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Making benzotrithiophene derivatives dopant-free for perovskite solar cells: Step-saving installation of π -spacers by a direct C–H arylation strategy†

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Previously, benzotrithiophene (BTT)-based hole-transporting materials (HTMs) had to be doped with three chemical agents for high-efficiency perovskite solar cells (PSC). This work describes significant progress by which the first dopant-free BTT core-based HTM (YKP03) with EDOT spacers was readily accessed by step-saving direct C–H arylation. PSCs with dopant-free YKP03 showed promising efficiencies of up to 16.15% with potential long-term storage stability.

Incorporation of a hole-transporting material (HTM) in perovskite-based solar cells has become a prerequisite for the enhancement of device performance and stability.¹ Among various organic hole-transporters, facile synthesis and device engineering of small-molecule HTMs is of particular interest since these π -conjugated oligo(hetero)aryls possess several advantages such as well-defined molecular weight, broad synthetic diversity, and lower cost.² Recently, perovskite solar cells (PSCs) using high planarity core-based HTMs, such as benzotrithiophenes,^{3,4} tetrathienylbenzenes,^{5–7} and truxenes,^{8–10} have been shown to exhibit promising power conversion efficiencies (PCE) of up to 18.8%. Among the above small molecules, we had much interest in the preparation, conjugation extension, and applications of benzotrithiophene (BTT) with C_{3h} symmetry, due to its simpler and cost-effective two-step synthesis using inexpensive starting materials and reagents.¹¹ In addition to the consideration of synthetic cost, the planarized BTT core usually demonstrated exceptional hole-transporting characteristics,^{3,4,12} both of which make BTT-

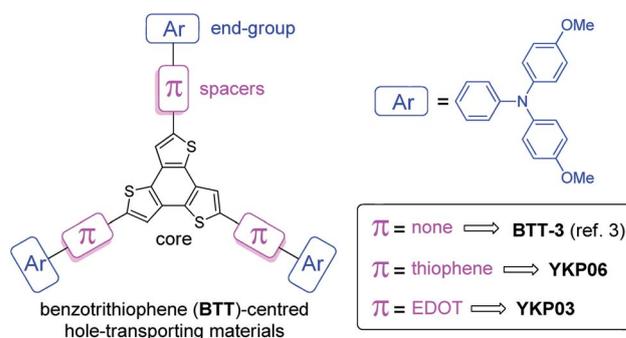
based HTMs a potential alternative to the commercially available **spiro-OMeTAD**.^{13,14} We noticed that, however, so far accessing BTT core-based HTMs must rely on a multistep approach involving tedious substrate prefunctionalization and the employment of either costly or somehow unstable organoboron reagents required in the Suzuki coupling reaction. Moreover, in order to achieve high efficiencies, previously reported perovskite solar devices using BTTs as hole-transporters must be doped with three kinds of chemical agents including 4-*tert*-butylpyridine (TBP), lithium bis(trifluoromethanesulfonyl) imide (Li-TFSI), and an expensive organometallic complex (FK209).^{3,4} Therefore, in this work, we wish to demonstrate significant progress regarding the synthesis and device properties of BTT-based HTMs (Fig. 1). The major breakthroughs and improvements are listed as follows: (1) a step-saving new synthetic route to three BTT core-based HTMs has been developed utilizing the more challenging but straightforward three-fold C–H activation/arylation reactions;¹⁵ (2) the first BTT-containing dopant-free HTM (YKP03) has been successfully synthesized by a modified methodology under pre-screened/

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★ Straightforward C–H/C–Br coupling reactions as key-step

★ Dopant-free HTMs obtained by inserting EDOT as π -spacer

Fig. 1 BTT core-based hole-transporting materials: step-saving new synthesis, facile installation of π -spacers, and dopant-free properties.

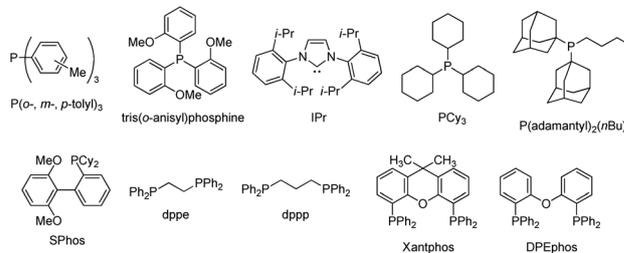
optimized reaction conditions. The 3,4-ethylenedioxythiophene (EDOT) moiety could be readily inserted as π -spacers for **YKP03** that led to stable PSC devices with a promising efficiency of 16.15%, free of addition of any commonly used chemical doping agents.

