

Supporting Information for
All-Polymer Solar Cells based on Wide Bandgap Polymerized Non-Fused
Electron Acceptors for Indoor Photovoltaics

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1. Materials and measurements

Materials: The synthetic procedures were performed under a nitrogen (N_2) atmosphere. Commercial chemicals (from *Sigma-Aldrich*, *J&K Chemical*, and *Energy Chemical*) were used as received. 1H -NMR spectra of intermedia products and monomers were recorded at 400 MHz and on a *Bruker AVANCE* spectrometer with TMS as the internal standard. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V/s and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode.

Fabrication of Solar Cells: OSCs use the conventional device as ITO/PEDOT:PSS/active layer/PFN-Br/Ag.^{S1} Photovoltaic devices were made by spin-coating the PEDOT:PSS aqueous solution through a 0.45- μ m filter, at 6000 rpm for 30 s onto pre-cleaned, patterned ITO substrates and then heating the ITO substrate in the air at 150 °C annealing for 15 min. The active layer materials (PBDB-T:acceptors,=1:1, 14 mg/mL in total) were dissolved in a solution of chlorobenzene (CB) with 1-chloronaphthalene (1-CN, 0.5%, v/v) additive. The blended solution was spin-coated on the PEDOT:PSS layer at 2500 rpm for 40 s. It was then annealed at 150 °C for 15 minutes. The thickness of the active layer is about 70 nm. Then PFN-Br methanol solution with a concentration of 1.0 mg/mL was deposited on the active layer at a speed of 3500 rpm for 30 seconds to provide a PFN-Br cathode modification layer. The thin films were then transferred into the N_2 -filled glove box. 80 nm of the Ag layer was then deposited onto the active layer by shadow masks.

Measurement of Solar Cells: The J - V curves were measured under AM1.5G illumination at 100 mW/cm² using an AAA solar simulator (*Enli Technology Co. Ltd*) calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology) and a Keithley 2400 source-measure unit. The EQE data were obtained using a solar cell spectral response measurement system (QE-R3011, *Enli Technology Co. Ltd*). The film thickness data were obtained via a surface profilometer (Dektak XT, Bruker).

SCLC: Space-charge-limited-current (SCLC) measurements were carried out using a Keithley 2400 source/measure. Electron-only devices were constructed using the ITO/PEDOT:PSS/active layer/MoO_x/Ag architecture, while hole-only devices were constructed using the ITO/ZnO/active layer/PFN-Br/Ag architecture. Current-voltage sweeps were carried out in the region of -6 V to 6 V in steps of 0.03 V at a slow rate. The carrier mobilities were measured using the space-charge-limited-current (SCLC) model, which is described by:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \quad (\text{eq. 1})$$

Where J is the current density, ε_0 is the permittivity of the vacuum (8.85×10^{-12} F/m), ε_r is the dielectric constant of the polymer, and L is the thickness of the polymer layer, μ is the hole or electron mobility, V is the internal voltage in the device and $V = V_{\text{appl}} - V_r - V_{\text{bi}}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes. The thickness of the photoactive layers for SCLC measurement was about 70 nm. The hole/electron mobilities were calculated with the *Mott-Gurney* equation in the SCLC region (slope = 2 in $\log J$ vs $\log V$ plots).^{S2,S3}

GIWAXS: GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with an X-ray wavelength of 1.5418 Å. The film samples were irradiated at a grazing angle of 0.12°-0.16°. All film samples were prepared by spin-coating CB/1-CN solutions on Si substrates.

AFM: Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nanoscope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

2. Synthetic Procedure

Synthesis of compound M3

M1 (500 mg, 0.84 mmol) and **M2** (1.62 g, 19.29 mmol) were dissolved in a toluene solution under nitrogen protection. After catalyst Pd(PPh₃)₄ (46.2 mg, 0.04 mmol) was added, the flask was purged with nitrogen gas five times to remove atmospheric air. The reaction mixture was stirred at 115 °C for 12 hours. After removing the solvent from the product, the purified compound was subjected to silica gel column chromatography for further purification, using a solvent mixture of PE/DCE (1:2, v/v) as the eluent. The dried product was dissolved in DCM (dichloromethane) and then transferred to a methanol solution for precipitation. After rinsing with methanol solvent, the product was dried (1.02 g, 80% yield). The product is directly used for the next reaction. ¹H NMR (400 MHz, CDCl₃), δ: 9.87 (s, 1H), 7.98 (d, *J* = 2.4 Hz, 2H), 7.60 (s, 2H), 3.60 (d, *J* = 7.6 Hz, 2H), 2.04 (d, 8H), 1.94 (s, 1H), 1.32-1.26 (m, 40H), 1.14-0.86 (m, 68H), 0.76-0.72 (m, 30H). MS *m/z*: [M]⁺, Calcd. For C₉₅H₁₄₉N₃O₅: 1513.54; Found: 1514.49.

