

New Benzotrithiophene-Based Hole-Transporting Materials for Perovskite Solar Cells: Succinct Synthesis and PCE Improvement

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We report a succinct synthesis of benzotrithiophene (BTT) core-based new hole-transporting materials (HTMs) with *t*-butyl terminal substituents, using boron- and tin-free threefold direct C–H/C–Br couplings as key transformations. One of the synthesized oligoaryls (YKP05) incorporating additional 3,4-

ethylenedioxythiophene (EDOT) moiety as π -spacers displayed significantly improved power conversion efficiency of up to 15.1% while fabricated in perovskite solar cells as hole-transporting layer.

Introduction

New design and synthesis of effective hole-transporting materials (HTMs) for use in perovskite solar cells (PSCs) has advanced significantly over the past few years.^[1] It has been well documented that perovskite-based solar devices are unable to display high efficiencies without the incorporation of a hole-transport layer that is responsible for prominent charge-separation processes.^[2] π -Conjugated small molecules have been hitherto the most popular organic HTMs because they are readily available either from commercial source or lab synthesis.^[3] Synthetically, it was much easier, in contrast to macromolecules, to carry out functional-group modifications where needed on their backbones. Besides, the fixed conjugation length of oligoaryls allowed facile and precise structural characterizations, thus encouraging scientists to create new small-molecule HTMs.^[4] Among a variety of thiophene-containing hole-transporting molecules, we were interested in the star-shaped benzotrithiophene (BTT) core-based HTMs owing to BTT's high planarity, undemanding synthesis, and promising power conversion efficiencies (PCEs) while fabricated as hole-transport layer in PSCs.^[5,6] However, we found that accessing these BTT-based small molecules must rely on traditional synthetic approaches involving Suzuki- or Stille-coupling reaction as key steps, which required costly organoboron or toxic organotin reagents. Recently our group developed a step-

saving synthetic protocol by which three C–H bonds of BTT can be directly arylated, giving effective HTMs in good isolated yields. These molecules were fabricated in perovskite-based solar devices that displayed PCEs of up to 16.2% without addition of any doping agents.^[7] Since direct C–H bond (hetero)arylation has been emerging as the most attractive synthetic tool towards step-economical preparation of π -conjugated small molecules for photovoltaic applications,^[8–10] we anticipate to further explore BTT-containing new oligoaryls for efficient PSCs utilizing direct C–H activation/arylation reaction as a key transformations. Hence, in this work, we facilely synthesized two BTT core-based new HTMs with *t*-butyl substituents (YKP02 and YKP05) through straightforward C–H/C–Br coupling reactions. This avoided preparing and treating any boron- or tin-related chemical agents and wastes. More interestingly, in device fabrications, we found the PCE of YKP05-based PSCs was significantly improved to 15.1% while 3,4-ethylenedioxythiophene (EDOT) had been inserted as π -spacers (Figure 1).

Results and Discussion

As shown in Scheme 1–1, the star-shaped HTMs (YKP02 & YKP05) were structurally divided into two moieties: core-(benzotrithiophene) and end-groups (triphenylamine derivatives), both of which must undergo a series of functional group transformations prior to the key cross-couplings. First, BTT (A) was brominated by *N*-bromosuccinimide (NBS) to give tribromo-BTT (B) as one coupling partner. Next, in order to introduce an EDOT moiety (F) to end-group as π -spacer by Suzuki coupling reaction, the bromotriphenylamine derivative (C) was transformed into its corresponding boron reagent (E) through tedious halogen-metal exchange and borylation reactions,^[11] in which an aryllithium intermediate was generated at -78°C . Moreover, EDOT must undergo a low-yield monobromination^[12] to afford (G) that readily reacted with above-prepared arylboron (E) under typical Pd-catalyzed Suzuki reaction conditions, giving desired EDOT-containing molecule (H). Furthermore, H was stannylated via (I) for subsequent Stille coupling reactions (key step) by an indispensable deprotonation/transmetallation