First, we performed a synthetic analysis/comparison taking the high-performance **BTT-3** (ref. 3) as an example (Scheme 1). Prior to the Suzuki coupling reaction, as reported in the literature, benzotrithiophene (**BTT**, **1a**) was brominated by the NBS reagent to generate tribromobenzotrithiophene (**1aa**). In addition, the end-group (**2a**) must be converted into its corresponding boronic ester derivative (**2aa**) through a three-step approach including Br/Li-exchange, transmetalation and ligand displacement with pinacol. Ultimately, the required organoboron reagent was produced. Coupling of **1aa** with **2aa** under general Suzuki reaction conditions afforded the desired **BTT-3**. Undoubtedly, this is a reliable synthetic strategy to access most target organic HTMs. However, in order to lower the cost of a promising HTM, and simultaneously, to avoid the preparation and treatment of toxic or unstable organometallic reagents such as organotin or organoborons during synthesis, we envisaged that **BTT** (**1a**) would directly undergo the threefold C–H bond activation/arylation reactions with **2a** under pre-optimized palladium catalysis conditions, by which **BTT-3** would be obtained in a more step-efficient and user-convenient manner.

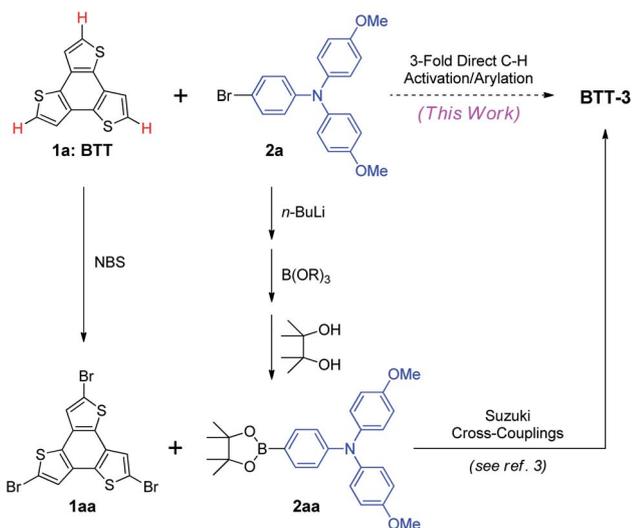
Hence, as shown in Table 1, we decided to perform ligand screening for the optimization of the threefold C–H/C–Br coupling reaction of **1a**. The first experiment was conducted with triphenylphosphine, giving **BTT-3** in only trace amount (entry 1). We examined other commonly used tri(aryl)phosphine ligands such as tritolylphosphines (entries 2–4). Among three regioisomers (*ortho*-, *meta*-, and *para*-), P(*o*-tolyl)₃ was found to be relatively promising since the target product was isolated in 30% yield (entry 2). The more electron-rich tris(*o*-

Table 1 Ligand screening for the threefold direct C–H/C–Br coupling reactions^a

Entry	Ligand	Yield (%) ^e
1	PPh ₃	Trace
2	P(<i>o</i> -tolyl) ₃	30
3	P(<i>m</i> -tolyl) ₃	Trace
4	P(<i>p</i> -tolyl) ₃	5
5	Tris(<i>o</i> -anisyl)phosphine	10
6	IPr	21
7	P(Cy) ₃	18
8	P(adamantyl) ₂ (<i>n</i> Bu)	27
9	SPhos	14
10	Dppe	Trace
11	Dppp	Trace
12	Xantphos	20
13	DPEphos	Trace
14 ^b	P(<i>o</i> -tolyl) ₃	60
15 ^c	P(<i>o</i> -tolyl) ₃	71
16 ^d	P(<i>o</i> -tolyl) ₃	55



^a Unless specified, the threefold C–H/C–Br coupling reactions were performed with **BTT** (**1a**: 0.30 mmol) and the end-group (**2a**: 1.05 mmol) in the presence of Pd(OAc)₂ (15 mol%), ligand (30 mol%), AcOH (60 mol%), and K₂CO₃ (1.08 mmol) in DMF (3 mL) at 125 °C under N₂ for 30 h. ^b DMF (1 mL). ^c DMF (1 mL) at 150 °C for 30 h. ^d DMF (1 mL) without AcOH. ^e Isolated yields.



