

## Supplementary Material

# Facile synthesis of benzotrithiophene core-based hole-transporting molecules with carbazole-wings for perovskite solar cells by Pd-catalyzed direct C-H/C-Br coupling reactions

Wei-Kai Chang,<sup>a</sup> Kun-Mu Lee,<sup>\*b</sup> Yin-Chi Wang,<sup>a</sup> Kun-Hua Chiang,<sup>a</sup> Chuan-Pin Lee,<sup>c</sup> and Ching-Yuan Liu<sup>\*a</sup>

<sup>a</sup> Department of Chemical and Materials Engineering, National Central University, Zhongli District, Taoyuan City, Taiwan (R.O.C)

<sup>b</sup> Department of Chemical and Materials Engineering, Chang Gung University, Guishan District, Taoyuan City, Taiwan (R.O.C)

<sup>c</sup> Radioactive Waste Disposal Technology R&D Center, National Tsing Hua University, Hsinchu City, Taiwan (R.O.C)

Email: [cyliau0312@ncu.edu.tw](mailto:cyliau0312@ncu.edu.tw)

## Table of Contents

### Part I: Experimental Section

General information.....	S2
<b>Figures S1-S2:</b> The UV-Vis absorption, photoluminescence spectra and cyclic voltammograms .....	S4
<b>Figures S3-S4</b> Thermogravimetric analysis and differential scanning calorimetry .....	S5
<b>Figure S5.</b> J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region .....	S6
<b>Figures S6-S7:</b> Steady-state PL and time-resolved PL spectra .....	S7
<b>Part II:</b>	
MALDI Spectra.....	S8
<sup>1</sup> H and <sup>13</sup> C NMR Spectra.....	S10

## 1. General information:

Unless otherwise noted, all reactions were conducted with magnetic stirring and in heat gun-dried glassware under nitrogen. Required chemicals such as Pd(OAc)<sub>2</sub>, P(*o*-tolyl)<sub>3</sub>, PivOH, and K<sub>2</sub>CO<sub>3</sub> are commercially available. Anhydrous solvents such as dichloromethane, mesitylene, and *N*-methyl-2-pyrrolidone (NMP) 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/AgNO<sub>3</sub> 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 and 0.01 M AgNO<sub>3</sub> dissolving in the acetonitrile as 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  $[-(E_{1/2} \text{ (vs. Fc/Fc}^+) + 5.16)] \text{ eV}$ ;  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$ . 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).

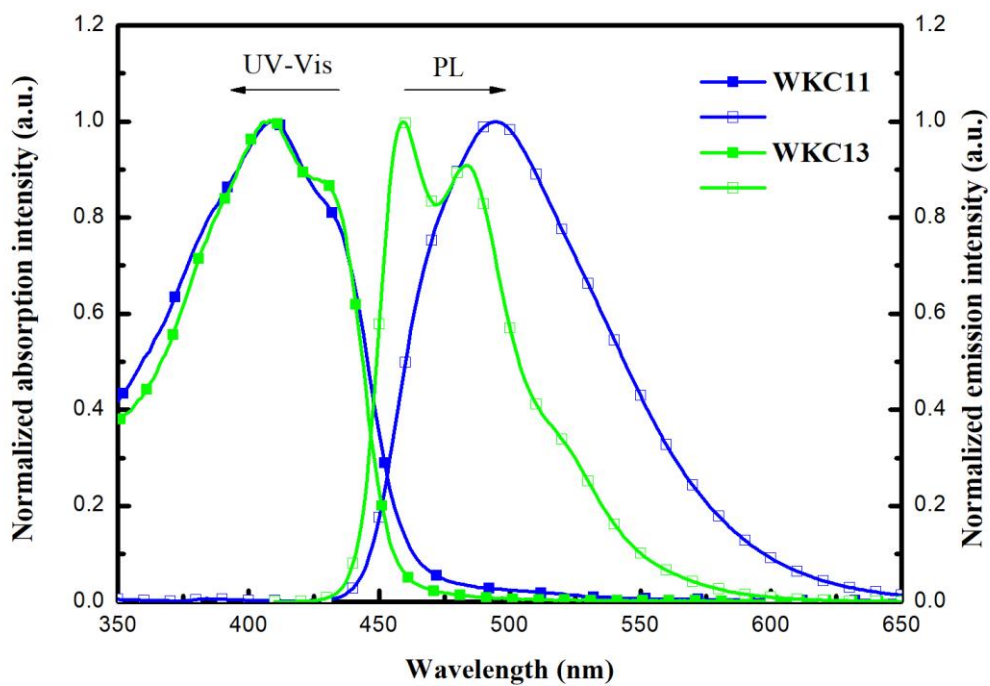
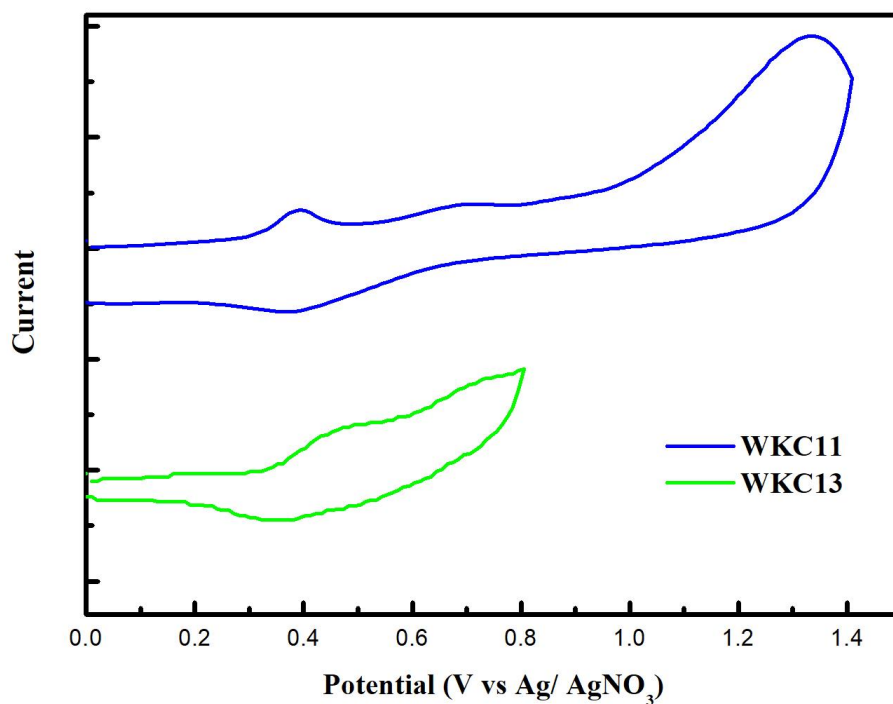
## 2. Device fabrication of the perovskite solar cells (PSCs):