Synthesis of compound M5

M3 (500 mg, 0.33 mmol) and **M4** (IO-Br, 371 mg, 1.65 mmol) were dissolved in a solvent mixture of chloroform (20 mL) and pyridine (2 mL). The mixture was stirred in the dark at 50 °C for 6 hours. After removing the solvent from the product, the purified compound was subjected to silica gel column chromatography for further purification, using a solvent mixture of PE/DCE (1:4, v/v) as the eluent (470mg, 75% yield). ¹H NMR (400 MHz, CDCl₃), δ: 8.09-7.80 (m, 12H), 3.62 (d, *J* = 7.2 Hz, 2H), 2.04 (d, *J* = 4.4 Hz, 8H), 1.94 (s, 1H), 1.32-1.26 (m, 32H), 1.14-0.86 (m, 68H), 0.76-0.72 (m, 30H). MS *m/z*: [M]⁺, Calcd. For C₁₁₂H₁₅₃Br₂NO₆S₅: 1929.57; Found: 1928.875.

Synthesis of Polymer WP1

M6 (60 mg, .031 mmol) and 2,5-bis(trimethylstannyl)thiophene (12.70 mg, 0.031 mmol) were dissolved in a toluene solution under nitrogen protection. After the

catalyst Pd₂(dba)₃ (0.91 mg, 0.0009 mmol) and P(*o*-tol)₃ (1.13 mg, 0.0037 mmol) were added, the flask was purged with nitrogen gas five times to remove atmospheric air. The reaction mixture was stirred at 115 °C for 14 hours. After cooling the mixture to room temperature, it was transferred to a methanol solution for precipitation and subsequently filtered through a Soxhlet thimble. The resulting polymer was separately dissolved in chlorobenzene after Soxhlet extraction with methanol and hexane. After precipitation with methanol once more, the polymer was subjected to vacuum filtration, and dried in a vacuum oven to obtain the polymer **WP1** (45 mg) subsequently.

Synthesis of Polymer WP2

M6 (60 mg, 0.031 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (15.25 mg, 0.031 mmol) were dissolved in a toluene solution under nitrogen protection. After the catalyst Pd₂(dba)₃ (0.91 mg, 0.0009 mmol) and P(*o*-tol)₃ (1.13 mg, 0.0037 mmol) was added, the flask was purged with nitrogen gas five times to remove atmospheric air. The reaction mixture was stirred at 115 °C for 14 hours. The purification methods for **WP2** were similar to those for WP1, ultimately resulting in the obtainment of **WP2** (47 mg).

Synthesis of Polymer WP3

(3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis-(trimethylstannane) (16.35 mg, 0.031 mmol) and **M6** (60 mg, 0.031 mmol) were dissolved in a toluene solution under nitrogen protection. After catalyst Pd₂(dba)₃ (0.91 mg, 0.0009 mmol) and P(*o*-tol)₃ (1.13 mg, 0.0037 mmol) were added, the flask was purged with nitrogen gas five times to remove atmospheric air. The reaction mixture was stirred at 115 °C for 14 hours. The purification methods for WP3 were similar to those for **WP1** and **WP2**, ultimately resulting in the obtainment of **WP3** (40 mg).

