

## Supporting Information

### One-Pot Synthesis of D- $\pi$ -D- $\pi$ -D Type Hole-Transporting Materials for Perovskite Solar Cells by Sequential C-H (Hetero)arylations

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## General Information

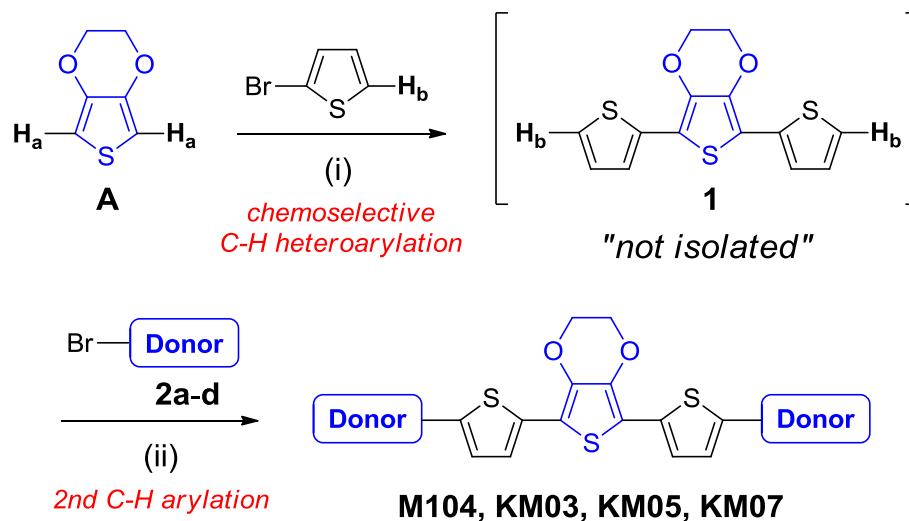
Unless otherwise noted, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Required chemicals such as Pd(OAc)<sub>2</sub>, phosphine ligands, PivOH, AcOH, K<sub>2</sub>CO<sub>3</sub>, and Cs<sub>2</sub>CO<sub>3</sub> are commercially available. Anhydrous 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), CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm for <sup>1</sup>H NMR, 54.0 ppm for <sup>13</sup>C NMR), or DMSO-d<sub>6</sub> (2.50 ppm for <sup>1</sup>H NMR, 39.4 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). Mass spectra were recorded on a JEOL JMS-700 for electron impact ionization (EI) and high resolution mass spectra (HRMS) on a JEOL JMS-700 spectrometers. The samples measured by fast atom bombardment (FAB) techniques were recorded in a 3-nitrobenzyl alcohol- or glycerine-matrix. 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 ( $E_g^{opt}$ ) 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 THF 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  $(E_{pa}+E_{pc})/2$ , where  $E_{pa}$  and  $E_{pc}$  are the potential energy of anodic and cathodic peaks, respectively. The HOMO energy level,  $E_{HOMO}$ , was calculated by  $-(E_{1/2} + 0.197 + 4.500 - 0.177)$  eV (*vs.* Ag/AgCl and NHE);  $E_{LUMO} = E_{HOMO} + E_g^{opt}$ . 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)

Device fabrications of the Perovskite solar cells (PSCs):

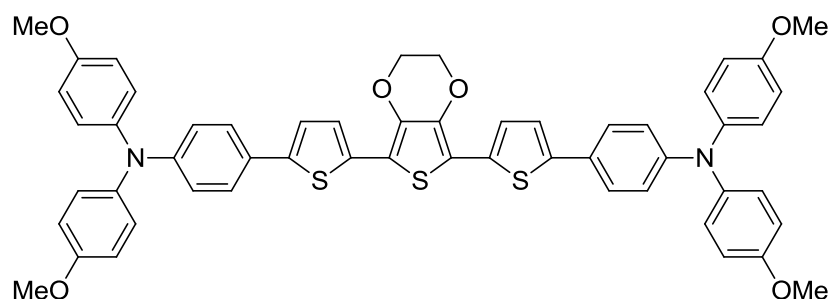
A TiO<sub>2</sub> compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt.% of Ti(acac)<sub>2</sub>O*i*Pr<sub>2</sub> in isopropanol). A 300 nm-thick mesoporous TiO<sub>2</sub> film (TiO<sub>2</sub> 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 cooled to room temperature, the substrate/films were transferred to a nitrogen-filled glove box. A solution consisting of PbI<sub>2</sub> (1.25 M) and CH<sub>3</sub>NH<sub>3</sub>I (1.25 M) in  $\gamma$ -butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the substrate/films by a two-step spin-coating process at 1000 and 5000 rpm for 10 and 20 sec, respectively. During the second spin-coating step, the substrate/films were treated with 50  $\mu$ L toluene drop-casting. The substrate/films were dried on a hot plate at 100 °C for 10 min. **M104**, **KM03**, **KM05**, **KM07**, and **Spiro-OMeTAD** (as reference cell) was dissolved in chlorobenzene (50 mg/mL), respectively. Each solution was heated to 80~90 °C for 20 min. Next on, 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 from previous step. This as-prepared HTM solution was spin-coated onto the substrate/films at 2000 rpm for 30 sec. In certain cases, the MoO<sub>3</sub> was deposited by thermal evaporation (~10 nm). 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>.

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 mW/cm<sup>2</sup>. 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).

## Two-Step in One-Pot Synthesis of D- $\pi$ -D- $\pi$ -D HTMs: M104, KM03, KM05, and KM07:

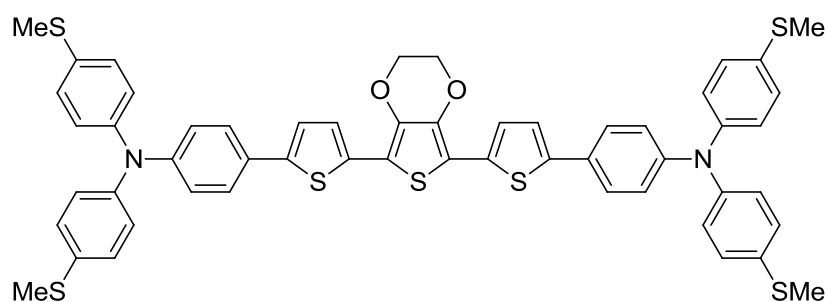


To a solution of Pd(OAc)<sub>2</sub> (0.10 mmol), P(Cy)<sub>3</sub> (0.20 mmol), PivOH (0.30 mmol), and K<sub>2</sub>CO<sub>3</sub> (3.00 mmol) in DMF (3 mL) in a flame-dried Schlenk tube were added ethylenedioxythiophene (EDOT) (A) (1.00 mmol) and 2-bromothiophene (2.20 mmol) under N<sub>2</sub>. The reaction mixture was then heated at 100 °C under N<sub>2</sub> for 3 h. After the oil bath had been removed, the corresponding donor-type aryl bromides **2a-d** (2.20 mmol) and additional K<sub>2</sub>CO<sub>3</sub> (3.00 mmol) were added to the reaction mixture which was then heated again to 100 °C and stirred at the same temperature under N<sub>2</sub> for another 24 hours. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate or 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 gave the desired products **M104**, **KM03**, **KM05**, and **KM07**.