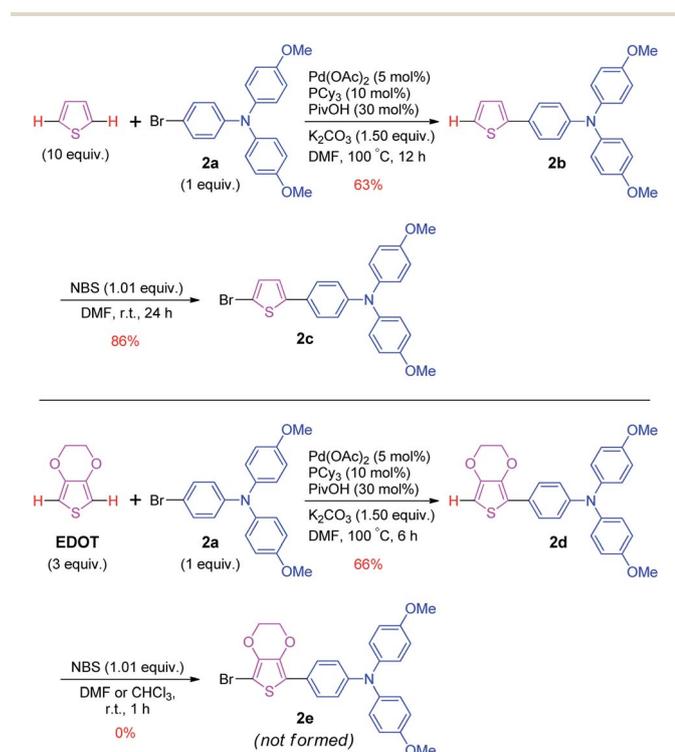
Scheme 1 Two approaches to access **BTT-3**: multistep synthesis vs. the straightforward threefold C–H/C–Br coupling reactions.

anisyl)phosphine led to the formation of **BTT-3** in unsatisfactory yield (10%, entry 5). In addition to phosphine ligands, the carbene-type ligand (IPr) was also tested. However, it did not further improve the yield (21%, entry 6) compared to the result of entry 2. Next, two kinds of tri(alkyl)phosphine ligands including P(Cy)₃ and P(adamantyl)₂(*n*Bu) were investigated, affording **BTT-3** in 18% and 27% yields, respectively (entries 7–8). A low yield was still obtained when the aryl–alkyl hybrid-type phosphine ligand (SPhos) was employed (14%, entry 9). Further, the coupling reaction was performed with a number of bidentate ligands, three of which were shown to be inefficient (trace, entries 10, 11, and 13), whereas the sterically rigid xantphos gave the product in 20% yield (entry 12). Therefore, P(*o*-tolyl)₃ was selected for subsequent optimizations including the alteration of the reaction concentration and temperature. We were pleased to observe a considerable yield improvement when the

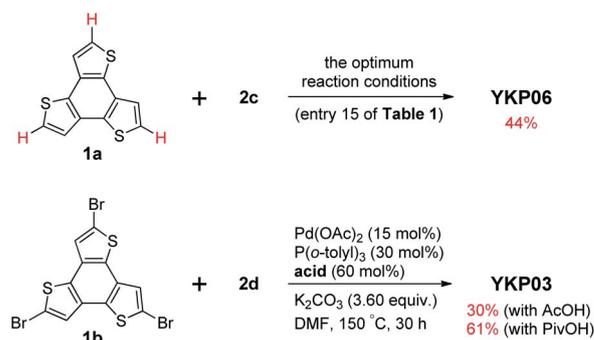
solvent loading was reduced from 3 mL to 1 mL (60%, entry 14), and meanwhile the yield can be further enhanced by setting the reaction temperature to 150 °C (71%, entry 15). Finally, we wondered if the reaction would proceed without the acid additive. It was found, however, that **BTT-3** was isolated with a diminished yield (55%, entry 16) in the absence of acetic acid.