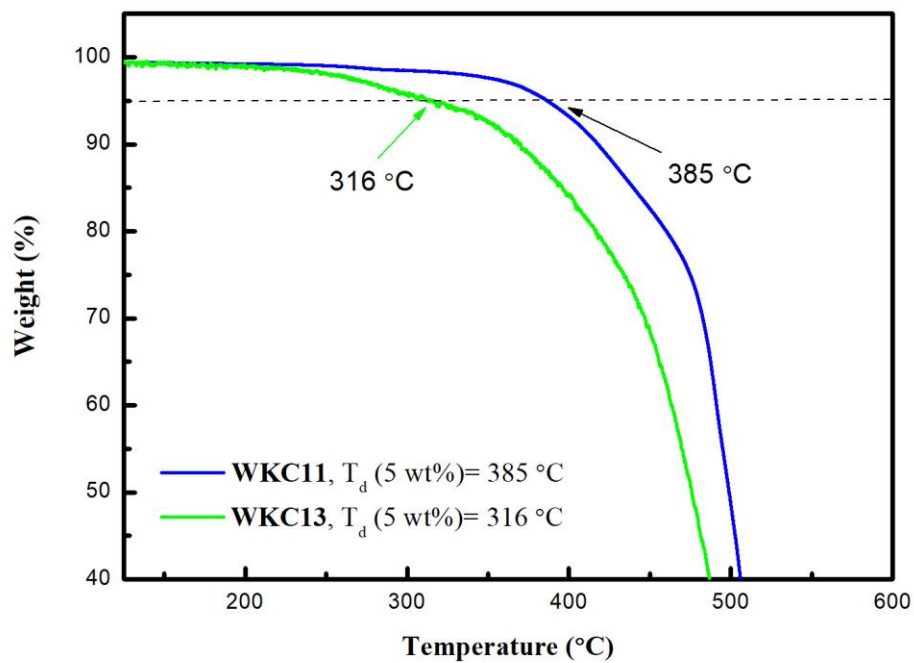
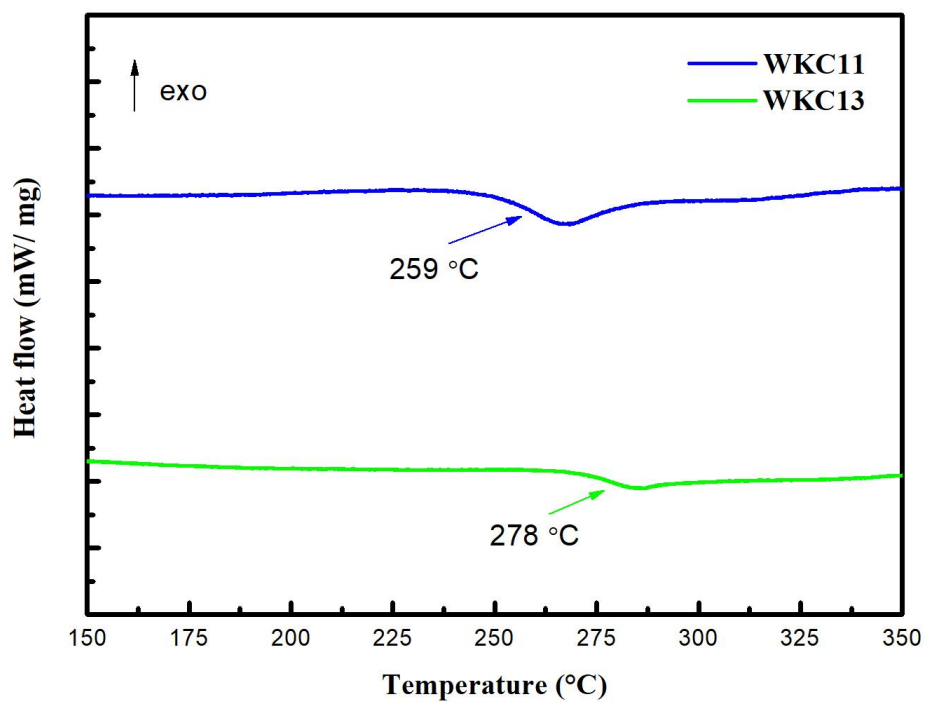
A TiO<sub>2</sub> compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt.% of Ti(acac)<sub>2</sub>O*i*Pr<sub>2</sub> in isopropanol). A 150 nm-thick mesoporous TiO<sub>2</sub> film (TiO<sub>2</sub> 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 μL 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. **WKC11**, **WKC13** and **spiro-OMeTAD** (as reference cell) was each dissolved in chlorobenzene (50 mg/mL). Each solution was stirred while heating to 130 °C for 20 min. Next, 17.5 μL of a solution of lithium

