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Two Methoxyaniline-Substituted Dibenzofuran Derivatives as Hole-Transport Materials for Perovskite Solar Cells⁺

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2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylam-ine)-9,9'-spirobifluorene (Spiro-OMeTAD), one classical organic photoelectric materials, has been widely used as hole transport material (HTM) in perovskite solar cells (PSCs) due to its relatively higher conductivity, easier film formation and weak absorption in the visible region, etc. However, the complex synthesis process and the high synthetic cost of Spiro-OMeTAD severely limit the commercialization of this material. In this work, two economical methoxyaniline-substituted dibenzofuran derivatives, BF-002 and BF-003, are synthesized and successfully used as hole-transport materials in perovskite solar cells (PSCs). The important properties including light absorption, thermal stability, energy level, conductivity, as well as photovoltaic performance are systematically demonstrated. The highest power conversion efficiencies of the PSCs based on BF-002 and BF-003 are 14.20% and 14.07%, respectively, comparable to that of the PSCs based on Spiro-OMeTAD.

Over the last three years, perovskite solar cells (PSCs), which utilize the organic-inorganic hybrid metal halide CH₃NH₃PbX₃ as light absorbing materials, have achieved remarkable progress in terms of high power conversion efficiencies (PCEs) of up to 20.1%.¹ Notable photovoltaic performances of PSCs mainly originate from the excellent characteristics, such as large absorption coefficients,² high carrier mobility,³ long carrier life-time,⁴ and moderate bandgap,⁵ of this new perovskite material. Hole-transport materials (HTMs) in PSCs are responsible for the extraction and transport of photogenerated holes, which are of considerable significance in determining the final PCE. In general, a good HTM should exhibit high hole mobility,⁶ suitable highest occupied molecular orbital (HOMO) energy levels, and stable thermodynamic and optical properties. At present, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD), one classical HTM in organic photoelectric devices, has been widely used in PSCs because of its relatively higher conductivity, better solubility, easier film formation and weak absorption in the visible region.7-10 However, the high synthetic cost of Spiro-OMeTAD severely limits the commercialization of this material and hinders the wide applications of relevant photoelectric devices subsequently.

To date, other kinds of alternatives to HTMs in PSCs have been developed and studied. Although conductive polymers, such as PTAA,^{11,12} P3HT,^{13,14} TFB,¹⁵ PCBTDPP,¹⁶ PDPPDBTE,¹⁷ and PCPDTBT¹¹ have been proven effective as HTMs in PSCs, small-molecule HTMs are considerably easier to synthesize and purify.

Moreover, the structures of small molecules are convenient to tailor for achieving satisfactory properties. Various small-molecule HTMs, such as pyrene arylamine derivative,¹⁸ 3,4-ethylenedioxythiophene,¹⁹ star-shaped triazine,²⁰ carbazole derivative,²¹ butadiene derivative,²² triphenylamine,²³ triptycene,²⁴ tetrathiafulvalene derivative,²⁵ and spiro-based derivative,²⁶ have been used in PSCs. To further reduce the cost of HTMs and enrich our understanding of the relationship between HTM structures and PSC performance, we should extend the scope of searching HTMs.



Fig. 1 Molecular structures of BF-002 and BF-003.

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For the first time in this study, we designed and synthesized two small-molecule HTMs of methoxyaniline-substituted dibenzofuran derivatives, BF-002 and BF-003, as shown in Fig. 1. The important properties including light absorption, thermal stability, energy level, conductivity, as well as photovoltaic performance are systematically demonstrated. Compared with Spiro-OMeTAD, the two new HTMs in this work are more facile and economical to synthesize. In addition to high solubility, the new HTMs demonstrate good filmforming property and high hole mobility. Based on BF-002 and BF-003, PSCs achieved PCEs of 14.20% and 14.07%, respectively, which are comparable to that obtained using conventional Spiro-OMeTAD. More importantly, the dibenzofuran derivatives are believed to possess a more flexible molecular structure design, as a variety of functional groups could be introduced into the structure.

