

## Supporting Information

### Making Benzotrithiophene Derivatives Dopant-Free for Perovskite Solar Cells? Step-Saving Installation of $\pi$ -Spacers by Direct C-H Arylation Strategy

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#### Part I: Experimental Section

1.1 General information.....	S2-S4
1.2 General procedure <b>A</b> for the synthesis of <b>BTT-3</b> & <b>YKP06</b> .....	S5
1.3 General procedure <b>B</b> for the synthesis of <b>YKP03</b> .....	S5
1.4 Compound characterizations.....	S6-S7
1.5 <b>Figures S1-S2</b> : The UV-Vis absorption, photoluminescence spectra and cyclic voltammograms,.....	S8
1.6 <b>Figures S3-S4</b> Thermogravimetric analysis and differential scanning calorimetry.....	S9
1.7 <b>Figure S5</b> . J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region.....	S10
1.8 <b>Figures S6-S7</b> : Steady-state PL and time-resolved PL spectra.....	S11
1.9 <b>Figure S8</b> . Device oxidation time vs. PCE.....	S13
1.10 <b>Figure S9</b> . Long-term storage stability test.....	S14
1.11 <b>Figure S10</b> . PL vs. time and hole-mobility vs. time.....	S15
1.12 <b>Figure S11</b> . Cross-section SEM picture.....	S16

#### Part II:

2.1 MALDI Spectra.....	S17-S18
2.2 <sup>1</sup> H and <sup>13</sup> C NMR Spectra.....	S19-S21

## 1. General information:

Unless otherwise noted, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Required chemicals such as Pd(OAc)<sub>2</sub>, phosphine ligands, PivOH, AcOH, and K<sub>2</sub>CO<sub>3</sub> are commercially available. Anhydrous or reagent-grade solvents such as dichloromethane, chloroform, and *N,N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich, Acros, or Alfa Aesar and used directly without further purifications. Syringes used to transfer reagents and solvents were purged with nitrogen prior to use. Reactions were monitored by thin layer chromatography (TLC, aluminum plates coated with silica gel, Merck 60, F-254). The spots were visualized by UV light. Flash column chromatography was performed using silica gel (spherical, 63-210 μm or 40-75 μm). Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. Chemical shifts were given relative to CDCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H NMR, 77.0 ppm for <sup>13</sup>C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), quint (quintet), m (multiplet), comp (complex), app (apparent), and br (broad). The mass spectrum recorded by Matrix-Assisted Laser Desorption/Ionization (MALDI) techniques was operated with a Bruker autoflex speed. Absorption spectra (UV-Vis) were measured on a Hitachi U-4100 UV-Vis spectrophotometer. Photoluminescence spectra (PL) were measured on a Hitachi F-7000 fluorescence spectrophotometer. The optical band gap ( $E_g^{\text{opt}}$ ) of the synthesized hole-transporting materials was calculated from the intersection of absorption and PL spectra. The experiments of cyclic voltammetry were carried out with an Autolab electrochemical analyzer using a Pt working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The measurements were conducted in dry CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte under a scan rate of 100 mVs<sup>-1</sup>. The half-wave potential,  $E_{1/2}$ , was calculated by  $(E_{\text{pa}} + E_{\text{pc}})/2$ , where  $E_{\text{pa}}$  and  $E_{\text{pc}}$  are the potential energy of anodic and cathodic peaks, respectively. The HOMO energy level,  $E_{\text{HOMO}}$ , was calculated by  $-[E_{1/2} (\text{vs. Ag/AgCl}_{\text{sat'd}}) + 0.197 (\text{vs. NHE}) + 4.500]$  eV;  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$ . Thermogravimetric analysis (TGA) was run on a TA Instrument Q500. Differential scanning calorimetry (DSC) was run on a Netzsch Instrument LT-DSC (Netzsch 204 F1).

## 2. Device fabrication of the perovskite solar cells (PSCs):

A TiO<sub>2</sub> compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75

wt.% of Ti(acac)<sub>2</sub>O*i*Pr<sub>2</sub> in isopropanol). A 150 nm-thick mesoporous TiO<sub>2</sub> film (TiO<sub>2</sub> particle size: ~20 nm, crystalline phase: anatase) was spin-coated onto the compact-TiO<sub>2</sub>/FTO substrate surface using home-made pastes and heated to 500 °C for 30 min. After sintering the TiO<sub>2</sub> layer, the films were cooled to room temperature and immersed in TiCl<sub>4</sub> solution (0.04 M in water) at 70 °C for 30 min. The films were then rinsed by deionized water and then annealed at 500 °C for 30 min again. After cooling to room temperature, the substrate/films were transferred to a nitrogen-filled glove box. A solution consisting of PbI<sub>2</sub> (1.80 M) and CH<sub>3</sub>NH<sub>3</sub>I (1.80 M) in  $\gamma$ -butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the TiO<sub>2</sub> substrate by a two-step spin-coating process at 1000 and 5000 rpm for 10 and 20 sec, respectively. At the second spin-coating step, the substrate/films were treated with 50  $\mu$ L toluene by drop-casting. The substrate/films were then left on standing for over 60 mins before dried on a hot plate at 100 °C for 10 min. **BTT-3**, **YKP06**, **YKP03** and **spiro-OMeTAD** (as reference cell) was each dissolved in chlorobenzene (50 mg/mL). Each solution was heated to 80~90 °C for 20 min. Next, 17.5  $\mu$ L of a solution of lithium bis(trifluoromethane)sulfonimide (Li-TFSI, 520 mg) in acetonitrile (1 mL) and 28.5  $\mu$ L 4-*tert*-butylpyridine (TBP) were added directly to the corresponding hole-transporting material (HTM) solutions prepared from previous step. This as-prepared HTM solution was spin-coated onto the substrate/films at 2000 rpm for 30 sec. Finally, the Ag cathode layer was deposited by thermal evaporation (~100 nm). The active area of each cell was fixed at 0.16 cm<sup>2</sup> by a metal mask.

In order to evaluate the hole-mobility of **BTT-3**, **YKP06**, **YKP03** and **spiro-OMeTAD**, hole-only devices were fabricated using the space-charge-limited current (SCLC) method based on the device structure of FTO/PEDOT:PSS/HTM/Ag. The hole-mobility data was obtained according to the Mott–Gurney law by fitting the equation (S1) to experimental data in the voltage range where the obtained slope in the double log plot is equal to 2.

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{d^3} \quad (\text{S1})$$

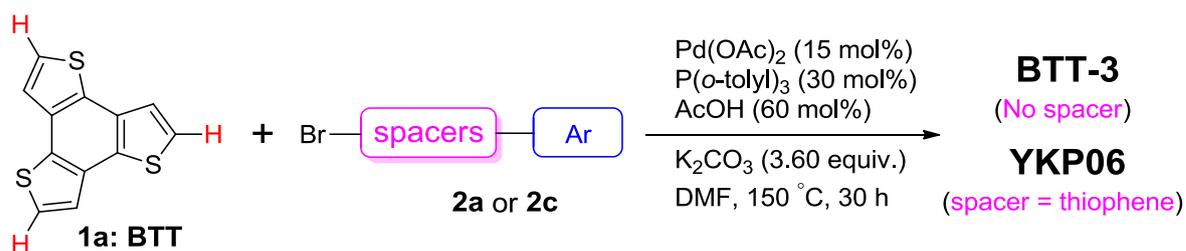
In equation (S1),  $J$  is the current density,  $\varepsilon_0$  is the permittivity of free space (8.85 x10<sup>-12</sup> F m<sup>-1</sup>),  $\varepsilon_r$  is the relative permittivity of the material (approaching 3 for organic semiconductors),  $\mu_h$  is the hole mobility,  $V$  is the applied voltage and  $d$  is the thickness of the active layer. The hole-only devices were fabricated by spin-coating PEDOT:PSS (Clevios P, VP A14083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (8  $\Omega$ /square). The HTM film was spin-coated on top from a chloroform solution with the concentration of 8 mg/mL. The film thickness was

varied by using different spin-coating speeds. Ag was deposited on top as a counter electrode by vacuum evaporation. The current density–voltage curves of the devices were recorded with a Keithley 2400 source.

### 3. PCE evaluation of the perovskite solar cells (PSCs):

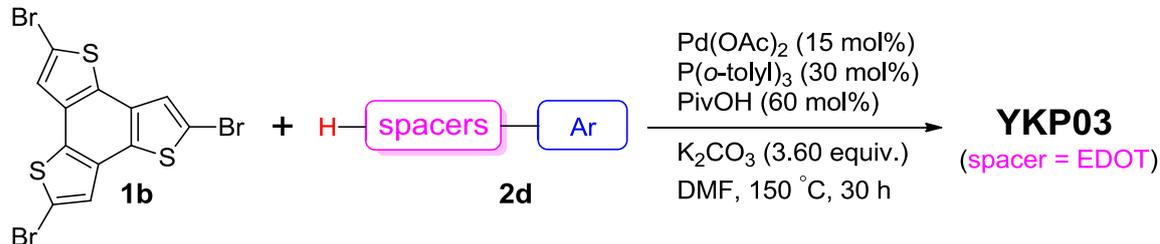
An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) calibrated with a single-crystal silicon reference cell was used for the incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. An AM 1.5G solar simulator (Yamashita Denso Corporation, YSS-50A) was used as the irradiation light source for the characteristic current density-voltage (J-V) measurements. The intensity of the simulated sunlight was calibrated to  $100 \text{ mW/cm}^2$ . The J-V characteristics of the cell under an illumination of AM 1.5G simulated sunlight were obtained by applying the external potential bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA).