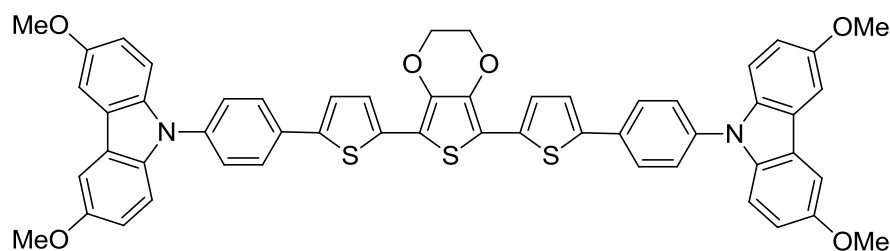


(**M104**)<sup>1</sup> was prepared from EDOT (A) (142 mg, 1.00 mmol), 2-bromothiophene (359 mg, 2.20 mmol), 4-bromo-*N,N*-bis(4-methoxyphenyl)aniline (**2a**) (845 mg, 2.20 mmol), Pd(OAc)<sub>2</sub> (24 mg, 0.10 mmol), P(Cy)<sub>3</sub> (56 mg, 0.20 mmol), PivOH (31 mg,

0.30 mmol), K<sub>2</sub>CO<sub>3</sub> (414 mg, 3.00 mmol, for each addition), and DMF (3 mL) according to the general procedure and giving after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **M104** (383 mg, 60 %, calculated based on the 70% conversion from **A** to **1**). Red solid; m.p.: 128.2-129.4 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, ppm): δ 7.43 (d, *J* = 8.0 Hz, 4 H), 7.24 (d, *J* = 3.0 Hz, 2 H), 7.15 (app s, 2 H), 7.03 (d, *J* = 8.5 Hz, 8 H), 6.91 (d, *J* = 8.5 Hz, 8 H), 6.76 (d, *J* = 8.0 Hz, 4 H), 4.42 (s, 4 H), 3.74 (s, 12 H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz, ppm): δ 155.9, 147.9, 142.0, 139.7, 137.6, 131.4, 126.8, 125.9, 125.1, 123.9, 122.3, 119.3, 115.0, 108.2, 65.0, 55.2; MS (FAB): 912 ([M-1]<sup>+</sup>, 5 %), 647 (2 %), 77 (100 %); HRMS (FAB): calcd. for C<sub>54</sub>H<sub>44</sub>N<sub>2</sub>O<sub>6</sub>S<sub>3</sub>: 912.2361, found: 912.2369.

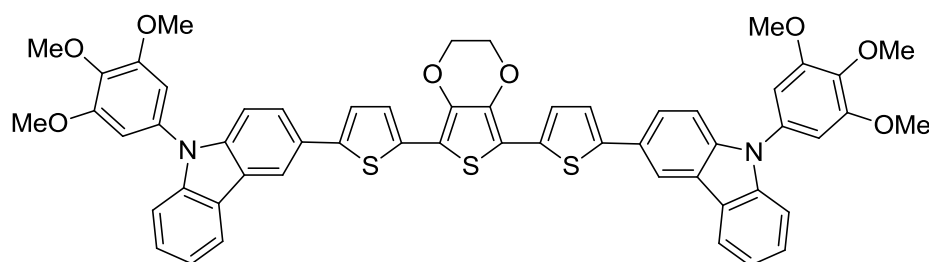


(**KM03**) was prepared from EDOT (**A**) (142 mg, 1.00 mmol), 2-bromothiophene (359 mg, 2.20 mmol), 4-bromo-*N,N*-bis(4-(methylthio)phenyl)aniline (**2b**) (915 mg, 2.20 mmol), Pd(OAc)<sub>2</sub> (24 mg, 0.10 mmol), P(Cy)<sub>3</sub> (56 mg, 0.20 mmol), PivOH (31 mg, 0.30 mmol), K<sub>2</sub>CO<sub>3</sub> (414 mg, 3.00 mmol, for each addition), and DMF (3 mL) according to the general procedure and giving after column chromatography (dichloromethane : hexanes = 50 : 50) the pure product **KM03** (212 mg, 31 %, calculated based on the 70% conversion from **A** to **1**). Orange solid; m.p.: 134.1-136.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 7.45 (d, *J* = 8.6 Hz, 4 H), 7.13-7.20 (comp, 12 H), 7.01-7.06 (comp, 12 H), 4.40 (s, 4 H), 2.48 (s, 12 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 146.6, 144.8, 142.2, 137.5, 133.0, 132.1, 128.4, 126.3, 124.8, 123.8, 123.4, 122.4, 109.7, 64.9, 16.7; MS (FAB): 978 ([M+1]<sup>+</sup>, 1 %), 713 (4 %), 393 (5 %), 89 (100 %); HRMS (FAB): calcd. for C<sub>54</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>S<sub>7</sub>: 976.1448, found: 976.1450.



(**KM05**) was prepared from EDOT (**A**) (142 mg, 1.00 mmol), 2-bromothiophene (359

mg, 2.20 mmol), 9-(4-bromophenyl)-3,6-dimethoxy-9*H*-carbazole (**2c**) (840 mg, 2.20 mmol), Pd(OAc)<sub>2</sub> (24 mg, 0.10 mmol), P(Cy)<sub>3</sub> (56 mg, 0.20 mmol), PivOH (31 mg, 0.30 mmol), K<sub>2</sub>CO<sub>3</sub> (414 mg, 3.00 mmol, for each addition), and DMF (3 mL) according to the general procedure and giving after column chromatography (ethyl acetate : dichloromethane : hexanes = 10 : 50 : 40) the pure product **KM05** (292 mg, 46 %, calculated based on the 70% conversion from **A** to **1**). Yellow solid; m.p.: 202.5-205.1 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 7.78 (d, *J* = 8.4 Hz, 4 H), 7.57 (d, *J* = 2.5 Hz, 4 H), 7.53 (d, *J* = 8.4 Hz, 4 H), 7.38 (d, *J* = 8.9 Hz, 4 H), 7.30 (d, *J* = 3.8 Hz, 2 H), 7.23 (d, *J* = 3.8 Hz, 2 H), 7.06 (dd, *J* = 8.9, 2.5 Hz, 4 H), 4.43 (s, 4 H), 3.96 (s, 12 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 154.0, 141.5, 137.8, 137.1, 136.0, 134.1, 132.7, 126.8, 126.6, 123.9, 123.7, 115.2, 114.9, 110.7, 109.8, 102.8, 65.0, 56.0; MS (FAB): 908 ([M-1]<sup>+</sup>, 14 %), 648 (8 %), 109 (6 %), 81 (100 %); HRMS (FAB): calcd. for C<sub>54</sub>H<sub>40</sub>N<sub>2</sub>O<sub>6</sub>S<sub>3</sub>: 908.2048, found: 908.2054.

