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1	View Article Online DOI: 10.1039/C6RA18823K Diketopyrrolopyrrole or benzodithiophene-arylamine small-molecular hole
2	transporting materials for stable perovskite solar cells
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18	Two simple small-molecular arylamine derivatives 4-methoxy-N-(4-methoxyphenyl)-
19	N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (OMeTPA-DPP)
20	and 4,4'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(N,N-
21	bis(4-methoxyphenyl)aniline) (OMeTPA-BDT) linked with diketopyrrolopyrrole or
22	benzodithiophene moieties have been synthesized. New compounds show better
23	thermal stability than spiro-OMeTAD. The steady-state and time-resolved
24	photoluminescence demonstrate that new compounds have good hole extraction
25	ability. The perovskite solar cells employing OMeTPA-BDT show a comparable 1

power conversion efficiency with that of spiro-OMeTAD. After more than 200 house watche Online of aging under one sun illumination, residual efficiency of the PSCs based on **OMeTPA-DPP, OMeTPA-BDT** and spiro-OMeTAD are 8.69%, 11.15% and 9.08%, respectively. The results demonstrate that the newly-developed compounds can act as efficient hole transporting materials for stable perovskite solar cells.

6 1. Introduction

Recently, organometal halide perovskite ($CH_3NH_3PbX_3$, X = Cl, Br, I) have 7 drawn great attention as light absorbing material for their direct band gaps, large 8 optical absorption, excellent ambipolar charge mobility and small exciton binding 9 energy.^[1-4] The breakthrough of perovskite solar cells (PSCs) is that Kim et al 10 reported solid-state devices using organic 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-11 amine) 9.9'-spirobifluorene (spiro-OMeTAD) as hole transporting materials (HTMs) 12 13 to replace the liquid electrolyte, leading to a promising power conversion efficiency (PCE) of 9.7%.^[1] Since then, the solid-state PSCs lead to a remarkable PCE of 14 exceeding 20%.^[5,6] Now HTMs are an important part of PSCs. Inorganic and organic 15 HTMs have been applied in PSCs. However, inorganic HTMs usually exhibit 16 relatively low efficiency in PSCs and are limited by materials selection (mainly Ni, 17 Cu compounds).^[7-11] Organic HTMs are widely used in PSCs for their superior 18 performance. They are classified into small molecules and polymers.^[12] The former 19 includes phenylamine derivatives,^[13-19] thiophene derivatives, [20-24] mainly 20 phthalocyanine derivatives,^[25-28] etc. The latter mainly includes tertiaryarylamine 21 polymer (PTAA),^[5] aniline polymer,^[29] diketopyrrolopyrrole and benzodithiophene 22 polymers.^[30-35] Among these compounds, spiro-OMeTAD is the most widely used 23 HTM in PSCs. Nevertheless, it is expensive due to its complicated multi-step 24 synthesis and difficult purification process. Moreover, the devices based on it show 25

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inferior stability. These defects limit the large-scale industrial production of cost/iew Article Online

2 effective PSCs. Hence, developing new organic HTMs is necessary for cost reduction

3 and improving the performance of the devices.

To develop cost-efficient and stable HTMs for PSCs, herein, we introduce low-4 cost DPP and BDT moieties as bridge into small-molecular compounds (OMeTPA-5 **DPP**, **OMeTPA-BDT**) and find these two compounds can act as HTM when applied 6 in PSCs. The structures of them are shown in Fig. 1. Two molecules show better 7 thermal stability than spiro-OMeTAD. The charge dynamics at the HTMs/perovskite 8 9 interface are investigated by steady-state photoluminescence (PL) and time-resolved PL measurements. And the long-term stability of the PSCs based on new HTMs are 10 superior to that of spiro-OMeTAD. 11



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13 Fig. 1 Molecular structures of OMeTPA-DPP and OMeTPA-BDT.