### General Procedure A for the Synthesis of BTT-3 & YKP06:

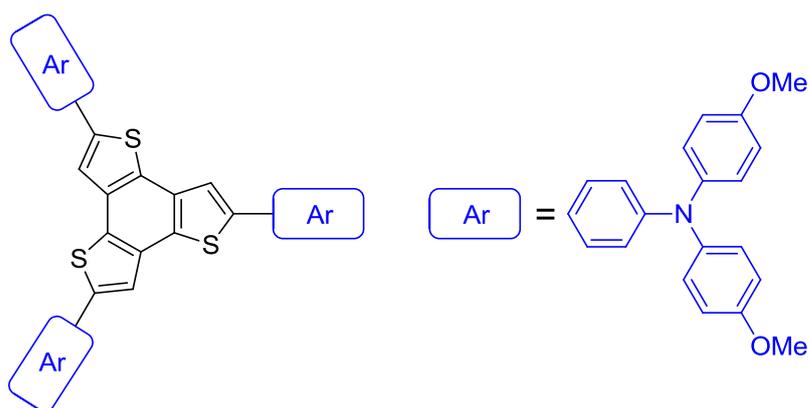


To a solution of Pd(OAc)<sub>2</sub> (15 mol%), P(*o*-tolyl)<sub>3</sub> (30 mol%), AcOH (60 mol%), and K<sub>2</sub>CO<sub>3</sub> (3.60 equiv.) in DMF (1 mL) in a flame-dried Schlenk flask/tube were added benzotrithiophene (**BTT**) (**1a**) (0.30 mmol) and the corresponding end-groups (**2a**, or **2c**) (1.05 mmol) under N<sub>2</sub>. The reaction mixture was then heated at 150 °C under N<sub>2</sub> for 30 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. Purification by flash chromatography afforded the desired products **BTT-3** or **YKP06**.

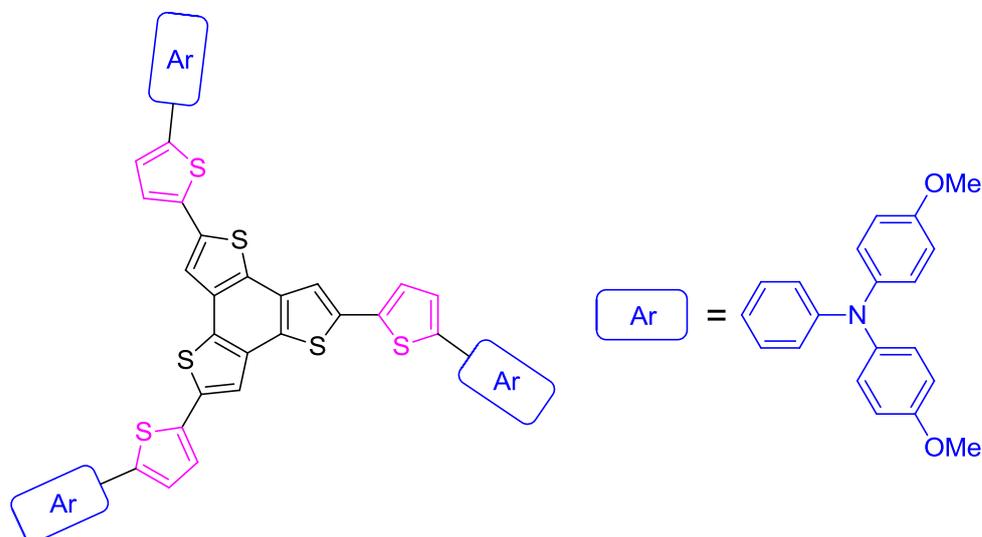
### General Procedure B for the Synthesis of YKP03:



To a solution of Pd(OAc)<sub>2</sub> (15 mol%), P(*o*-tolyl)<sub>3</sub> (30 mol%), PivOH (60 mol%), and K<sub>2</sub>CO<sub>3</sub> (3.60 equiv.) in DMF (3 mL) in a flame-dried Schlenk flask/tube were added tribromobenzotrithiophene (**1b**) (0.50 mmol) and the corresponding end-group (**2d**) (1.75 mmol) under N<sub>2</sub>. The reaction mixture was then heated at 150 °C under N<sub>2</sub> 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 (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. Purification by flash chromatography afforded the desired products **YKP03**.

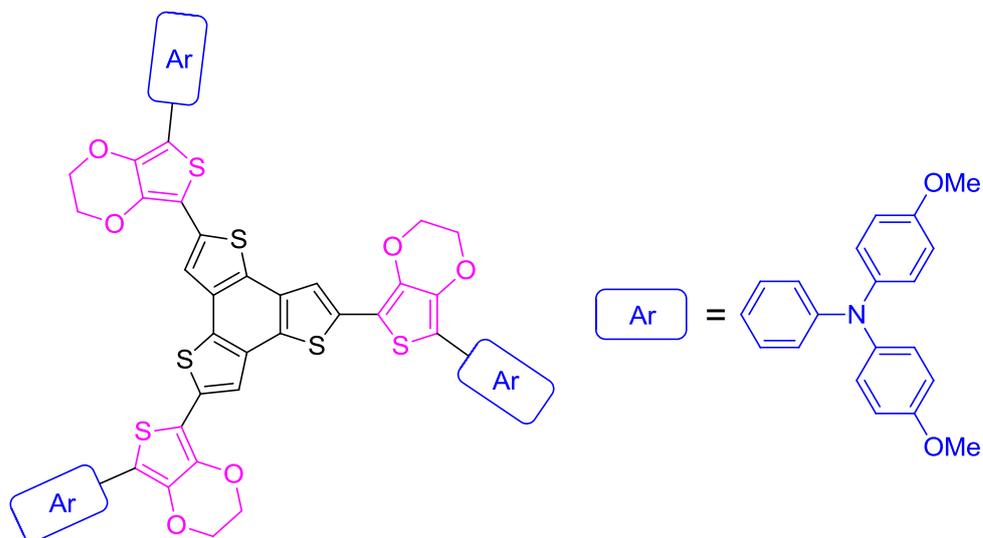


**(BTT-3)**<sup>1</sup> was prepared from benzotrithiophene<sup>2</sup> (**BTT**) (**1a**) (74 mg, 0.30 mmol), **2a** (403 mg, 1.05 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), AcOH (11 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (1 mL) according to **General Procedure A** (150 °C, 30 h) and giving after column chromatography (dichloromethane : ethyl acetate : hexanes = 40 : 5 : 55) the pure product **BTT-3** (246 mg, 71 %). Yellow solid; m.p.: 296.1-297.3 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 7.60 (s, 3 H), 7.56 (d, *J* = 8.7 Hz, 6 H), 7.11 (d, *J* = 8.9 Hz, 12 H), 6.97 (d, *J* = 8.7 Hz, 6 H), 6.86 (d, *J* = 8.9 Hz, 12 H), 3.82 (s, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 156.1, 148.8, 143.6, 140.5, 132.5, 129.6, 126.9, 126.8, 126.0, 120.2, 116.0, 114.8, 55.5.



**(YKP06)** was prepared from benzotrithiophene (**BTT**) (**1a**) (74 mg, 0.30 mmol), **2c** (489 mg, 1.05 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), P(*o*-tolyl)<sub>3</sub> (27 mg, 0.09 mmol), AcOH (11 mg, 0.18 mmol), K<sub>2</sub>CO<sub>3</sub> (149 mg, 1.08 mmol), and DMF (1 mL) according to **General Procedure A** (150 °C, 30 h) and giving after column chromatography (dichloromethane : hexanes = 75 : 25) the pure product **YKP06** (185 mg, 44 %). Yellow solid; m.p.: 181.2-183.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ

7.31 (d,  $J = 8.5$  Hz, 6 H), 7.22 (s, 3 H), 7.04-7.07 (comp, 15 H), 6.95 (d,  $J = 3.6$  Hz, 3 H), 6.88 (d,  $J = 8.5$  Hz, 6 H), 6.84 (d,  $J = 8.9$  Hz, 12 H), 3.80 (s, 18 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, ppm):  $\delta$  155.9, 148.1, 144.1, 140.5, 136.6, 134.9, 131.5, 129.5, 126.7, 126.2, 125.9, 125.4, 122.2, 120.2, 116.7, 114.7, 55.4; HRMS (MALDI): calcd. for  $\text{C}_{84}\text{H}_{63}\text{N}_3\text{O}_6\text{S}_6$ : 1401.3036, found: 1401.3052 ( $\text{M}^+$ ).

