

Electronic Supplementary Information

Rational Strategy to Enhance the Thermal Stability of Solar Cell Performance Using a Photocrosslinkable Conjugated Polymer

Hong Diem Chau, Su Hong Park, Sung Hoon Jung, Jin Young Park, Min Ji Kang, Amit Kumar Harit, Han Young Woo, Min Ju Cho*, and Dong Hoon Choi*

Department of Chemistry, Research Institute for Natural Sciences, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

*Corresponding authors: M. J. Cho, chominju@korea.ac.kr; D. H. Choi dhchoi8803@korea.ac.kr

Contents

1. Instrumentation	2
2. Experimental Section.....	4
3. Supporting Figures and Tables.	11
4. References.....	26

1. Instrumentation

^1H NMR and ^{13}C NMR spectra of the compounds and polymers were recorded using a Bruker 500 MHz spectrometer (Ascend 500, Bruker). Mass spectra (MS) of the synthesized compounds were recorded using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF/TOF™ 5800, ABSCIEX) at the Korea Basic Science Institute (Seoul). The number average molecular weight (M_n) and polydispersity index (PDI) values of PM6-X0 and PM6-X30 were estimated by gel permeation chromatography (GPC; Agilent GPC 1200 series) at 80 °C using 1,2-dichlorobenzene (*o*-DCB) as the eluent and polystyrene (PS) as the standard. The absorption and photoluminescence (PL) spectra of the active materials in chloroform (CF) solutions and thin films were recorded at room temperature (298 K) using a UV-vis absorption spectrometer (Agilent 8453, photodiode array, $\lambda = 190\text{--}1100$ nm) and a fluorescence spectrophotometer (Hitachi F-7000), respectively. The electrochemical properties were characterized by cyclic voltammetry (eDAQ EA161) at a scanning rate of 50 mV s⁻¹, using a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as the electrolyte, Pt wire as the counter, and Ag/AgCl as the reference electrode.

Grazing-incidence wide-angle X-ray diffraction (GIWAXD) of the films on the SiO_2 wafer was carried out using a PLS-II 9A ultra-small-angle X-ray scattering beamline at the Pohang Accelerator Laboratory (energy = 11.07 keV, pixel size = 0.0886 mm, $\lambda = 1.122$ Å, $2\theta = 0\text{--}20^\circ$). The surface morphologies of the films were investigated by atomic force microscopy (AFM; XE-100, Advanced Scanning Probe Microscope, PSIA) with a silicon cantilever.

PSC fabrication and characterization

The device was fabricated using a solution process with the conventional configuration of ITO/PEDOT:PSS/active layer/PDINN/Ag. PM6-X0:Y6-BO and PM6-X30:Y6-BO (donor:acceptor = 1:1.2 wt. ratio) were dissolved in the solvent chlorobenzene (CB) with the

addition of 0.5% v/v 1-chloronaphthalene (CN) at a total blend concentration of 22 mg mL⁻¹ and stirred overnight at 80°C. ITO (150 nm)-coated glass was cleaned by ultrasonication in deionized water and isopropyl alcohol for 10 min, dried at 120 °C overnight, and subjected to a UV-ozone treatment for 20 min. poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, Clevios P VP Al 4083) was spin coated onto ITO-coated glass substrates at 3000 rpm for 40 s and baked at 150 °C for 20 min. The substrates were transferred to a glove box. Then, the active layer was spin-coated onto the PEDOT:PSS layer, and the films were thermally annealed at 120 °C for 10 min. The UV crosslinked active layer was subjected to the UV irradiation ($\lambda = 365$ nm) at 120 °C for another 10 min. *N,N'*-bis(7-(dimethylamino)-4-azaheptyl)-3,4,9,10-perylene tetracarboxylic diimide (PDINN, 1 mg mL⁻¹ solution in methanol) was spin-coated on top of the active layers at 3000 rpm for 30 s. Finally, a Ag (100 nm) layer was deposited on the PDINN layer using a vacuum evaporator to form a 4 mm² active region through a shadow mask. The J - V curves of the devices were measured using a Keithley 2400 source meter under simulated AM 1.5G illumination (100 mW cm⁻²). External quantum efficiency (EQE) spectra were recorded using a certified EQE instrument (EQX 3100, McScience, Inc.).

Measurement of charge carrier mobility by space-charge-limited current (SCLC)

The hole-only devices (HODs), employing the device architectures ITO/PEDOT:PSS/polymer/Au, were measured using the space charge limited current (SCLC) method. The mobility was obtained by fitting the current-voltage (J - V) curves using the Mott-Gurney equation, $J = (9/8)\epsilon_0\epsilon_r\mu(V^2/L^3)$, where J is the current density, ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, μ is the mobility, V is the applied voltage, and L is the active layer thickness.^{S1} The hole mobility was calculated from the slopes of the J - V logarithmic plots.

2. Experimental Section

2.1. Materials

All chemicals were purchased from Sigma-Aldrich, Acros Organics Co., and Tokyo Chemical Industry, and were used as received without further purification. PM6-X0 was purchased from Derthon OPV Co., Ltd., and the PEDOT:PSS solution (Clevios P VP (A1 4083)) was purchased from Heraeus. The reagent-grade solvents used in this experiment were freshly dried using standard distillation methods. 2,5-dibromothiophene-3,4-dicarboxylic acid (1), 2,5-bis(6-bromohexyl)thiophene (3), and 4-oxo-4-(penta-1,4-dien-3-yloxy)butanoic acid (9) were synthesized according to the literature.^{S2-S4}