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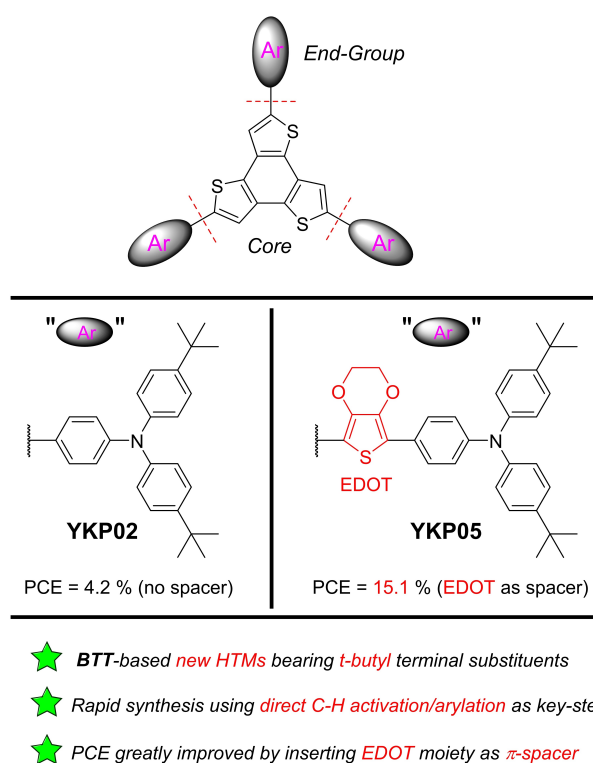


Figure 1. New benzotrithiophene (BTT) core-based hole-transporting materials with *t*-butyl substituents: rapid synthesis and PCE improvement.

process. Eventually, the required aryltin coupling-partner (**J**) was produced.

Based on the pre-functionalizations shown in Scheme 1–1, we carried out a synthetic analysis/comparison of **YKP02** and **YKP05**, focusing on the demonstration of two different pathways (Scheme 1–2). In contrast to traditional multistep synthesis using organoboron or organotin reagents (**E** and **J**) required in Suzuki- and Stille coupling reactions, we designed two boron- and tin-free alternative routes to **YKP02** and **YKP05**, respectively, through direct C–H bond activation/arylation reactions. Step-economically, **YKP02** could be obtained in one pot just by mixing core (**A**) with end (**C**). For the EDOT-inserted **YKP05**, our synthetic approach could omit complex chemical transformations. In other words, as a prominent building block, compound (**H**) was directly generated by the C–H monoarylation of EDOT (**F**) with the end-group (**C**). **H** further underwent the second C–H arylation with tribromo-BTT (**B**) to afford desired **YKP05**. The proposed synthetic routes displayed exceptional atom- and step-economies through succinct and viable direct C–H/C–Br coupling reactions.

Indeed, as demonstrated in Scheme 2, we carried out an efficient synthesis of two target HTM molecules by reacting BTT-based cores (**A** or **B**: synthesized according to^[5a]) with the corresponding end-groups (**C**^[8g] or **H**^[8d]) under previously optimized C–H arylation conditions,^[7] giving **YKP02** and **YKP05** in moderate isolated yields (54%, 67%).

After obtaining **YKP02** and **YKP05**, we investigated their optical, electrochemical, electrical and thermal properties. The

results were summarized in Table 1. It was found that the incorporation of EDOT units made the optical bandgap of **YKP05** narrower ($\Delta E_g = 2.63$ eV) due to its upshifted E_{HOMO} (–5.23 eV) and downshifted E_{LUMO} (–2.60 eV). This relatively higher-lying E_{HOMO} of –5.23 eV well fitted the energy level between E_{HOMO} of the perovskite layer ($\text{CH}_3\text{NH}_3\text{PbI}_3$, $E_{\text{HOMO}} = -5.42$ eV) and the silver electrode ($E_{\text{HOMO}} = -4.20$ eV). We anticipated that **YKP05** would be capable of extracting holes more efficiently from $\text{CH}_3\text{NH}_3\text{PbI}_3$ to HTM layer. Besides, insertion of EDOT into **YKP05** also improved the hole mobility ($\mu_h = 4.52 \times 10^{-5}$). For the thermal properties, **YKP02** exhibited higher decomposition temperature ($T_d = 481^\circ\text{C}$) than that of **YKP05** ($T_d = 403^\circ\text{C}$). However, both molecules displayed similar glass transition temperature ($T_g = 217^\circ\text{C}$ for **YKP02**; 226°C for **YKP05**). In general, these two small molecules possessed comparable/better thermal stabilities than those of the commercially available HTM spiro-OMeTAD ($T_d = 417^\circ\text{C}$; $T_g = 126^\circ\text{C}$).

