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## Efficient, symmetric oligomer hole transporting materials with different cores for high performance perovskite solar cells†

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**Novel symmetric oligomer hole transporting materials (HTMs) incorporating 3,4-ethylenedioxythiophene (EDOT) and 2,1,3-benzothiadiazole (BTD) cores have been synthesized and tested for high performance perovskite solar cells. A maximum energy conversion efficiency of 14.23% has been achieved by employing DPEDOT-B[BMPDP]<sub>2</sub> with the electron donating EDOT unit as the core, which is comparable to that of the traditional spiro-OMeTAD (14.55%).**

Organometal halide perovskites (CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, X = Cl, Br, I) possess special features, such as a direct band gap and intense light harvesting ability.<sup>1</sup> Thereby they can be utilized as both efficient light absorbers and electron–hole transporting materials for thin-film organic–inorganic hybrid solar cells.<sup>2</sup> Therefore, organometal halide perovskite solar cells have been recently receiving great attention owing to their outstanding features such as high efficiency and low cost.<sup>3</sup> In the perovskite solar cells, hole transporting materials (HTMs) play a key role in determining the photovoltaic performance. In this regard, the development of cost-effective and efficient HTMs is urgently needed. The most effective HTM for the hybrid solar cells is 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenyl-amine)-9,9'-spirobifluorene (**spiro-OMeTAD**) in terms of the efficiency and stability.<sup>4</sup> However, **spiro-OMeTAD** is quite expensive owing to the difficulty in its purification. For commercial purposes, the exploration of alternative HTMs with high performance and cheap synthetic price is strongly required. Recently, impressive photovoltaic performance has been achieved using small molecule HTMs, such as azomethine,<sup>5</sup> 3,4-ethylenedioxythiophene,<sup>6</sup> pyrene,<sup>7</sup> linear  $\pi$ -conjugated,<sup>8</sup> butadiene,<sup>9</sup> **spiro-OMeTAD** derivative,<sup>10</sup> carbazole derivative,<sup>11</sup> tetrathiafulvalene,<sup>12</sup> tetraphenyl-benzidine,<sup>13</sup> oligothiophene

derivative,<sup>14</sup> and spiro-thiophene derivative<sup>15</sup> based HTMs showing efficiencies in the range of 10–15%. Recently, we<sup>16</sup> have reported quinolizino acridine-, star-shaped triphenylamino-, and triazine based HTMs, exhibiting high conversion efficiencies of ~14%. Nevertheless, most of the small molecule HTMs are still expensive, with low conversion efficiency and low stability compared to **spiro-OMeTAD**. Therefore, the development of cheap HTMs with operation stability is still very important.

Herein, we report three types of hole transporting materials by incorporating an electron donating unit or an electron-withdrawing unit into tetraphenyl benzidine or substituting four triphenylamines into the phenyl unit. The molecular structures of the three HTMs are shown in Fig. 1.

The synthetic scheme for the preparation of **B[BMPDP]<sub>2</sub>**, **DPEDOT-B[BMPDP]<sub>2</sub>** and **DPBTD-B[BMPDP]<sub>2</sub>** is shown in Scheme 1. The primary step for their syntheses is the Suzuki coupling reaction<sup>17</sup> of bis(4-bromophenyl)amine and *N*-bis-(methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine. The final two HTMs were synthesized by the Buchwald–Hartwig amination<sup>18</sup> of **1** and dihalo derivatives.

The UV-vis absorption spectra of the three HTMs recorded in chlorobenzene are displayed in Fig. 2a. As summarized in Table S1 (ESI†), the UV-vis light absorption peaks of **B[BMPDP]<sub>2</sub>**, **DPEDOT-B[BMPDP]<sub>2</sub>** and **DPBTD-B[BMPDP]<sub>2</sub>** were observed at 376, 377, and 473 nm, respectively. The  $\lambda_{\text{abs}}$  of **DPBTD-B[BMPDP]<sub>2</sub>** is more red shifted than that of **DPEDOT-B[BMPDP]<sub>2</sub>**. This bathochromic shift seems to be attributed to an intramolecular charge transfer in

