

Cite this: *J. Mater. Chem. A*, 2019, 7, 5934Received 20th December 2018
Accepted 20th February 2019

DOI: 10.1039/c8ta12274a

rsc.li/materials-a

Spiro-*t*BuBED: a new derivative of a spirobifluorene-based hole-transporting material for efficient perovskite solar cells†

Po-Han Lin,^{‡a} Kun-Mu Lee,^{‡*} Chang-Chieh Ting^a and Ching-Yuan Liu^{‡*a}

A new spirobifluorene-based hole-transporting material (**spiro-*t*BuBED**) was efficiently synthesized on the gram scale *via* straightforward C–H activations/arylations. Perovskite solar cells with **spiro-*t*BuBED** showed a promising power conversion efficiency of 18.6% without a device oxidation process previously considered to be indispensable.

The hole-transporting material (HTM) is the most important component of the perovskite solar cell (PSC), as it is required to enhance the power conversion efficiency (PCE) and stability of PSC devices.^{1–9} With targeted development based on the extensively used small-molecule hole transporters, efficient perovskite solar cells based on, for instance, H101,¹⁰ B[BMPDP]₂,¹¹ KR133,¹² azulenes,¹³ or FDT¹⁴ have achieved PCEs of up to 20%. However, we have noticed that preparation of these HTMs must employ traditional synthetic techniques, which have required tedious substrate pre-functionalizations such as lithiation, borylation, or stannylation prior to Suzuki or Stille reactions. On the other hand, and more importantly, in device fabrications, solar cells based on these small-molecule HTMs have been observed to usually remain ineffective until a device oxidation process of 1–4 hours was performed. These disadvantages with respect to synthesis and device preparation might reduce the commercialization opportunities of these potentially useful HTMs. Therefore, in the current work, we set out to overcome the above hurdles, and achieved several major improvements: (1) a step-economical synthesis of a new spiro-linked molecule *via* straightforward C–H bond activations/arylations, (2) aging-/

oxidation-free device fabrications, and (3) gram-scale synthesis of our target molecule.

As shown in Fig. 1, we designed a new spirobifluorene-core-based oligoaryl compound incorporating 3,4-ethylenedioxythiophene (EDOT) as a π -spacer and *t*-butyl (*t*Bu) groups as end substituents. This molecule was named spirobis(triphenylamine)ethylenedioxythiophenediphenyl, which was further abbreviated to **spiro-*t*BuBED**. **Spiro-*t*BuBED** was facilely synthesized in two steps free of starting material metalations through direct C–H bond activation/arylation reactions.¹⁵ In addition, unlike devices employing other spirobifluorene-based small molecules, we found that perovskite solar cells using **spiro-*t*BuBED** as the HTM did not need any device oxidation treatment, and displayed a high PCE of 18.6% immediately after being fabricated.

The two synthetic routes to our target HTM are detailed in Scheme 1. Had **spiro-*t*BuBED** been prepared using the traditional synthetic approaches, Suzuki- or Stille cross couplings would have necessarily been involved as key reactions requiring substrate prefunctionalization steps such as bromination, Li/Br-exchange, and borylation (compounds 3, 4). Moreover, use of the Stille reaction would have required the synthesis of toxic