The HTMs are synthesized through a simple reaction of 2, 8dibromodibenzofuran with *N*,*N*-*bis*[4-(di-4-anisylamino)phenyl]amie and N3, N6-*bis*(di-4-anisylamino)-9H-carbazole. The UV-vis absorption spectra of the two HTMs in chlorobenzene are shown in Fig. 2a. BF-002 and BF-003 exhibit maximum absorption peaks at 323 and 306 nm, respectively. These peaks probably result from the π - π * electron transition of the large molecular conjugate system.²⁷ Notably, the HTMs almost show no absorption in the visible region. On the other hand, the maximum absorption peak of BF-002 exhibits a red shift of 17 nm versus that of BF-003. This bathochromic shift could be attributed to one more planar configuration of BF-002. The absorption onset wavelengths of BF-002 and BF-003 were found at 475 and 461 nm, which correspond to optical bandgaps (*E*_g) of 2.61 eV and 2.69 eV, respectively. The thermal properties of BF-002 and BF-003 are measured by thermogravimetic analysis (TGA). As demonstrated in Fig. 2b, TGA results show that the decomposition temperature of BF-002 and BF-003 is about 400 °C, thereby suggesting good thermal stability. This feature is thought to be positive for the long-term durability of PSCs.

The conductive property is important for HTMs because it will considerably influence the performance of PSCs. The conductivity of films are determined by using a two-contact electrical conductivity set-up.21 Fig. 3a shows the current-voltage characteristics of BF-002 and BF-003 doped with lithium bis(trifluoromethylsulphonyl)imide (Li-TFSI), 4-tert-butylpyridine (tBP), and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridin-e)cobalt(III) bis(trifluoromethylsulphonyl) imide (FK209). The conductivity of BF-003 is observed to be slightly higher than that of Spiro-OMeTAD and BF-002, which is more favorable to hole transport in HTMs. So as to study the electrical properties of BF-002 and BF-003, HOMO energy levels were determined by using cyclic voltammetry (CV) conducted in dilute solutions. As shown in Fig. 3b, the pair of redox peaks of the two HTMs are highly reversible, indicating good electrochemical stability. The HOMO energy level can be calculated on the basis of the following equation: $E_{HOMO} =$ $-5.1-(E_{\text{ox,HTM}} \text{ vs. Fc/Fc}^+)$ (eV), where $E_{\text{ox,HTM}}$ versus Fc/Fc⁺ is the onset of oxidation potential with reference to ferrocene.²⁸ The HOMO energy level of BF-002 and BF-003 were calculated to be -5.01 and -5.14 eV, respectively. In PSCs, the open circuit voltage $(V_{\rm oc})$ is determined by the difference between the Fermi level of TiO₂ and the HOMO of HTMs.²⁹ The HOMO energy level of BF-003 is lower than that of BF-002 by about 130 mV. Therefore, we





Fig. 2 (a) UV-vis absorption spectra of HTMs dissolved in chlorobenzene; (b) Thermogravimetric analysis of BF-002 and BF-003.

Fig. 3 (a) Current–voltage characteristics of doped HTM films; (b) Cyclic voltammograms of HTMs with ferrocene as reference.



Fig. 4 (a) Energy level diagram of perovskite solar cells with two HTMs; (b) Cross-sectional SEM image of the perovskite solar cells.

anticipate a higher $V_{\rm oc}$ value for devices with BF-003 in comparison with those with BF-002.

Fig. 4a shows the energy level diagram of the corresponding components in perovskite solar cells. The HOMO energy levels of BF-002 and BF-003 were measured to be -5.01 eV and -5.14 eV by CV. The reported HOMO energy level for CH₃NH₃PbI₃ is -5.44 eV,⁴ obviously, the HOMO energy levels of our new HTMs are located above the ground-state level of the perovskite, implying that the two HTMs possess favorable energetics for hole transfer from perovskite into the HTM layer. In this work, PSCs were constructed with a conventional configuration of FTO/compact TiO₂/mesoporous TiO₂+perovskite/HTM/Ag. To be mentioned, the CH₃NH₃PbI₃ was subsequently deposited by using a two-step sequential method as reported.³⁰ The resulting perovskite films were coated with HTMs in the presence of Li-TFSI, tBP, and FK209. Fig. 4b shows the crosssectional scanning electron microscopy (SEM) image of the prepared mesoporous PSCs, which exhibit a well-defined multi-layer structure with clear interfaces. The perovskite layer penetrates well into the mesoporous TiO₂ and forms an overlayer. Then, HTMs infiltrate into the pores in the TiO₂/perovskite layer and form a thin capping layer on the top.