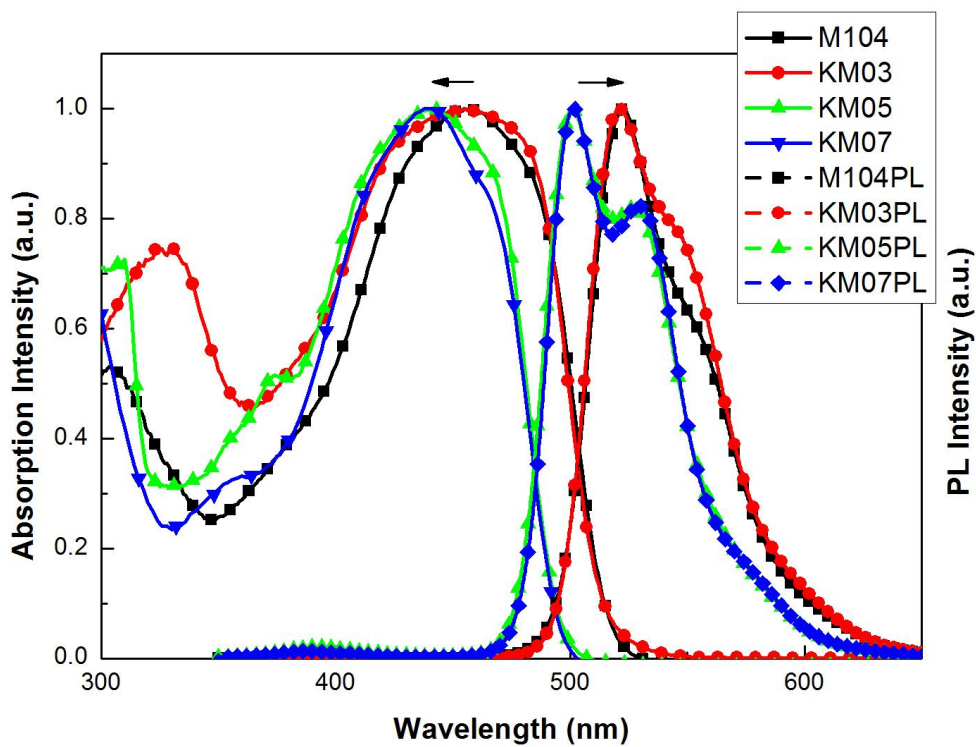


(**KM07**) was prepared from EDOT (**A**) (142 mg, 1.00 mmol), 2-bromothiophene (359 mg, 2.20 mmol), 3-bromo-9-(3,4,5-trimethoxyphenyl)-9*H*-carbazole (**2d**) (906 mg, 2.20 mmol), Pd(OAc)<sub>2</sub> (24 mg, 0.10 mmol), P(Cy)<sub>3</sub> (56 mg, 0.20 mmol), PivOH (31 mg, 0.30 mmol), K<sub>2</sub>CO<sub>3</sub> (414 mg, 3.00 mmol, for each addition), and DMF (3 mL) according to the general procedure and giving after column chromatography (ethyl acetate : hexanes = 30 : 70) the pure product **KM07** (224 mg, 33 %, calculated based on the 70% conversion from **A** to **1**). Light brown solid; m.p.: 148.3-151.5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 8.38 (d, *J* = 1.5 Hz, 2 H), 8.19 (d, *J* = 7.7 Hz, 2 H), 7.71 (dd, *J* = 8.6, 1.7 Hz, 2 H), 7.39-7.47 (comp, 6 H), 7.29-7.36 (comp, 4 H), 7.24 (d, *J* = 3.8 Hz, 2 H), 6.78 (s, 4 H), 4.48 (s, 4 H), 3.99 (s, 6 H), 3.89 (s, 12 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 154.1, 143.7, 141.5, 140.5, 137.43, 137.35, 133.0, 132.8, 126.6, 126.3, 124.2, 123.9, 123.7, 123.1, 122.4, 120.5, 120.1, 117.4, 110.2, 110.0, 109.7, 104.4, 65.1., 61.0, 56.3; MS (FAB): 968 ([M-1]<sup>+</sup>, 5 %), 662 (5 %), 107 (62 %), 77 (100 %); HRMS (FAB): calcd. for C<sub>56</sub>H<sub>44</sub>N<sub>2</sub>O<sub>8</sub>S<sub>3</sub>: 968.2260, found: 968.2253.

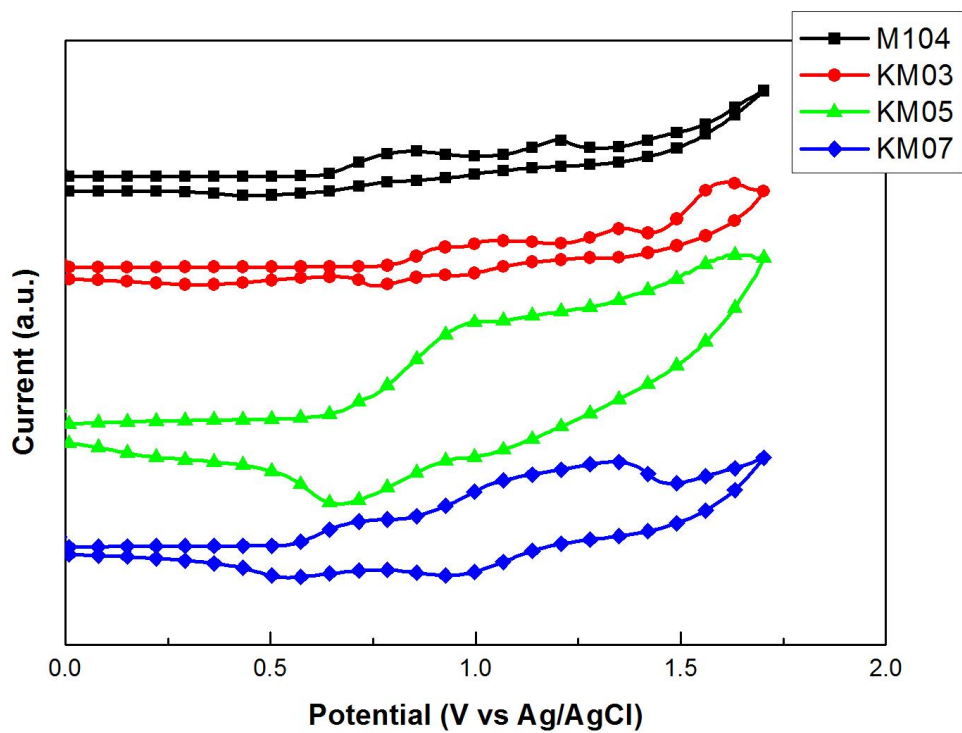
## References:

1. Y. Wu, Z. Wang, M. Liang, H. Cheng, M. Li, L. Liu, B. Wang, J. Wu, R. P. Ghimire, X. Wang, Z. Sun, S. Xue, Q. Qiao, *Acs Appl. Mater. Interfaces* **2018**, *10*, 17883.

