub>H<sub>40</sub>F<sub>24</sub>N<sub>10</sub>O<sub>8</sub>, 1556.3; Found 1556.9.

DOI: 10.1039/C7TC03931J

ARTICLE

The polyimidazoline product ((1), 10 g, 6.4mmol) was dissolved in 200 mL THF. Then pumped HCl gas (100 mL, 2.5 mol L<sup>-1</sup> - prepared by adding 21.0 mL of concentrated HCl to 79.0 mL H<sub>2</sub>O). The reaction solution reflux for 12 h. The reaction solution was cooled to room temperature, then an orange solid formed. The reaction mixture was filtered and recrystallized from diethyl ether, compound (2) obtained (3.8 g, 93.0%): mp 197-199 °C, IR: 2803.99, 2722.76, 1693.86; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 10.15 (s, 2H), 9.91 (s, 2H), 7.80 (d, *J* = 8.5 Hz, 4H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 4H), 7.32-7.21 (m, 8H), 7.19-7.04 (m, 4H), 2.60 (s, 6H); ESI-MS (*m*/*z*): [M+H]<sup>+</sup> Calcd for C<sub>42</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>, 628.2; Found, 629.5.

#### Wittig regents (3)

Wittig reagents (3) were synthesized according to literature.<sup>31</sup>

#### N,N-di(phenyl)-N',N'-di(4-(4-N,N-di(4-(4-methoxy-phenyl))amino) phenyl)ethenyl) -1,1'-biphenyl-4,4'-diamine (TPD-4MeTPA)

4-[N,N-di(p-tolyl)amino]benzyl(triphenyl)phosphonium bromide (W1, 2.64 g, 4 mmol) and compound (2) (0.31 g, 0.5 mmol) were added into a 100 mL round-bottom flask under N2. Anhydrous THF (40 mL) was added to above flask, cooled down to 0 °C. The THF solution of *t*-BuOK (16 mmol, 0.8 mol  $L^{-1}$ ) was added dropwise to above flask, stirred for 30 min at 0 °C, followed with stirred at room temperature until compound (2) was consumed completely (monitored by thin-layer chromatography). The reaction was terminate with ice water. The crude product was heated under reflux for 8 h in THF with a catalytic amount of iodine. Then the remaining iodine was removed by sodium hydroxide (NaOH) solution (Wt = 10%, 100 mL) by stirring for 2 h. After that, the product was purified by chromatographed on a silica gel column (petroleum ether: ethyl acetate =50:1 as eluent) to give the title compound as a pure *E* stereoisomer TPD-4MeTPA (0.59 g, 69%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.67 (dd, J = 11.9, 7.9 Hz, 2H), 7.58-7.42 (m, 6H), 7.40-7.28 (m, 10H), 7.20-6.76 (m, 60H), 2.30 (q, J = 5.0 Hz, 30H). HRMS (m/z): Calcd for C<sub>124</sub>H<sub>108</sub>N<sub>6</sub>, 1705.86690; Found 1705.86589.

TPD-4MeOTPA and TPD-4EtCz were synthesized by **W2** (4-[*N*,*N*-di(*p*-

methoxyphenyl)amino]benzyl(triphenyl)phosphoniumbromide), **W3** (3-[(9-ethyl)-carbazole]methyl(triphenyl)phosphonium bromide) and compound **2** using the same method.

**TPD-4MeOTPA:** (0.63 g, 73%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.53-7.43 (m, 6H), 7.37 (d, J = 8.3 Hz, 4H), 7.31 (t, J = 7.2 Hz, 8H), 7.10 (dd, J = 35.0, 7.7 Hz, 26H), 6.91 (s, 16H), 6.83 (d, J = 8.6 Hz, 18H), 3.79 (s, 24H), 2.33 (d, J = 11.3 Hz, 6H). HRMS (m/z): Calcd for C<sub>126</sub>H<sub>108</sub>N<sub>6</sub>O<sub>8</sub>, 1833.82622; Found 1833.82536.