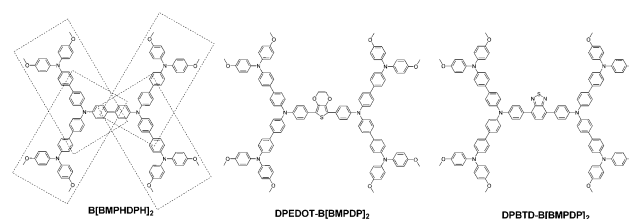
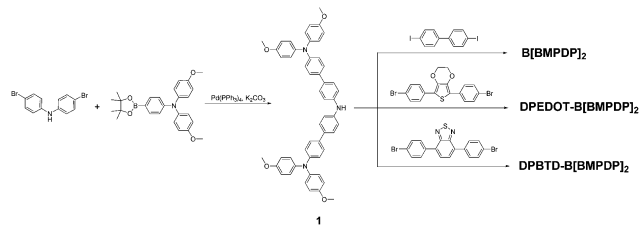


Fig. 1 Chemical structures of **B[BMPDP]<sub>2</sub>**, **DPEDOT-B[BMPDP]<sub>2</sub>** and **DPBTD-B[BMPDP]<sub>2</sub>** moieties studied in the present work.

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Scheme 1 Schematic diagram for the synthesis of **B[BMPDP]<sub>2</sub>**, **DPEDOT-B[BMPDP]<sub>2</sub>** and **DPBTD-B[BMPDP]<sub>2</sub>**.

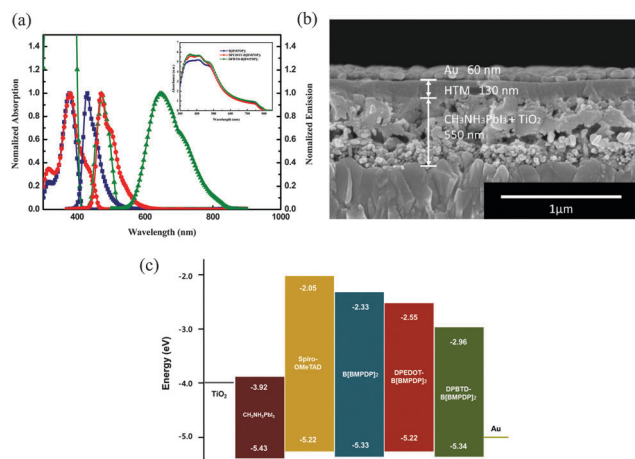


Fig. 2 (a) Absorption and emission spectra of the HTMs in chlorobenzene. Inset: UV-vis absorption spectra of the HTMs coated on mp-TiO<sub>2</sub>/MAPbI<sub>3</sub> films. (b) Cross-sectional field-emission scanning electron microscopy (FE-SEM) image of mp-TiO<sub>2</sub>/MAPbI<sub>3</sub>/HTM/Au. (c) Energy level diagram of each component.

**DPBTD-B[BMPDP]<sub>2</sub>**. The fluorescence spectra of **B[BMPDP]<sub>2</sub>** and **DPEDOT-B[BMPDP]<sub>2</sub>** exhibit an emission at 429 and 472 nm with a small Stokes shift of 53–95 nm compared with a large Stokes shift of 175 nm in **DPBTD-B[BMPDP]<sub>2</sub>**, demonstrating that a small structural change in the excited state occurs in the two former compounds. The inset of Fig. 2a shows the absorption spectra of the perovskite-coated mesoporous TiO<sub>2</sub> films with the three HTMs. Three HTM-coated films exhibit an enhanced absorption band from 350 to 580 nm.

The cross-sectional field-emission scanning electron microscopy (FE-SEM) image of the prepared perovskite solar cell is displayed in Fig. 2b, showing a well-defined multi-layer structure with clear interfaces. The thickness of the TiO<sub>2</sub> scaffold film incorporated with perovskite, HTM layer and Au is 550 nm and 130 nm and 60 nm, respectively. Fig. 2c shows a comparative diagram of the energy levels of the corresponding components in the device. The HOMO levels of **B[BMPDP]<sub>2</sub>**, **DPEDOT-B[BMPDP]<sub>2</sub>** and **DPBTD-B[BMPDP]<sub>2</sub>** are measured to be  $-5.33$ ,  $-5.22$  and  $-5.34$  eV, respectively, which are well matched with CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> ( $-5.43$  eV).