The photovoltaic performances of PSCs employing BF-002 and BF-003 as HTMs are measured under AM 1.5, 100 mW cm⁻² simulated light illumination. Fig. 5a shows the current–voltage (J–V) characteristics obtained from champion solar cells using each HTM. The corresponding and average photovoltaic parameters are summarized in Table 1. For comparison, a reference cell with Spiro-OMeTAD as HTM was also fabricated under similar conditions. The



Fig. 5 (a) *J–V* curves for PSCs fabricated with BF-002, BF-003, and Spiro-OMeTAD; (b) Corresponding IPCE spectra; (c) Corresponding integrated photocurrent density curves.

 Table 1
 Summary of photovoltaic parameters of PSCs employing different

 HTMs
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нтм		J _{SC} (mA cm ⁻²)	$V_{oc}(\mathbf{V})$	FF	PCE(%)
Spiro- OMeTAD	Champion	23.22	0.99	0.66	15.04
	Average	$\textbf{20.94} \pm \textbf{1.46}$	$\textbf{0.93} \pm \textbf{0.04}$	$\textbf{0.68} \pm \textbf{0.03}$	13.23 ± 0.72
BF-002	Champion	21.56	1.01	0.65	14.20
	Average	20.73 ± 0.93	$\textbf{0.98} \pm \textbf{0.03}$	$\textbf{0.63} \pm \textbf{0.02}$	12.77 ± 0.72
BF-003	Champion	21.22	1.03	0.64	14.07
	Average	19.70 ± 1.48	1.01 ± 0.02	$\textbf{0.67} \pm \textbf{0.02}$	13.08 ± 0.81

PCE of the champion cell with BF-002 is 14.20%, with a shortcircuit current density (J_{sc}) of 21.56 mA cm⁻², an open circuit voltage (V_{oc}) of 1.01 V, and a fill factor of (FF) 0.65. The champion cell prepared with BF-003 yielded a J_{sc} of 21.22 mA cm⁻², a V_{oc} of 1.03 V, and a *FF* of 0.64, leading to a PCE of 14.07%. The results are comparable with that of PSCs based on Spiro-OMeTAD

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fabricated under the same conditions, with a J_{sc} of 23.22 mA cm⁻², a V_{oc} of 0.99 V, and an FF of 0.66 and yielding a PCE of 15.04%. As excepted, the BF-003-based device shows a slightly higher average V_{oc} in comparison with that of the BF-002 based device. This higher V_{oc} can be attributed to the lower HOMO energy level of BF-003 than that of BF-002, which is consistent with the electrochemical measurement result. The higher V_{oc} of the BF-003-based device is responsible for the slightly higher average PCE than that of the BF-002 based device. The average *FF* of the BF-003-based cell is also slightly higher than that of BF-002, which may be caused by higher conductivity of the former. On the other hand, the reproducibility in PCE of the devices based on each HTM molecule is satisfactory, as can be seen in Fig. S1.

The incident photon to current conversion efficiency (IPCE) spectra of the PSCs based on the three HTMs are presented in Fig. 5b. The devices based on BF-002 and BF-003 exhibit a broad



Fig. 6 *J-V* characteristics of the solar cells with Spiro-OMeTAD, BF-002, and BF-003 as the HTMs, respectively, evaluated under one sun condition with different scan directions.

 Table 2 Summary of photovoltaic parameters of the solar cells with Spiro-OMeTAD, BF-002, and BF-003 as the HTMs, respectively, evaluated under one sun condition with different scan directions.