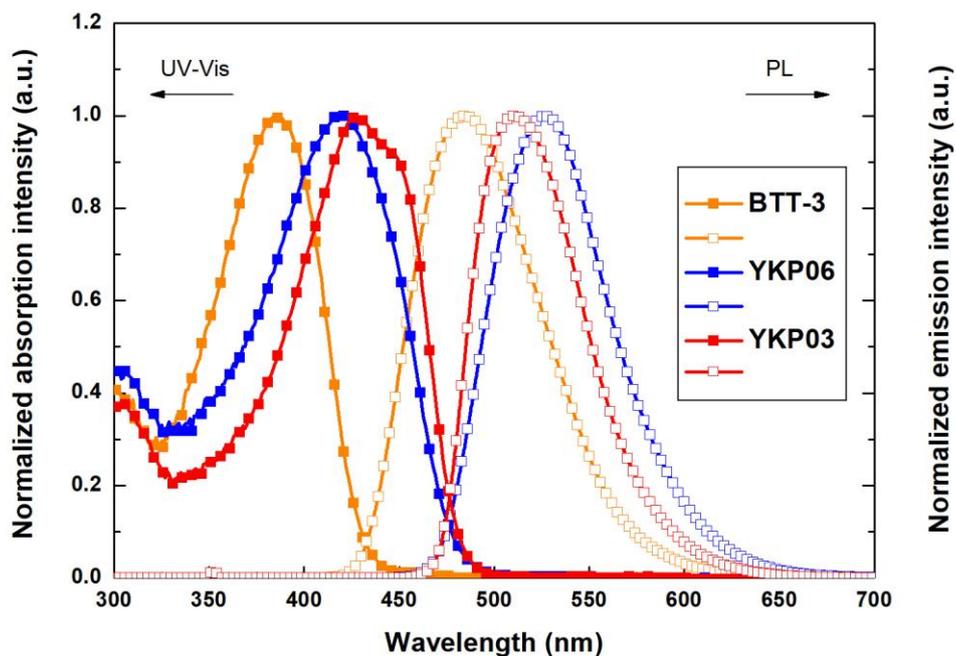


(**YKP03**) was prepared from tribromobenzotrithiophene<sup>1</sup> (**1b**) (242 mg, 0.50 mmol), **2d**<sup>3</sup> (780 mg, 1.75 mmol),  $\text{Pd}(\text{OAc})_2$  (17 mg, 0.075 mmol),  $\text{P}(o\text{-tolyl})_3$  (46 mg, 0.15 mmol),  $\text{PivOH}$  (31 mg, 0.30 mmol),  $\text{K}_2\text{CO}_3$  (248 mg, 1.80 mmol), and DMF (3 mL) according to **General Procedure B** (150 °C, 30 h) and giving after column chromatography (dichloromethane : ethyl acetate : hexanes = 50 : 4 : 46) the pure product **YKP03** (481 mg, 61 %). Yellow solid; m.p.: 340.6-341.5 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  7.50 (d,  $J = 8.5$  Hz, 6 H), 7.39 (s, 3 H), 7.06 (d,  $J = 8.7$  Hz, 12 H), 6.90 (d,  $J = 8.5$  Hz, 6 H), 6.83 (d,  $J = 8.7$  Hz, 12 H), 4.35 (app s, 6 H), 4.23 (app s, 6 H), 3.79 (s, 18 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, ppm):  $\delta$  155.8, 147.1, 140.7, 138.7, 137.1, 133.7, 131.0, 128.9, 126.7, 126.4, 125.0, 120.5, 116.1, 115.8, 114.6, 109.2, 64.8, 64.5, 55.4; HRMS (MALDI): calcd. for  $\text{C}_{90}\text{H}_{69}\text{N}_3\text{O}_{12}\text{S}_6$ : 1576.3278, found: 1576.3262 ( $[\text{M}+\text{H}]^+$ ).

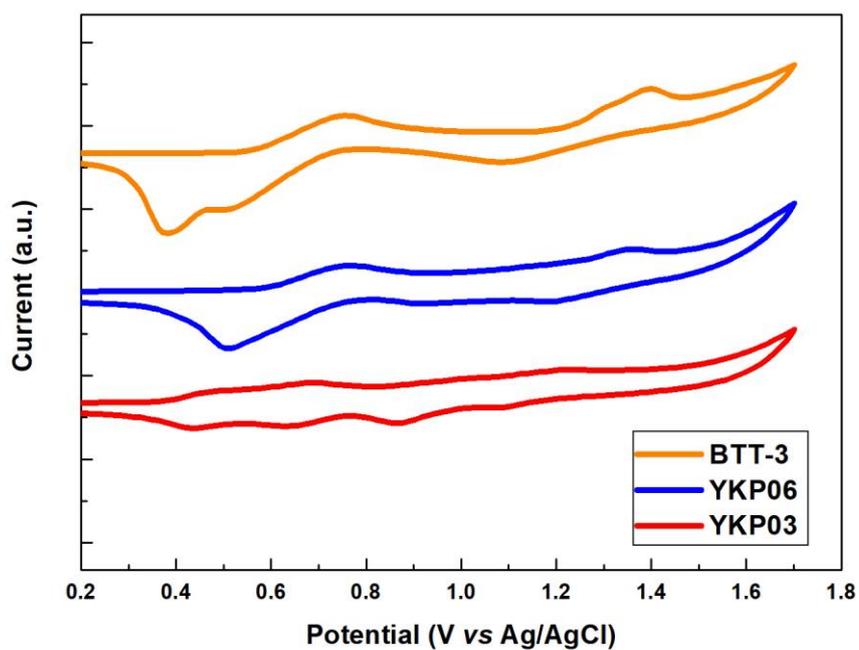
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1. Molina-Ontoria, A.; Zimmermann, I.; Garcia-Benito, I.; Gratia, P.; Roldán-Carmona, C.; Aghazada, S.; Grätzel, M.; Nazeeruddin, M. K.; Martín, N. *Angew. Chem. Int. Ed.* **2016**, *55*, 6270.
2. Zou, S.; Wang, Y.; Gao, J.; Liu, X.; Hao, W.; Zhang, H.; Zhang, H.; Xie, H.; Yang, C.; Li, H.; Hu, W. *J. Mater. Chem. C*, **2014**, *2*, 10011.
3. Chang, Y.-C.; Lee, K.-M.; Lai, C.-H.; Liu, C.-Y. *Chem. Asian J.* **2018**, *13*, 1510.

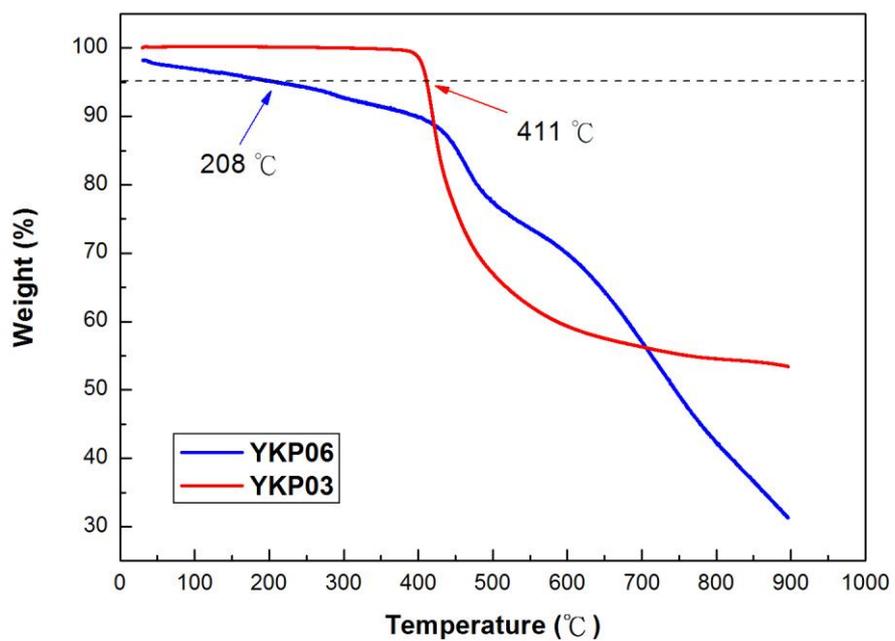
**Figure S1.** The UV-Vis absorption and photoluminescence spectra of **BTT-3**, **YKP06**, and **YKP03** in  $\text{CH}_2\text{Cl}_2$  solution.



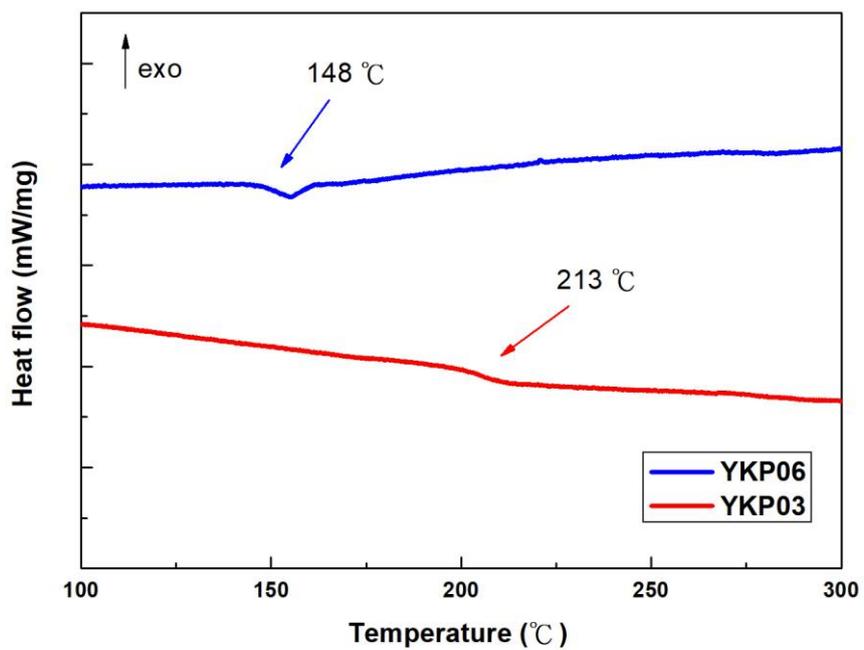
**Figure S2.** Cyclic voltammetry spectra of **BTT-3**, **YKP06**, and **YKP03** in  $\text{CH}_2\text{Cl}_2$  solution.