3. GPC and CV

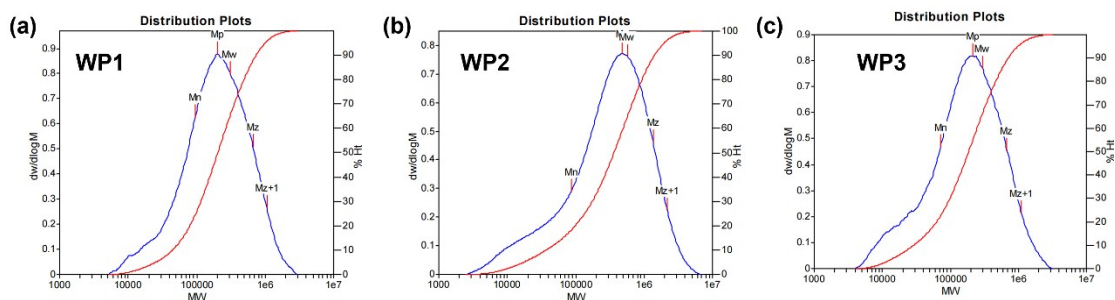


Figure S1. GPC curves of NFRA-type polymer (a) WP1, (b) WP2, and (c) WP3.

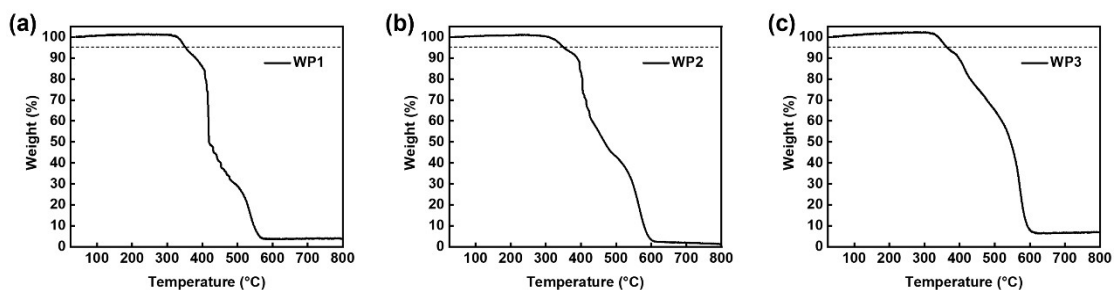


Figure S2. TGA plot for (a) WP1, (b) WP2, and (c) WP3 with a heating rate of 10 °C/min under N_2 atmosphere, respectively. Temperatures for 5% weight loss of WP1-3 are 350.83, 350.17, and 365.33 °C, respectively.

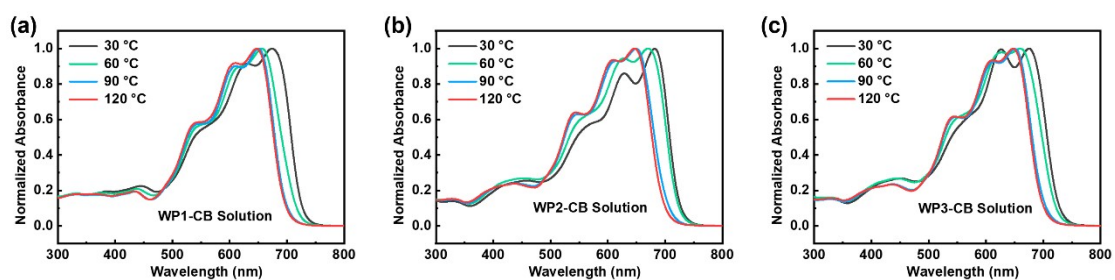


Figure S3. Temperature-dependent optical absorption spectra for WP1-3 recorded in CB solutions, respectively.

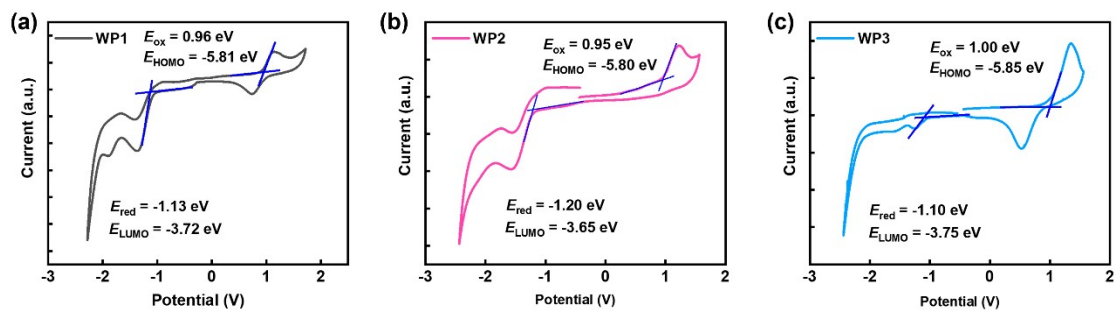


Figure S4. Cyclic voltammogram of NFRA-type polymer (a) **WP1**, (b) **WP2**, and (c) **WP3**. Potential vs. Fc/Fc⁺.