2.2. Synthesis

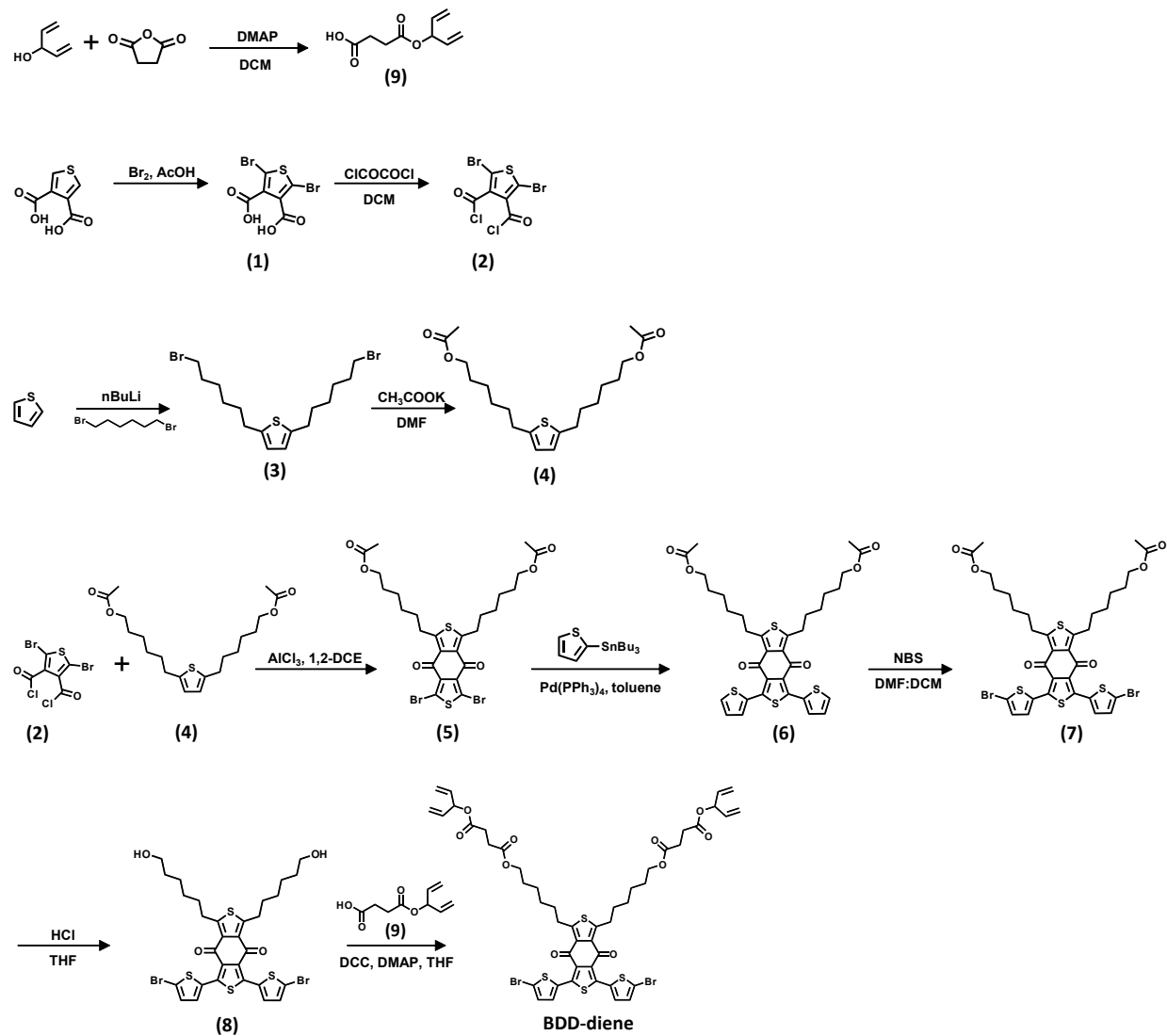


Fig. S1 Synthesis scheme of the crosslinkable monomer BDD-diene

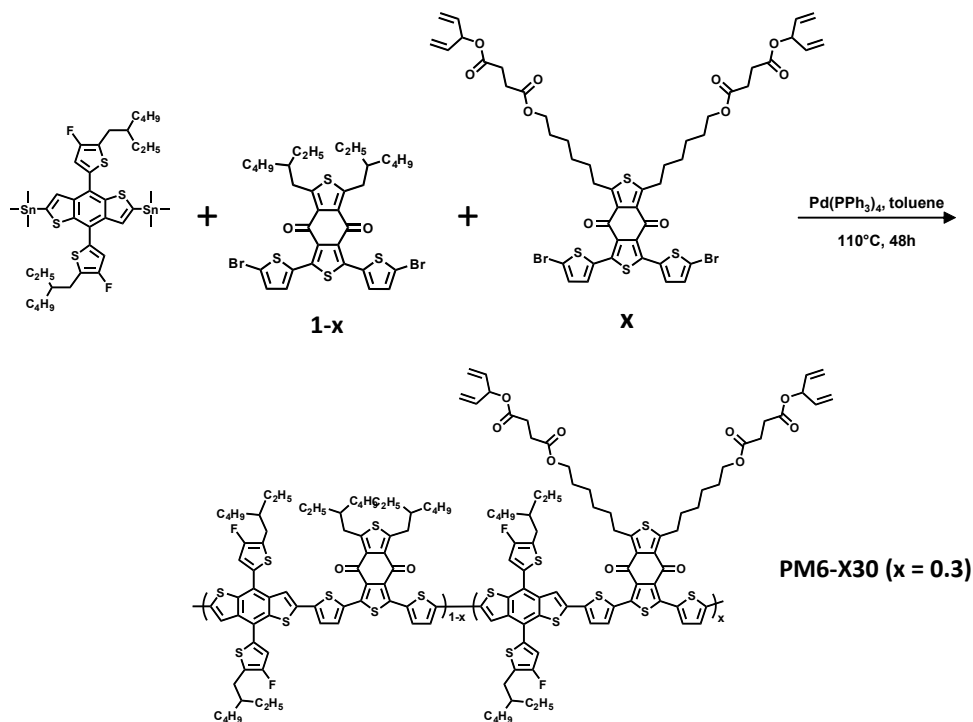


Fig. S2 Synthesis scheme of the crosslinkable polymer donor PM6-X30

Thiophene-2,5-diylbis(hexane-6,1-diyl) diacetate (4). Compound **3** (1.64 g, 4.0 mmol) and potassium acetate (1.18 g, 0.12 mmol) were dispersed in DMF (20 mL). The mixture was stirred at 90 °C overnight. After cooling to room temperature (RT), n-hexane (100 mL) was added and the organic layer was extracted and dried over anhydrous sodium sulfate. After evaporation of the solvent, the product was purified by column chromatography (eluent: dichloromethane (DCM)) on silica gel to obtain compound **4** as a pale yellow oil (**4**: 1.41 g, 96% yield). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 6.55 (s, 2H), 4.05 (t, *J* = 6.9 Hz, 4H), 2.74 (t, *J* = 7.6 Hz, 4H), 2.04 (s, 6H), 1.60 - 1.69 (m, 8H), 1.38 ppm (dt, *J* = 7.4, 3.5 Hz, 8H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 171.2, 143.0, 123.4, 77.2, 64.5, 31.5, 30.0, 28.6, 28.5, 25.6, 21.0; MALDI-TOF MS: *m/z* calcd for C₂₀H₃₂O₄S: 368.20; found: 368.19 [M⁺]; Elemental Anal. Calcd for C₂₀H₃₂O₄S: C, 65.18; H, 8.75; O, 17.37; S, 8.70. Found: C, 63.56; H, 7.56; S, 8.59.