15 2.1 Optical electrochemical and thermal properties of the compounds

Fig. 2a shows the UV-Vis absorption and fluorescence emission spectra of OMeTPA-DPP and OMeTPA-BDT dissolved in dichloromethane (DCM), and the characteristic of them are listed in Table 1. OMeTPA-DPP and OMeTPA-BDT exhibit absorption peaks at 642 nm and 414 nm, respectively. The absorption spectrum of OMeTPA-DPP shows stronger red shift than OMeTPA-BDT due to

^{14 2.} Results and discussion

functionalized diketopyrrolopyrrologyrrols9/C6RA18823K powerful absorbing of 1 more capacity configurations than benzodithiophene configurations. The fluorescence spectra of 2 3 both the new compounds show large stokes shifts (64 nm and 69 nm), which suggest that they can occur relatively large structural change upon excitation. The absorption 4 spectra confirm that the compounds don't significantly absorb the visible light. The 5 optical band gap (Eg) of HTMs estimated from the intersection of the corresponding 6 7 normalized absorption and fluorescence emission spectra are 1.82 eV and 2.74 eV, 8 respectively.



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Fig. 2 (a) Normalized UV-vis absorption and photoluminescence, (b) cyclic
voltammogram with ferrocene as the reference in DCM and (c) thermogravimetric
analysis (TGA) of OMeTPA-DPP, OMeTPA-BDT and spiro-OMeTAD.

5 **Table 1.** Summary of the optical, electrochemical and thermal properties of new 6 compounds

HTM	$\lambda_{max}{[a]}/$ nm	$\lambda_{PL}^{[a,b]}/$ nm	Eg ^[c] / eV	HOMO ^[d] / eV	LUMO ^[e] / eV	$T_d^{[f]}/$ °C	Tg[g]/ °C	Tm[g]/ °C
OMeTPA- DPP	642	706	1.82	-5.13	-3.31	305	157	169
OMeTPA- BDT	414	483	2.74	-5.19	-2.45	399	158	215

[a] UV-vis absorption spectra and fluorescence spectra were measured in CH_2Cl_2 solution. [b] Excitation at λ_{max} . [c] From the intersection of absorption and emission spectra. [d] From CV measurement and referenced to ferrocene. [e] $E_{LUMO} = E_{HOMO}$ $+E_g$. [f] Decomposition temperature, from TGA. [g] Glass-transition temperature and melting temperature, from DSC.

12 Cyclic voltammograms (CV) measurements (Fig. 2b) were carried out to get the 13 electrochemical properties of new compounds and spiro-OMeTAD. The pair of redox

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peaks of OMeTPA-DPP and OMeTPA-BDT is highly reversible, indicating that we warticle Online 1 they have excellent electrochemical stability. The HOMO energy levels are calculated 2 by the following equation^[36]: E_{HOMO} =-5.1-($E_{ox.HTM}$ vs. Fc/Fc⁺) (eV), where $E_{ox.HTM}$ vs. 3 Fc/Fc^+ is onset of oxidation potential with reference to ferrocene as standard. The 4 highest occupied molecular orbital (HOMO) energy levels of them calculated from 5 CV are -5.13 eV and -5.19 eV. Interesting, electron-withdrawing diketopyrrolopyrrole 6 bridge do not lower HOMO level of OMeTPA-DPP compared to OMeTPA-BDT, 7 and repeated CV data are shown in Fig. S2. HOMO levels of new compounds are 8 9 more positive than the conductive band of perovskite, indicating a favorable driving force that may generate for electron-hole separation at the HTMs/perovskite interface. 10 And both of them are deeper than spiro-OMeTAD (-5.08 eV). It indicates that the 11 compounds have appropriate HOMO levels relating to the valence band of perovskite 12 and lead to higher open circuit voltage than that of spiro-OMeTAD. The lowest 13 unoccupied molecular orbital (LUMO) levels calculated from HOMO and Eg are 14 found to be -3.31 eV and -2.45 eV for OMeTPA-DPP and OMeTPA-BDT, 15 respectively. 16