The perovskite solar cells using **YKP02** or **YKP05** as hole-transporting material were fabricated and their photovoltaic parameters are collected in Table 2. **YKP02**-based devices showed relatively lower short-circuit current ($J_{\text{sc}} = 15.05$ mA/cm²) and fill factor (FF = 27.50%), which led to inferior power conversion efficiency (PCE) of 4.17%. Presumably this was owing to its lower-lying E_{HOMO} of –5.43 eV that is even lower than the E_{HOMO} of perovskite layer (–5.42 eV), thus resulting in an inefficient hole-transporting behavior. On the other hand, the PSC devices with **YKP05** incorporating additional EDOT moieties as π -spacers demonstrated higher open-circuit voltage ($V_{\text{oc}} = 1.02$ V), J_{sc} (20.90 mA/cm²), and FF (70.40%), giving a significantly improved PCE of 15.07%. However, under dopant-free conditions, PSCs with either **YKP02** or **YKP05** exhibited poor PCEs (< 1%).

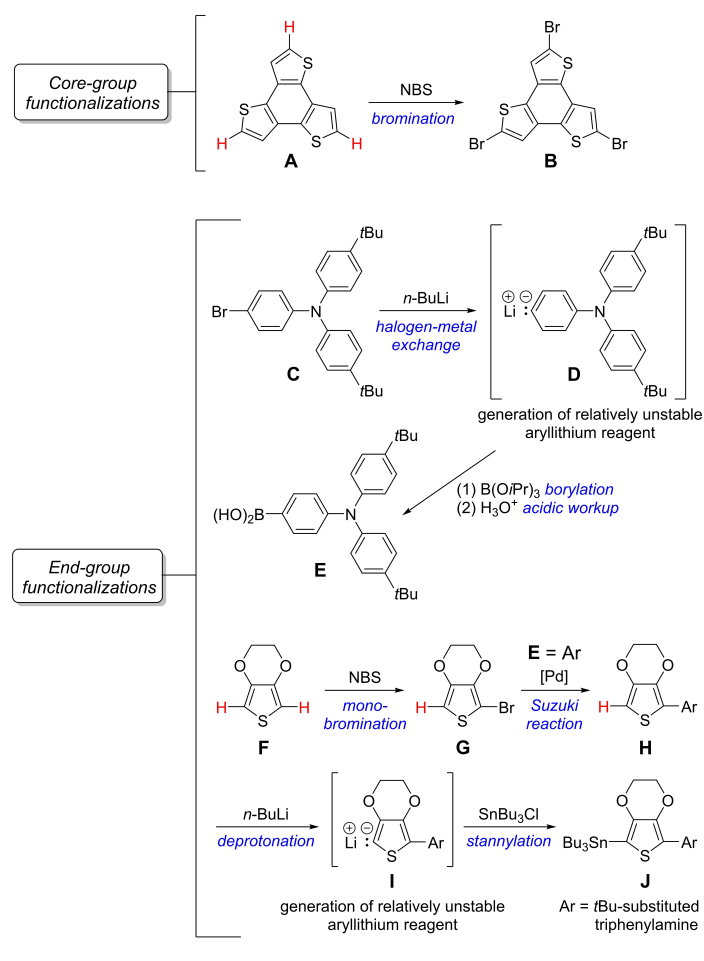
Further, we investigated the incident photon-to-current conversion efficiency (IPCE) of our solar devices based on **YKP02** and **YKP05**, respectively (Figure 2). Compared with **YKP02**, PSCs with **YKP05** displayed excellent IPCEs in the wavelength region between 350–800 nm. This result reflected the higher J_{sc} values (20.90 mA/cm²) of **YKP05**-based devices shown in Table 2.

The experiments of steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) for **YKP02** and **YKP05** were also carried out to evaluate their hole-extraction abilities. Compared with **YKP02**, as presented in Figure 3a, we

Table 1. Data of the optical, electrochemical and thermal properties of **YKP02** and **YKP05**.