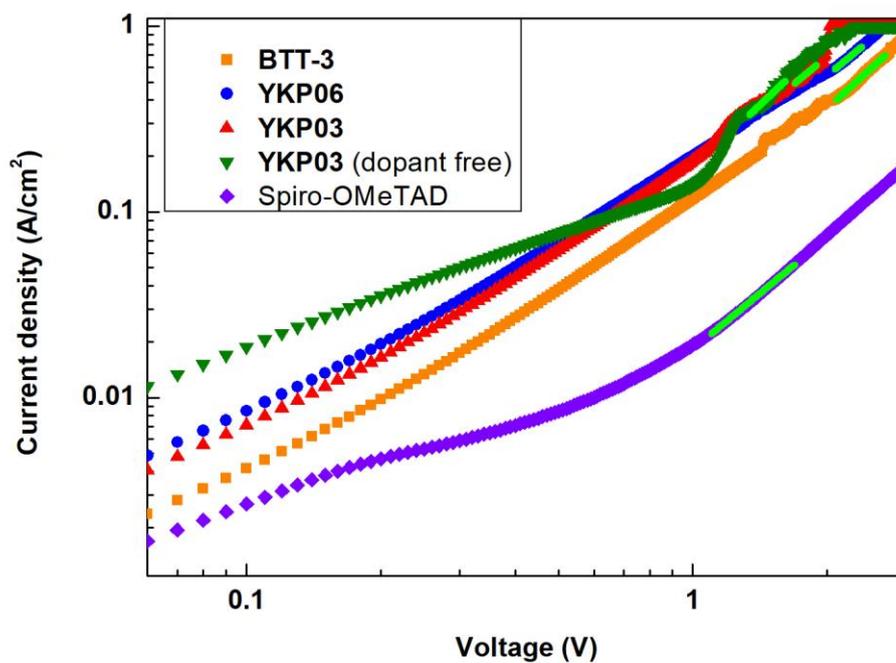
**Figure S3.** Thermogravimetric analysis curves of **YKP06** and **YKP03**.



**Figure S4.** Differential scanning calorimetry curves of **YKP06** and **YKP03**.

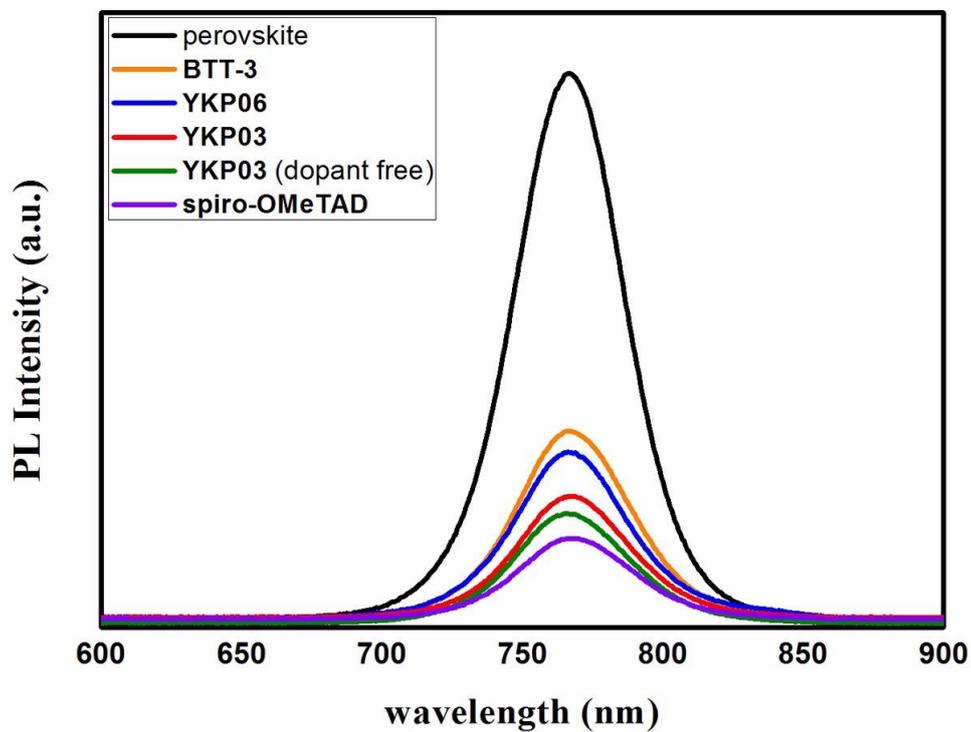


**Figure S5.** J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region.

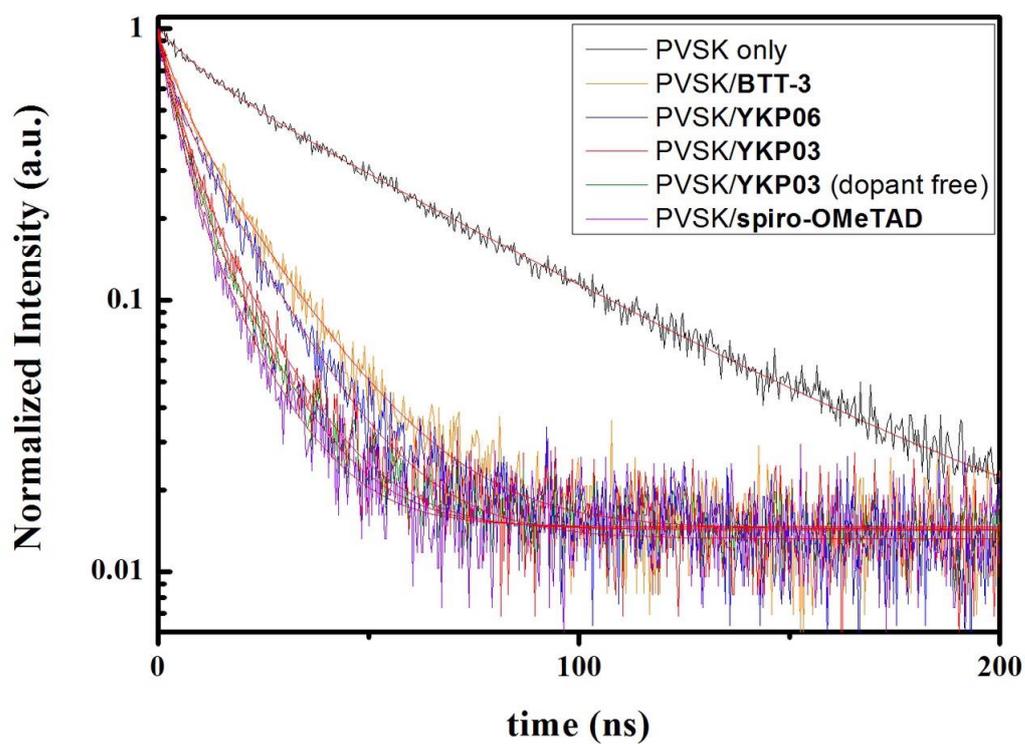


HTMs	hole mobility, $\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
<b>BTT-3</b>	$2.66 \times 10^{-4}$
<b>YKP06</b>	$4.53 \times 10^{-4}$
<b>YKP03</b>	$5.80 \times 10^{-4}$
<b>YKP03 (dopant-free)</b>	$5.74 \times 10^{-4}$
<b>spiro-OMeTAD</b>	$6.48 \times 10^{-4}$