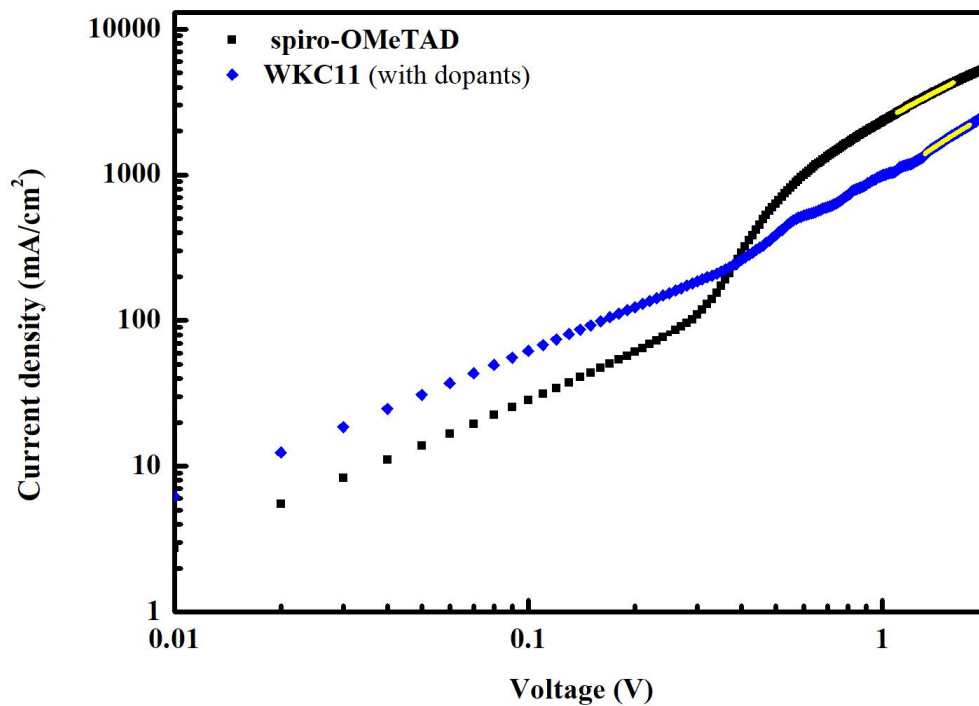
bis(trifluoromethane)sulfonimide (Li-TFSI, 520 mg) in acetonitrile (1 mL) and 28.5  $\mu$ L 4-*tert*-butylpyridine (TBP) were added directly to the corresponding hole-transporting material (HTM) solutions prepared from previous step. This as-prepared HTM solution was spin-coated onto the substrate/films at 2000 rpm for 30 sec. Finally, the Ag cathode layer was deposited by thermal evaporation ( $\sim$ 100 nm). The active area of each cell was fixed at 0.16 cm<sup>2</sup> by a metal mask.