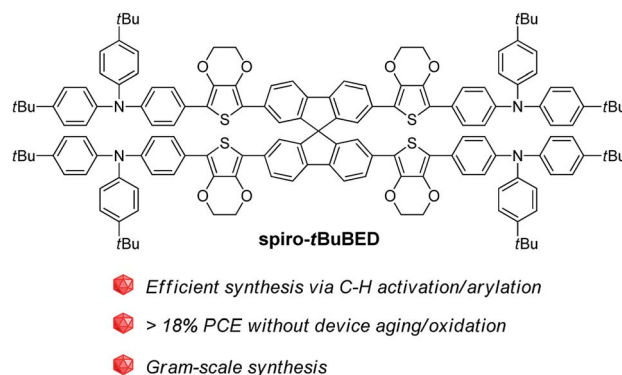


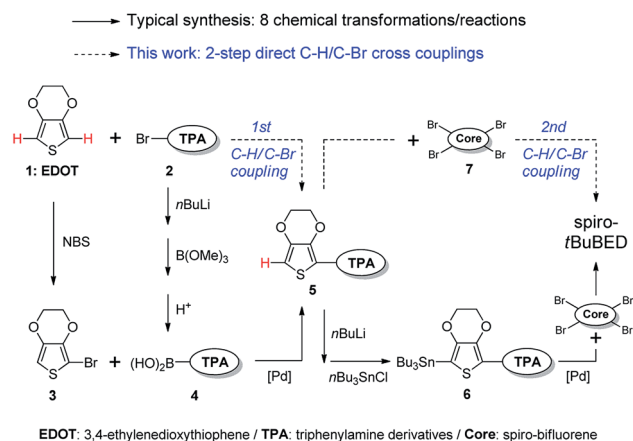
Fig. 1 Spiro-*t*BuBED: a new *t*-butyl-substituted spirobifluorene-core-based oligoaryl compound as an efficient hole-transporting material.

^aDepartment of Chemical and Materials Engineering, National Central University, Zhongli District, Taoyuan 320, Taiwan, Republic of China. E-mail: cyliu0312@ncu.edu.tw

^bDepartment of Chemical & Materials Engineering, Chang Gung University, Department of Pediatrics, Chang Gung Memorial Hospital, Linkou, Taoyuan 333, Taiwan, Republic of China. E-mail: kmlee@mail.cgu.edu.tw

† Electronic supplementary information (ESI) available: NMR spectra (¹H and ¹³C) of compounds 5 and **spiro-*t*BuBED**. See DOI: 10.1039/c8ta12274a

‡ These authors contributed equally to this work.



Scheme 1 Two synthetic routes to **spiro-tBuBED**. Reaction conditions for the direct C–H/C–Br couplings: (i) 1st C–H/C–Br: **1** (3.00 mmol), **2** (1.00 mmol), Pd(OAc)₂ (0.05 mmol), P(Cy)₃ (0.10 mmol), PivOH (0.30 mmol), K₂CO₃ (1.50 mmol), DMF (3 mL), 100 °C, 6 h; (ii) 2nd C–H/C–Br: **5** (2.10 mmol), **7** (0.50 mmol), Pd(OAc)₂ (0.05 mmol), P(*o*-tolyl)₃ (0.10 mmol), PivOH (0.30 mmol), K₂CO₃ (2.25 mmol), DMF (4.5 mL), 100 °C, 48 h.

organotin reagents **6** or treatment of related tin chemical wastes. Following this method would have taken at least eight chemical transformations/operations. In contrast, we report herein a step-saving access to **spiro-tBuBED** using a two-step C–H/C–Br cross-coupling strategy. Direct C–H monoarylation of EDOT **1** with bromotriphenylamine derivative **2** afforded the key building block **5** in 71% yield. Through a second C–H bond activation/arylation, **5** further reacted with 2,2',7,7'-tetrabromo-9,9'-spirobifluorene **7** to give the target molecule in moderate yield (65%). This synthesis shortcut was developed to provide a rapid and user-friendly alternative route to spiro-bifluorene-based hole-transporting materials.