(5,7-dibromo-4,8-dioxo-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-1,3-diyl)bis(hexane-6,1-diyl) diacetate (5). Under nitrogen atmosphere, compound **1** (1.0 g, 3.0 mmol), oxalyl chloride (2.0 mL, 12.0 mmol), one drop of DMF were added to 15 mL of dry DCM. After stirring overnight at RT, the solvent and excess oxalyl chloride were removed by evaporation. The crude solid compound **2** was directly added into the solution of compound **4** (1.2 g, 3.0 mmol) in 1,2-dichloroethane (10 mL). The mixture was cooled down to 0 °C, and AlCl₃ (1.6 g, 12.0 mmol) was added in small portions. The mixture solution was kept stirring at 0 °C for 30 min more before warmed to room temperature and stirred for further 4 h. After completion of the reaction, it was quenched with ice and extracted using DCM. The combined organic layer was concentrated, and the obtained crude product was further purified by column chromatography (eluent: DCM:ethyl acetate (EA), 20:1, v/v) to obtain the target compound **5** as a pale yellow solid (**5**: 1.69 g, 85% yield). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 4.06 (t, J = 6.7 Hz, 4H), 3.31 - 3.37 (m, 4H), 2.05 (s, 6H), 1.75 (d, J = 7.3 Hz, 4H), 1.61 - 1.69 (m, 4H), 1.40 - 1.51 ppm (m, 8H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 175.4, 171.2, 155.1, 134.7, 132.2, 119.6, 77.3, 64.5, 30.4, 29.8, 29.0, 28.5, 25.7, 21.0; MALDI-TOF MS: m/z calcd for C₂₆H₃₀Br₂O₆S₂: 659.99; found: 659.04 [M⁺]; Elemental Anal. Calcd for C₂₆H₃₀Br₂O₆S₂: C, 47.14; H, 4.56; O, 14.49; S, 9.68. Found: C, 47.17; H, 4.73; S, 9.67.

(4,8-dioxo-5,7-di(thiophen-2-yl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-1,3-diyl)bis(hexane-6,1-diyl) diacetate (6). Compound **5** (1.32 mg, 2.0 mmol) and tributyl (thiophen-2-yl)stannane (1.64 mg, 4.4 mmol) were dissolved in 20 mL of dry toluene under a nitrogen atmosphere. Subsequently, a catalytic amount of Pd(PPh₃)₄ was added to the reaction mixture. The solution was stirred at 90 °C overnight. After vacuum evaporation of the solvent,

the residue was further purified by column chromatography (eluent: DCM: EA, 25:1, v/v). The desired product **6** was obtained as a yellow solid (6: 1.14 g, 93% yield). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.73 (dd, J = 1.22, 3.97 Hz, 2H), 7.51 (dd, J = 1.22, 5.19 Hz, 2H), 7.13 (dd, J = 3.81, 5.04 Hz, 2H), 4.07 (t, J = 6.71 Hz, 4H), 3.32 - 3.39 (m, 4H), 2.05 (s, 6H), 1.77 (t, J = 7.32 Hz, 4H), 1.62 - 1.70 (m, 4H), 1.41 - 1.52 (m, 8H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 177.6, 171.2, 153.5, 142.6, 133.2, 132.6, 132.6, 130.6, 129.3, 127.2, 77.2, 64.5, 30.5, 29.6, 28.9, 28.5, 25.7, 21.0; MALDI-TOF MS: m/z calcd for C₃₄H₃₆O₆S₄: 668.14; found: 669.13 [M⁺]; Elemental Anal. Calcd for C₃₄H₃₆O₆S₄: C, 61.05; H, 5.43; O, 14.35; S, 19.17. Found: C, 61.03; H, 5.71; S, 15.63.

(5,7-bis(5-bromothiophen-2-yl)-4,8-dioxo-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-1,3-diyl)bis(hexane-6,1-diyl) diacetate (7). Compound **6** (1.0 mg, 1.5 mmol) and *N*-bromosuccinimide (0.59 g, 3.3 mmol) was dissolved into DMF:DCM (1:1, v/v). The resulting solution was stirred overnight at RT. Subsequently, DCM (50 mL) was added and the organic layer was extracted and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography (eluent: DCM:EA, 30:1, v/v) on silica gel to obtain compound **7** as a bright yellow solid (7: 1.52 g, 92% yield). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.45 (d, J = 3.97 Hz, 2H), 7.08 (d, J = 4.27 Hz, 2H), 4.08 (t, J = 6.71 Hz, 4H), 3.31 - 3.40 (m, 4H), 2.05 (s, 6H), 1.77 (t, J = 7.32 Hz, 4H), 1.67 (quin, J = 7.02 Hz, 4H), 1.40 - 1.53 (m, 8H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 177.4, 171.2, 154.1, 141.5, 134.4, 132.1, 131.8, 130.4, 129.8, 118.2, 77.2, 64.5, 30.4, 29.7, 29.0, 28.5, 25.7, 21.1; MALDI-TOF MS: m/z calcd for C₃₄H₃₄Br₂O₆S₄: 823.96; found: 824.91 [M⁺]; Elemental Anal. Calcd for C₃₄H₃₄Br₂O₆S₄: C, 49.40; H, 4.15; O, 11.61; S, 15.51. Found: C, 49.25; H, 4.22; S, 15.63.