**Figure S6.** Steady-state PL spectra of the devices fabricated as glass/perovskite/HTMs.

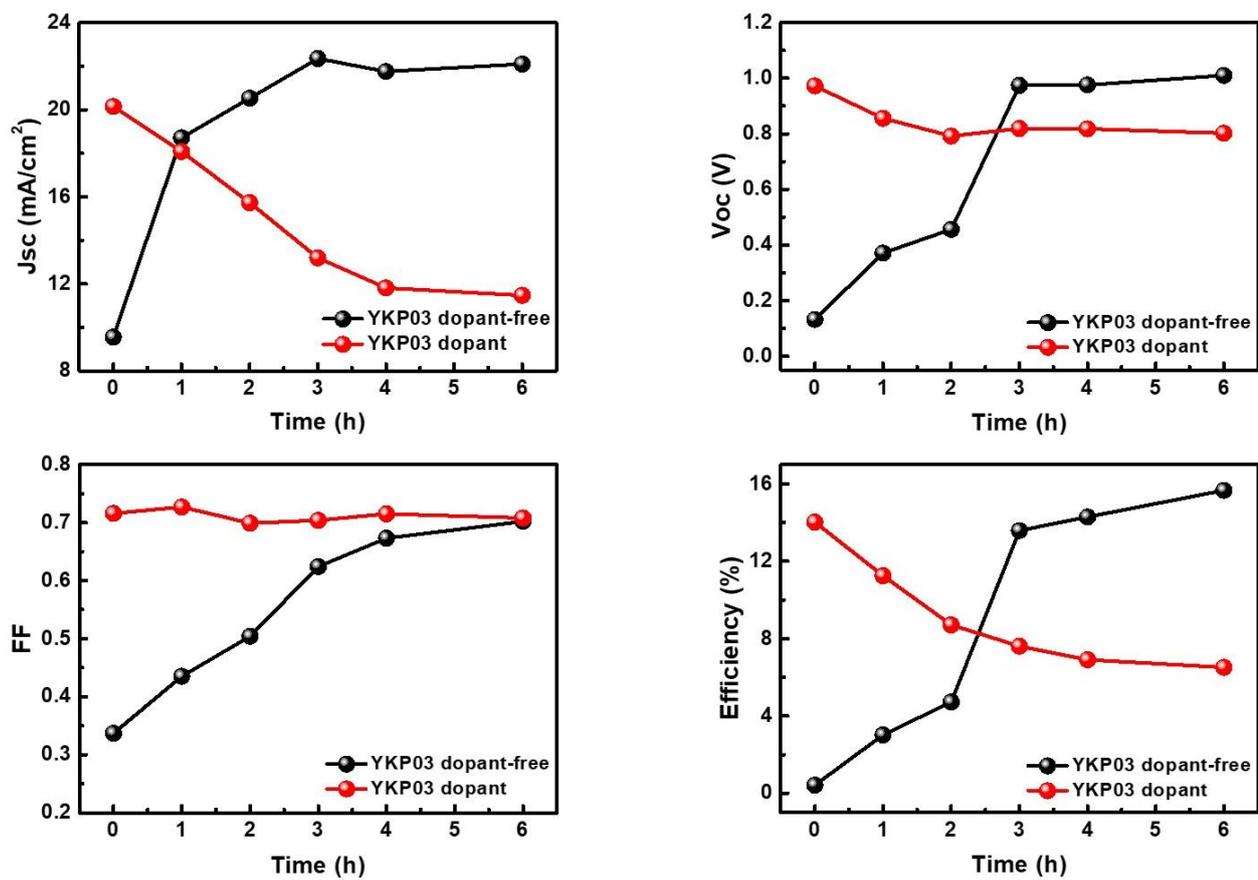


**Figure S7.** Time-resolved PL spectra of the devices fabricated as glass/perovskite/HTMs.

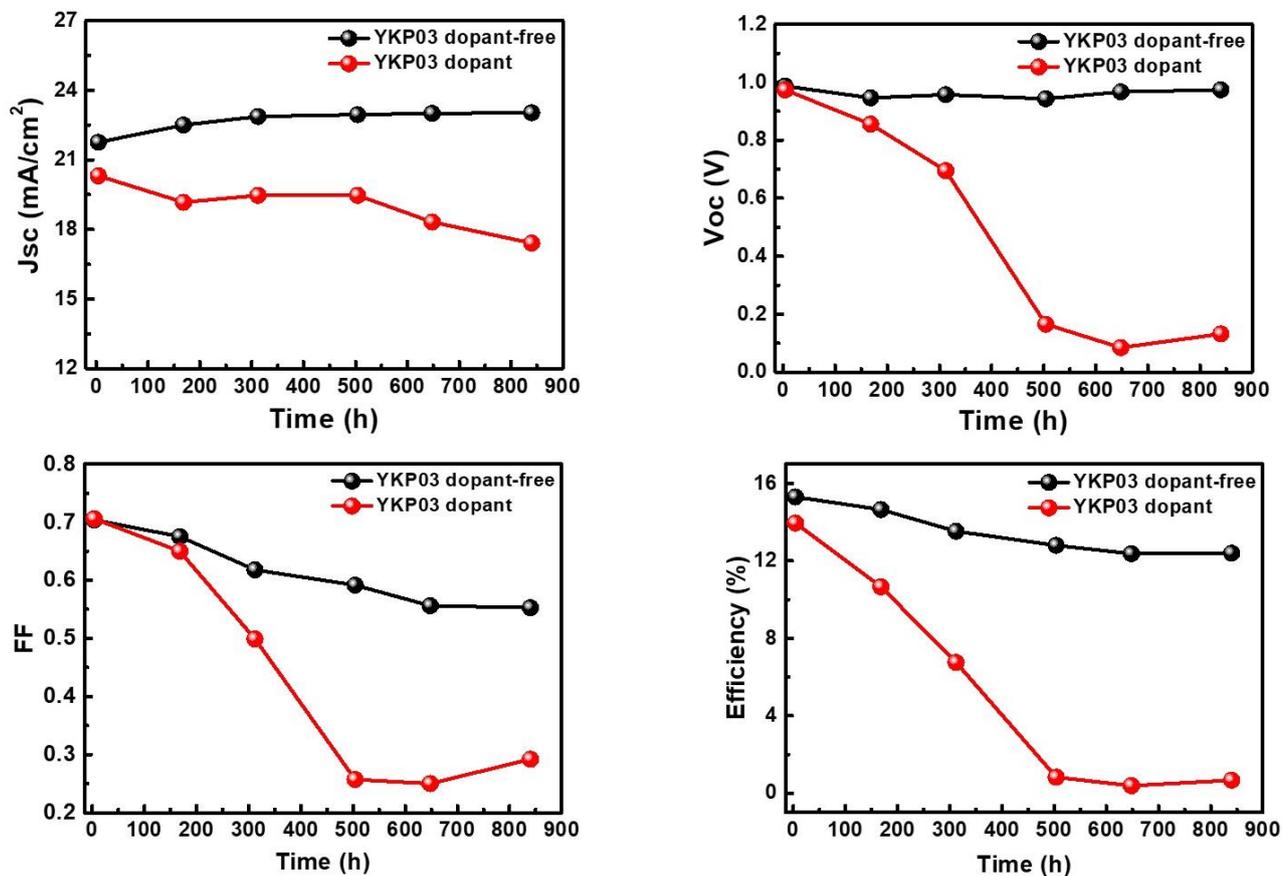


Sample	$A_1$ (%)	$\tau_1$ (ns)	$A_2$ (%)	$\tau_2$ (ns)	$\tau_{avg}$ (ns)
perovskite only	24.5	10.10	75.5	51.44	41.31
perovskite / <b>BTT-3</b>	37.8	4.79	62.2	17.97	12.99
perovskite / <b>YKP06</b>	70.7	14.87	29.3	2.84	11.35
perovskite / <b>YKP03</b>	47.8	13.29	52.2	4.11	8.50
perovskite / <b>YKP03</b> (dopant-free)	56.7	4.06	43.3	12.8	7.84
perovskite / <b>spiro-OMeTAD</b>	39.0	12.11	61.0	4.01	7.17

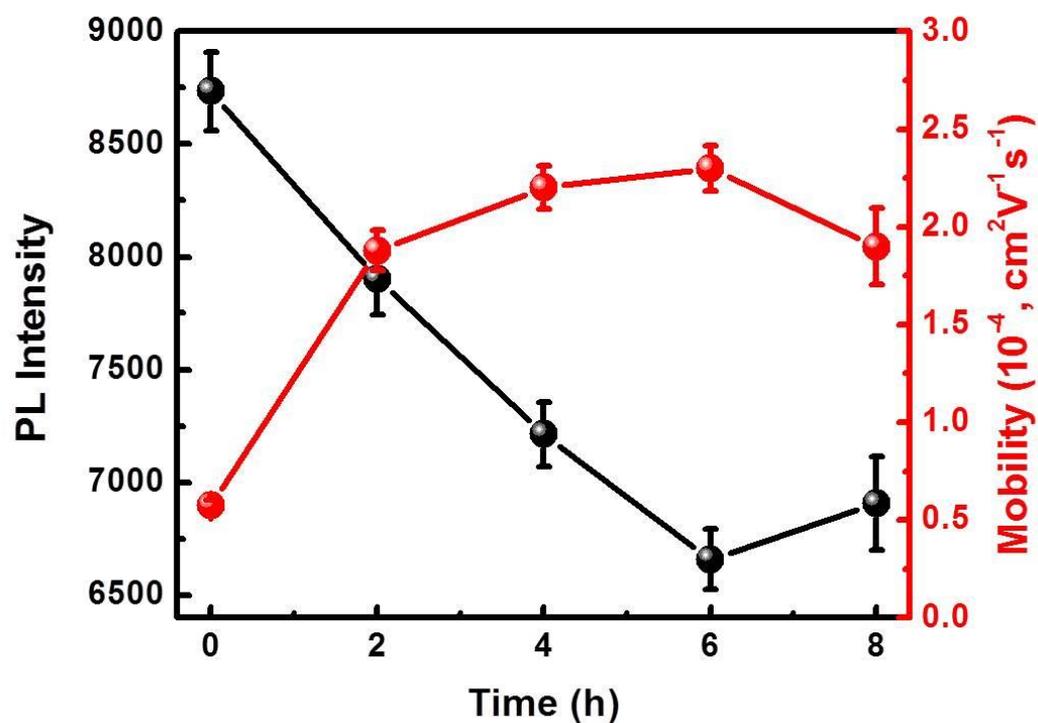
**Figure S8.** The influence of device oxidation time on photovoltaic characteristics of the perovskite solar cells based on **YKP03** with the conditions of dopants vs. dopant-free (under ambient atmosphere:  $25\pm 2$  °C and 50~70% RH).