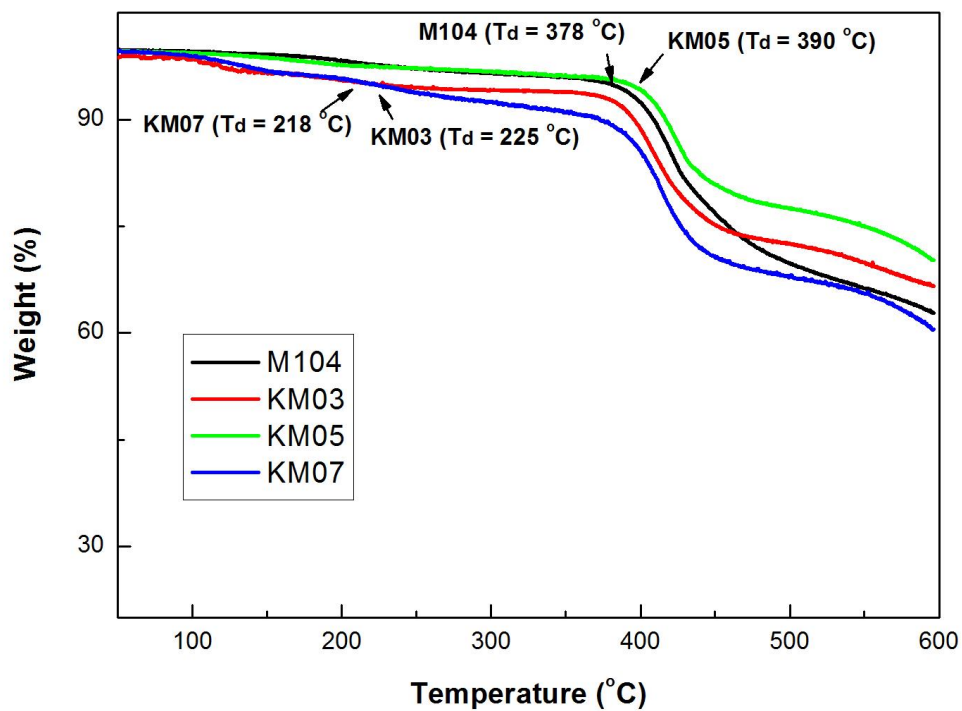
**Figure S1.** The UV-Vis absorption and photoluminescence spectra of **M104**, **KM03**, **KM05** and **KM07** in THF solution.



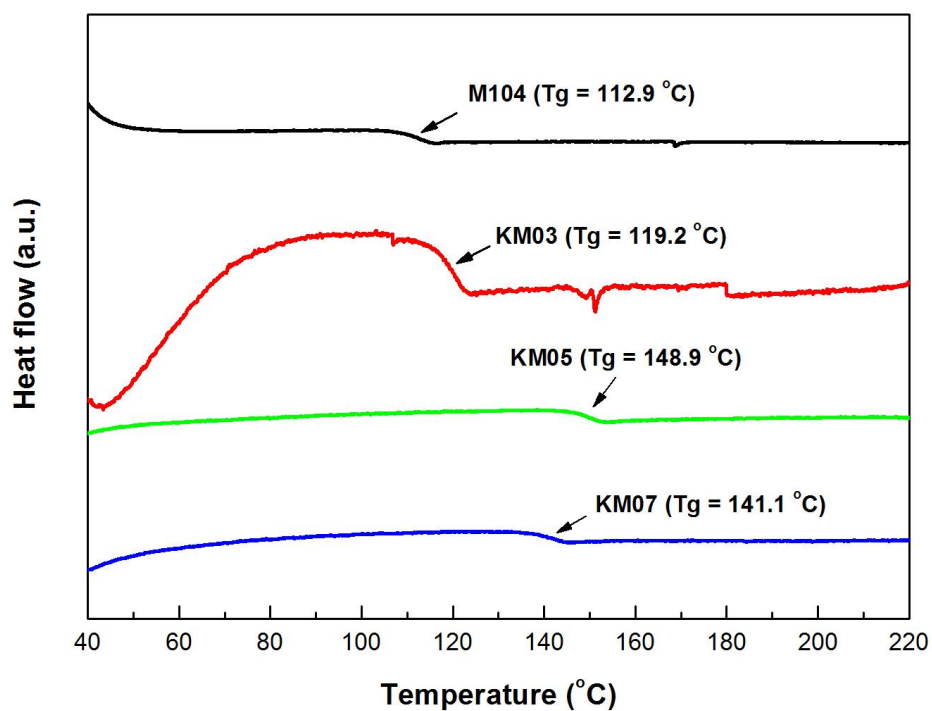
**Figure S2.** Cyclic voltammetry spectra of **M104**, **KM03**, **KM05** and **KM07** in THF solution.