17 The thermal properties of the compounds are investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As demonstrated in Fig. 18 2c and Fig. S1, the results show that these two HTMs exhibit more than 150 °C of 19 glass-transition temperature (T_g) and more than 300 °C of decomposition temperature, 20 respectively. The spiro-OMeTAD show a low Tg of 122 °C (shown in Fig. S1), which 21 is similar with the reported value ($T_g = 126 \text{ °C}$).^[37] The introduction of DPP or BDT 22 moieties into these new molecules as cores can lower the twisting force and increase 23 the π -conjugation ability than spiro-core. Moreover, the existence of heterocyclic 24 aromatic DPP or BDT into molecular main chain could decrease mobility of chain 25

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segment and molecular flexibility of these two new compounds than spiro-OMeTAD^{iew Article Online} which lead to high T_g than spiro-OMeTAD.^{38,39} And high thermal stability is beneficial to the long-term durability of PSCs.

4 **2.2 Charge dynamics**

To investigate the charge transfer dynamics at the HTM/perovskite interface, we 5 measure charge generation of the perovskite film via steady-state and time-resolved 6 photoluminescence (PL). Theoretically, the quenching of steady-state PL and 7 reduction of PL lifetime indicate the efficient charge separation. From the steady-state 8 9 PL spectra in Fig. 3a, we can find that both of **OMeTPA-DPP** and **OMeTPA-BDT** showed almost completely quenched (quenching efficiency 85% of OMeTPA-DPP 10 and 96% of OMeTPA-BDT) compared with a perovskite film without any HTM, 11 which indicate efficient charge transfer at HTM/perovskite interface. ^{40, 41} The higher 12 13 quenching efficiency of OMeTPA-BDT may be more beneficial for effective PCEs than that of OMeTPA-DPP. Moreover, the steady-state PL spectra of perovskite 14 films coated with HTMs reveal a hypochromatic shift, which may result from the 15 optical properties of the perovskite/HTM interface ⁴² and the chemical interaction 16 between perovskite surface and HTM.43 17

Fig. 3b shows the time-resolved PL decay spectra of perovskite film coated with OMeTPA-DPP, OMeTPA-BDT and one without any HTM layer. In the absence of HTM layer, the excited perovskite has no other possibility than recombining with electron within perovskite layer, indicating a longer decay time. Pristine perovskite exhibits a lifetime of 3.77 ns, illustrates relatively slow carrier recombination in perovskite layer. However, when the HTMs exhibit, the perovskite can be quenched by the HTMs layer, resulting in a faster decay process. All the perovskite coated with

HTMs show significantly reduced lifetime, meaning faster decay rates (1.99 ns. fog9/c6RA18823K
OMeTPA-DPP and 0.96 ns for OMeTPA-BDT). Combined with the steady-state PL
spectra, the faster decay rates of perovskite coating with new HTMs show the
dynamical possibility of the charge transfer at HTM/perovskite interface.





Fig. 3 (a) Time-integrated PL spectra. Excitation wavelength: 600 nm. (b) Timeresolved PL spectra. Monitored at 765 nm, excitation at 445 nm.

9 **2.3 Device performance**

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To prove the potential of **OMeTPA-DPP** and **OMeTPA-BDT** acting as HTMs. We watche Contine PSCs, we compare the devices with new compounds and spiro-OMeTAD as HTM, together with a cell without HTM. The cross-sectional field-emission scanning electron microscopy (SEM) image of a conventional mesoscopic PSC (shown in Fig. 4a) shows typical structural configuration with clear interfaces. The thickness of mesoporous TiO₂ composed of perovskite and the HTM layer are about 500 nm and 150 nm. The device configuration of hybrid solar cells is shown in Fig. 4b. And Fig. 4c shows the energy level diagram of the materials used in our devices according to





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Fig. 4 (a) Cross-sectional SEM image of the perovskite solar cells. (b) Scheme of the
PSCs configuration. (c) Energy level diagram of the corresponding materials used in
devices.

15 Fig. 5a shows the current-density-voltage (*J-V*) curves of fore-mentioned devices.

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The photovoltaic parameters of the PSCs are summarized in Table 2. As the PSC we write online have exhibited a greatly improvement in PCE by increasing the hole-conductivity of HTMs *via* doping the additives such as lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) and 4-tert-butylpiridine (TBP). We fabricate the devices by doping the two additives into **OMeTPA-DPP** and **OMeTPA-BDT**, spiro-OMeTAD HTMs to enhance cells performance.