НТМ	Scan direction	J _{SC} (mA cm ⁻²)	Voc (V)	FF	PCE(%)
Spiro-	Reverse	22.73	0.96	0.68	14.89
OMeTAD	Forward	24.44	0.92	0.53	11.88
DE 002	Reverse	21.56	1.01	0.65	14.20
BF-002	Forward	22.44	0.97	0.52	11.21
DE 002	Reverse	19.83	1.03	0.64	12.98
BF-003	Forward	20.73	1.01	0.54	11.15

conversion range from 350 nm to 700 nm. The maximum intensities of the IPCE spectra obtained at about 500 nm for the three devices all exceed 80%. As shown in Fig. 5c, the integrated photocurrent densities of BF-002 and BF-003 are 21.08 mA cm⁻² and 20.58 mA cm^{-2} , respectively, which are in good agreement with the J_{sc} values acquired from the J-V curves. Stability is another important issue for evaluating new HTM materials. Bu it should be mentioned firstly that the stability of PSCs using Spiro-OMeTAD reported up to now demonstrates mixed results probably due to the different fabrication methods and test conditions.^{17,25} In this work, PSCs based on the three HTM molecules were fabricated and tested under the same conditions for parallel comparison. After fabrication, the devices were stored in air without light illumination and the stability test was conducted by measuring the J-V curves per 12 h. It can be seen from Fig. S1, PSCs using BF-002 and BF-003 showed slightly better stability within 100 h.

As often reported, hysteresis in the current-voltage measurement is a phenomenon frequently observed in PSCs. Uncovering the intrinsic reasons for the anomalous hysteresis is still on-going. To date, some conclusions have been put forward. For example, some groups ascribed hysteresis to the ions migration of within perovskite film, or the transient ferroelectric polarization. In the meantime, it is widely accepted that the slow kinetic processes, like charge transport or interfacial separation, will lead to pronounced hysteresis certainly. In this work, the J-V curves obtained through forward and reverse scans for PSCs employing the three HTMs are shown in Fig. 6. Notably, the J-V curves of the two PSCs show hysteretic behaviours. Detailed photovoltaic parameters are summarized in Table 2. In good accordance with the results demonstrated in Fig. 3a, the device based on BF-003 is less pronounced in terms of hysteresis, which could be ascribed to its higher conductivity that facilities hole transport, one important dynamic process of charge transfer in PSCs. To further suppress hysteresis in PSCs, some strategies can be used through improving perovskite crystallinity and surface coverage,²³⁻²⁴ passivating trap states at perovskite grain boundaries,²⁵ accelerating charge extraction,²⁶ or optimizing cell structures.²⁴

Conclusions

In summary, we designed and synthesized two new smallmolecule HTMs based on methoxyaniline-substituted dibenzofuran derivatives. Then, we have successfully fabricated perovskite solar cells with the derivatives as HTMs. The devices fabricated from BF-002 and BF-003 show PCEs of 14.20% and 14.07%, which are comparable to that (15.04%) of the Spiro-OMeTAD based cell.

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Moreover, BF-002 and BF-003 exhibit stable thermodynamic and optical properties, high conductivity, and moderate HOMO energy levels, indicating the two materials can be promising HTMs in PSCs. We believe that these new materials will offer a new design strategy toward developing potential alternatives to expensive traditional HTMs for the fabrication of cost-effective and high-performance photovoltaic devices.

Experimental section

HTMs Synthesis and Characterization

The synthetic routes for BF-002 and BF-003 are shown in Fig. 7. **Synthesis of** *N-tert*-**Butoxycarbonyl**-*N*,*N-bis*(4-bromophenyl)amine (1).^[31] To a solution of *N*,*N-bis*(4-bromophenyl)amine (20.0 g, 62.0 mmol) and di-*tert*-butyl dicarbonate (20.1 g, 92.0 mmol) in THF (90 mL), 4-(dimethylamino)pyridine (1.5 g, 12.0 mmol) was added slowly. Then the mixture was heated to reflux for 3 h with stirring. After cooling, the solvent was removed under reduced pressure. The crude product was filtered through a pad of silica gel using dichloromethane as the eluent and concentrated in vacuo. The residue was stirred in methanol at 60 °C to give compound 1 (23.7 g, 90%) as a white powder. ¹H NMR (500 MHz, CDCl3): δ 7.35 (d, *J* = 8.5 Hz, 4H), 6.99 (d, *J* = 8.5 Hz, 4H), 1.37 (s, 9H). MS: *m/z* 449.95 [M+Na]⁺, 876.91 [2M+Na]⁺.