Based on the optimum reaction conditions obtained in entry 15, we proceeded to synthesize other target HTMs incorporating π -spacers (**YKP06** and **YKP03**). Prior to the key steps, a series of building blocks (**2b–d**: π -spacer + end-group) were efficiently prepared by direct C–H monoarylation. As shown in Scheme 2, the reaction of methoxy-substituted bromotriphenylamine **2a** with excess thiophene under typical palladium-catalyzed C–H activation conditions furnished the desired one-side-arylated thiophene derivative **2b** (63%). Bromination of **2b** with NBS gave **2c** in good yield (86%). Likewise, 3,4-ethylenedioxythiophene (EDOT) underwent direct C–H activation/arylation with **2a**, leading to the formation of product **2d** in moderate yield (66%). It is worth noting that by adjusting the reaction time (6 h), generation of the undesired diarylated EDOT byproduct could be suppressed. However, we failed to obtain **2e** after carrying out NBS bromination of **2d**. We found that molecule **2e** was prone to decomposition shortly after isolation (viscous dark liquid was observed).

In Scheme 3, the threefold C–H arylation was performed by the coupling of **1a** (**BTT**) with building block **2c** under optimum reaction parameters (entry 15, Table 1), affording **YKP06** (thiophene as the π -spacer) in 44% yield. On the other hand, the synthetic route to **YKP03** (EDOT as the π -spacer) was modified



Scheme 2 Synthesis of building blocks **2b–e** (π -spacer + end-group) using direct C–H monoarylation as the key step.



Scheme 3 Synthesis of **YKP06** and **YKP03** by the optimized threefold direct C–H/C–Br coupling reactions.

since we were unable to access **2e**. We then decided to exchange the role of both reactants: direct C–H arylation of molecule **2d** with the tribrominated **BTT 1b** led to the production of target **YKP03** in 30% yield (with acetic acid). The isolated yield was improved (61%) as pivalic acid was employed. We assumed that different acid additives might exhibit dissimilar reactivities toward a single C–H activation/arylation substrate (**2d**).¹⁶

Prior to device fabrication, **BTT-3**, **YKP06** and **YKP03** were evaluated by measuring their optical, electrochemical, thermal and electrical properties and the results are collected in Table 2. **YKP06** and **YKP03** possess smaller optical bandgaps ($\Delta E_{\text{g}}^{\text{opt}} = 2.60$ eV) than **BTT-3** ($\Delta E_{\text{g}}^{\text{opt}} = 2.87$ eV) due to the inserted π -spacers (thiophene for **YKP06**; EDOT for **YKP03**) that extended the conjugation lengths. The highest occupied molecular orbital energy (E_{HOMO}) of each HTM was estimated by performing cyclic voltammetry (CV), showing that all HTMs exhibited appropriate HOMO energy levels ($E_{\text{HOMO}} = -5.16 \sim -5.37$ eV) located between the E_{HOMO} of the perovskite layer ($E_{\text{HOMO}} = -5.43$ eV) and gold electrode ($E_{\text{HOMO}} = -5.10$ eV). The thermal characteristics of the three molecules were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compared to the data for **BTT-3** provided in the literature ($T_{\text{d}} = 470$ °C; $T_{\text{g}} = 159$ °C),³ we found that introduction of a thiophene unit as the π -spacer considerably lowered the decomposition temperature of **YKP06** ($T_{\text{d}} = 208$ °C) while the glass transition temperature was slightly reduced ($T_{\text{g}} = 148$ °C). On the other hand, **YKP03** also displayed a relatively lower T_{d} of 411 °C, whereas its T_{g} was shown to be significantly enhanced (213 °C), implying that EDOT might be regarded as a superior π -spacer candidate for benzotrithiophene-based HTMs. In addition, hole mobility data of HTMs in the space-charge limited current (SCLC) region were obtained by fabricating each molecule with the device configuration of FTO/PEDOT:PSS/HTM/Ag. We were pleased to find that **YKP06** and **YKP03** demonstrated better hole mobilities ($\mu_{\text{h}} = 4.53 \times 10^{-4}$; 5.80×10^{-4} cm² V⁻¹ s⁻¹) than the reported **BTT-3** ($\mu_{\text{h}} = 2.66 \times 10^{-4}$ cm² V⁻¹ s⁻¹), indicating that the installation of π -spacers enabled an improvement in the conductivity of **BTT**-based HTMs. It is worth noting that, under dopant-free conditions, **YKP03** has been shown to exhibit a comparable hole mobility ($\mu_{\text{h}} = 5.74 \times 10^{-4}$ cm² V⁻¹ s⁻¹), making it promising for subsequent solar cell applications.