1,3-bis(5-bromothiophen-2-yl)-5,7-bis(6-hydroxyhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (8). Compound **7** (1.0 mg, 1.2 mmol) was dissolved in 30 mL of tetrahydrofuran (THF). Subsequently, 10 mL HCl 5M was slowly added to the mixture. The reaction was heated to reflux at 70 °C overnight. After completion, the precipitate was filtered and washed several times with DCM to obtain a yellow solid with a very low solubility. Crude product **8** was used in the subsequent reaction without further purification. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.44 (d, J = 3.97 Hz, 2H), 7.08 (d, J = 3.97 Hz, 2H), 3.67 (t, J = 6.26 Hz, 4H), 3.36 (t, J = 7.63 Hz, 4H), 1.73 - 1.82 (m, 4H), 1.58 - 1.66 (m, 4H), 1.47 (br. s., 8H); Elemental Anal. Calcd for C₃₀H₃₀Br₂O₄S₄: C, 48.52; H, 4.07; O, 8.62; S, 17.27. Found: C, 49.45; H, 7.22; S, 18.28.

o,o'-((5,7-bis(5-bromothiophen-2-yl)-4,8-dioxo-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-1,3-diyl)bis(hexane-6,1-diyl) di(penta-1,4-dien-3-yl) disuccinate (BDD-diene). Compound **8** (890 mg, 1.2 mmol) and compound **9** (1.10 g, 6.0 mmol) were dissolved in 100 mL of distilled THF under a nitrogen atmosphere. Then, dicyclohexylcarbodiimide (DCC, 1.23 g, 0.6 mmol) and 4-dimethylaminopyridine (DMAP, 147 mg, 1.2 mmol) were added to the mixture. The reaction was stirred at 60 °C overnight. After completion, the resulting mixture was filtered through celite to remove solids and purified by column chromatography (eluent: DCM:EA, 30:1, v/v). The obtained compound was then recrystallized and washed several times with ethanol to yield the monomer BDD-diene as a yellow solid (BDD-diene: 1.03 g, 80% yield). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.45 (d, J = 3.97 Hz, 2H), 7.08 (d, J = 3.97 Hz, 2H), 5.78 - 5.87 (m, 4H), 5.69 - 5.74 (m, 2H), 5.30 (td, J = 1.34, 17.17 Hz, 4H), 5.23 (td, J = 1.22, 10.38 Hz, 4H), 4.10 (t, J = 6.71 Hz, 4H), 3.32 - 3.38 (m, 4H), 2.61 - 2.69 (m, 8H), 1.75 (d, J = 7.32 Hz, 4H), 1.62 - 1.70 (m, 4H), 1.40 - 1.52 (m, 8H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ

= 177.4, 172.3, 171.2, 154.1, 141.5, 134.9, 134.5, 132.1, 131.9, 130.4, 129.8, 118.1, 117.5, 77.2, 75.3, 64.8, 30.4, 29.7, 29.4, 29.1, 29.0, 28.5, 25.7; MALDI-TOF MS: m/z calcd for $C_{48}H_{50}Br_2O_{10}S_4$: 1072.07; found: 1073.03 [M⁺]; Elemental Anal. Calcd for $C_{48}H_{50}Br_2O_{10}S_4$: C, 53.63; H, 4.69; O, 14.88; S, 11.93. Found: C, 53.40; H, 4.79; S, 11.67.

Synthesis of the polymer PM6-X30. The monomer BDT-2F (1 equiv.), BDD (0.7 equiv.), BDD-diene (0.3 equiv.), and Pd(PPh₃)₄ (5 mol%) were added to a Schlenk tube. Subsequently, anhydrous toluene (5 mL) was injected into one portion and the mixture was degassed for 10 min under bubbling nitrogen. The reaction was refluxed for 48 h at 110 °C. After cooling to room temperature, the resulting solution was precipitated in methanol (300 mL). The residue was collected and purified by Soxhlet extraction using acetone, n-hexane, DCM, and chloroform (CF). The concentrated CF fraction was then precipitated in methanol (300 mL), collected, and dried under vacuum at 60 °C for 24 h. M_n : 11.3 kDa; PDI: 1.74. Elemental Anal. Calcd for Chemical Formula: $C_{722}H_{798}F_{20}O_{44}S_{80}$: C, 66.07; H, 6.13; F, 2.89; S, 19.54; O, 5.36. Found: C, 65.89; H, 6.54; S, 19.88; O, 5.45.