### 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 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).

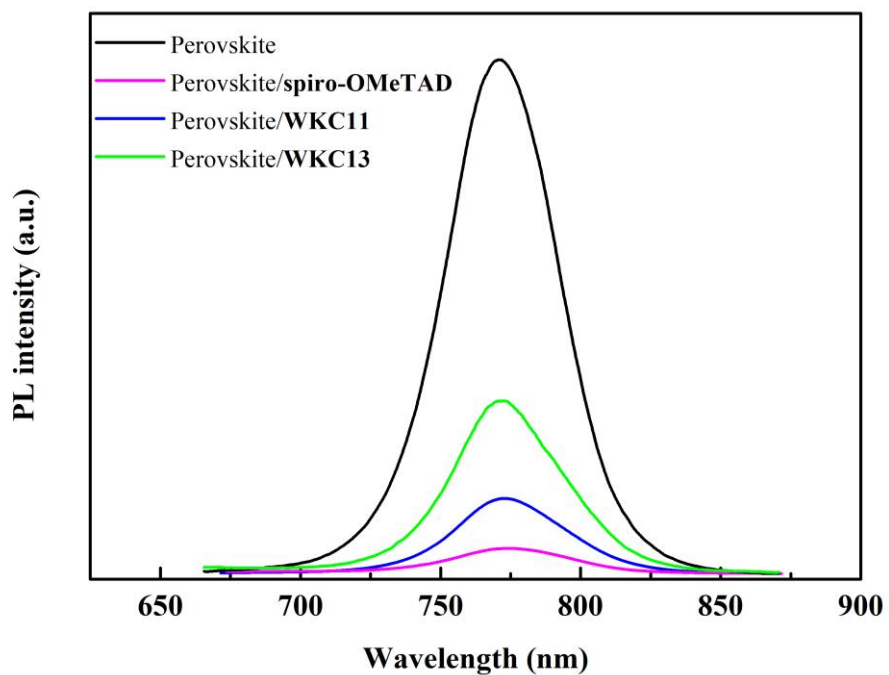
**Figure S1.** The UV-Vis absorption and photoluminescence spectra of **WKC11** and **WKC13** in  $\text{CH}_2\text{Cl}_2$  solution.**Figure S2.** Cyclic voltammety spectra of **WKC11** and **WKC13** in  $\text{CH}_2\text{Cl}_2$  solution.

**Figure S3.** Thermogravimetric analysis curves of **WKC11** and **WKC13**.**Figure S4.** Differential scanning calorimetry curves of **WKC11** and **WKC13**.

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

HTMs	hole mobility, $\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
<b>WKC11</b>	$6.13 \times 10^{-4}$
<b>WKC13</b>	$9.59 \times 10^{-5}$
<b>spiro-OMeTAD</b>	$1.17 \times 10^{-3}$