After preliminary optimization of devices, the PCEs of the PSCs with OMeTPA-7 **DPP**, **OMeTPA-BDT** and spiro-OMeTAD as HTM are 8.63%, 10.89% and 13.45%, 8 9 respectively. The device fabricated without any HTM shows a PCE of only 5.41%. Obviously, the improved PCEs of devices with **OMeTPA-DPP** or **OMeTPA-BDT** 10 than a device without HTM demonstrate that the new compounds have the potential to 11 be efficient HTMs in PSCs. The short circuit current (J_{sc}) of the devices fabricated 12 with OMeTPA-DPP, OMeTPA-BDT and spiro-OMeTAD are 14.87, 16.60, and 13 19.93 mA cm⁻². The incident photon to current efficiency (IPCE) spectra represents 14 the ratio of extracted electrons to incident photons at the electrode surface at a given 15 wavelength. And corresponding IPCE spectra of the devices with OMeTPA-DPP, 16 17 **OMeTPA-BDT**, spiro-OMeTAD and without HTMs is shown in Fig. 5b. Compared with hole-conductor-free device, the IPCE spectra of the PSCs with HTMs are 18 significantly improved in 400-800 nm. The devices with new compounds show lower 19 IPCE response in 400-800 nm than that of spiro-MeOTAD, which may result from 20 lower HOMO level of them than spiro-OMeTAD. So there is lower driving force for 21 electron injection efficiency between the perovskite layer and the OMeTPA-22 **DPP/OMeTPA-BDT** layer. In addition, the integrated IPCE spectra of the devices 23 are in good agreement with the J_{sc} from each device. In perovskite solar cells, the 24 open circuit voltage (V_{oc}) mainly depends on the HOMO energy level of HTMs and 25

the Fermi level of TiO₂. The HOMO energy level of **OMeTPA-BDT** is lower that we write Online that of spiro-OMeTAD by about 150 mV. Therefore, the difference of 110 meV between them lead to the average V_{oc} of device based on **OMeTPA-BDT** are higher than that of spiro-OMeTAD. The hysteresis characteristics of the PSC devices with new HTMs and spiro-OMeTAD were evaluated from the forward and reverse scan directions, as shown in Fig. S3 and table S1. There are similar hysteresis behavior among the devices with new HTMs and spiro-OMeTAD

8 **Table 2.** The current–voltage (J-V) characteristics of CH₃NH₃PbI₃-based devices 9 with **OMeTPA-DPP**, **OMeTPA-BDT** and spiro-OMeTAD as HTM and with any 10 HTM for comparison measured under simulated AM 1.5G irradiation.

HTM	$V_{ m oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF(%)	PCE(%)
no HTM	0.75	11.21	63.9	5.41
OMeTPA-DPP	0.92	14.87	63.0	8.63
OMeTPA-BDT	0.96	16.60	68.5	10.89
spiro-OMeTAD	0.95	19.93	71.1	13.45

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a 20 Current density (mA·cm⁻²) 15 10 no HTM 5 **OMeTPA-DPP** 0 **OMeTPA-BDT** spiro-OMeTAD -5 0.4 0.6 0.0 0.2 0.8 1.0 Voltage (V) b 80 60 IPCE (%) 40 no HTM **OMeTPA-DPP** 20 **OMeTPA-BDT** spiro-OMeTAD 0 **–** 300 400 500 600 700 800 Wavelength (nm)

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3 Fig. 5 (a) Current density-voltage of cells based on OMeTPA-DPP, OMeTPA-BDT, spiro-OMeTAD and a cell without any HTM. (b) Corresponding incident photo-to-4 current conversion efficiency (IPCE) spectrum of the devices. 5