3. Supporting Figures and Tables

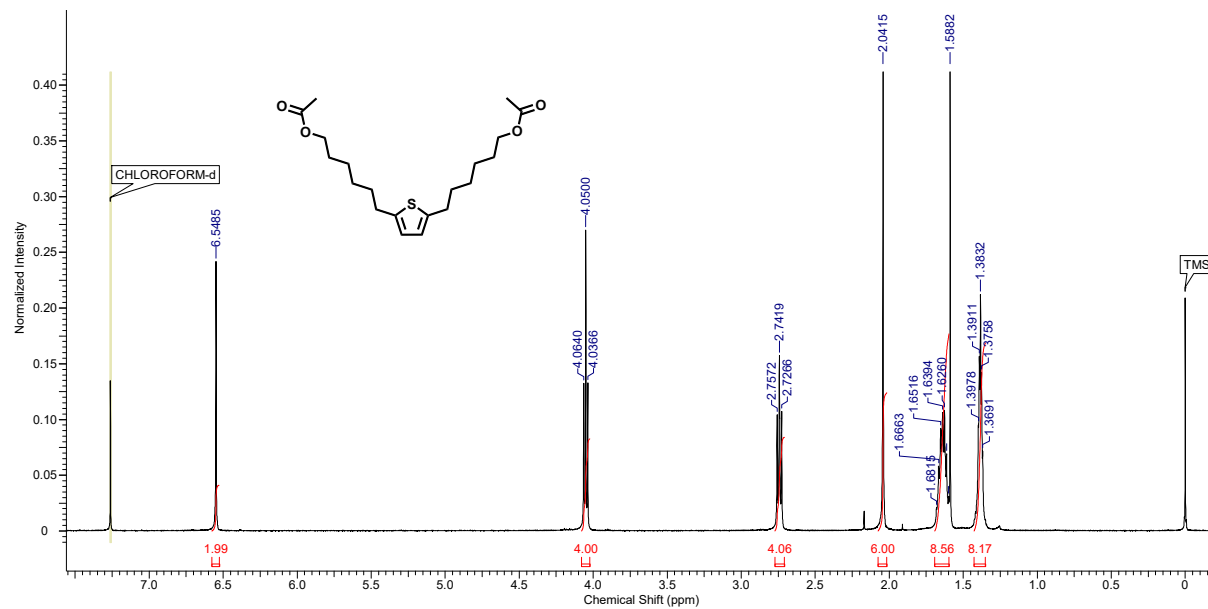


Fig. S3 ^1H NMR spectrum of compound 4

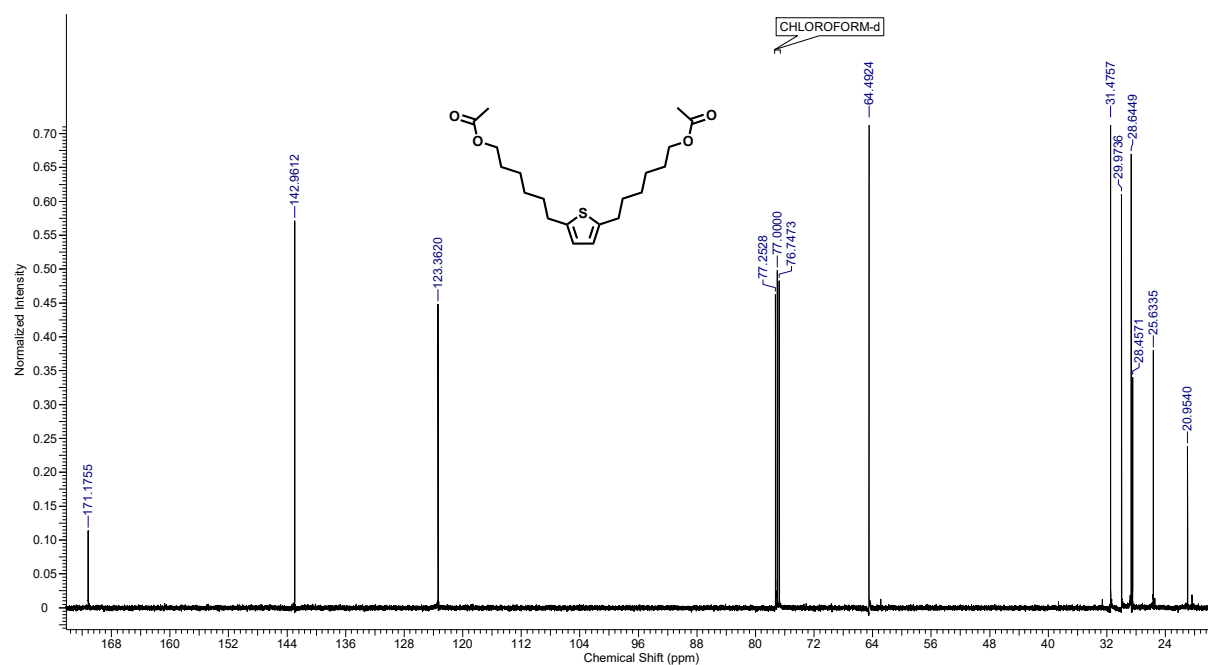


Fig. S4 ^{13}C NMR spectrum of compound 4