**Figure S6.** Steady-state PL spectra of the devices fabricated as glass/perovskite/HTMs (HTMs spin-coated from PhCl).



**Figure S7.** Time-resolved PL spectra of the devices fabricated as glass/perovskite/HTMs (HTMs spin-coated from PhCl).

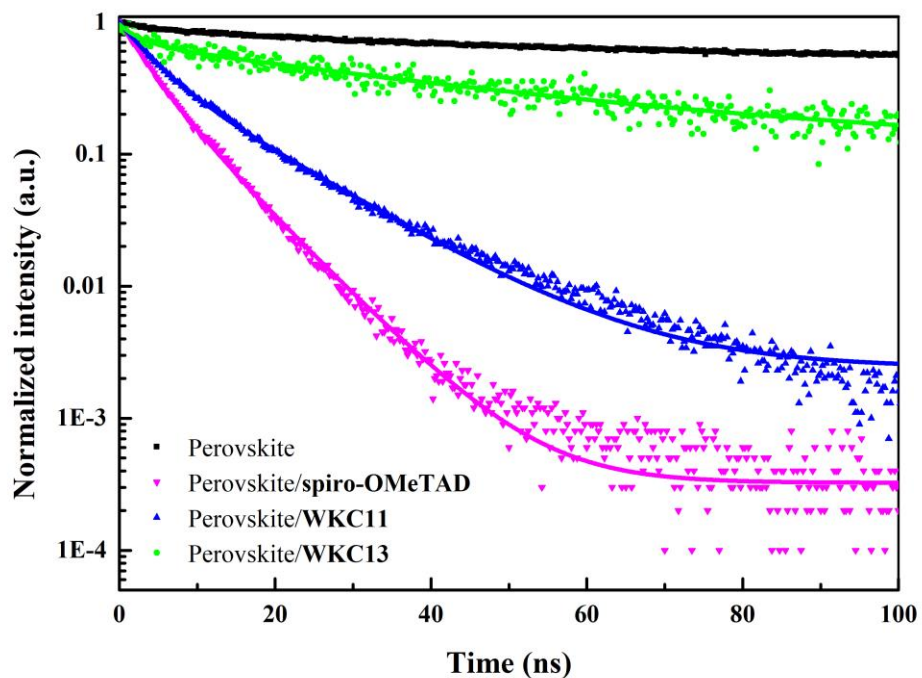
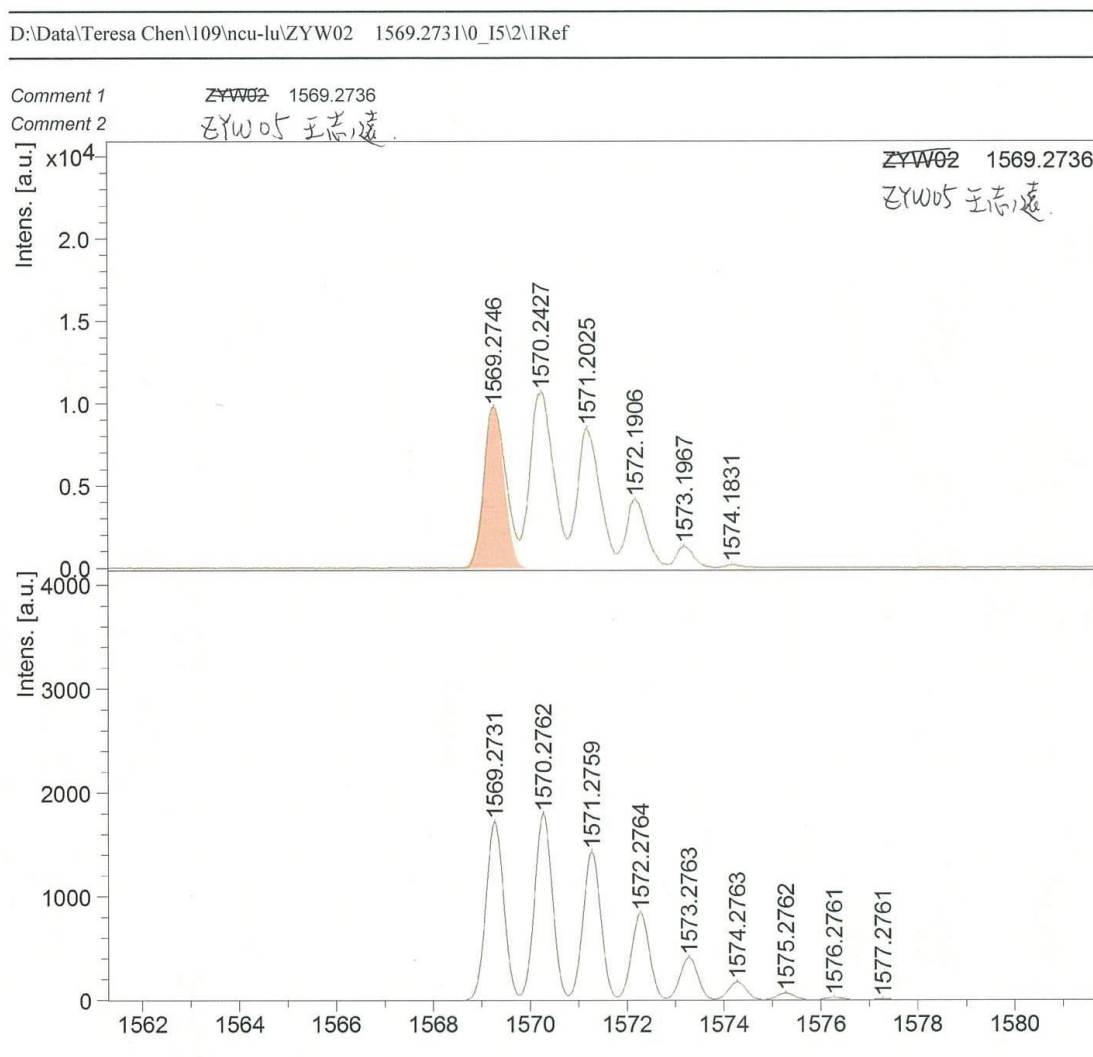


Figure S8. Mass Spectrum of **WKC11** (MALDI).