To study the stability of devices base on different HTMs, we further optimize the 6 device fabrication and gain a PCE of 10.05%, 12.81% and 14.20% for OMeTPA-7 DPP, OMeTPA-BDT and spiro-OMeTAD, respectively (shown in Fig. S5). Then we 8 9 put these cells without encapsulation under one sun illumination. As shown in Fig. 6 10 and Table S5, we noted that the devices with OMeTPA-DPP and OMeTPA-BDT



show a 14% and 13% loss of PCE, however, the spiro-OMeTAD-based showed the Wave Article Online
most significant deterioration (36% loss of PCE) after 10 days of aging. The excellent
stability of the OMeTPA-DPP and OMeTPA-BDT based cells than that of spiroOMeTAD are attributable to excellent thermal stability and the existence of

5 hydrophobic alkyl chains on them.



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Fig. 6. Stability test for devices based on OMeTPA-DPP (■), OMeTPA-BDT (●),
and spiro-OMeTAD (▲).

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10 **3. Conclusions**

In summary, we develop two simple small-molecular hole transporting materials with 11 high thermal stability by introducing DPP or BDT moieties into molecules. These two 12 HTMs can be synthesized by short route with high-yielding. Photoluminescence study 13 14 indicate that OMeTPA-DPP and OMeTPA-BDT can act efficient HTM in PSCs. After 10 days of aging, residual efficiency of the PSCs based on **OMeTPA-DPP**, 15 **OMeTPA-BDT** and spiro-OMeTAD are 8.69%, 11.15% and 9.08%, respectively. 16 17 These HTMs are thus promising HTMs with the potential to replace spiro-OMeTAD due to their good performance and simple synthesis route. This work also provide a 18 strategy for designing and developing new efficient and stable HTMs for PSCs. 19

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1 4. Experimental section

2 4.1 Materials and reagents

All reagents and chemicals were purchased from Sigma-Aldrich, Alfa, Sinopharm Chemical Reagent Co., Ltd., TCI and Derthon Optoelectronic Materials Science Technology Co., Ltd. without further purification. FTO coated glass substrates with a sheet resistance of $15 \Omega \cdot \text{sq}^{-1}$ were purchased from TEC company.

7 4.2 Hole transporting materials synthesis

The synthesis of **OMeTPA-DPP** and **OMeTPA-BDT** are simple with high yields by well-know reaction (Suzuki cross-coupling reactions). The synthesis route of them is shown in Scheme 1. And the molecular structures were confirmed by ¹H and ¹³C NMR spectroscopy and mass spectrometry (MALDI-TOF). Detailed synthesis procedures for both HTMs are shown as follows.



14 Scheme 1. Synthetic routes to OMeTPA-DPP and OMeTPA-BDT.

Synthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)phenyl)aniline (compound **2**). Under the protection of Ar, compound **1** (3 mmol, 1.728 g), bis(pinacolato)diboron (3.75 mmol, 0.96 g), KOAc (9.36 mmol, 0.9 g), dry 1,4-dioxane were added into a 50 mL flask. Then Pd₂dba₃ (14 mg) and X-Phos (30 mg) were added to the system and stirring at 80 °C overnight.

The reaction mixture was then cooled down to room temperature and extracted withew Article Online
CH₂Cl₂, remove the solvent. The residue mixture was purified by column
chromatography (CH₂Cl₂/hexane=1:1) to obtain the white solid (product 2, 1.10 g,
74%). ¹H NMR (400 MHz, DMSO) δ 7.47 (d, 2H), 6.93 (d, 4H), 6.70 (d, 4H), 6.68 (d,
2H), 3.76 (s, 6H), 1.26 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 156.23, 151.44,
140.43, 135.80, 127.20, 119.47, 118.65, 114.77, 83.41, 55.48, 24.89.