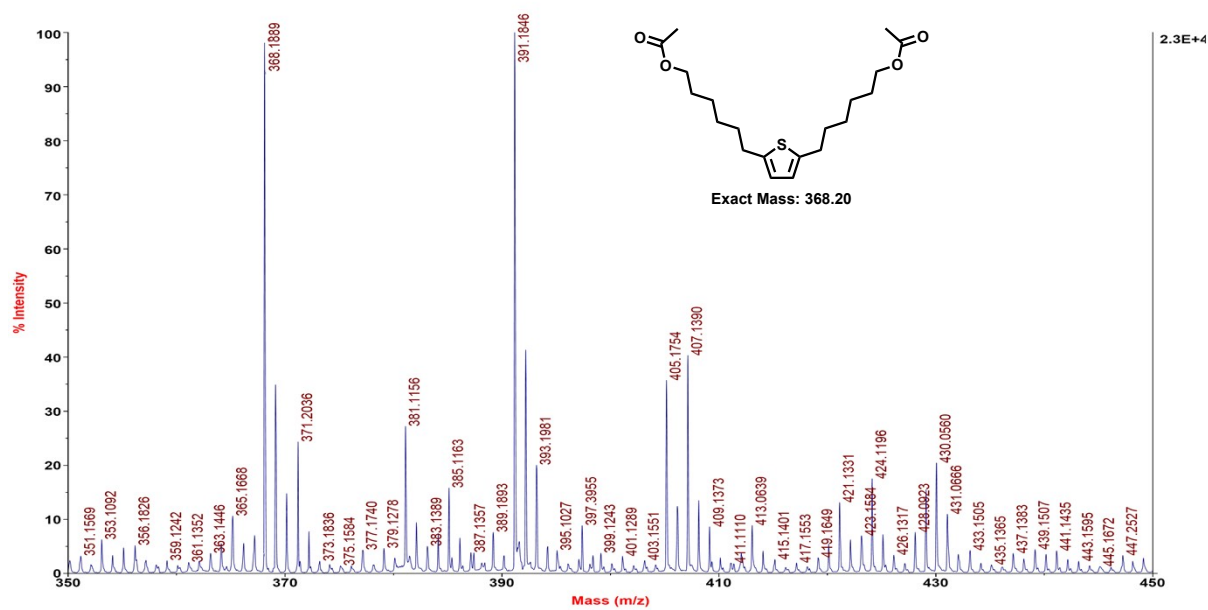


Fig. S5 Mass spectrum of compound 4

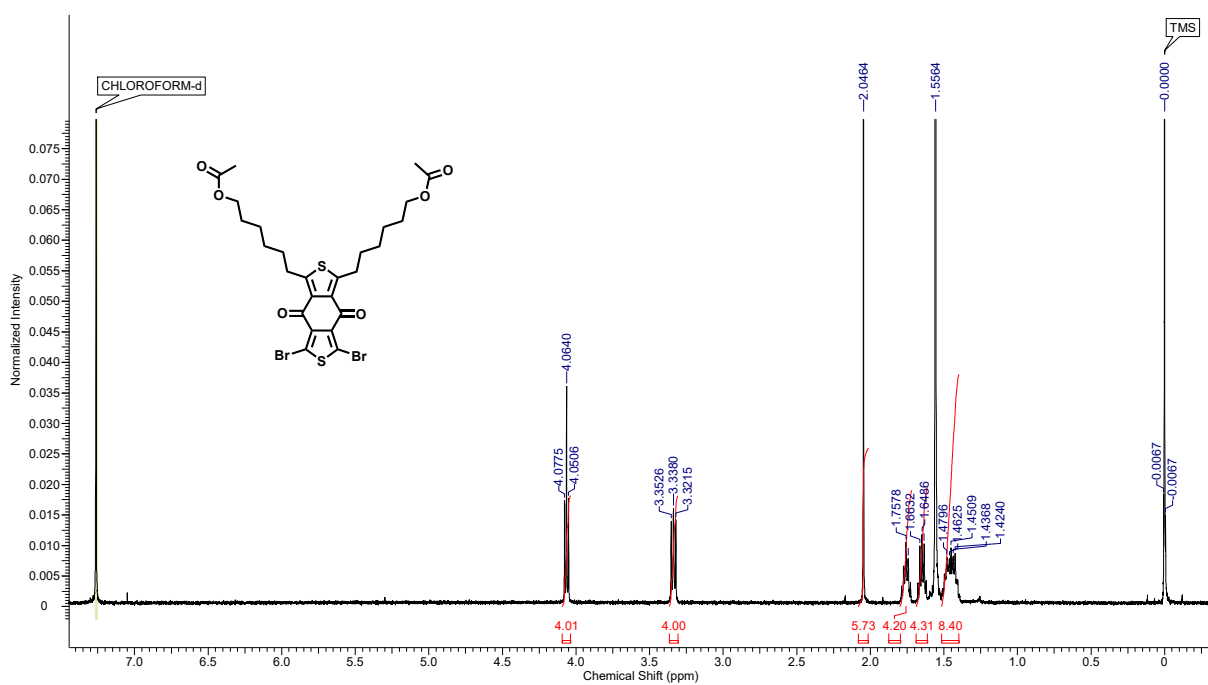


Fig. S6 ¹H NMR spectrum of compound 5

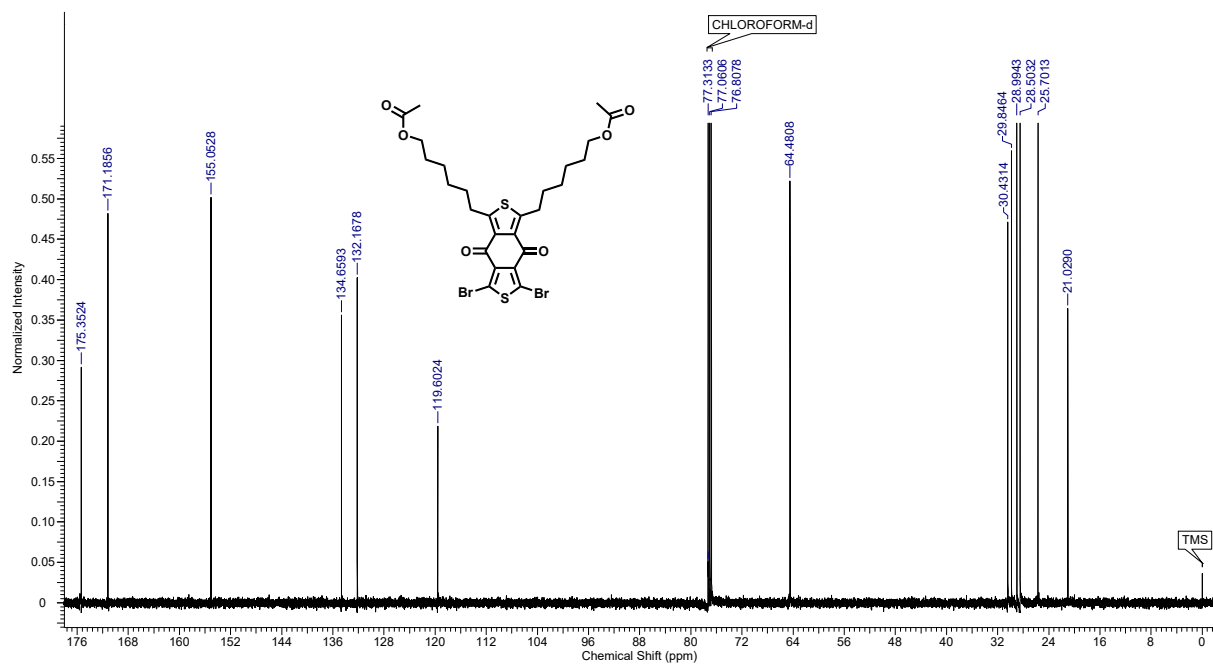


Fig. S7 ^{13}C NMR spectrum of compound 5