**Figure S3.** Thermogravimetric analysis curves of **M104**, **KM03**, **KM05** and **KM07**.

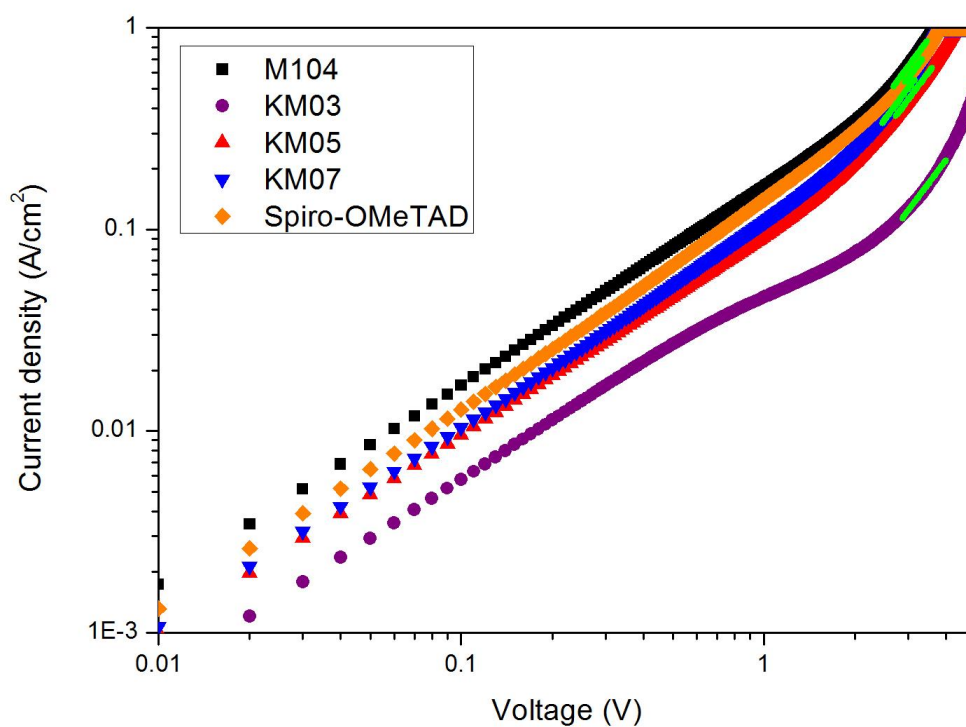


**Figure S4.** Differential scanning calorimetry curves of **M104**, **KM03**, **KM05** and **KM07**.



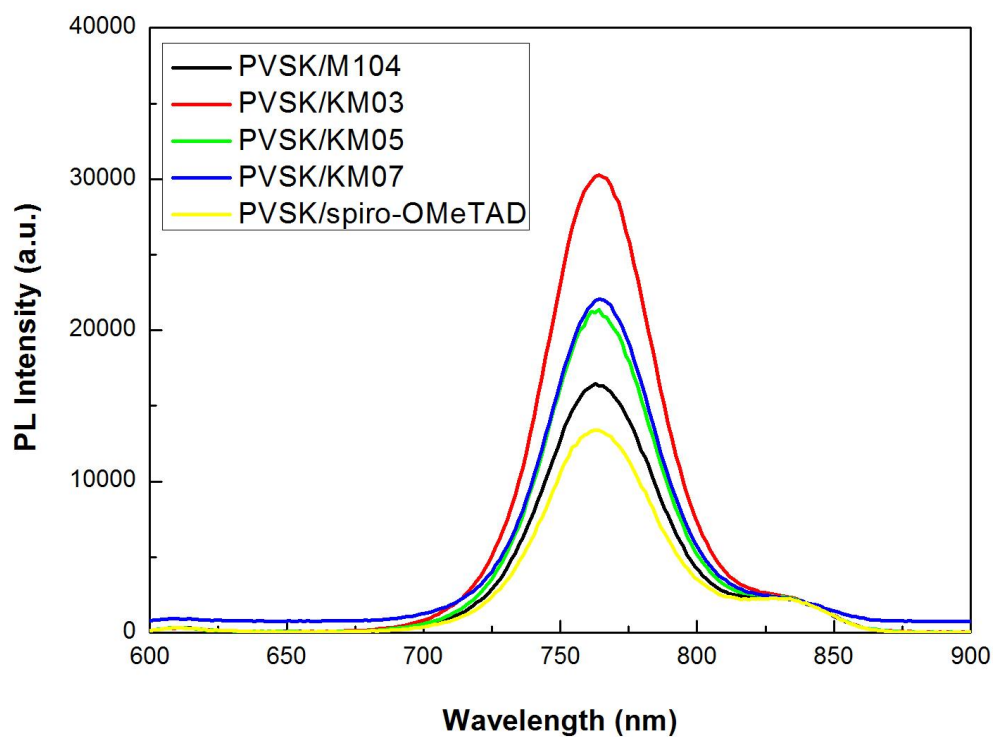


**Figure S5.** J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region.

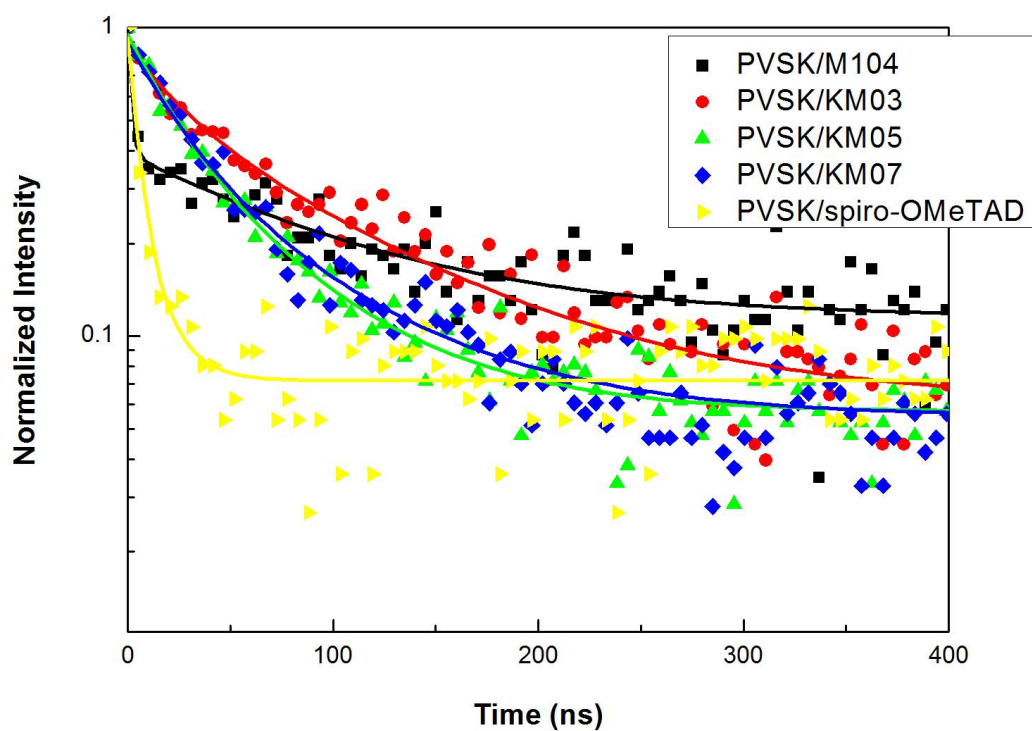


HTMs	hole mobility, $\mu$ ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )
<b>M104</b>	$2.36 \times 10^{-4}$
<b>KM03</b>	$4.54 \times 10^{-5}$
<b>KM05</b>	$1.61 \times 10^{-4}$
<b>KM07</b>	$1.78 \times 10^{-4}$
<b>Spiro-OMeTAD</b>	$2.11 \times 10^{-4}$

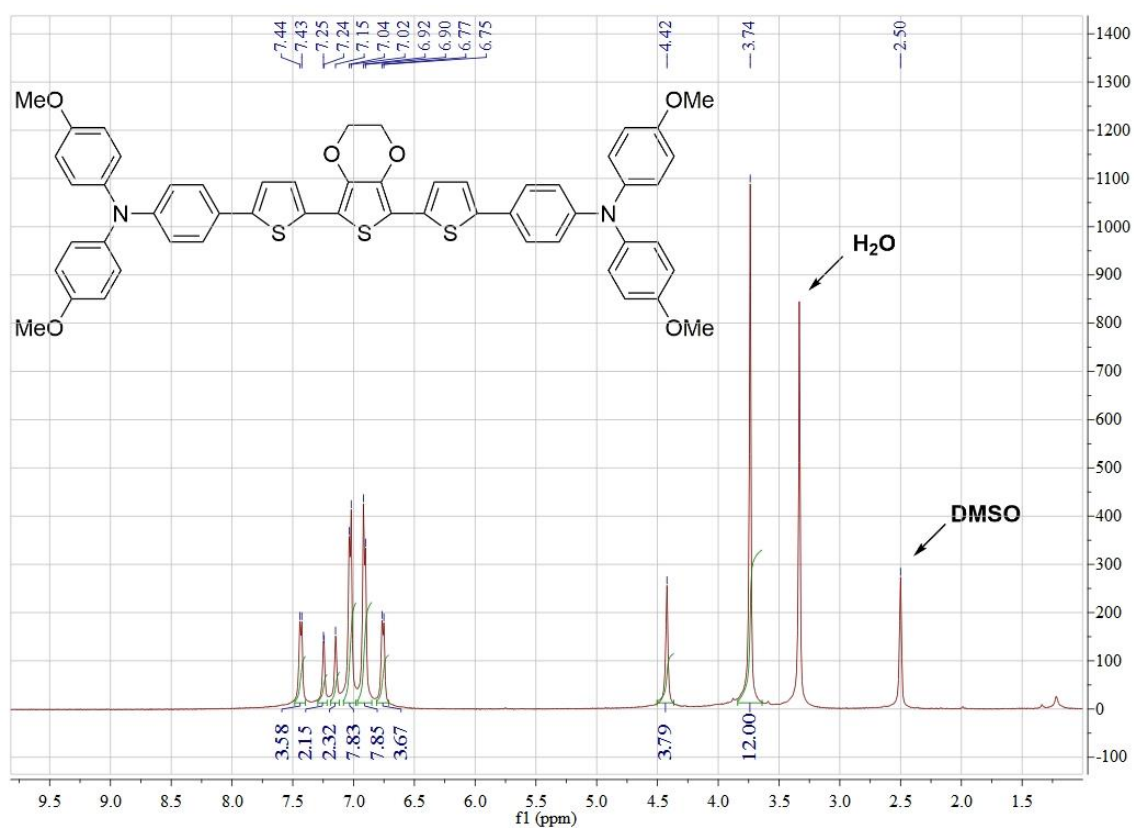
**Figure S6.** Steady-state PL spectra of the devices fabricated as FTO/perovskite/HTMs.