**Figure S9.** Long-term storage stability of the perovskite solar cells based on YKP03 with the conditions of dopants vs. dopant-free (under N<sub>2</sub> in glove box: 25±2 °C and ~5% RH).



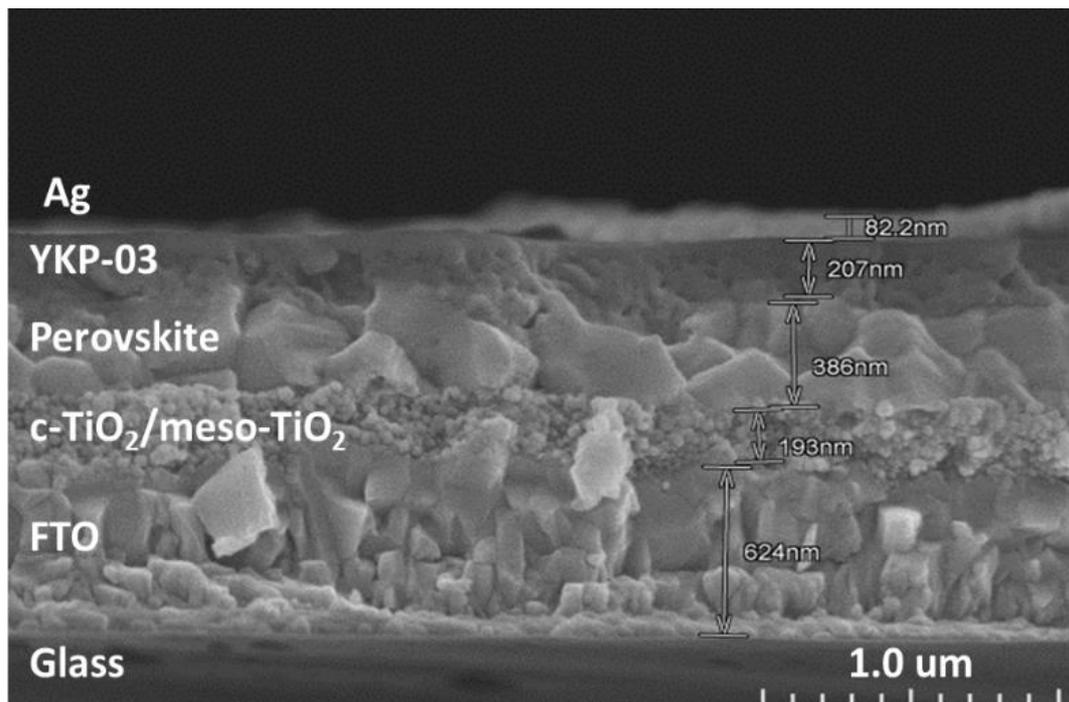
**Figure S10.** Steady-state PL vs. time & the hole-mobility vs. time of dopant-free YKP03 (at  $25\pm 2$  °C and 50% RH).



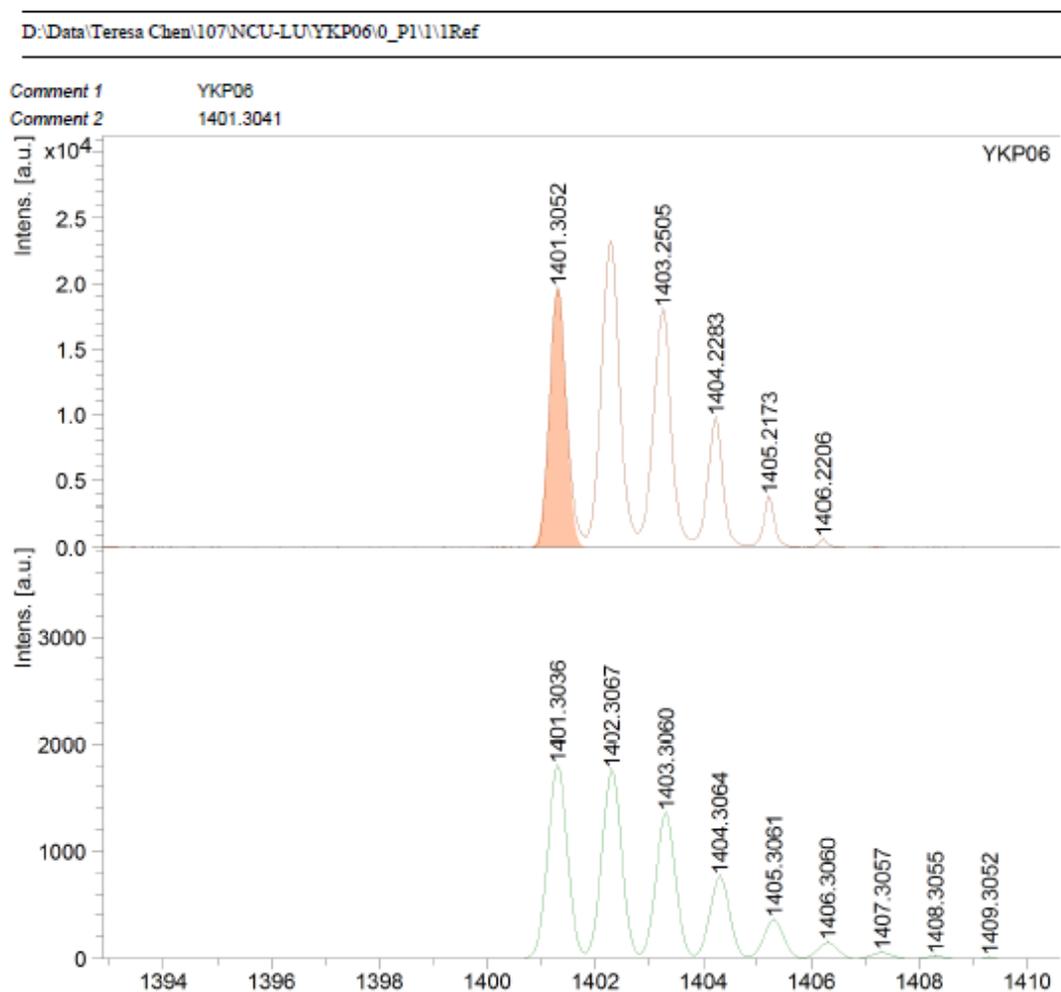
**Black curve:** steady-state PL data obtained based on the device structure of FTO/perovskite/YKP03.