Fig. 7 The synthetic routes of BF-002 and BF-003. Reaction conditions: (a) 4-(dimethylamino)pyridine, THF, reflux; (b) potassium *tert*-butoxide, $Pd_2(dba)_3/(t-Bu)_3PH\cdotBF_4$, toluene, reflux; (c) TFA, rt, 10 min.; (d) potassium *tert*-butoxide, $Pd_2(dba)_3$ (*t*-Bu)_3PH·BF_4, toluene, reflux, 9 h; (e) 4-(dimethylamino)pyridine, THF, reflux; (f) sodium *tert*-butoxide, $Pd_2(dba)_3/(t-Bu)_3PH\cdotBF_4$, toluene, reflux; (g) potassium *tert*-butoxide, toluene, reflux; (h) sodium *tert*-butoxide, $Pd_2(dba)_3/(t-Bu)_3PH\cdotBF_4$, toluene, reflux, 20 h.

Synthesis of *N-tert*-Butoxycarbonyl-*N*,*N-bis*[4-(di-4-anisylamino) phenyl]amine (2).^[32] To a 1 L three-necked round-bottomed flask, di-4-anisylamine (23.7 g, 100 mmol), compound 1 (20.0 g, 47.0 mmol), potassium *tert*-butoxide (15.8 g, 141 mmol) and dry toluene (450 mL) were added. The mixture was purged with N₂ for 10 min. and then (*t*-Bu)₃PH·BF₄ (0.54 g, 1.88 mmol) and Pd₂(dba)₃ (0.86 g, 0.94 mmol) were added. The reaction mixture was heated to reflux for 4 h under N₂. After cooling, the reaction was poured into water, extracted with dichloromethane, washed with brine and concentrated in vacuo. The crude product was suspended in hexane, then heated to reflux and filtered to give compound 2 as a white powder (27.2 g, 80%). ¹H NMR (500 MHz, CDCl3): δ 7.02 (dd, *J* = 8.3 Hz, 12H), 6.85 (d, *J* = 9 Hz, 4H), 6.80 (d, *J* = 9 Hz, 8H), 3.78 (s, 12H), 1.44 (s, 9H). MS: *m/z* 723.33 [M⁺].

Synthesis of *N,N-Bis*[4-(di-4-anisylamino)phenyl]amine (3).^[32] To a 250 mL three-necked round-bottomed flask, compound 2 (4.1 g, 5.67 mmol) was dissolved in dichloromethane (20 mL). Then trifluoroacetic acid (63 mL, 97 g) was added. The reaction mixture was stirred at room temperature for 10 min. Evaporation of the solvent and recrystallization from toluene and hexane afforded compound 3 as a white solid (3.1 g, 88.6%). ¹H NMR (400 MHz, D6-DMSO): δ 7.24 ~ 6.83 (m, 24H), 3.78 (s, 12H). MS: *m/z* 623.28 [M⁺].

Synthesis of BF-002. To a 250 mL three-necked round-bottomed flask, 2,8-dibromo- dibenzofuran (2.1 g, 6.4 mmol),^[33] compound 3 (8.8 g, 14 mmol) and potassium *tert*-butoxide (1.8 g, 16 mmol) and dry toluene (115 mL) were added. The mixture was flushed with N₂ for 10 min, and then $(t-Bu)_3PH\cdot BF_4$ (0.074 g, 0.26 mmol) and Pd₂(dba)₃ (0.12 g, 0.13 mmol) were added. The reaction mixture was heated to reflux for 9 h under N₂. After cooling, the solution was filtered to remove insoluble solids. The solvent of the filtrate was removed and the resulting solid was purified by column chromatography (silica gel, toluene) to give a yellow solid. Recrystallization from hexane and ethyl acetate afforded BF-002 as a light yellow solid (4.8 g, 53.2%). The overall yield of BF-002 was 33.9%. HPLC: 99.3%. ¹H NMR (400 MHz, (CD₃)₂CO): δ 7.00 (d, 18H), 6.89 ~ 6.80 (m, 36H), 3.75 (s, 24H). MS: *m/z* 1410.58 [M⁺].