4. All-PSCs

Table S1. Characteristics of PBDB-T:WP2-based all-PSCs spin-coated from CB with different ratios of donor-acceptor, annealed at 150 °C for 15 minutes.

Ratio	Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
1:1	60-80	1.16	10.48	0.52	6.32
1:1.2	60-80	1.15	10.37	0.51	6.06

Table S2. Characteristics of PBDB-T:WP2-based (1:1 ratio) all-PSCs spin-coated from CB with different annealed temperatures, similar film thickness.

Temp. (°C)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
80	1.15	10.32	0.52	6.23
100	1.14	9.85	0.53	6.18
150	1.14	11.24	0.53	6.82
180	1.14	10.48	0.53	6.33

Table S3. Characteristics of PBDB-T:WP2-based (1:1 ratio) all-PSCs spin-coated from CB with different proportions of additives, annealed at 150 °C for 15 minutes.

Solvent	Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
CB	50-60	1.12	11.06	0.47	5.85
CB:0.5% 1-CN	50-60	1.15	10.32	0.52	6.23
CB:1% 1-CN	50-60	1.14	11.00	0.48	5.99
CB:2% 1-CN	50-60	1.15	9.87	0.49	5.59

Table S4. Characteristics of PBDB-T:WP2-based (1:1 ratio) all-PSCs spin-coated from CB with different thicknesses of the active layer, annealed at 150 °C for 15 minutes.

Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
80-90	1.14	11.27	0.53	6.85
60-80	1.14	11.79	0.52	6.93
50-60	1.14	11.23	0.53	6.82
40-50	1.14	10.95	0.53	6.58

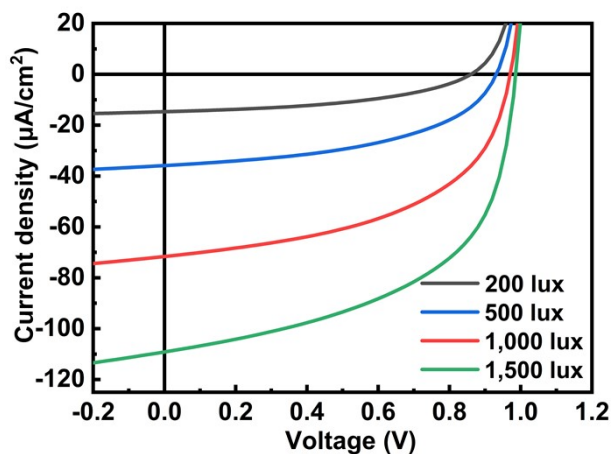


Figure S5. J - V curves of PBDB-T:WP2-based all-PSCs under different illumination intensities in LED 3000 K light source.

Table S5. Photovoltaic performance of PBDB-T:WP2-based all-PSCs under different 3,000 K light source illumination intensities.

Intensity (lux)	V_{OC} (V)	J_{SC} (μA/cm ²)	J_{calc} (μA/cm ²)	FF	PCE (%)
200	0.87	88.69	14.71	0.45	10.15
500	0.93	109.16	36.07	0.49	11.69
1,000	0.97	90.27	74.46	0.54	13.77
1,500	0.99	109.16	98.32	0.54	14.17

Table S6. Static photovoltaic performance of PBDB-T:WP1-based under indoor illuminations (3,000 K, 1,500 lux).

V_{oc} (V)	J_{sc} ($\mu\text{A}/\text{cm}^2$)	FF	PCE (%)
0.97	89.17	0.45	9.56
0.97	92.44	0.45	9.83
0.98	89.02	0.47	9.90
0.98	89.31	0.46	9.89
0.99	88.69	0.46	9.71

Table S7. Static photovoltaic performance of PBDB-T:WP2-based under indoor illuminations (3,000 K, 1,500 lux).

V_{oc} (V)	J_{sc} ($\mu\text{A}/\text{cm}^2$)	FF	PCE (%)
0.98	106.4	0.54	13.77
0.98	107.6	0.54	13.91
0.98	105.4	0.54	13.62
0.99	109.2	0.54	14.17
0.99	108.8	0.54	14.13

Table S8. Static photovoltaic performance of PBDB-T:WP3-based under indoor illuminations (3,000 K, 1,500 lux).