Table 2 The optical, electrochemical, thermal and electrical properties of BTT-3, YKP06 and YKP03

HTMs	ΔE_g^{opta} [eV]	E_{HOMO}^b [eV]	E_{LUMO}^c [eV]	T_d^d [°C]	T_g [°C]	Hole mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
BTT-3	2.87	-5.37	-2.50	470	159	2.66×10^{-4}
YKP06	2.60	-5.34	-2.74	208	148	4.53×10^{-4}
YKP03	2.60	-5.16	-2.56	411	213	5.80×10^{-4}

^a $\Delta E_g^{opt} = 1240/\lambda_{\text{intersect}}$, $\lambda_{\text{intersect}}$ refers to the intersection of UV/Vis absorption and photoluminescence spectra (measurements performed in CH_2Cl_2). ^b $E_{HOMO} = -[E_{1/2} \text{ (vs. Ag/AgCl}_{\text{sat'd}}) + 0.197 \text{ (vs. NHE)} + 4.500]$ eV (CV measurements performed in CH_2Cl_2). ^c $E_{LUMO} = E_{HOMO} + \Delta E_g^{opt}$. ^d T_d was obtained at 5% weight loss of HTMs.

Perovskite solar cells using **BTT-3**, **YKP06** and **YKP03** as hole-transport layers were fabricated. The photovoltaic performance data are summarized in Table 3. In general, each molecule was dissolved in chlorobenzene and then heated to 90 °C for 20 minutes in order to obtain a clear solution. Two doping agents, 4-*t*-butylpyridine and lithium bis(trifluoromethanesulfonyl)imide, were added to the above solution before spin-coating was carried out. Perovskite solar cells based on **BTT-3** showed a power conversion efficiency (PCE) of 13.79% which is lower than the literature reported value of 18.20%. We speculated that the enhanced PCE might be attributed to the use of an additional additive (FK209 as the third dopant).³ Compared to **BTT-3**, solar cells with **YKP06** or **YKP03** exhibited superior open-circuit voltage ($V_{oc} = 0.990$ – 1.020 V) and fill factor (FF = 67.20–68.90%) while the short-circuit current density ($J_{sc} = 20.86$ – 20.96 mA cm^{-2}) was shown to be lower than that of **BTT-3**, which led to PCEs of 13.92–14.63%. We assumed that the **YKP** series had higher hole mobilities because of their better film formation. For the PSCs with **YKP06**, we assumed that charge recombination might take place at the perovskite/HTM interface due to its lower-lying E_{LUMO} (–2.74 eV, Table 2), thus giving a relatively lower value of J_{sc} . In the case of **YKP03** fabricated under dopant-free conditions, the devices demonstrated improved photovoltaic parameters ($V_{oc} = 1.030$ V/ $J_{sc} = 23.07$ mA cm^{-2} /FF = 68%), resulting in a promising PCE of 16.15% which is better than that of the doped solar cells with other HTMs synthesized in this work. Moreover, the performance of **YKP03**-based dopant-free PSCs was close to that of the reference cells using the commercially available **spiro-OMeTAD** as the HTM (PCE = 17.59%).

Under forward and reverse scanning, as shown in Fig. 2a, the devices demonstrated small hysteresis effects and the **YKP03**-based dopant-free PSCs exhibited the best performance. In Fig. 2b, we show the spectra of the photon-to-current conversion efficiency (IPCE) of perovskite solar cells fabricated with each HTM. It was found that the devices based on **YKP03** (dopant-free conditions) achieved nearly 80% IPCE from the wavelength of 450 nm to 650 nm and exhibited a higher IPCE value from 670 nm to 770 nm than those using other HTMs. This is consistent with their remarkable J_{sc} value shown in Table 3. As shown in Fig. 2c, we also measured the steady-state power output of PSC devices using the more efficient **YKP03** as the HTM through a continuous PCE (η) vs. time (t) experiment (voltage set at 0.82 V). It was found that both curves (**YKP03** with and without dopants) reached J_{max} quickly and remained stable for over 300 seconds.