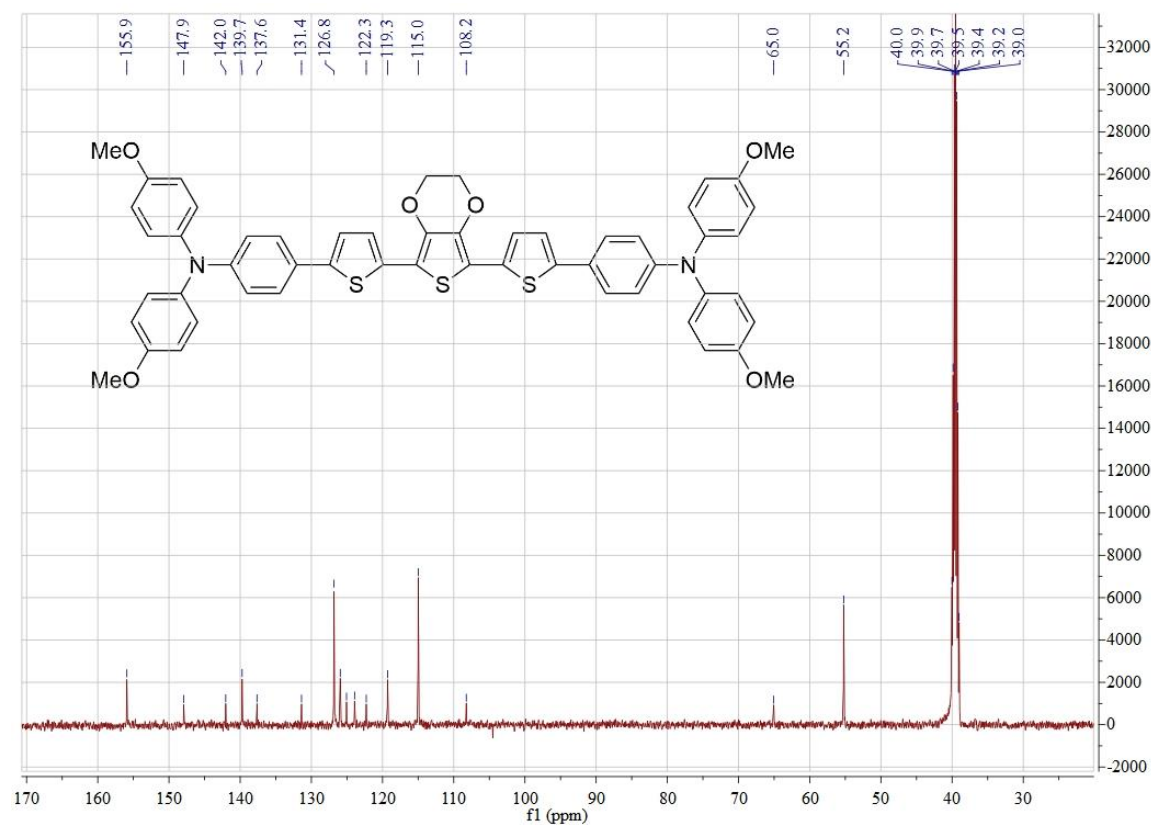
**Figure S7.** Time-resolved PL spectra of the devices fabricated as FTO/perovskite/HTMs.



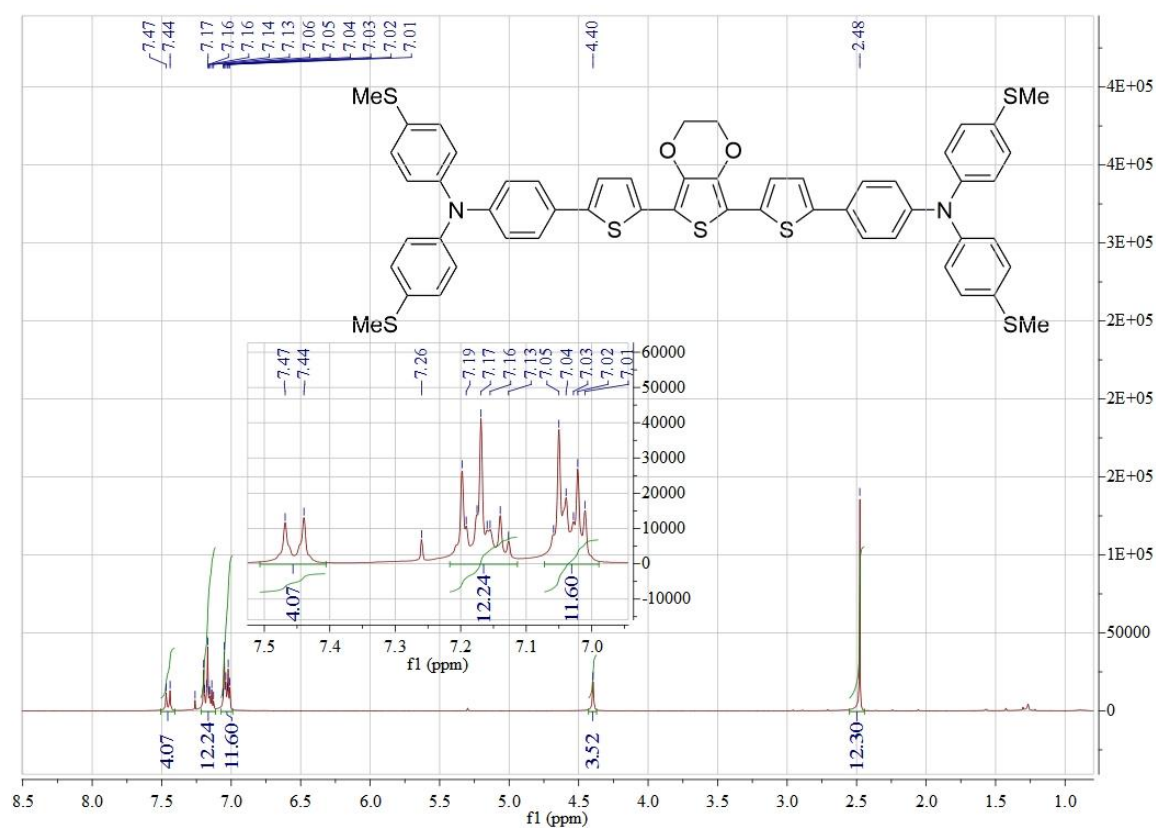
**Figure S8.**  $^1\text{H}$  NMR Spectrum of M104 (500 MHz,  $\text{DMSO-d}_6$ )