**TPD-4EtCz:** (0.51 g, 65%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):

Page 6 of 8

8.15 (dd, J = 24.0, 17.1 Hz, 6H), 7.73-7.63 (m, 4H), 7.59 (t, J = 9.7 Hz, 2H), 7.56-7.27 (m, 22H), 7.22-6.92 (m, 14H), 4.34 (t, J = 12.2 Hz, 8H), 2.39 (d, J = 25.3 Hz, 6H), 1.50-1.35 (m, 12H). HRMS (m/z): Calcd for C<sub>102</sub>H<sub>84</sub>N<sub>6</sub>, 1393.67910; Found 1393.67831.

#### 3.4 Quantum chemical calculation

Quantum chemical calculation was performed on a Gaussian 03 program with the Beck's three-parameter exchange functional and the Lee-Yang-Parr's correlation functional (B3LYP) using 6-31G (d) basis sets.<sup>64</sup>

#### 3.5 Solar cell fabrication details

A 30 nm-thickness compact TiO<sub>2</sub> layer, 200-300 nm mesoporous TiO<sub>2</sub> layers and perovskite laver  $([(FAI)_{0.85}(PbI_2)_{0.85}(MABr)_{0.15}(PbBr_2)_{0.15}])$  were prepared according to the reported methods.<sup>53</sup> The HTMs layers were spin-coated on the top of TiO<sub>2</sub>/perovskite films at 3000 rpm for 20 s with a concentration of 20 mg mL<sup>-1</sup>. For comparison, perovskite solar cells based on spiro-OMeTAD were also fabricated by using a chlorobenzene solution doped with Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (tBP) under the same conditions. All the above fabrication processes were carried out in air. Finally, 80 nm-thickness Au photocathode was deposited by thermal evaporation.

#### 4. Conclusions

We synthesized three TPD-core HTMs (TPD-4MeTPA, TPD-4MeOTPA and TPD-4EtCz) with simple synthetic procedures and low cost. The PSC based on dopant-free TPD-4MeOTPA as the HTM affords an impressive PCE of 15.28%, which is a little lower than that obtained employing the well-known p-doped *spiro*-OMeTAD. The devices based on as-synthesized HTMs obtained a higher stability than the device based on *spiro*-OMeTAD afer 600 h at room temperature in ambient air with 30% relative humidity without encapsulation. The introduction of these three novel HTMs with improved synthesis and excellent performance highlight their potential use in the future deployment of PSCs.

#### Acknowledgements

The authors gratefully acknowledge the financial support from the National Key R&D Program of China (2016YFB0401303), the National Natural Science Foundation of China (21676188) and Key Projects in Natural Science Foundation of Tianjin (16JCZDJC37100). The calculation in this work was supported by high performance computing center of Tianjin University, China.

#### Notes and references

- 1 F. Zhang, S. R. Wang, X. G. Li and Y. Xiao, *Curr. Nanosci.*, 2016, **12**, 137-156.
- 2 M. A. Green, A. Ho-Baillie and H. J. Snaith, *Nat. Photonics*, 2014, **8**, 506-514.
- 3 Y. G. Rong, L. F. Liu, A. Mei, X. Li and H. W. Han, Adv. Energy Mater., 2015, 5, 1501066.
- 4 F. D. Giacomo, A. Fakharuddin, R. Jose and T. M. Brown, *Energy Environ. Sci.*, 2016, **9**, 3007-3035.