Synthesis of *N-tert*-Butoxycarbonyl-3,6-dibromo-9H-carbazole (4). To a solution of 3,6-dibromo-9H-carbazole (11.5 g, 35.4 mmol) and di-*tert*-butyl dicarbonate (11.6 g, 53.1 mmol) in THF (50 mL), 4-(dimethylamino)pyridine (0.86 g, 7.1 mmol) was added. Then the mixture was heated to reflux for 3 h with stirring. After cooling, the solvent was removed under reduced pressure. The crude product was filtered through a pad of silica gel using dichloromethane as the eluent and concentrated in vacuo. The residue was stirred in methanol and water at 60°C to give compound 4 (14.0 g, 93%) as a light yellow solid. ¹H NMR (500 MHz, CDC13): δ 8.06 (d, J = 9 Hz, 2H), 7.92 (d, J = 2 Hz, 2H), 7.48 (dd, J = 9, 2 Hz, 2H), 1.67 (s, 9H). MS: m/z 447.93 [M+Na]⁺, 872.88 [2M+Na]⁺.

Synthesis of *N-tert*-Butoxycarbonyl-*N3,N6-bis*(di-4-anisylamino)-9H-carbazole (5).^[32] To a 500 mL three-necked round-bottomed flask, di-4-anisylamine (28.3 g, 124 mmol), compound 4 (25.0 g, 58.8 mmol), sodium *tert*-butoxide (17.0 g, 176 mmol) and dry toluene (250 mL) were added. The mixture was purged with N₂ for 10 min. and then $(t-Bu)_3$ PH·BF₄ (1.36 g, 4.7 mmol) and Pd₂(dba)₃ (2.15 g, 2.35 mmol) were added. The reaction mixture was heated to reflux for 5 h under N₂. After cooling, the reaction was poured into

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water, extracted with toluene, washed with brine and concentrated in vacuo. The crude product was filtered through a pad of silica gel. Then washed with hot hexane and ethyl acetate throughly to afford compound 5 as a light yellow solid (31.1 g, 73.8%). ¹H NMR (500 MHz, CDCl3): δ 8.03 (d, J = 8.5 Hz, 2H), 7.368 (s, 2H), 7.03 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 7Hz, 8H), 6.71 (d, J = 9Hz, 8H), 3.70 (s, 12H), 1.63 (s, 9H). MS: m/z 721.31 [M⁺].

Synthesis of *N3,N6-bis*(di-4-anisylamino)-9H-carbazole (6).^[32] To a 1 L three-necked round-bottom flask, compound 5 (31.1 g, 43 mmol), potassium *tert*-butoxide (14.5 g, 129 mmol) and dry toluene (600 mL) were added. The reaction mixture was heated to reflux for 1 h. After cooling, the solution was poured into water, extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was washed with hot toluene to give compound 6 as a light yellow solid (25.1 g, 93.7%). ¹H NMR (400 MHz, D6-DMSO): δ 11.17 (s, 1H), 7.64 (s, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 8.8Hz, 2H), 6.87 ~ 6.79 (m, 16H), 3.70 (s, 12H). MS: *m/z* 621.26 [M⁺].

Synthesis of BF-003. To a 250 mL three-necked round-bottom flask,

2,8-dibromo- dibenzofuran (0.5 g, 1.53 mmol),^[33] compound 6 (2.1 g, 3.38 mmol) and sodium *tert*-butoxide (0.37 g, 3.84 mmol) and dry toluene (100 mL) were added. The mixture was flushed with N₂ for 10 min. and then (*t*-Bu)₃PH·BF₄ (0.018 g, 0.06 mmol) and Pd₂(dba)₃ (0.028 g, 0.03 mmol) were added. The reaction mixture was heated to reflux for 20 h. After cooling, the solution was filtered to remove insoluble solids. The solvent of the filtrate was removed and the resulting solid was purified by column chromatography (silica gel, hexane : ethyl acetate = 4:1(v:v) as eluent) to give BF-003 as a light yellow solid (1.5 g, 55.5%). The overall yield of BF-002 was 35.7%. HPLC: 99.69%. ¹H NMR (500 MHz, D6-DMSO): δ 8.55 (s, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 9.15 Hz, 6H), 7.29 (d, *J* = 8.1 Hz, 4H), 7.08 ~ 6.81 (m, 36H), 3.68 (s, 24H). ¹³C NMR (126 MHz, CDCl3): δ 155.77, 125.31, 124.48, 114.51, 113.25, 110.37, 77.32, 77.06, 76.81,55.54. MS: *m/z* 1406.55 [M⁺].