In order to study the hole-transfer process at device interfaces, steady-state photoluminescence (PL) was measured based on the device structures of glass/perovskite and glass/perovskite/HTM (PL spectra provided in Fig. S6†). The perovskite-only device showed a strong PL band, while the ones fabricated with HTMs displayed a significant reduction of the PL emission. Compared with other synthesized HTMs, **YKP03** exhibited a more effective PL quenching, implying that it may extract holes efficiently from the perovskite layer. Besides, we also carried out time-resolved PL (TRPL) experiments (Fig. S7†). The fitted average lifetime for **YKP03**/perovskite is 7.84–8.50 ns, which is superior than those for **BTT-3**/perovskite and **YKP06**/perovskite (12.99 ns and 11.35 ns). This result also indicated that **YKP03** possesses a better charge extraction capability.

Table 3 The photovoltaic performance of perovskite solar cells using BTT-3, YKP06 or YKP03 as the hole-transport layer^{a,b,c}

HTMs		V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
BTT-3	Best	0.960	22.56	63.67	13.79
	Average	0.940 ± 0.030	21.82 ± 1.21	63.91 ± 3.36	13.11 ± 0.69
YKP06	Best	0.990	20.96	67.20	13.92
	Average	1.000 ± 0.020	20.44 ± 0.43	65.0 ± 2.57	13.28 ± 0.64
YKP03	Best	1.020	20.86	68.90	14.63
	Average	0.980 ± 0.040	20.40 ± 1.12	70.40 ± 3.51	14.07 ± 0.81
YKP03 (dopant-free)	Best	1.030	23.07	68.00	16.15
	Average	1.010 ± 0.030	22.75 ± 0.40	69.06 ± 1.71	15.86 ± 0.41
spiro-OMeTAD	Best	1.050	23.24	72.10	17.59
	Average	1.050 ± 0.020	22.26 ± 0.76	73.64 ± 2.67	17.21 ± 0.26

^a The statistical data were obtained based on 6–8 cells. ^b Unless specified, the perovskite solar cells were fabricated with the addition of two doping agents: 4-*t*-butylpyridine and lithium bis(trifluoromethanesulfonyl)imide. ^c Reverse scans.

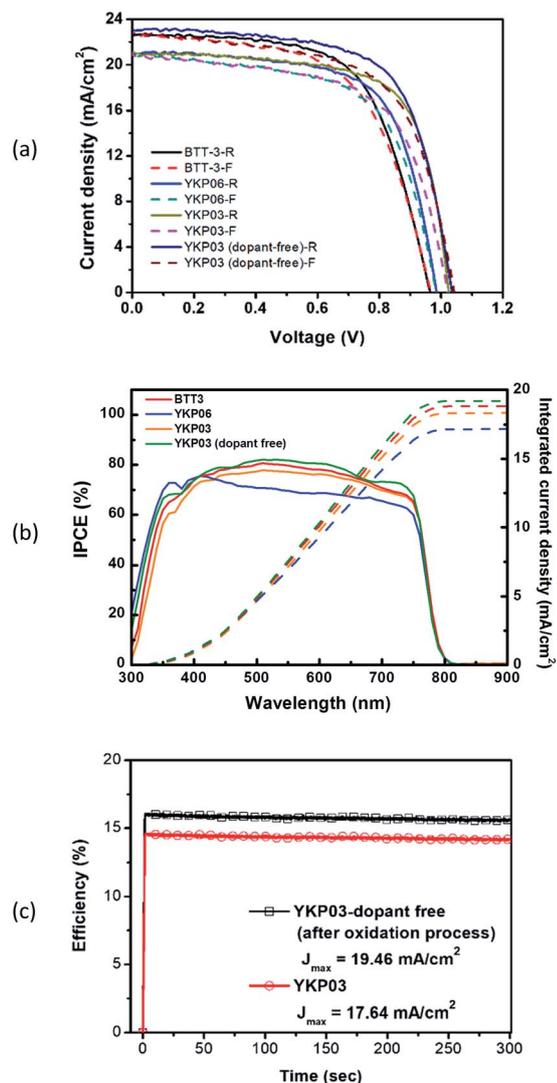


Fig. 2 (a) The photocurrent density vs. voltage (J - V) characteristic curves; (b) the incident photon-to-current conversion efficiency (IPCE) spectra of perovskite solar cells based on BTT-3, YKP06 or YKP03; (c) the steady-state power output: PCE (η) vs. time (t) curves of perovskite solar cells based on YKP03.