After carrying out this synthesis, we calculated the optical bandgap (ΔE_g) of **spiro-tBuBED** by evaluating its UV/Vis absorption and photoluminescence properties ($\Delta E_g = 1240/\lambda_{\text{intersect}} = 2.58$ eV). The electrochemistry of **spiro-tBuBED** was investigated by conducting cyclic voltammetry, which yielded a highest occupied molecular orbital (HOMO) energy of -5.30 eV, a value between that of the perovskite layer ($E_{\text{HOMO}} = -5.43$ eV) and that of the Au electrode ($E_{\text{HOMO}} = -5.10$ eV). In addition, we also obtained the thermal properties of **spiro-tBuBED** by performing thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compared with the commercial hole-transporting material **spiro-OMeTAD**

($T_d = 417$ °C; $T_g = 126$ °C), we were pleased to find that our HTM exhibited comparable thermal stability ($T_d = 416$ °C) and a superior glass transition temperature ($T_g = 258$ °C). The hole mobility of **spiro-tBuBED** was estimated by carrying out a space-charge-limited current (SCLC) investigation. This analysis yielded a hole-transport ability ($\mu_h = 2.29 \times 10^{-4}$ cm² V⁻¹ s⁻¹) similar to that of **spiro-OMeTAD** ($\mu_h = 3.53 \times 10^{-4}$ cm² V⁻¹ s⁻¹). The corresponding spectra are provided in ESI†

Furthermore, perovskite solar cells using **spiro-tBuBED** as the HTM were fabricated, and their performance measures are shown in Table 1. **Spiro-tBuBED**-based solar cells displayed a remarkable open-circuit voltage ($V_{oc} = 1.102$ V), higher than that of cells based of **spiro-OMeTAD** ($V_{oc} = 1.022$ V). We also measured notable short-circuit current ($J_{sc} = 22.99$ mA cm⁻²) and fill factor (FF = 0.735) values, corresponding to a power conversion efficiency (PCE) of 18.60% and superior to the cells with **spiro-OMeTAD**. Under forward and reverse scanning, as shown in Fig. 2a, our devices demonstrated minimal hysteresis effects, smaller than those of solar cells with **spiro-OMeTAD**. Acquired photon-to-current conversion efficiency (IPCE) spectra (Fig. 2b) showed that solar cells employing **spiro-tBuBED** as the hole-transporting layer were able to achieve approximately 85% IPCE for absorption wavelengths of 450–700 nm, with this IPCE value comparable to those of the cells with **spiro-OMeTAD**. Importantly, we also performed time-resolved PL (TRPL) experiments with the **spiro-tBuBED**-based devices. **Spiro-tBuBED**/perovskite showed a better quenching behavior than did **spiro-OMeTAD**/perovskite. The fitted average lifetime of **spiro-tBuBED**/perovskite was determined to be 14.5 ns, better than the 20.6 ns value for **spiro-OMeTAD**/perovskite. This result indicated a superior charge extraction capability for **spiro-tBuBED** than for **spiro-OMeTAD** (the corresponding TRPL spectra are shown in Fig. S7 in ESI†).

To shed light on the uniqueness of **spiro-tBuBED**-based photovoltaic devices, we carried out experiments involving measuring PCEs for various device oxidation times (Fig. 3). Our previous experience with device preparation suggested oxidation treatment to be indispensable for increasing the conductivity of hole-transport materials. But surprisingly, compared to the perovskite solar cells using commercial **spiro-OMeTAD** as the HTM, the cells with **spiro-tBuBED** did not require any device oxidation process, having demonstrated a >18% PCE immediately after the device fabrication was complete. Moreover, the PCEs based on forward and reverse scans remained stable for at least 4 hours. The cells with **spiro-OMeTAD**, in contrast, needed at least 1 hour of oxidation under an atmospheric environment to achieve their best power conversion efficiencies with the

Table 1 Photovoltaic performance measures of perovskite solar cells using **spiro-tBuBED** as the HTM.^{a,b}

HTM		V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE (%)
Spiro-tBuBED	Best	1.102	22.99	0.735	18.60
	Average	1.090 ± 0.008	23.15 ± 0.42	0.720 ± 0.02	18.17 ± 0.55
Spiro-OMeTAD	Best	1.022	22.97	0.764	17.94(21.9) ^c
	Average	1.032 ± 0.024	22.74 ± 0.35	0.742 ± 0.02	17.41 ± 0.57

^a Reverse scans. ^b The statistical data were obtained from 8 cells. ^c See ref. 16 for the best PCE obtained by Tavakoli and Grätzel.