Characterization

¹H and ¹³C NMR spectra were recorded on a Varian INOVA 400MHz or Varian INOVA 500MHz Spectrometer. Matrix assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF) were performed on a Waters MALDI micro MX instrument. The UV-Vis absorbance spectra of the two HTMs in chlorobenzene were measured with a UV-Vis spectrophotometer (HP 8543, Hewlett Packard, USA). The thermal analysis was performed through TGA (TGA/SDT851, Switzerland) at a heating rate of 10 °C min⁻¹ in a temperature range of 0 °C to 800 °C under nitrogen atmosphere. Tafel measurements were employed using an electrochemical workstation (CHI 630D, Chenhua, Shanghai) with the structure of FTO/HTM//FTO, with an effective working area of 1.9 cm² and at a scan rate of 10 mV·s⁻¹. Cyclic voltammetry was carried out with a electrochemical workstation (CHI 630D) using a conventional threeelectrode configuration. A three-electrode system consisting of a glassy carbon working electrode, a Ag/AgCl reference electrode and a Pt wire counter electrode was used. Redox potential of materials was measured in dichloromethane solution with 0.1M (n-C₄H₉)₄NPF₆ as the supporting salt at a scan rate of 50 mV s⁻¹. Potentials were calibrated with reference to the Fc⁺/Fc couple.

Device Fabrication

To fabricate the devices, Fluorinedoped Tin Oxide (FTO) glass was patterned by etching with Zn powder and hydrochloric acid (4 M). Then the substrate was cleaned in a detergent solution using an ultrasonic bath for 30 min, rinsed with deionized water, acetone, and isopropanol. The compact TiO₂ layer was deposited by spin coating TiO₂ organic sol on the substrate at 3000 rpm for 30 s, followed by sintering in a furnace at 450°C for 2 h. Organic sol for TiO₂ compact layer was prepared according to previous literature.^[34] Mesoporous TiO₂ film was prepared by spin coating a commercial TiO₂ paste (Dyesol-18NRT, 1:3.5 w/w diluted in ethanol) at 5000 rpm for 30 s. The film was successively sintered at 500°C for 30 min. CH₃NH₃PbI₃ layer was fabricated by two step method reported in the literature.^[30] The TiO₂/FTO substrate was infiltrated with PbI_2 by spin coating at 5000 rpm for 5 s and dried on a hot plate at 70°C for 30 min. After cooling down, the film was dipped in a solution of CH₃NH₃I in 2-propanol (10 mg ml⁻¹) for 60 s, rinsed with 2propanol, and dried at 70°C for 30 min to form the crystallized CH₃NH₃PbI₃. The HTM layers were deposited by spin coating at 3000 rpm for 30 s. The spin-coating formulation was prepared by dissolving 72.3 mg BF-002, BF-003 or spiro-MeOTAD, 28.8 µL 4*tert*-butylpyridine (tBP), 17.5 μ L of a stock solution of 520 mg mL⁻¹ lithium bis (trifluoromethylsulphonyl)imide(Li-TFSI) in acetonitrile, and 20 µL of a stock solution of 300 mg mL⁻¹ tris(2-(1H-pyrazol-1yl)-4-tert-butylpyridine)cobalt(III) *bis*(trifluoromethylsulphonyl) imide(FK209) in acetonitrile in 1 mL chlorobenzene. Finally, 50 nm Ag was thermally evaporated on top of the device to form the back contact. The active area of these solar cells was 0.12 cm². All devices were fabricated in a glove box.

Device Performance Measurement

Microscopic morphologies of the typical device cross sections were characterized by scanning electron microscopy (SEM, FEI Quanta 450). The current density–voltage (J–V) curves of PSCs were measured under simulated AM 1.5 illumination (100 mW·cm⁻², PEC-L15, Peccell, Japan) using a Keithley digital source meter (Keithley 2601, USA). IPCE values were measured as a function of wavelength from 300 nm to 800 nm using the monochromatic light from a system made of a xenon lamp, a monochromator, and appropriate filters.

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Graphical Abstract



Two low-cost methoxyaniline-substituted dibenzofuran derivatives were synthesized and used as hole-transport materials for efficient perovskite solar cells