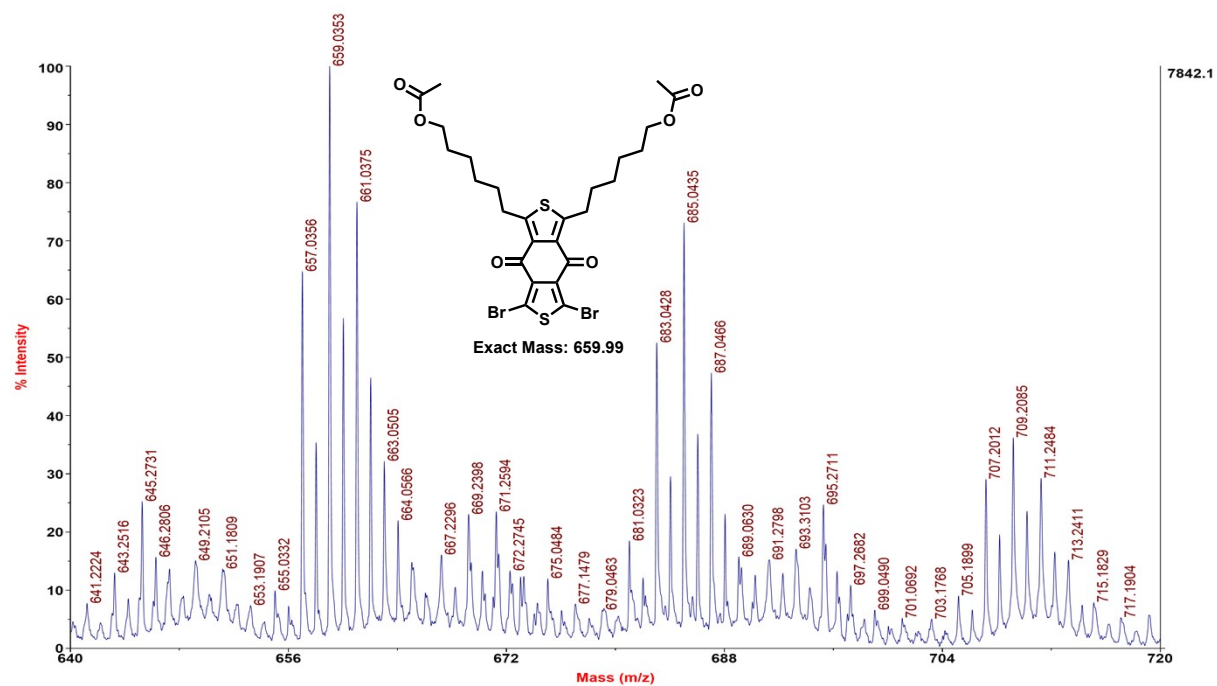


Fig. S8 Mass spectrum of compound 5

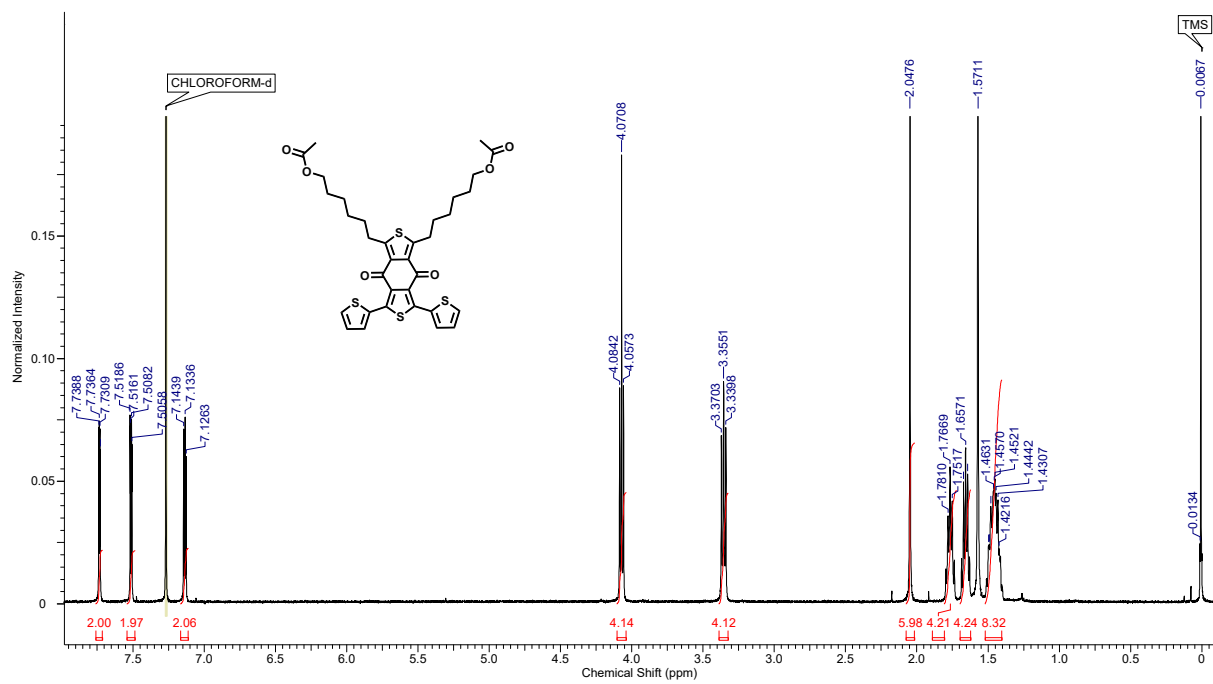


Fig. S9 ^1H NMR spectrum of compound 6

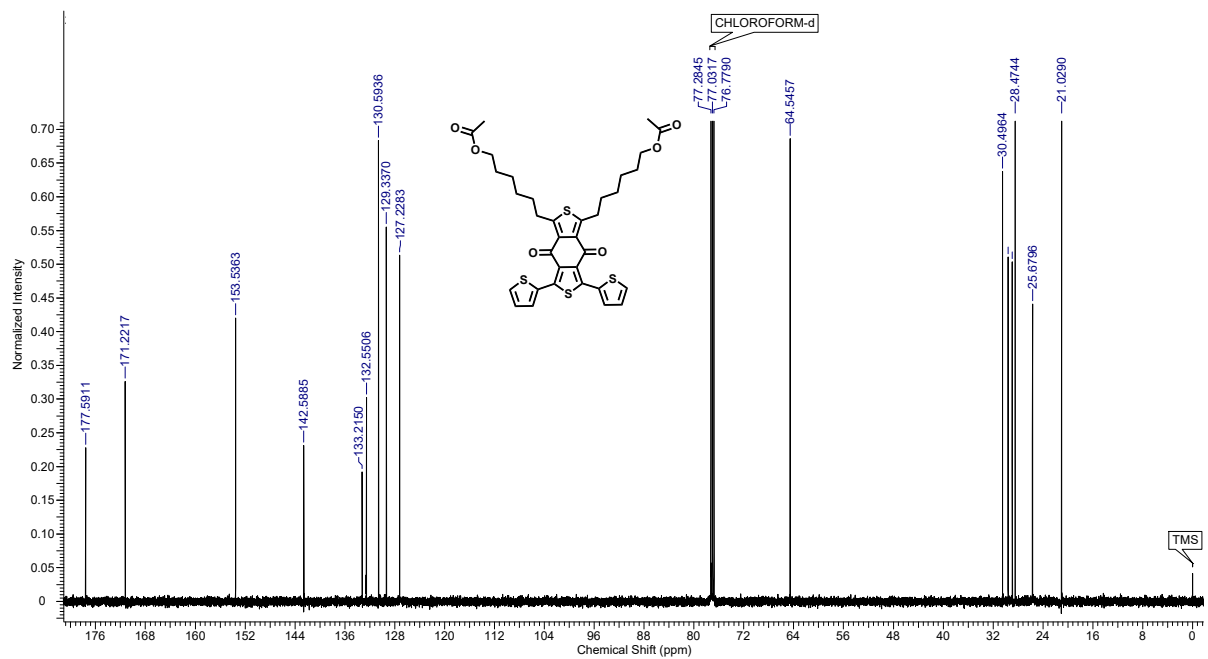