Fig. 3a shows the photocurrent–voltage ( $J$ – $V$ ) curves of the perovskite solar cells employing the HTMs. For reference, the device with **spiro-OMeTAD** as the HTM is fabricated. The detailed photovoltaic parameters of the devices are also summarized

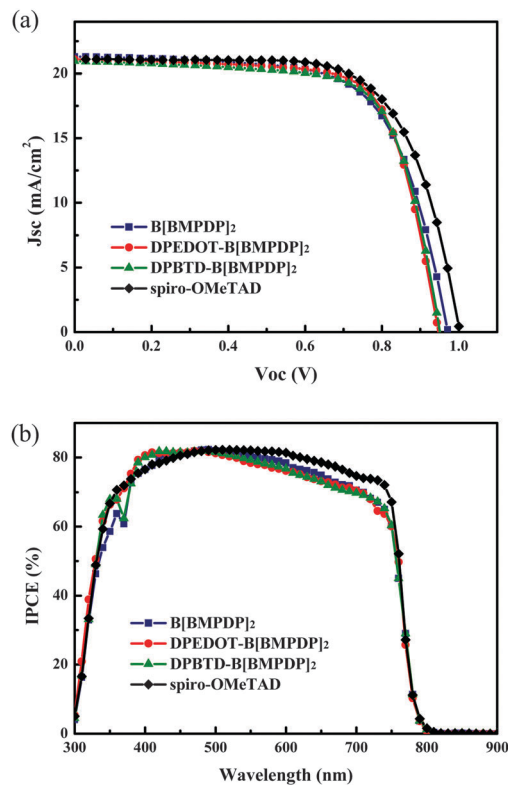


Fig. 3 (a) Photocurrent–voltage ( $J$ – $V$ ) curves of the solar cells with **B[BMPDP]<sub>2</sub>** (■), **DPEDOT-B[BMPDP]<sub>2</sub>** (●), **DPBTD-B[BMPDP]<sub>2</sub>** (▲) and **spiro-OMeTAD** (◆) as the HTMs, respectively. (b) Corresponding IPCE spectra.

in Table 1. We have fabricated 30 solar cells for each HTM and the histogram of energy conversion efficiencies for the cells is shown in Fig. S3 (ESI<sup>†</sup>). The energy conversion efficiencies of the cells employing three HTMs were shown to be almost comparable with that of the **spiro-OMeTAD** based reference cell. The average efficiencies for **B[BMPDP]<sub>2</sub>**, **DPEDOT-B[BMPDP]<sub>2</sub>**, and **DPBTD-B[BMPDP]<sub>2</sub>** and **spiro-OMeTAD** were observed to be 12.37, 13.12, 13.09, and 13.43%, respectively.

The highest energy conversion efficiency (14.23%) was achieved by employing the **DPEDOT-B[BMPDP]<sub>2</sub>** under one sun illumination. The incident photon-to-current efficiency (IPCE) spectra of

Table 1 Summary of photovoltaic parameters of the solar cells employing different HTMs

HTM		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF	$\eta$ (%)
<b>B[BMPDP]<sub>2</sub></b>	Average	20.69	0.938	0.637	12.37
	Best	21.29	0.972	0.667	13.81
<b>DPEDOT-B[BMPDP]<sub>2</sub></b>	Average	20.87	0.955	0.660	13.12
	Best	21.07	0.947	0.713	14.23
<b>DPBTD-B[BMPDP]<sub>2</sub></b>	Average	20.69	0.965	0.657	13.09
	Best	20.96	0.951	0.702	13.99
<b>spiro-OMeTAD</b>	Average	20.82	0.939	0.688	13.43
	Best	21.17	1.003	0.685	14.55

Performances of devices were measured with 0.16 cm<sup>2</sup> working area.



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