- 5 F. Zhang, S. R. Wang, X. G. Li and Y. Xiao, *Synth. Met.*, 2016, **220**, 187-193.
- 6 Y. X. Zhao and K. Zhu, Chem. Soc. Rev., 2016, 45, 655-689.
- 7 Y. K. Song, S. T. Lv, X. C. Liu, X. G. Li, S. R. Wang, H. Wei, D. M. Li, Y. Xiao and Q. B. Meng, *Chem. Commun.*, 2014, **50**, 15239-15242.
- 8 P. M. Da and G. F. Zheng, *Nano Res.*, 2017, **10**, 1471-1497.
- 9 T.Ye, S. Y. Ma, X. Jiang, M. Petrovic, C. Vijila, S. Ramakrishna and L. Wei, *Nanoscale*, 2017, 9, 412-420.
- 10 J. Y. Liu, J. J. Shi, D. M. Li, F. Zhang, X. G. Li, Y. Xiao, S. R. Wang, Synth. Met., 2016, 215, 56-63.
- 11 Y. Li, Z. Xu, S. L. Zhao, B. Qiao, D. Huang, L. Zhao, J. Zhao, P. Wang, Y. Q. Zhu, X. G. Li, X. X. Liu and X. R. Xu, *Small*, 2016, **12**, 4902-4908.
- 12 F. Zhang, W. D.Shi, J. S. Luo, N. Pellet, C. Y. Yi, X. Li, X. M. Zhao, T. J. S. Dennis, X. G. Li, S. R. Wang, Y. Xiao, S. M. Zakeeruddin, D. Q. Bi and M. Grätzel, *Adv. Mater.*, 2017, **29**, 1606806.
- 13 F. Zhang, Z. Q. Wang, H. W. Zhu, N.-P. Pellet, J. S. Luo, C. Y. Yi, X. C. Liu, H. L. Liu, S. R. Wang, X. G. Li, Y. Xiao, S. M. Zakeeruddin, D. Q. Bi and M. Grätzel, *Nano Energy*, 2017, DOI: 10.1016/j. nanoen.2017.09.035.
- 14 D. Q. Bi, C. Y. Yi, J. S. Luo, J. D. Décoppet, F. Zhang, S. M. Zakeeruddin, X. Li, A. Hagfeldt and M. Grätzel, *Nat. Energy*, 2016, **1**, 16142.
- 15 T. Swetha adn S. P. Singh, J. Mater. Chem. A, 2015, **3**, 18329-18344.
- 16 S. Ameen, M. A. Rub, S. A. Kosa, K. A. Alamry, M. S. Akhtar, H. S. Shin, H. K. Seo, A. M. Asiri and M. K. Nazeeruddin, *ChemSusChem*, 2016, 9, 10-27.
- 17 X. M. Zhao, F. Zhang, C. Y. Yi, D. Q. Bi, X. D. Bi, P. Wei, J. S. Luo, X. C. Liu, S. R. Wang, X. G. Li, S. M. Zakeeruddin and M. Grätzel, *J. Mater. Chem. A*, 2016, **4**, 16330-16334.
- 18 S. Shi, Y. Li, X. Li and H. Wang, *Mater. Horiz.*, 2015, **2**, 378-405.
- 19 J. J. Wang, S. R.Wang, X. G. Li, L. F. Zhu, Q. B. Meng, Y. Xiao and D. M. Li, *Chem. Commun.*, 2014, **50**, 5829-5832.
- 20 J. Liu, Q. Q. Ge, W. F. Zhang, J. Y. Ma, J. Ding, G. Yu and J. S. Hu, *Nano Res.* **2017**, 10.1007/s12274-017-1618-z.
- 21 W. B. Yan, Y. Li, Y. L. Li, S. Y. Ye, Z. W. Liu, S. F. Wang, Z. Q. Bian and C. H. Huang, *Nano Res.*, 2015, **8**, 2474-2480.
- 22 Y. S. Kwon, J. Lim, H. J. Yun, Y. H. Kim and T. Park, *Energy Environ. Sci.*, 2014, **7**, 1454-1460.
- 23 J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C. S. Lim, J. A. Chang, Y. H. Lee, H. J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel and S. II Seok, *Nat. Photonics*, 2013, **7**, 486-491.
- 24 P. Qin, S. Tanaka, S. Ito, N. Tetreault, K. Manabe, H. Nishino, M. K. Nazeeruddin and M. Grätzel, *Nat. Commun.*, 2014, 5, 3834.
- 25 K. T. Cho, O. Trukhina, C. Roldán-Carmona, M. Ince, P. Gratia, G. Grancini, P. Gao, T. Marzalek, W. Pisula, P. Y. Reddy, T. Torres and M. K. Nazeeruddin, *Adv. Energy Mater.*, 2017, 7, 1601733.
- 26 X. Q. Jiang, Z. Yu, J. B. Lai, Y. C. Zhang, M. W. Hu, N. Lei, D. P. Wang, X. C. Yang and L. C. Sun, *ChemSusChem*, 2017, **10**, 1838–1845.
- 27 X. Q. Jiang, Z. Yu, H.-B. Li, Y. W. Zhao, J. S. Qu, J. B. Lai, W. Y. Ma, D. P. Wang, X. C. Yang and L. C. Sun, *J. Mater. Chem. A*, 2017, **5**, 17862-17866.
- 28 X. Q. Jiang, Z. Yu, Y. C. Zhang, J. B. Lai, J. J. Li, G. G. Gurzadyan, X. C. Yang and L. C. Sun, *Sci. Rep.*, 2017, **7**, 42564.
- 29 G.-W. Kim, G. Kang, J. Kim, G.-Y. Lee, H. II Kim, L. Pyeon, J. Lee and T. Park, *Energy Environ. Sci.*, 2016, **9**, 2326-2333.
- 30 Z. Yu and L.C. Sun, Adv. Energy Mater., 2015, 5, 1500213.
- 31 X. C. Liu, J. You, Y. Xiao, S. R. Wang, W. Z. Gao, J. B. Peng and X. G. Li, *Dyes Pigm.*, 2016, **125**, 36-43.
- 32 X. C. Liu, J. F. Liang, J. You, L. Ying, Y. Xiao, S. R. Wang and X. G. Li, *Dyes Pigm.*, 2016, **131**, 41-48.