HTMs	ΔE_g [eV] ^[a]	E_{HOMO} [eV] ^[b]	E_{LUMO} [eV] ^[c]	hole mobility (cm ² V ⁻¹ s ⁻¹)	T_d [°C]	T_g [°C]
YKP02	2.93	–5.43	–2.50	3.19×10^{-5}	481	217
YKP05	2.63	–5.23	–2.60	4.52×10^{-5}	403	226

^[a] The optical bandgap ΔE_g was determined based on the UV/Vis absorption and photoluminescence spectra (measurements conducted in CH_2Cl_2). ^[b] $E_{\text{HOMO}} = -[E_{1/2}(\text{vs. Ag/AgCl}_{\text{sat'd}}) + 0.197(\text{vs. NHE}) + 4.500]$ eV (measurements conducted in CH_2Cl_2). ^[c] $E_{\text{LUMO}} = E_{\text{HOMO}} + \Delta E_g$.



Scheme 1. The commonly used synthetic steps to prepare the target intermediates **B**, **E**, **G**, **H**, and **J**.

Table 2. Photovoltaic performances of the perovskite solar cells employing **YKP02** or **YKP05** as hole-transporting materials.^{[a], [b]}

HTMs		V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
YKP02	best	1.01	15.05	27.50	4.17
	average	0.89 ± 0.07	11.86 ± 2.15	36.48 ± 0.07	3.75 ± 0.42
YKP05	best	1.02	20.90	70.40	15.07
	average	0.98 ± 0.04	20.81 ± 0.66	66.38 ± 2.89	13.49 ± 0.89
spiro-OMeTAD	best	1.05	22.50	74.50	17.65
	average	1.03 ± 0.03	21.95 ± 0.36	74.98 ± 1.51	16.98 ± 0.64

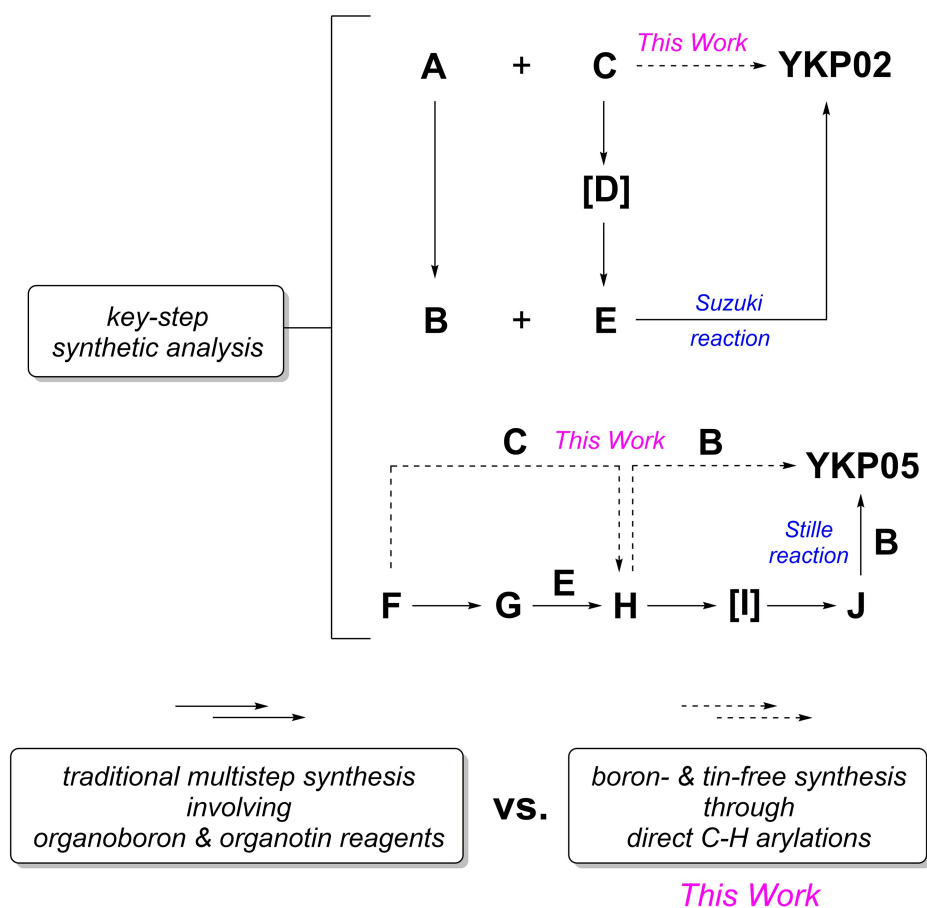
^[a] Reverse scans. **YKP02** and **YKP05** were doped with Li-TFSI and *t*-butylpyridine (TBP). ^[b] The statistical data were calculated based on 5–6 cells.