Synthesis of 3,6-bis(5-(4-(bis(4-methoxyphenyl)amino)phenyl)thiophen-2-yl)-2,5-7 bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (OMeTPA-DPP). 8 Compound 2 (1.2 mmol, 0.517 g), compound 3 (0.5 mmol, 0.34 g), 2M solution of 9 10 K₂CO₃ (8 mmol, 1.1 g) in H₂O, [Pd(PPh₃)₄] (0.05 mmol, 58 mg), DMF (20 mL) were 11 added into a 100 mL Ar-protected flask. The reaction solution was kept with stirring at 90 °C overnight. The reaction mixture was then cooled down to room temperature 12 and poured into cool water, extracted with CH₂Cl₂. The organic layer was dried with 13 MgSO₄, and the solvent was removed by rotary evaporator. The residue mixture was 14 purified by column chromatography (CH₂Cl₂/hexane=1:1) to obtain the product as 15 atropurpureus solid (OMeTPA-DPP, 415 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 16 7.44 (d, 4H), 7.29 (d, 4H), 7.10 (d, 8H), 6.87 (t, 12H), 4.06 (m, 4H), 3.81 (s, 12H), 17 18 1.95 (s, 2H), 1.47 – 1.27 (m, 16H), 0.95 – 0.81 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) 19 δ 161.69, 156.38, 150.18, 149.40, 140.06, 139.49, 137.07, 127.34, 127.05, 126.78, 124.70, 122.87, 119.69, 114.84, 107.71, 55.49, 45.93, 40.93, 39.19, 30.30, 28.48, 20 21 23.08, 14.07, 10.60. HRMS (MALDI-TOF): [M-H] m/z calcd for C₇₀H₇₃N₄O₆S₂: 1130.4898; found: 1130.4796. 22

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23 Synthesis of 4,4'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,624 diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (OMeTPA-BDT).

25 Compound 4 (0.6 mmol, 0.36 g), compound 2 (1.5 mmol, 0.65 g), 2M solution of

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K₂CO₃ (8 mmol, 1.1 g) in H₂O, [Pd(PPh₃)₄] (0.05 mmol, 58 mg), DMF (20 mJ₂), werver View Article Online View Articl 1 added into a 50 ml Ar-protected flask and following the same procedure to make 2 3 **OMeTPA-DPP**. The **OMeTPA-BDT** was obtained as a green solid (554 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.46 (m, 6H), 7.10 (d, 8H), 6.95 (d, 4H), 6.85 (d, 4 8H), 4.18 (s, 4H), 3.81 (s, 12H), 1.82 (dd, 2H), 1.75 – 1.65 (m, 2H), 1.58 (dd, 4H), 5 1.53 (d, 2H), 1.40 (s, 8H), 1.02 (t, 6H), 0.93 (d, 6H). ¹³C NMR (100 MHz, CDCl3) δ 6 156.22, 148.93, 143.96, 143.36, 140.50, 132.60, 129.17, 127.08, 126.99, 126.21, 7 120.16, 114.83, 113.95, 75.92, 55.52, 40.71, 30.52, 29.26, 23.93, 23.19, 14.21, 11.38. 8 9 HRMS (MALDI-TOF): [M-H] m/z calcd for C₆₆H₇₁N₂O₆S₂: 1052.4177; found: 1052.4655. 10

11 4.3 Device Fabrication

The fluorine-coated SnO_2 glass substrate (FTO) with high transparency in the visible range (2 cm × 1.5 cm) were etched in specific pattern with zinc powder and 1 M aqueous solution of HCl for 20 seconds. Then glass substrates were washed using an ultrasonic bath for 30 min, rinsed with ethanol, annealed at 510 °C for 30 min.

The compact TiO₂ layer was deposited on the etched FTO substrate by aerosol 16 spray-pyrolysis using O₂ as the carrier gas at 450 °C from a precursor solution of 1.2 17 18 ml titanium diisopropoxide and 0.8 ml bis(acetylacetonate) in 14 ml anhydrous 19 isopropanol, and then sintered at 510 °C for 30 min. The mesoporous TiO₂ film was deposited by spin coating at 4000 rpm for 30 s with a ramp of 2000 rpm s⁻¹ from a 20 21 diluted commercial TiO₂ paste in ethanol (Dyesol 18NR-T, 2:7, weight ratio), gradually heated to 510 °C, keep 15 min and cooled to room temperature in air. Then 22 the TiO₂ films were treated in a 0.04 M aqueous solution of TiCl₄ at 70 °C for 30 min, 23 24 rinsed with deionized water and following annealed at 510 °C for 30 min.