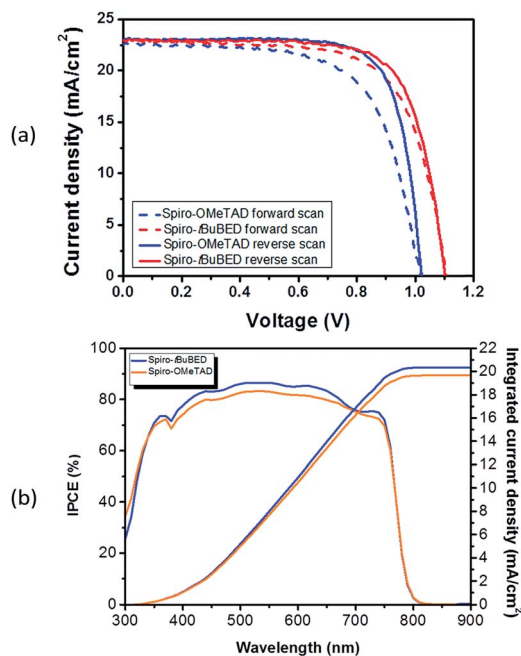


Fig. 2 (a) Photocurrent density vs. voltage curves and (b) incident photon-to-current conversion efficiency (IPCE) spectra of the two indicated solar cells.

highest value of hole-mobility of the HTM. In addition, the PCE based on the forward scan started to decline after 1 hour under oxidation. We believe that the fabrication of perovskite solar cells without the need to perform pre-oxidations would be beneficial to the subsequent roll-to-roll device encapsulation processing and commercialization.

Furthermore, as shown in Fig. 4, we produced current density–time ($i-t$) and efficiency–time ($\eta-t$) plots of the PSC with **spiro-tBuBED** and of that with **spiro-OMeTAD**, under continuous one sun illumination. They both showed quick response, and stable output values for over 600 s. In addition, the efficiency levels of both PSCs decreased by 4–5% after the devices were stored in a box under 30% RH at 25–28 °C for 4 weeks (Fig. S8†). We speculated that the decreased efficiency might have been due to the leakage of additives. We also acquired top-

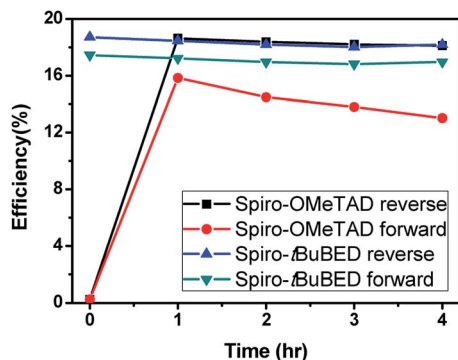


Fig. 3 PCE vs. aging/oxidation time for **spiro-OMeTAD**- and **spiro-tBuBED**-based perovskite solar devices.

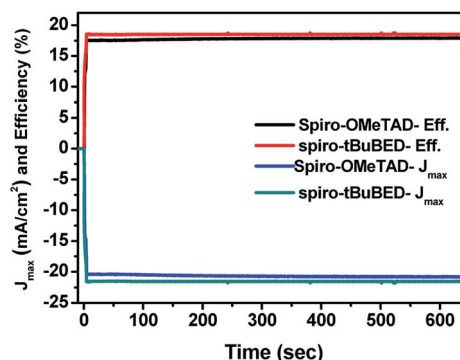


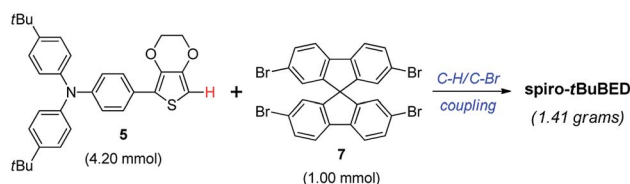
Fig. 4 ($i-t$) and ($\eta-t$) plots of PSCs based on **spiro-tBuBED** and **spiro-OMeTAD**.

view SEM images of the HTMs and a cross-section SEM image of the devices, as shown in ESI (Fig. S9 and S10†). Compared to **spiro-OMeTAD**, the **spiro-tBuBED**-based film was observed to be smoother, which apparently led to its higher V_{oc} and better device stability.