We further explored the device oxidation time and long-term stability focusing on perovskite solar cells with the most promising YKP03 (Fig. 3). With two doping agents, perovskite solar cells showed the best PCE of 14.63% without the need for the device oxidation process (Fig. 3a). However, the efficiency rapidly declined to $\sim 7\%$ when the device was exposed to an ambient atmosphere for 4 h (25 \pm 2 $^{\circ}\text{C}$ and 50–70% RH), presumably owing to the hygroscopic chemical dopants that caused device instability. In contrast, although the dopant-free solar cells required at least 3 h of oxidation to achieve a comparable PCE ($\sim 14\%$) to that of the doped ones, they appeared to remain stable and the PCE continued climbing to the highest value (16.15%) thereafter within 3 h. More importantly, as shown in Fig. 3b, experiments for long-term storage stability were also conducted in a glove box under 5% RH. The result indicated that, under dopant-free conditions, perovskite

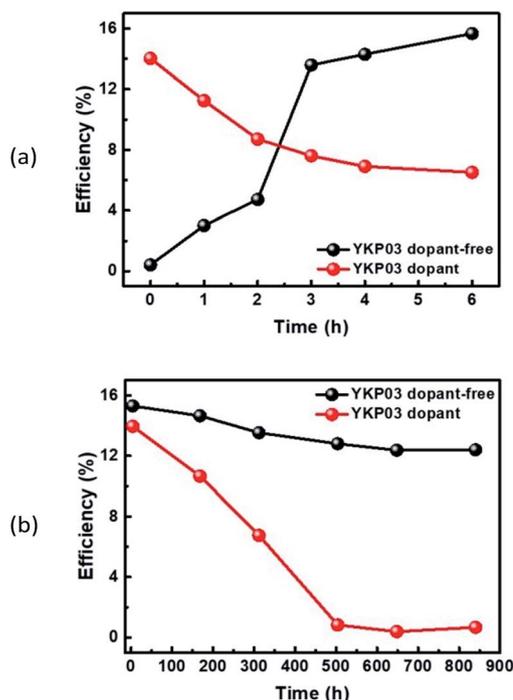


Fig. 3 (a) PCE vs. device oxidation time curves and (b) PCE vs. long-term storage stability of the perovskite solar cells using YKP03 as the HTM.

solar cells exhibited exceptional stability and the PCEs retained over 80% of the best value for more than 800 h, whereas the devices with two doping agents were found to be far less stable since their PCEs dropped drastically within 500 h. The chemical dopants (TBP and Li-TFSI) are nitrogen-containing compounds which may absorb water during the device oxidation process and long-term storage test. In particular, the Li-TFSI salt is very hygroscopic because of its ionic characteristics. Therefore, we speculated that both hygroscopic chemical dopants might influence the film formation/quality of YKP03-based devices (in particular the hydrophilic perovskite-based layer might be partly destroyed), thus leading to an inferior PCE. In contrast, under dopant-free conditions, YKP03-based PSCs exhibited better PCEs and potential long-term storage stabilities.

In summary, we provide a step-saving new route to benzo-triithiophene (BTT) core-based hole-transporting materials (BTT-3, YKP06 and YKP03) via Pd-catalyzed direct C–H arylation under optimized reaction conditions. Among three HTMs, YKP03 incorporating EDOT as the π -spacer demonstrated promising power conversion efficiencies of up to 16.15% when employed in perovskite solar devices, without the use of any chemical doping agents. Moreover, YKP03-based dopant-free solar cells also displayed impressive long-term stabilities, making it one of the potential candidates for replacing the costly and doping-necessary spiro-OMeTAD.

Conflicts of interest

There are no conflicts to declare.

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