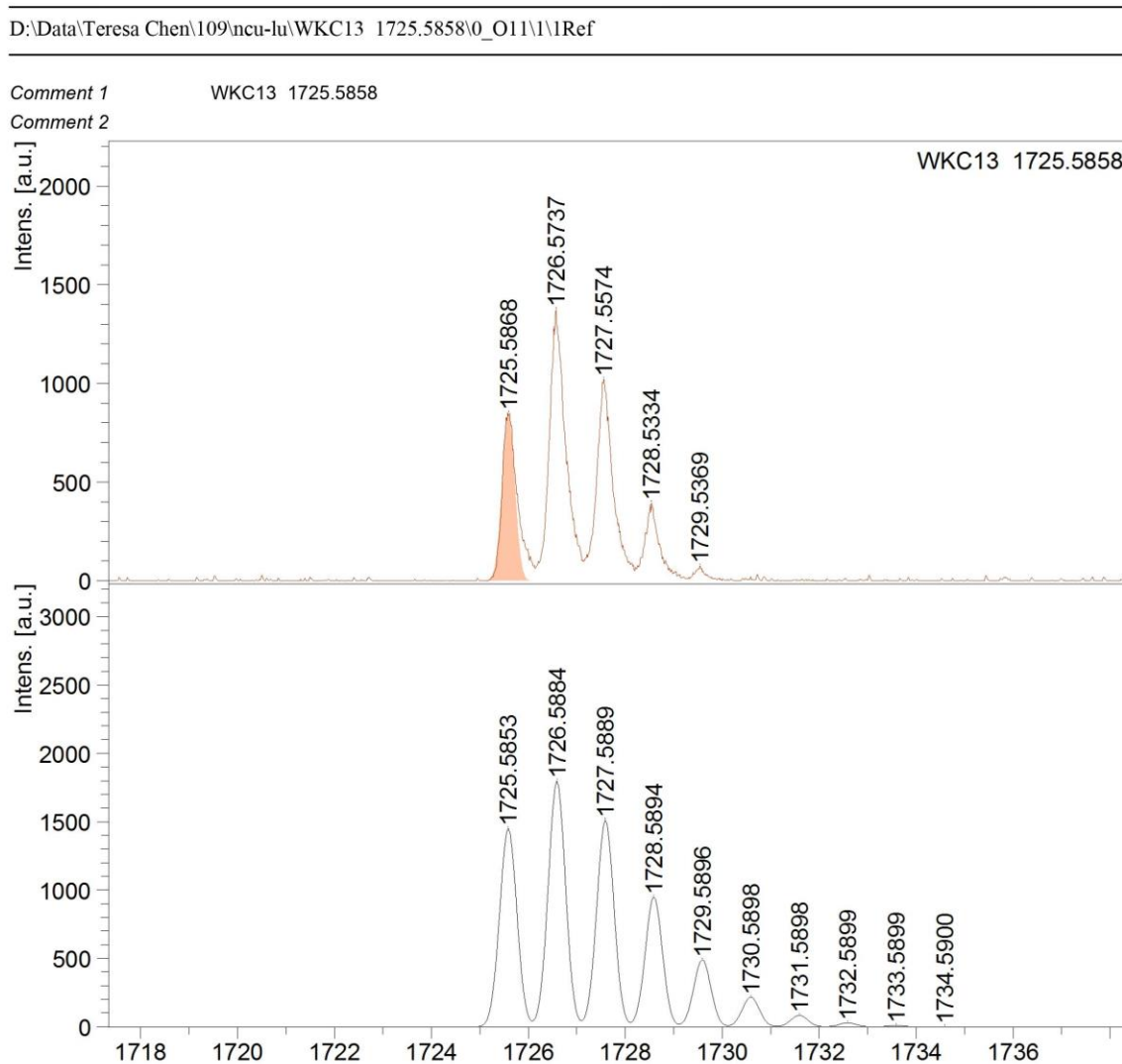
**Acquisition Parameter**

Date of acquisition 2020-04-07T15:09:42.000  
 Acquisition method name D:\Methods\flexControlMethods\Teresa\RP\_PEG 1500-2018 May 31.par  
 Acquisition operation mode Reflector  
 Voltage polarity POS  
 Number of shots 1000  
 Name of spectrum used for calibration  
 Calibration reference list used PEG-Na -Calibration Mono

**Instrument Info**

User NCU  
 Instrument ATS-00670  
 Instrument type autoflex



Figure S9. Mass Spectrum of **WKC13** (MALDI).**Acquisition Parameter**

Date of acquisition 2020-10-22T17:03:15.709+08:00  
Acquisition method name D:\Methods\flexControlMethods\Teresac\RP\_PEG 1000-2018 May 31.par  
Acquisition operation mode Reflector  
Voltage polarity POS  
Number of shots 1000  
Name of spectrum used for calibration  
Calibration reference list used PEG-Na -Calibration Mono-T