Encouraged by the results shown in Table 1, Fig. 3 and 4, we further scaled up the essential C–H arylation reaction of the end-group molecule **5** with core molecule **7** (Scheme 2). The C–H/C–Br coupling reaction proceeded smoothly to yield 1.41 grams (61% yield) of the desired **spiro-tBuBED** HTM after column chromatography purification. Procedures for the gram-scale synthesis are detailed in ESI.†

Finally, we compared our **spiro-tBuBED** with other high-performance small-molecule HTMs in terms of synthesis, estimated cost/price, and PCEs (Table 2). The non-spiro-type molecules such as **BTT-3** (ref. 17) and **ATT-OMe**¹⁸ were prepared using 7 synthetic steps on a relatively small scale (0.38–0.39 grams at key-steps), thus leading to higher estimated costs (568–598 USD per mmol HTM). Nevertheless, the solar cells with **BTT-3** or **ATT-OMe** demonstrated very promising PCEs over 18%. On the other hand, the commercial **spiro-OMeTAD**¹⁸ and our **spiro-tBuBED** were accessed by using only 3 chemical transformations and on larger synthetic scales (1.07–1.41 grams). The cost of **spiro-tBuBED** was estimated to be much lower than the costs of other HTMs.

In summary, we have demonstrated a new spiro-bifluorene-based symmetrical molecule (**spiro-tBuBED**) incorporating EDOT as π -bridges and di-*t*-butyl-triphenylamine as end groups. **Spiro-tBuBED** can be successfully synthesized through sequential C–H arylations on the gram scale, and we expect this synthesis to become a viable and sustainable alternative approach for use both in academia and industry. Perovskite-



Scheme 2 Gram-scale synthesis of **spiro-tBuBED**.

Table 2 Comparison of spiro-tBuBED with other small-molecule HTMs

HTM	Synthetic steps	Synthetic scale ^a (g)	Cost ^b (USD)	Best PCE (%)
BTT-3 (ref. 17)	7 steps	0.38	598	18.20
ATT-OMe ¹⁸	7 steps	0.39	568	18.13
spiro-OMeTAD ¹⁹	3 steps	1.07	291 ^c /382 ^d	15.20
spiro-tBuBED	3 steps	1.41	167	18.60

^a The synthetic scale reported in the literature refers to the key step that produces the target HTM. ^b The cost was estimated based on taking into consideration all reagents, chemicals and solvents employed in each synthesis and purification step for the production of 1.00 mmol of the target HTM. ^c The estimated home-made cost. ^d The commercial price from companies.

based solar cells using **spiro-tBuBED** as the hole-transporting layer displayed – without the need for any device oxidation treatment – a power conversion efficiency of 18.6%, exceeding the PCEs acquired from the cells with the most-used **spiro-OMeTAD**. The design and step-economical synthesis of new organic molecules for application as efficient HTMs are currently underway in our laboratory.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

Financial support provided by the Ministry of Science and Technology (MOST), Taiwan (MOST 106-2113-M-008-002 and 106-2218-E-182-005-MY2), the National Central University (NCU), Chang Gung University (QZRPD181) and Chang Gung Memorial Hospital, Linkou, Taiwan (CMRPD2G0301) is gratefully acknowledged.