V_{oc} (V)	J_{sc} ($\mu\text{A}/\text{cm}^2$)	FF	PCE (%)
0.97	89.70	0.43	9.18
0.96	88.33	0.45	9.37
0.98	90.91	0.44	9.68
0.98	90.27	0.44	9.41
0.97	94.98	0.43	9.59

5. SCLC

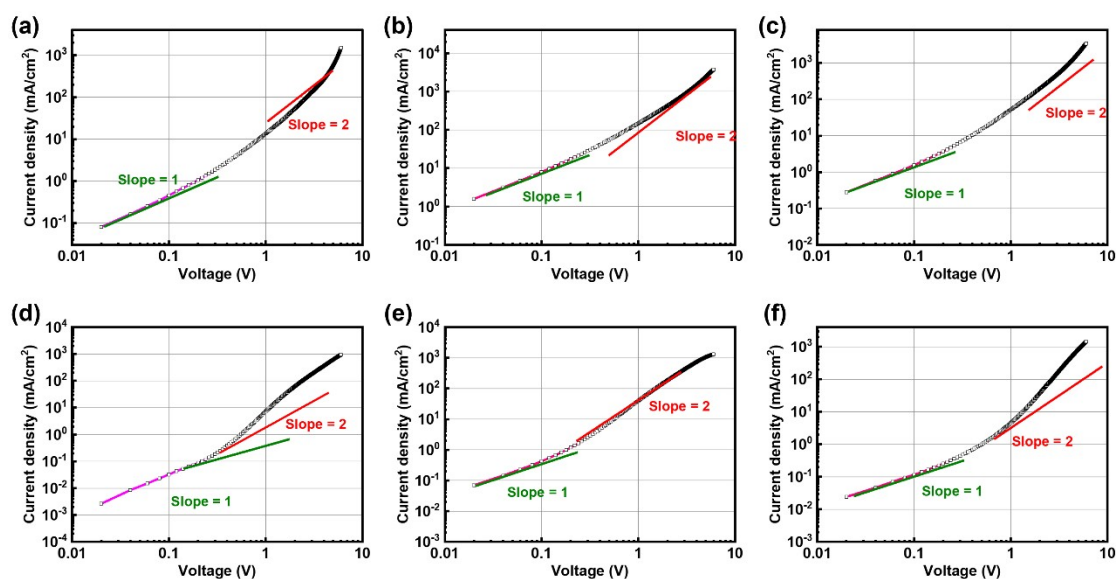


Figure S6. (a-c) Hole and (d-f) electron mobility based on (a, d) PBDB-T:WP1, (b, e) PBDB-T:WP2, and (c, f) PBDB-T:WP3 extracted from SCLC measurement.

Table S9. Hole and electron mobility for PBDB-T:Polymer acceptors extracted from SCLC measurement.

Blends	$\mu_h (\times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s}))$	$\mu_e (\times 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s}))$
PBDB-T:WP1	1.78	0.379
PBDB-T:WP2	8.48	5.87
PBDB-T:WP3	4.76	1.32