found that **YKP05** showed much stronger PL quenching effect, which is comparable to that of **spiro-OMeTAD**. This indicated that **YKP05** could efficiently extract holes at the interface between $\text{CH}_3\text{NH}_3\text{PbI}_3$ (perovskite layer) and the hole-transport layer. In addition, the TRPL spectra (Figure 3b) demonstrated that **YKP05**-based devices had the average lifetime of 36 ns ($\tau_{\text{average}} = 36$ ns) which was superior than the $\tau_{\text{average}} = 88$ ns for the devices with **YKP02** ($\tau_{\text{average}} = 18$ ns for **spiro-OMeTAD**-based devices). Compared to **YKP02**, **YKP05** with additional EDOT moieties has a better solubility in common organic solvents, which contributed to obtain a smoother film quality

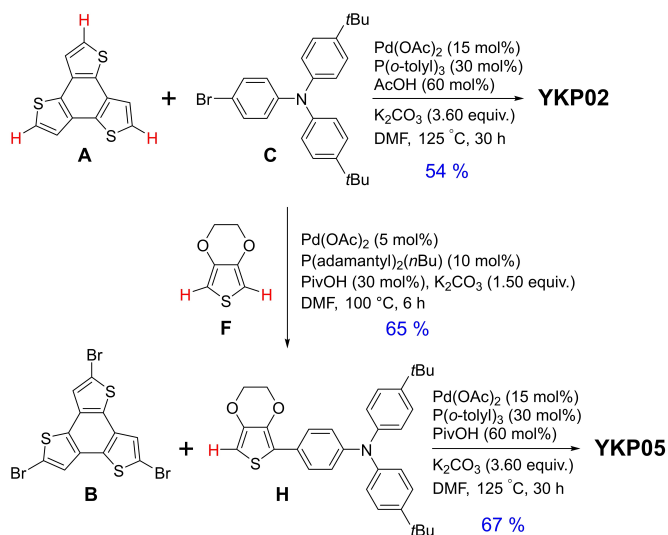
during spin-coating process. We speculated this might be one of the reasons the PSC devices with **YKP05** exhibited the improved hole-extraction, PL quenching abilities and PCEs.

Conclusions

In summary, in contrast to the commonly used methoxy group (-OMe) introduced into small-molecular HTMs, the work reports new hole-transporting materials based on **BTT** bearing *t*-butyl moiety as terminal substituents. Through step-economical synthetic strategies involving [Pd]-catalysed threefold direct



Scheme 2. Key-step synthetic analysis for **YKP02&05**: Suzuki- and Stille reactions versus direct C–H activation/arylations.



Scheme 3. Efficient synthesis of target HTMs (**YKP02&05**) by direct C–H/C–Br coupling reactions.

C–H/C–Br coupling as key transformations, **YKP02** and **YKP05** were readily obtained in moderate to good isolated yields, free of the generation and treatment of any organoboron or

organotin reagents required in Suzuki or Stille reactions. For photovoltaic applications, **YKP05** consisting of EDOT as π -spacers was fabricated as hole-transport layers in perovskite solar cells, displaying a greatly improved power conversion efficiency of up to 15.1%. Development of step-saving new synthetic routes for high-efficiency HTMs/PSCs is currently underway in our laboratory.

Experimental Section

General procedure for the synthesis of YKP05: To a solution of Pd(OAc)₂ (15 mol%), P(*o*-tolyl)₃ (30 mol%), PivOH (60 mol%), and K₂CO₃ (3.60 equiv.) in DMF (5 mL) in a flame-dried Schlenk flask/tube were added tribromobenzotrithiophene (**B**) (0.50 mmol) and the corresponding end group (**H**) (1.75 mmol) under N₂. The reaction mixture was then heated at 125 °C under N₂ for 30 h. After the reaction mixture had cooled to room temperature, water (15 mL) was added. The mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na₂SO₄) and concentrated in *vacuo*. Purification by column chromatography afforded the desired product **YKP05**.