Notes and references

- 1 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.
- 2 S. F. Völker, S. Collavini and J. L. Delgado, *ChemSusChem*, 2015, **8**, 3012.
- 3 Z. Yu and L. Sun, *Adv. Energy Mater.*, 2015, **5**, 1500213.
- 4 L. Calió, S. Kazim, M. Grätzel and S. Ahmad, *Angew. Chem., Int. Ed.*, 2016, **55**, 14522.
- 5 C. R. Seco, L. Cabau, A. V. Ferran and E. Palomares, *Acc. Chem. Res.*, 2018, **51**, 869.
- 6 G.-W. Kim, G. Kang, J. Kim, G.-Y. Lee, H. I. Kim, L. Pyeon, J. Lee and T. Park, *Energy Environ. Sci.*, 2016, **9**, 2326.
- 7 W. Zhou, Z. Wen and P. Gao, *Adv. Energy Mater.*, 2018, **8**, 1702512.
- 8 C. Huang, W. Fu, C.-Z. Li, Z. Zhang, W. Qiu, M. Shi, P. Heremans, A. K.-Y. Jen and H. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 2528.
- 9 D. Bi, A. Mishra, P. Gao, M. Franckevičius, C. Steck, S. M. Zakeeruddin, M. K. Nazeeruddin, P. Bäuerle, M. Grätzel and A. Hagfeldt, *ChemSusChem*, 2016, **9**, 433.
- 10 H. Li, K. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar and A. C. Grimsdale, *Angew. Chem., Int. Ed.*, 2014, **53**, 4085.
- 11 H. Choi, S. Park, M.-S. Kang and J. Ko, *Chem. Commun.*, 2015, **51**, 15506.
- 12 K. Rakstys, A. Abate, M. L. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2015, **137**, 16172.
- 13 H. Nishimura, N. Ishida, A. Shimazaki, A. Wakamiya, A. Saeki, L. T. Scott and Y. Murata, *J. Am. Chem. Soc.*, 2015, **137**, 15656.
- 14 M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. C. Baena, P. Gao, R. Scopelliti, E. Mosconi, K.-H. Dahmen, F. D. Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Grätzel and M. K. Nazeeruddin, *Nat. Energy*, 2016, **1**, 15017.
- 15 L. Ackermann, R. Vicente and A. R. Kapdi, *Angew. Chem., Int. Ed.*, 2009, **48**, 9792; K. Murakami, S. Yamada, T. Kaneda and K. Itami, *Chem. Rev.*, 2017, **117**, 9302; S. Tokuji, H. Awane, H. Yorimitsu and A. Osuka, *Chem.-Eur. J.*, 2013, **19**, 64; T. Yanagi, S. Otsuka, Y. Kasuga, K. Fujimoto, K. Murakami, K. Nogi, H. Yorimitsu and A. Osuka, *J. Am. Chem. Soc.*, 2016, **138**, 14582; A. Mori and A. Sugie, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 548; F. Shibahara and T. Murai, *Asian J. Org. Chem.*, 2013, **2**, 624; A. Nitti, M. Signorile, M. Boiocchi, G. Bianchi, R. Po and D. Pasini, *J. Org. Chem.*, 2016, **81**, 11035; A. Nitti, G. Bianchi, R. Po, T. M. Swager and D. Pasini, *J. Am. Chem. Soc.*, 2017, **139**, 8788.
- 16 M. M. Tavakoli, W. Tress, J. V. Milic, D. Kubicki, L. Emsley and M. Grätzel, *Energy Environ. Sci.*, 2018, **11**, 3310.
- 17 A. M. Ontoria, I. Zimmermann, I. G. Benito, P. Gratia, C. R. Carmona, S. Aghazada, M. Grätzel, M. K. Nazeeruddin and N. Martin, *Angew. Chem., Int. Ed.*, 2016, **55**, 1.
- 18 I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Aragón, G. Grancini, A. Molina-Ontoria, E. Orti, N. Martin and M. K. Nazeeruddin, *Adv. Energy Mater.*, 2016, 1601674.
- 19 N. J. Jeon, H. G. Lee, Y. C. Kim, J. Seo, J. H. Noh, J. Lee and S. I. Seok, *J. Am. Chem. Soc.*, 2014, **136**, 7837.