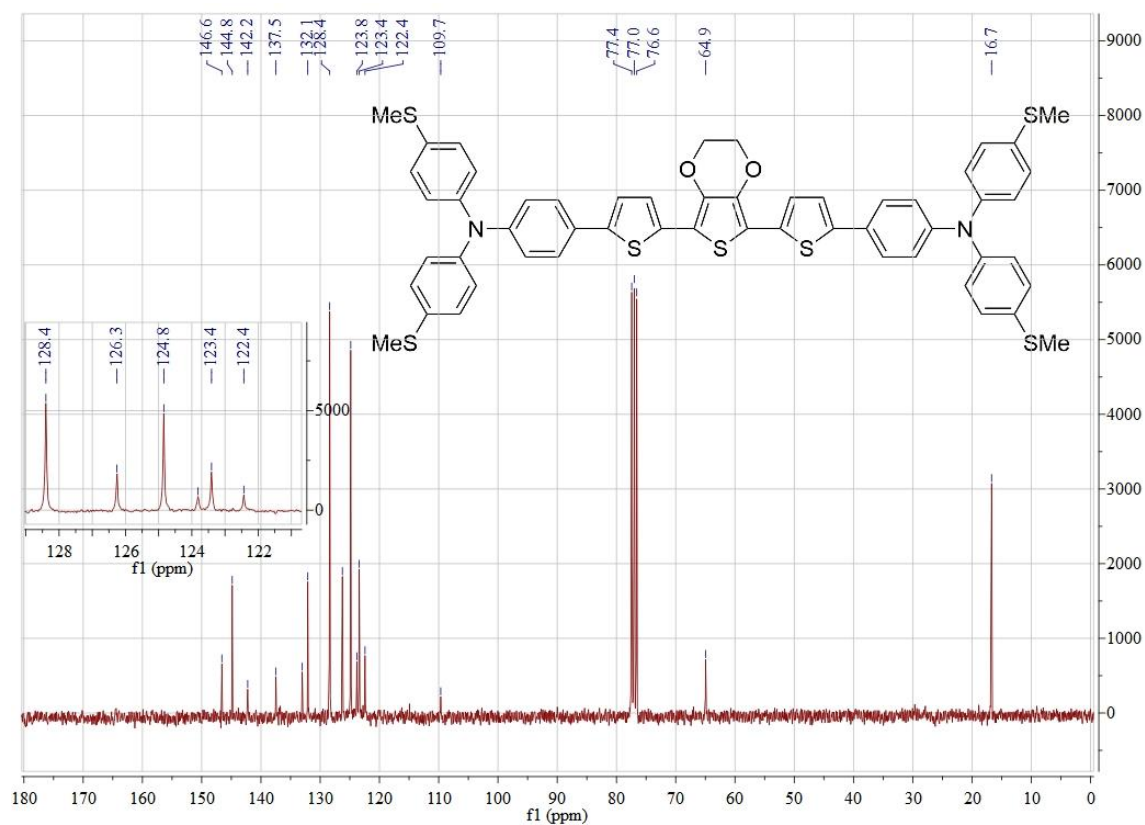
**Figure S9.**  $^{13}\text{C}$  NMR Spectrum of M104 (125 MHz,  $\text{DMSO-d}_6$ )



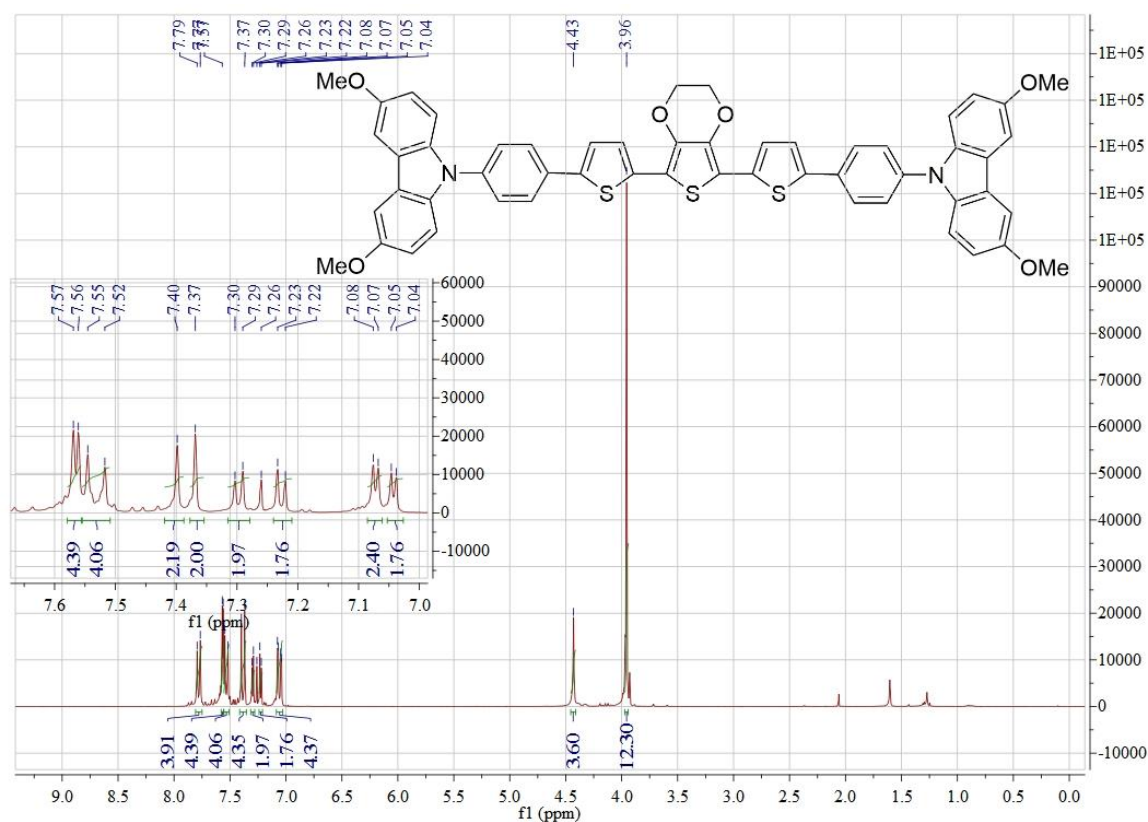
**Figure S10.**  $^1\text{H}$  NMR Spectrum of **KM03** (300 MHz,  $\text{CDCl}_3$ )