6. NMR and MS

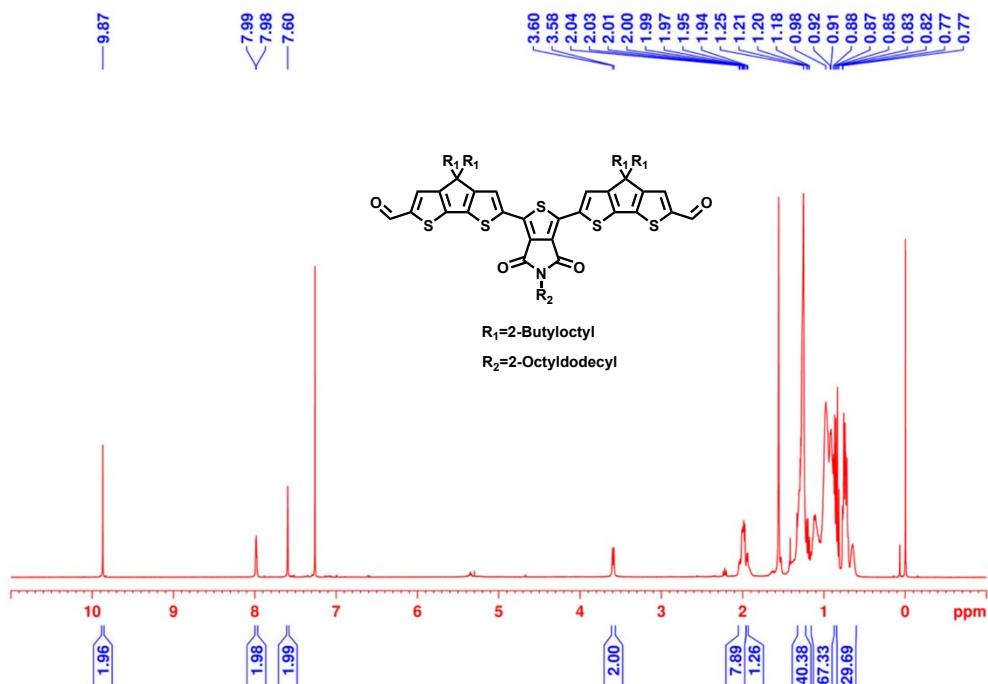


Figure S7. $^1\text{H-NMR}$ spectra of **M3** recorded in CDCl_3 .

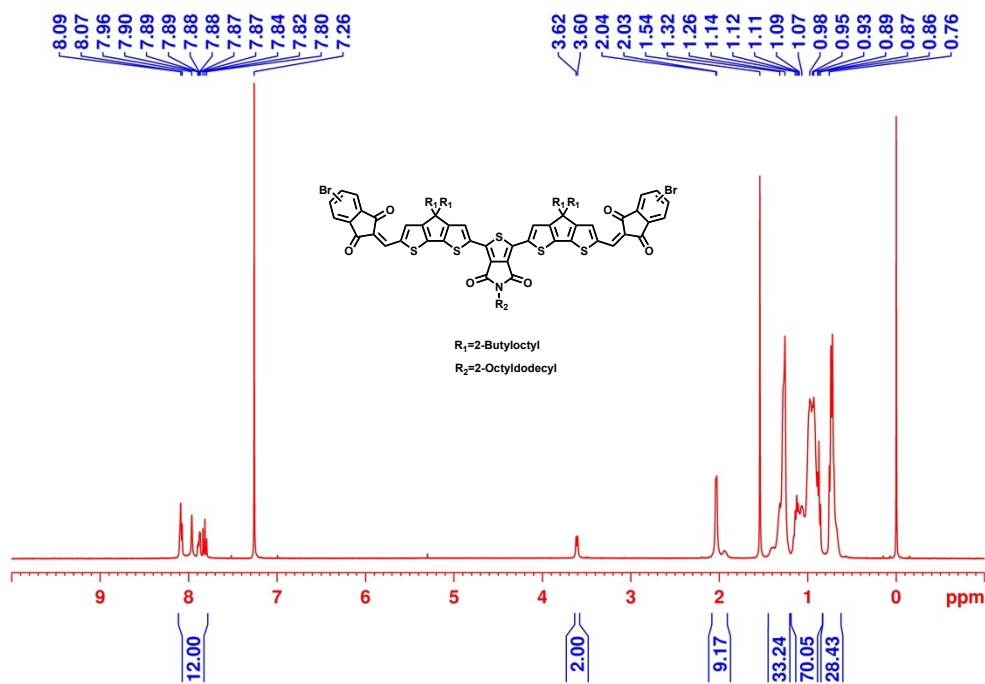


Figure S8. $^1\text{H-NMR}$ spectra of **M6** recorded in CDCl_3 .