**Instrument Info**

User NCU  
Instrument ATS-00670  
Instrument type autoflex

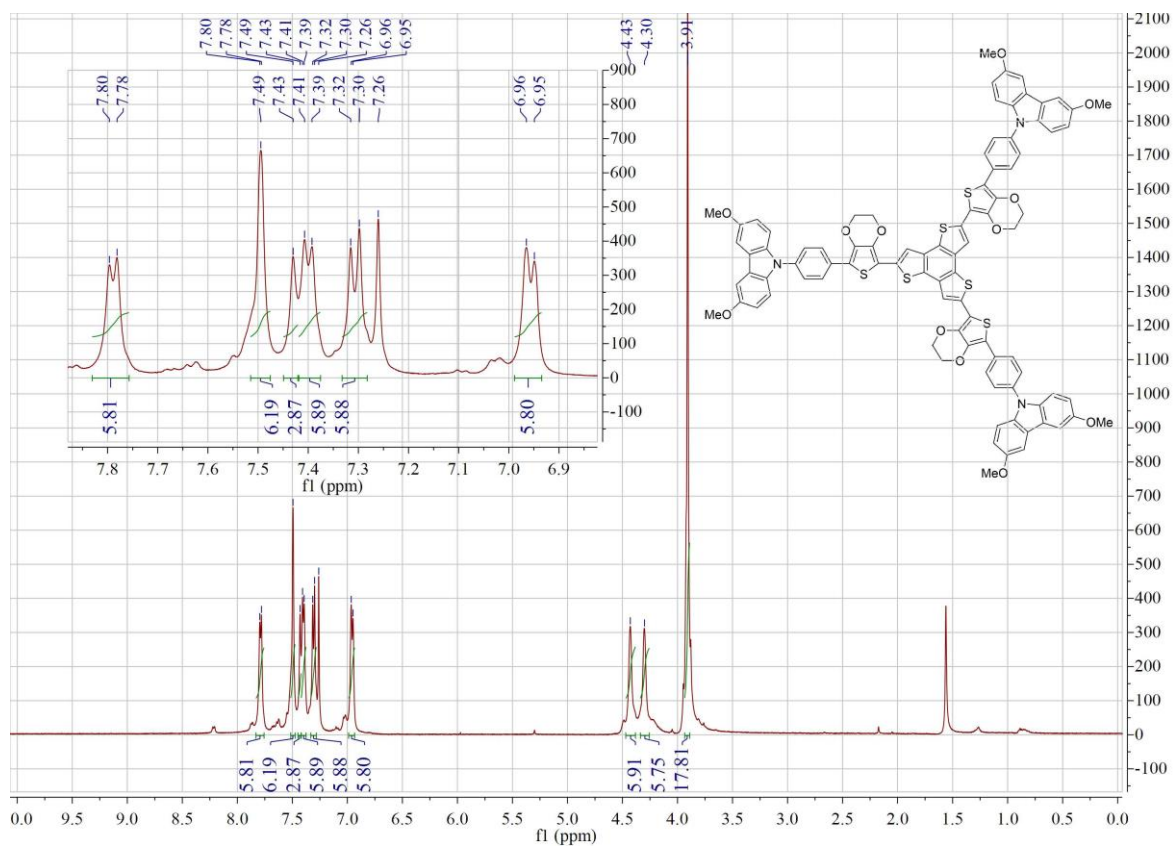
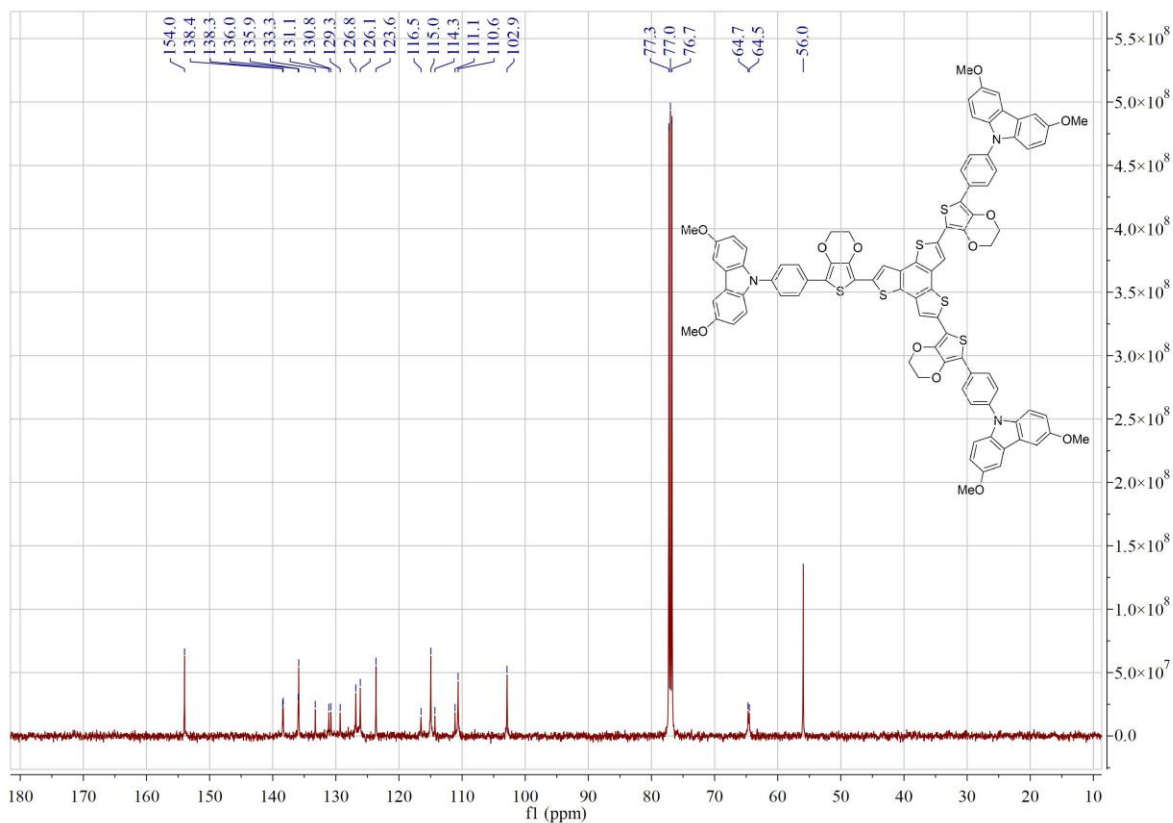
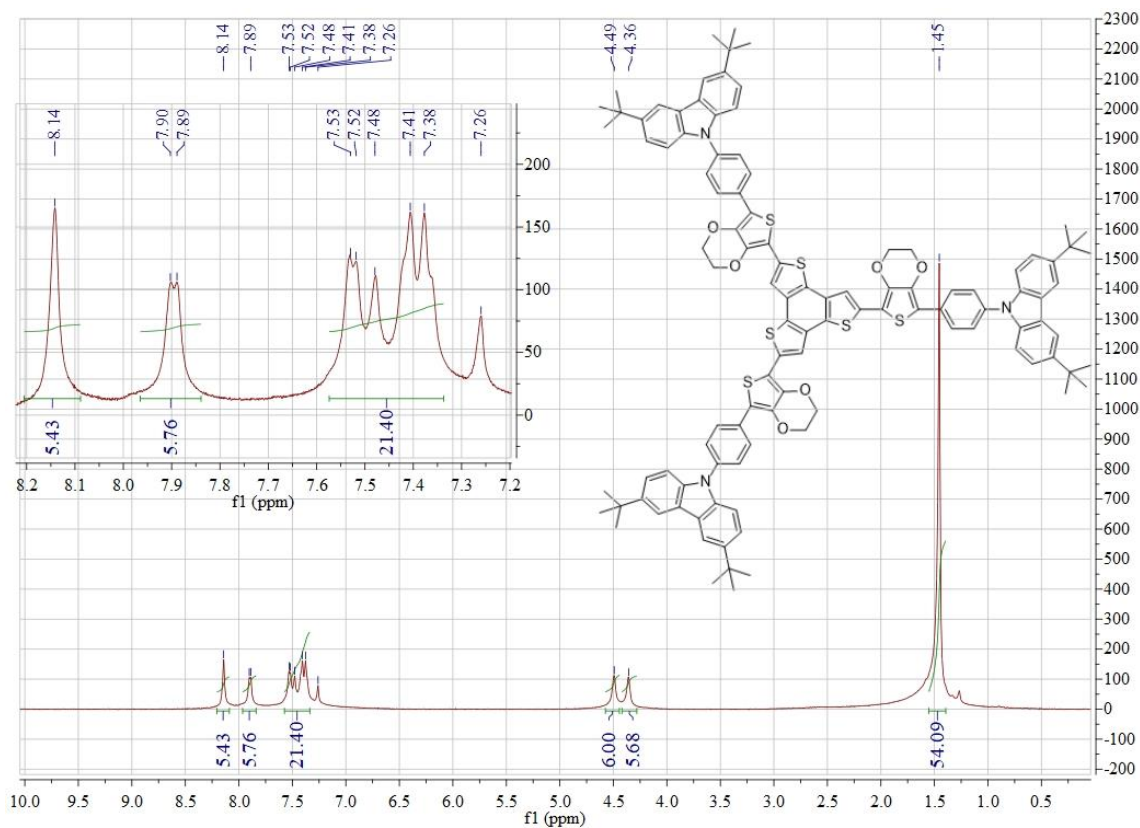
Figure S10.  $^1\text{H}$  NMR Spectrum of **WKC11** (500 MHz,  $\text{CDCl}_3$ )Figure S11.  $^{13}\text{C}$  NMR Spectrum of **WKC11** (125 MHz,  $\text{CDCl}_3$ )

Figure S12.  $^1\text{H}$  NMR Spectrum of **WKC13** (500 MHz,  $\text{CDCl}_3$ )Figure S13.  $^{13}\text{C}$  NMR Spectrum of **WKC13** (125 MHz,  $\text{CDCl}_3$ )