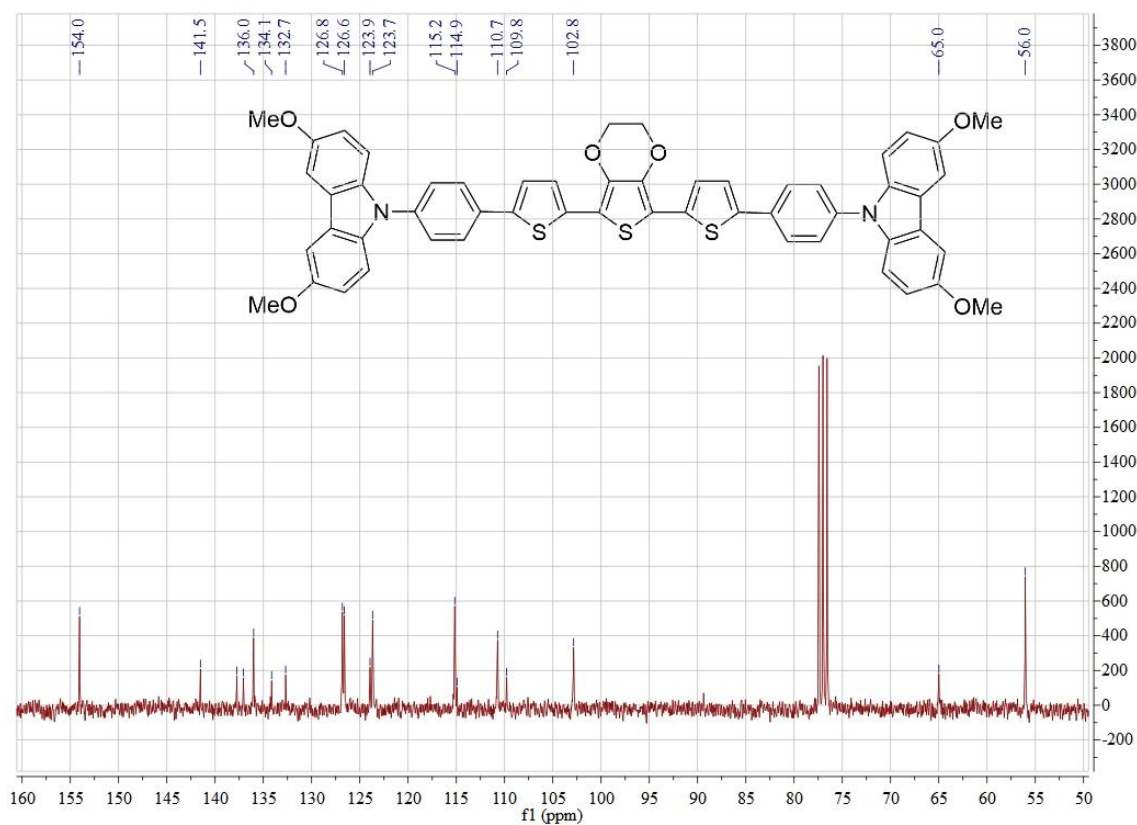
**Figure S11.**  $^{13}\text{C}$  NMR Spectrum of **KM03** (75 MHz,  $\text{CDCl}_3$ )



**Figure S12.**  $^1\text{H}$  NMR Spectrum of **KM05** (300 MHz,  $\text{CDCl}_3$ )

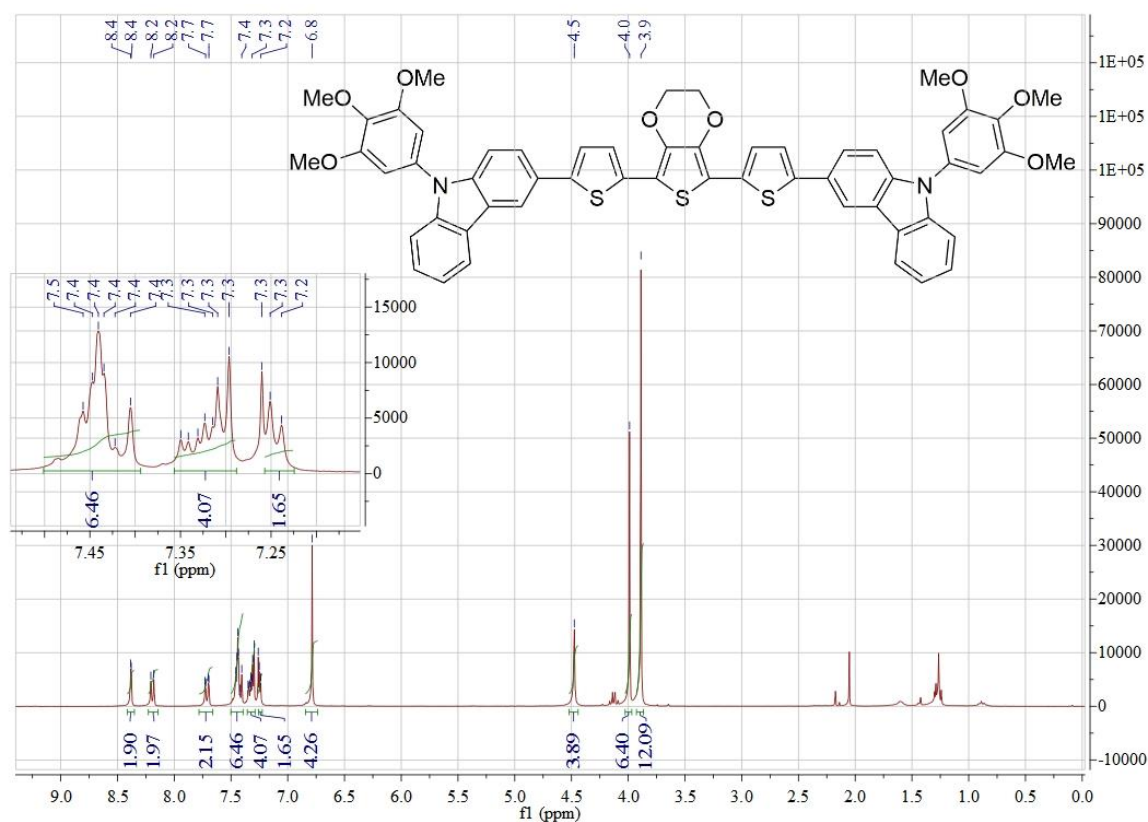


**Figure S13.**  $^{13}\text{C}$  NMR Spectrum of **KM05** (75 MHz,  $\text{CDCl}_3$ )





**Figure S14.**  $^1\text{H}$  NMR Spectrum of **KM07** (300 MHz,  $\text{CDCl}_3$ )



**Figure S15.**  $^{13}\text{C}$  NMR Spectrum of **KM07** (75 MHz,  $\text{CDCl}_3$ )