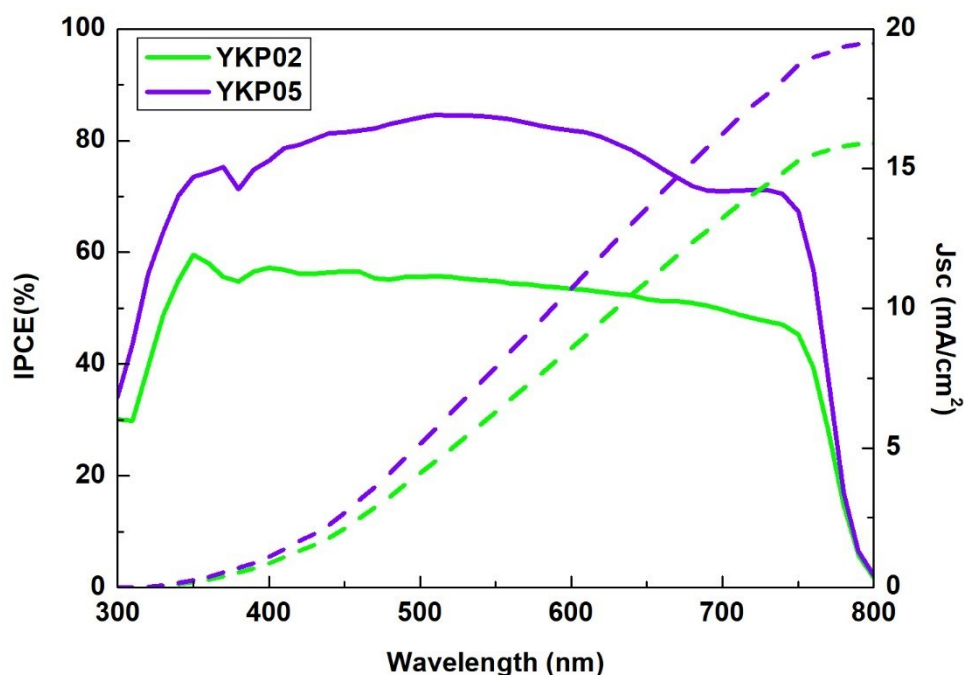


Figure 2. The spectra of incident photon-to-current conversion efficiency (IPCE) of perovskite solar cells with YKP02 or YKP05.

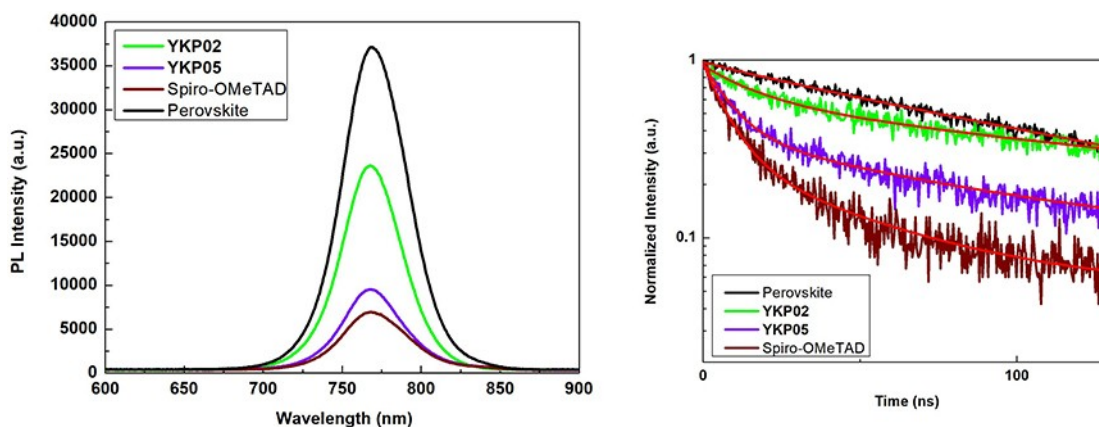


Figure 3. (a) Steady-state photoluminescence (PL) spectra; (b) Time-resolved PL spectra of the devices fabricated as glass/(CH₃)NH₃PbI₃/HTM.

Supporting Information Summary

Supplementary materials available: Optical (UV/Vis), electrochemical (CV), thermal properties (TGA&DSC), NMR (¹H and ¹³C), and mass spectra (MALDI).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Benzotrithiophenes · Direct C–H Arylations · Hole-Transporting Materials · Perovskite Solar Cells

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