**Red curve:** hole-mobility data obtained using SCLC method based on the device structure of FTO/PEDOT:PSS/ YKP03/Ag.

**Figure S11.** Cross-section SEM image of **YKP03**-based PSC devices (dopant-free).



**Figure S12.** MALDI Spectrum of YKP06.



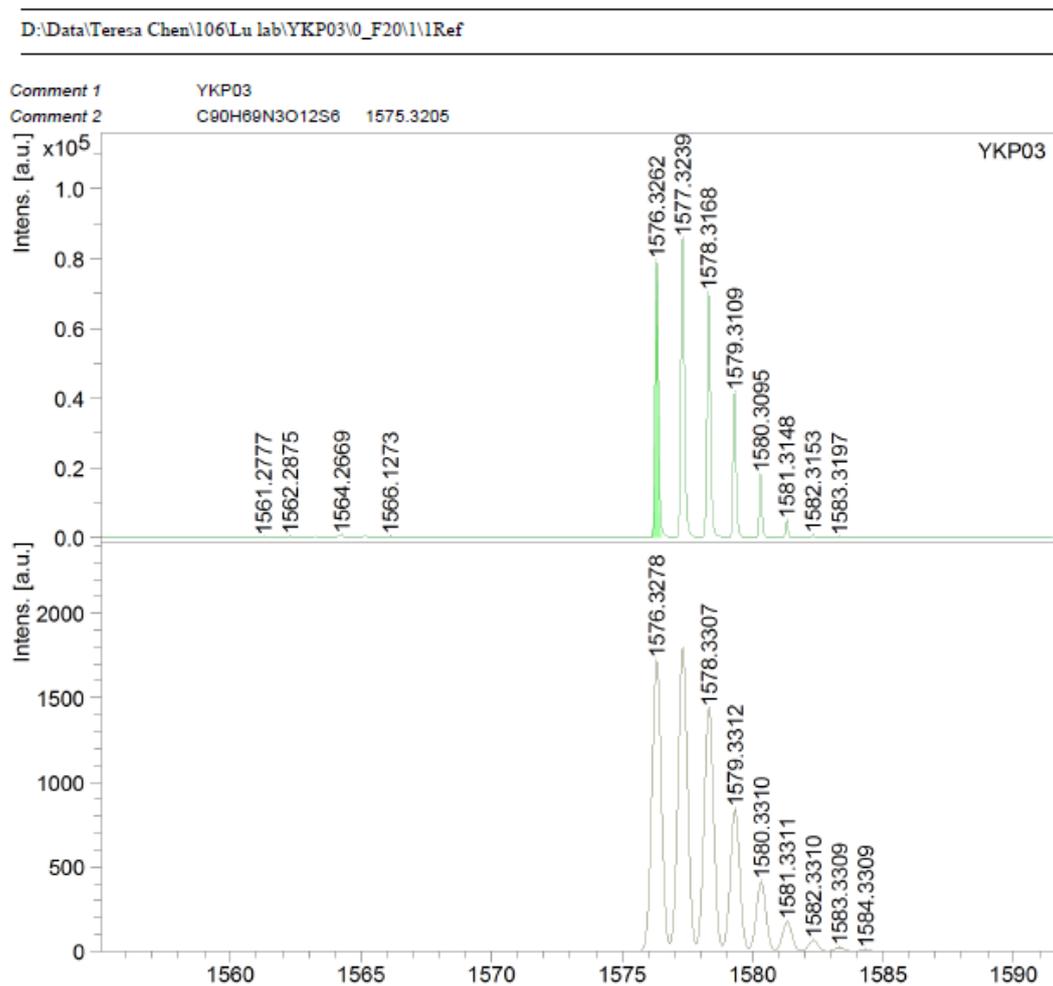
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 Voltage polarity POS  
 Number of shots 1000  
 Name of spectrum used for calibration  
 Calibration reference list used PEG-Na -Calibration Mono\_800-1900Da

**Instrument Info**

User NCU  
 Instrument ATS-00670  
 Instrument type autoflex

**Figure S13. MALDI Spectrum of YKP03.**



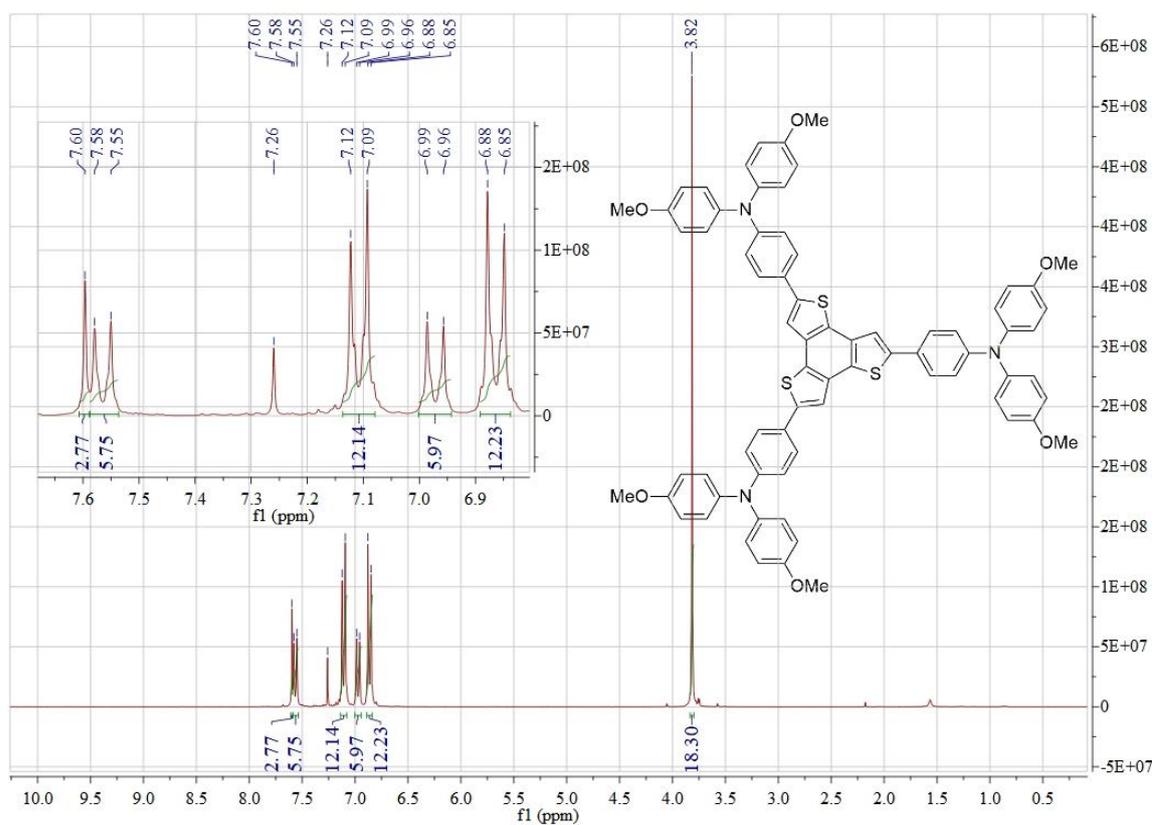
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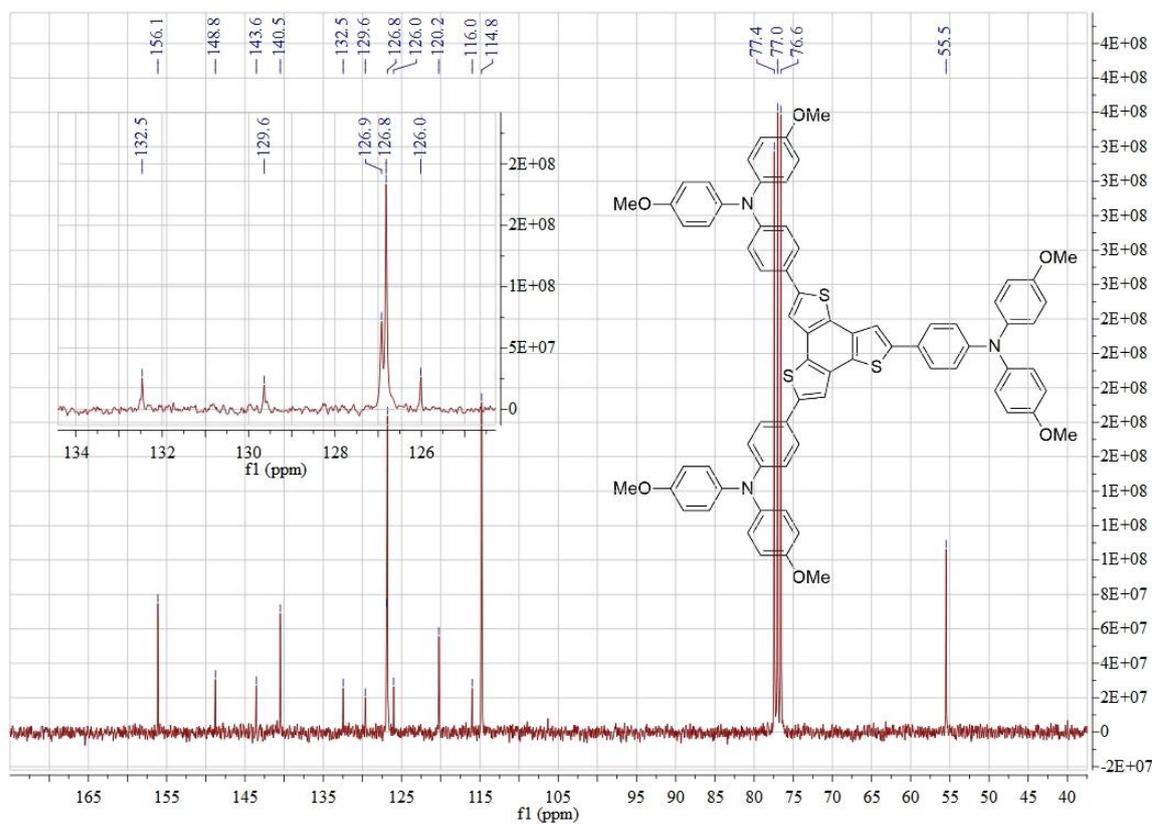
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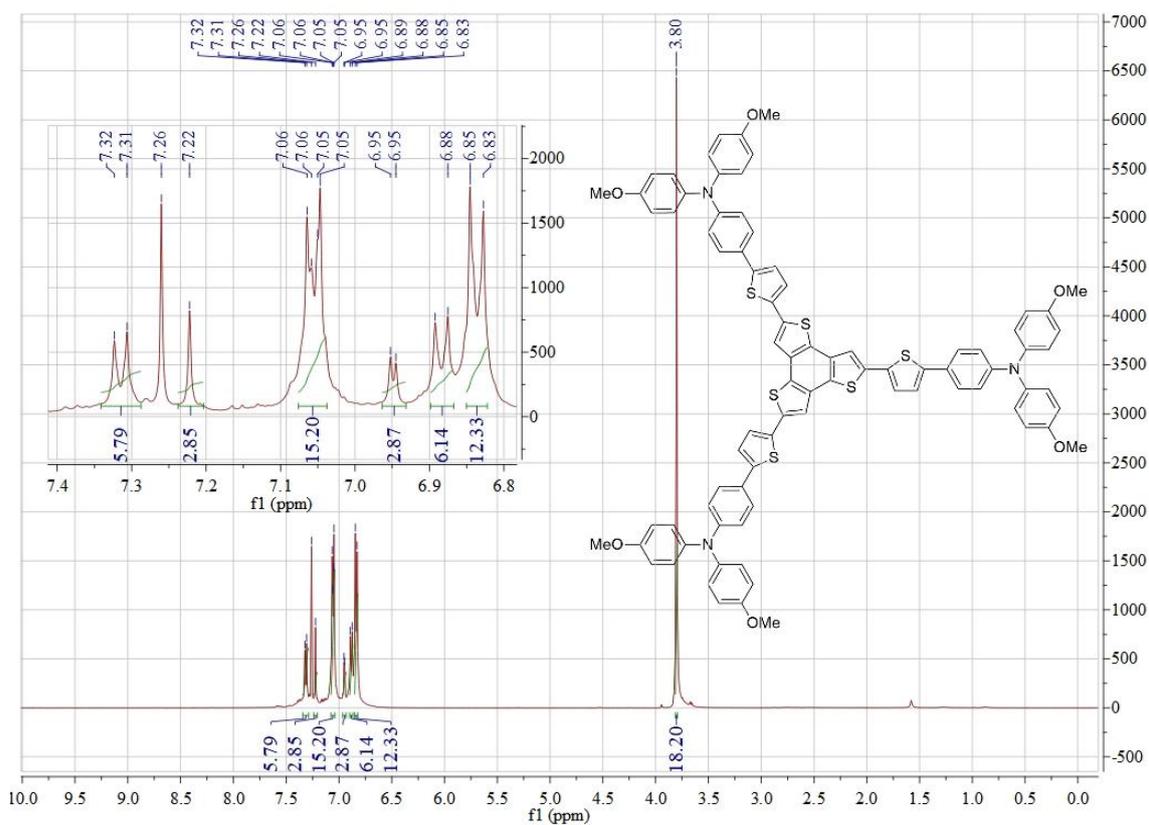
**Figure S14.**  $^1\text{H}$  NMR Spectrum of **BTT-3** (300 MHz,  $\text{CDCl}_3$ )