This journal is © The Royal Society of Chemistry 20xx

- 33 Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953-1010.
- 34 W.-J. Chi, P.-P. Sun and Z.-S. Li, *Nanoscale*, 2016, **8**, 17752-17756.
- 35 L. Zheng, Y. H. Chung, Y. Ma, L. Zhang, L. Xiao, Z. Chen, S. Wang, B. Qu and Q. A Gong, *Chem. Commun.*, 2014, **50**, 11196-11199.
- 36 J. A. Christians, R. C. M. Fung and P. V. Kamat, J. Am. Chem. Soc., 2014, 136, 758-764.
- 37 J. J. Guo, X. F. Meng, J. Niu, Y. Yin, M. M. Han, X. H. Ma, G. S. Song and F. Zhang, *Synth. Met.*, 2016, **220**, 462-468.
- 38 L. Petrikyte, I. Zimmermann, K. Rakstys, M. Daskeviciene, T. Malinauskas, V. Jankauskas, V. Getautis and M. K. Nazeeruddin, *Nanoscale*, 2016, 8, 8530-8535.
- 39 S. Kazim, F. J. Ramos, P. Gao, M. K. Nazeeruddin, M. Grätzel and S. Ahmad, *Energy Environ. Sci.*, 2015, **8**, 2946-2953.
- 40 F. Zhang, C. Y. Yi, P. Wei, X. D. Bi, J. S. Luo, G. Jacopin, S. R. Wang, X. G. Li, Y. Xiao, S. M. Zakeeruddin and M. Grätzel, *Adv. Energy Mater.*, 2016, 6, 1600401.
- 41 C. H. Huang, W. F. Fu, C. Z. Li, Z. Q. Zhang, W. M. Qiu, M. M. Shi, P. Heremans, A. Jen and H. Z. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 2528-2531.
- 42 F. Zhang, X. M. Zhao, C. Y. Yi, D. Q. Bi, X. D. Bi, P. Wei, X. C. Liu, S. R. Wang, X. G. Li, S. M. Zakeeruddin and M. Grätzel, *Dyes Pigm.*, 2017, **136**, 273-277.
- 43 M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, J. Mater. Chem. A, 2015, **3**, 12159-12162.
- 44 T. P.Osedach, T. L. Andrew and V. Bulovic, *Energy Environ. Sci.*, 2013, **6**, 711-718.
- 45 H. Li, K. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar and A. C. Grimsdale, *Angewandte Chemie.*, 2014, **53**, 4085-4088.
- 46 http://www.sigmaaldrich.com/catalog/product/aldrich/7920 71?lang=zh&region =CN.
- 47 W. Z. Gao, S. R. Wang, Y. Xiao and X. G. Li, *Dyes Pigm.*, 2013, **97**, 92-99.
- 48 M. S. Subeesh, K. Shanmugasundaram, C. D. Sunesh, Y. S. Won and Y. Choe, *J. Mater. Chem. C*, 2015, **3**, 4683-4687.
- 49 K. P. Li, J. L. Qu, B. Xu, Y. H. Zhou, L. J. Liu, P. Peng and W. J. Tian, *New J. Chem.*, 2009, **33**, 2120-2127.
- 50 P. Ganesan, K. Fu, P. Gao, I. Raabe, K. Schenk, R. Scopelliti, J. Luo, L. H. Wong, M. Grätzel and M. K. Nazeeruddina, *Energy Environ. Sci.*, 2015, **8**, 1986-1991.