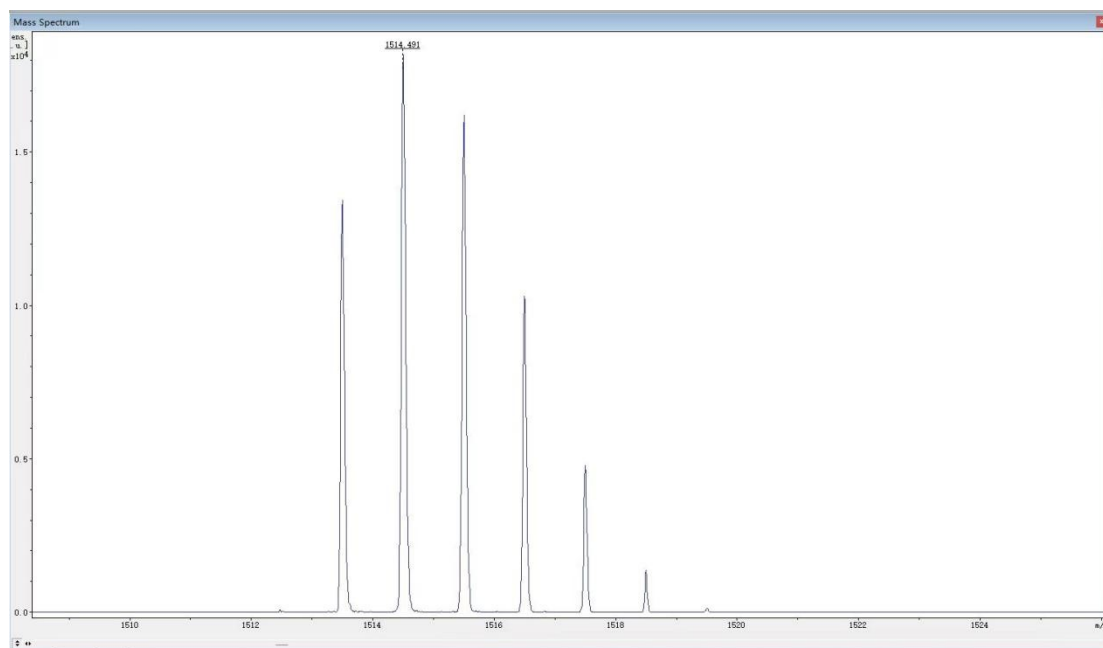


Figure S9. MALDI-TOF-MS spectra of **M3**.

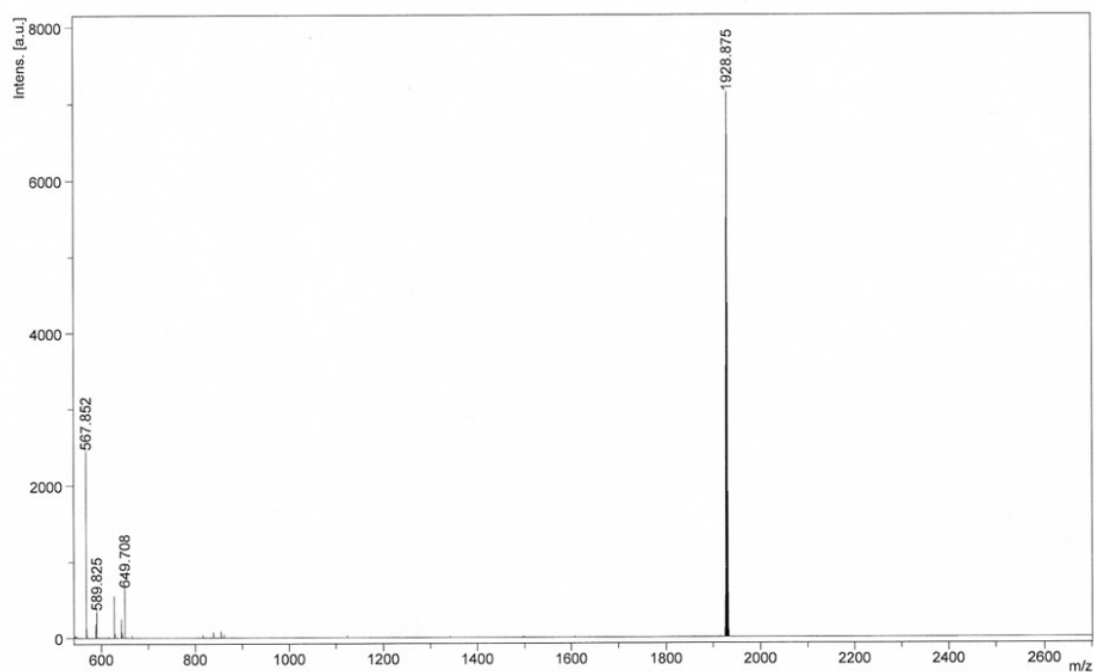


Figure S10. MALDI-TOF-MS spectra of **M6**.

7. Reference

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- S2. N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, Clarendon Press, 1948.
- S3. P. N. Murgatroyd, *J. Phys. D: Appl. Phys.*, 1970, **3**, 151-156.