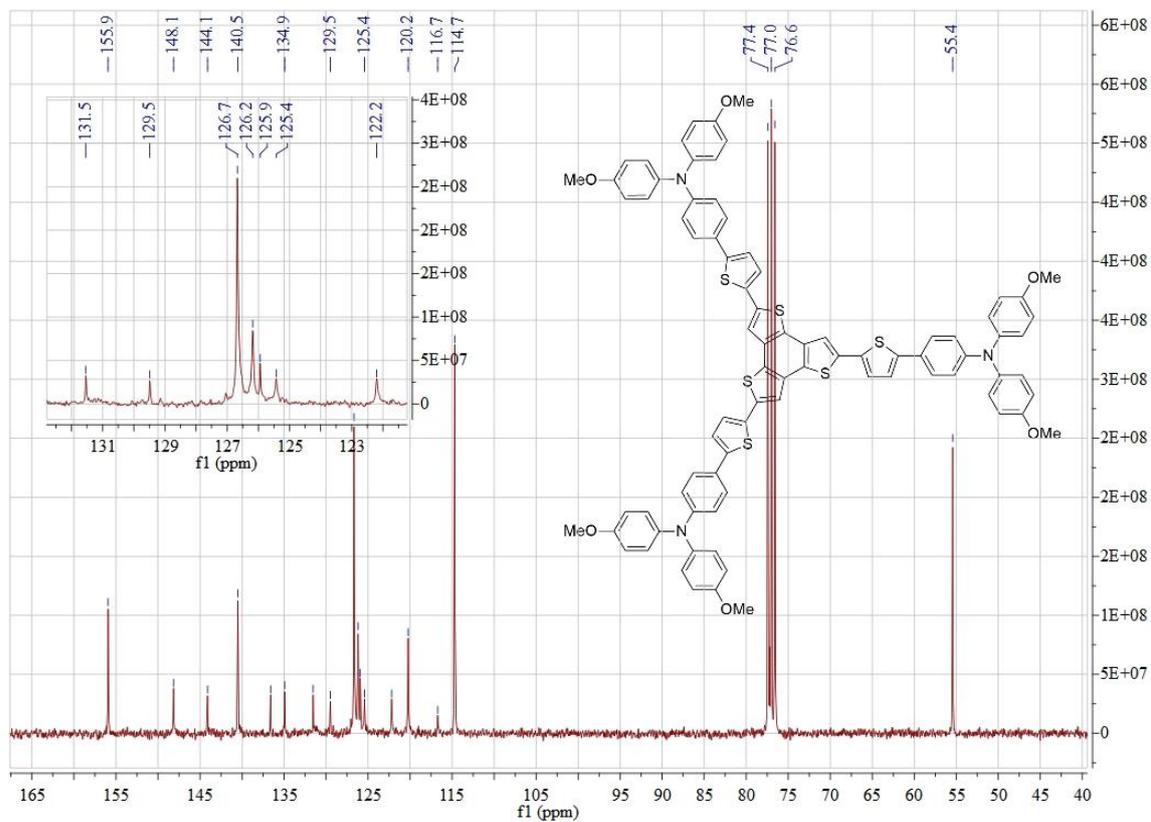
**Figure S15.**  $^{13}\text{C}$  NMR Spectrum of **BTT-3** (75 MHz,  $\text{CDCl}_3$ )



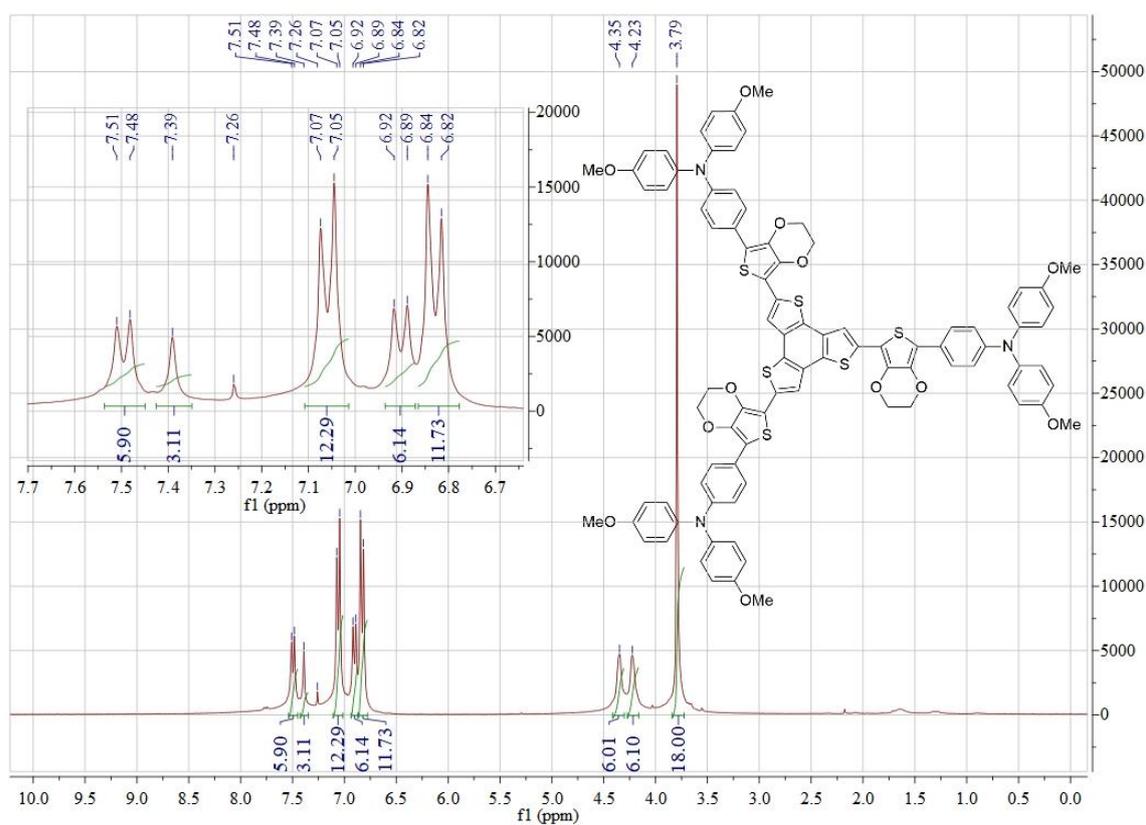
**Figure S16.**  $^1\text{H}$  NMR Spectrum of YKP06 (500 MHz,  $\text{CDCl}_3$ )



**Figure S17.**  $^{13}\text{C}$  NMR Spectrum of YKP06 (75 MHz,  $\text{CDCl}_3$ )



**Figure S18.**  $^1\text{H}$  NMR Spectrum of YKP03 (300 MHz,  $\text{CDCl}_3$ )



**Figure S19.**  $^{13}\text{C}$  NMR Spectrum of YKP03 (75 MHz,  $\text{CDCl}_3$ )