- 51 A. Krishna, D. Sabba, H. Li, J. Yin, P. P. Boix, C. Soci, S. G. Mhaisalkar and A. C. Grimsdale, *Chem. Sci.*, 2014, **5**, 2702-2709.
- 52 P. Gratia, A. Magomedov, T. Malinauskas, M. Daskeviciene, A. Abate, S. Ahmad, M. Grätzel, V. Getautis and M. K. Nazeeruddin, *Angewandte Chemie.*, 2015, **54**, 11409-11413.
- 53 D. Q. Bi, W. Tress, M. I. Dar, P. Gao, J. S. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J. C. Baena, J. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Sci. Adv.*, 2016, **2**, 1501170.
- 54 F. Zhang, X. C. Liu, C. Y. Yi, D. Q. Bi, J. S. Luo, S. R. Wang, X. G. Li, Y. Xiao, S. M. Zakeeruddin and M. Grätzel, *Chemsuschem*, 2016, **9**, 2578-2585.
- 55 Y. S. Liu, Q. Chen, H. S. Duan, H. P. Zhou, Y. Yang, H. J. Chen, S. Luo, T. B. Song, L. Dou, Z. R. Hong, Y. Yang, *J. Mater. Chem. A*, 2015, **3**, 11940-11947.
- 56 J. Liu, Y. Z. Wu, C. J. Qin, X. D. Yang, T. Yasuda, A. Islam, K. Zhang, W. Q. Peng, W. Chen and L. Y. Han, *Energy Environ. Sci.*, 2014, **7**, 2963-2967.
- 57 J. J. Guo, Z. C. Bai, X. F. Meng, M. M. Sun, J. H. Song, Z. S. Shen, N. Ma, Z. L. Chen, F. Zhang, J. Sol. Energy, 2017, 155, 121–129.
- 58 P. Qi, F. Zhang, X. M. Zhao, X. C. Liu, X. D. Bi, P.Wei, Y. Xiao, X. G. Li and S. R. Wang, *Energy Technol.*, 2017, DOI: 10.1002/ente.201600517

- 59 H. W. Zhu, F. Zhang, X. C. Liu, M. N. Sun, J. L. Han, J. You, S. R. Wang, Y. Xiao and X. G. Li, *Energy Technol.*, 2017, DOI: 10.1002/ente.201600555.
- 60 X. C.Liu, L. F. Zhu, F. Zhang, J. You, Y. Xiao, D. M. Li, S. R. Wang, Q. B. Meng and X. G. Li, *Energy Technol.*, 2017, 5, 312-320.
- 61 P. Qi, F. Zhang, X. G. Li, Y. Xiao, J. J. Guo and S. R. Wang, Synth. Met., 2017, 226, 1–6.
- 62 Y. Liu, Z. Hong, Q. Chen, H. Chen, W. H. Chang, Y. Yang, T. B. Song and Y. Yang, *Adv. Mater.*, 2016, **28**, 440–446.
- 63 F. G. Zhang, X. C. Yang, M. Cheng, W. H. Wang and L. C. Sun, Nano Energy, 2016, **20**, 108-116.
- 64 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, et al. Gaussian 03, revision E. 01. Wallingford, CT: Gaussian, Inc.; 2004.



TPD based molecular "bee" as dopant-free HTMs for PSCs exhibit the PCE of 15.28% which is comparable to doped *spiro*-OMeTAD.