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The PbI₂ in DMF solution (461 mg mL⁻¹) was dropped on the TiO₂/FTO

substrate by spin-coated at 3000 rpm for 30 s, put in room temperature for 5, million Article Online 1 annealed on a hot plate at 70 °C for 30 min. After cooling down, the film was dipped 2 in 9 mg mL⁻¹ CH₃NH₃I (prepared according to the previously reports ⁴⁴) in 2-propanol 3 solution for 30 s, spin coating at 3000 rpm for 30 s and dried at 70 °C for 30 min. The 4 HTM layer was coated by spin-coating at 5000 rpm for 30 s. The concentration of 5 new HTMs and spiro-OMeTAD are 70 mg mL⁻¹ in 1 mL of chlorobenzene with 6 heating to 70°C overnight, then 28.8 µL of 4-tert-butylpyridine, 17.5 µL of lithium 7 bis(trifluoromethylsulphonyl)imide (520 mg Li-TFSI in 1 mL of acetonitrile) were 8 9 added to the solution. The HTMs were spin-coated on the CH₃NH₃PbI₃/TiO₂/FTO substrate at 4000 rpm for 30 s. All device fabrications were performed below 15% of 10 relative humidity. 11

Finally, Au layer with a thickness of 60 nm was deposited on HTM layer by thermal evaporator to form the back contact. The active area of the device was defined by a black mask with a size of 0.09 cm² for all measurement.

15 4.4 Analytical measurement

¹H NMR and ¹³C NMR spectra were measured by a Bruker DPX 400 MHz 16 chemical shifts against tetramethylsilane 17 spectrometer with the (TMS). 18 HRMS(MALDI-TOF) experiments were performed using a MS Bruker Daltonik Reflex III and Bruker solariX spectrometer. The absorption spectra of the compounds 19 were recorded by a UV-Vis spectrophotometer (U-3900H, Hitachi, Japan). Cyclic 20 21 voltammograms (CV) were carried out on a CHI660D (Shanghai Chenhua Device Company, China) in a three-electrode electrochemical cell with a Pt disk working 22 electrode, an SCE reference electrode and a platinum wire sphere with supporting 23 electrolyte of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (TBAPF₆) in 24 CH₂Cl₂ at a scan rate of 50 mV s⁻¹ using ferrocene as inner standard at the end of each 25

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measurement. The cross-sectional morphologies of the devices were observed with yiew Article Online 1 field emission scanning electron microscopy (FE-SEM, sirion200, FEI Corp., 2 Holland). The photocurrent-voltage (J-V) characteristics of the PSCs were measured 3 under AM 1.5 (100 mW cm⁻²) illumination which was provided by an AAA grade 4 solar simulator (Newport, USA, 94043A, calibrated with a standard crystalline silicon 5 solar cell). The incident photon to current conversion efficiency (IPCE) was 6 performed on QE/IPCE measurement kit (Newport, USA, CA). The steady-state 7 photoluminescence (PL) emission and time-resolved PL decay measurements were 8 9 carried out on a Fluorescence Detector (QM400 and LaserStrobe, Photo Technology International, USA). Time-integrated PL emission spectra of film were recorded by a 10 standard 450 W xenon CW lamp. Time-resolved PL decay measurements were 11 carried out on a pulsed nitrogen/dye laser. Differential scanning calorimetry of HTMs 12 was recorded with scan rate of 20 °C min⁻¹ (DSC, TA Instruments-Waters LLC, USA, 13 14 Q2000). The decomposition temperature of the compounds were carried out on a Thermal Gravimetric Analyzer (TGA, Q5000IR) at a heating rate of 10 °C min⁻¹ in a 15 temperature range of 0 °C to 800 °C under nitrogen atmosphere. 16

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Two new hole transporting materials with diketopyrrolopyrrole or benzodithiophene moieties were developed for stable perovskite solar cells.