Fig. S10 ^{13}C NMR spectrum of compound 6

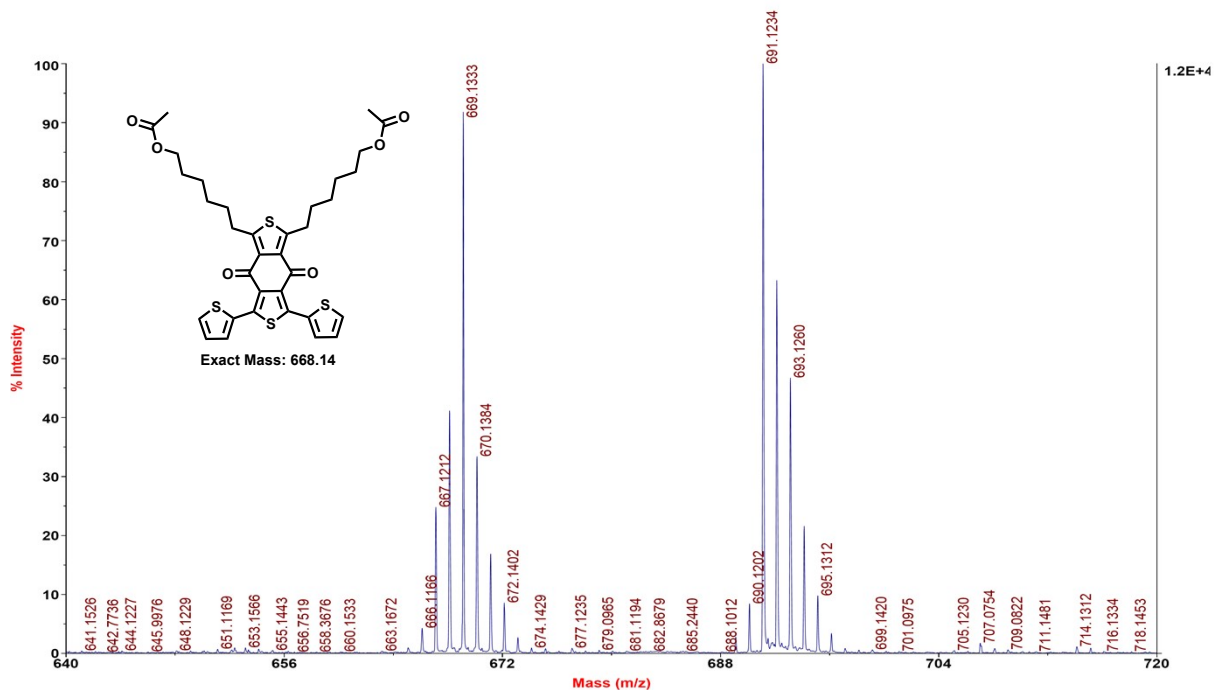


Fig. S11 Mass spectrum of compound 6

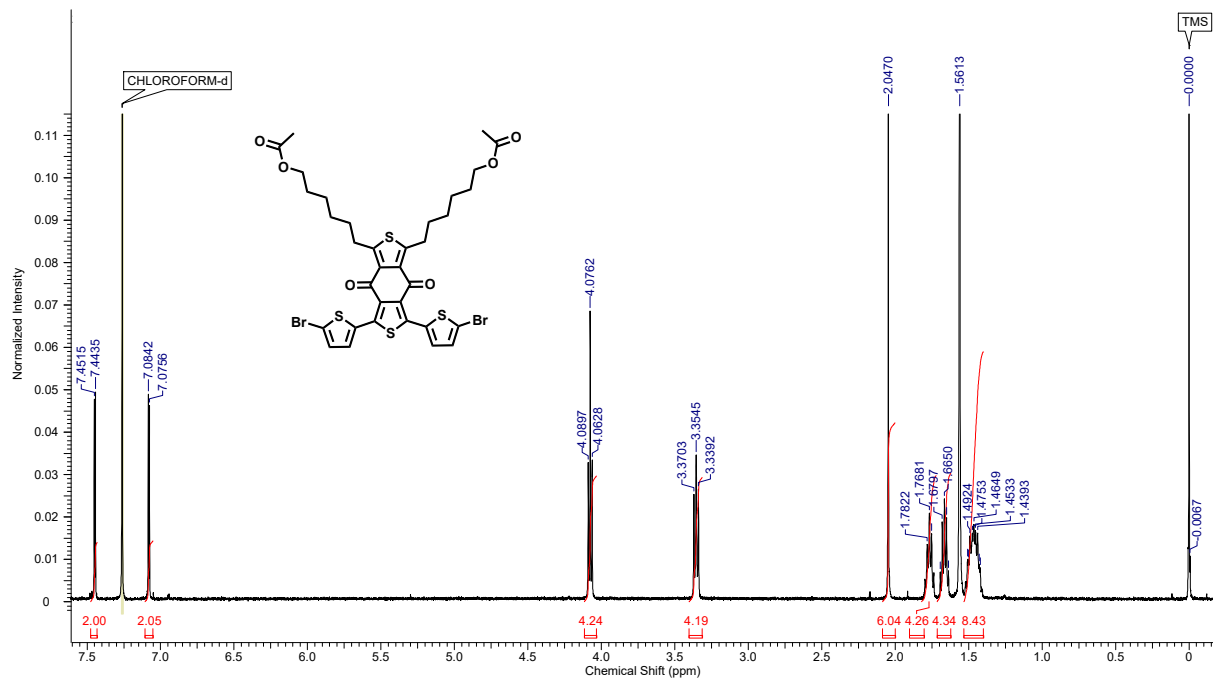


Fig. S12 ¹H NMR spectrum of compound 7

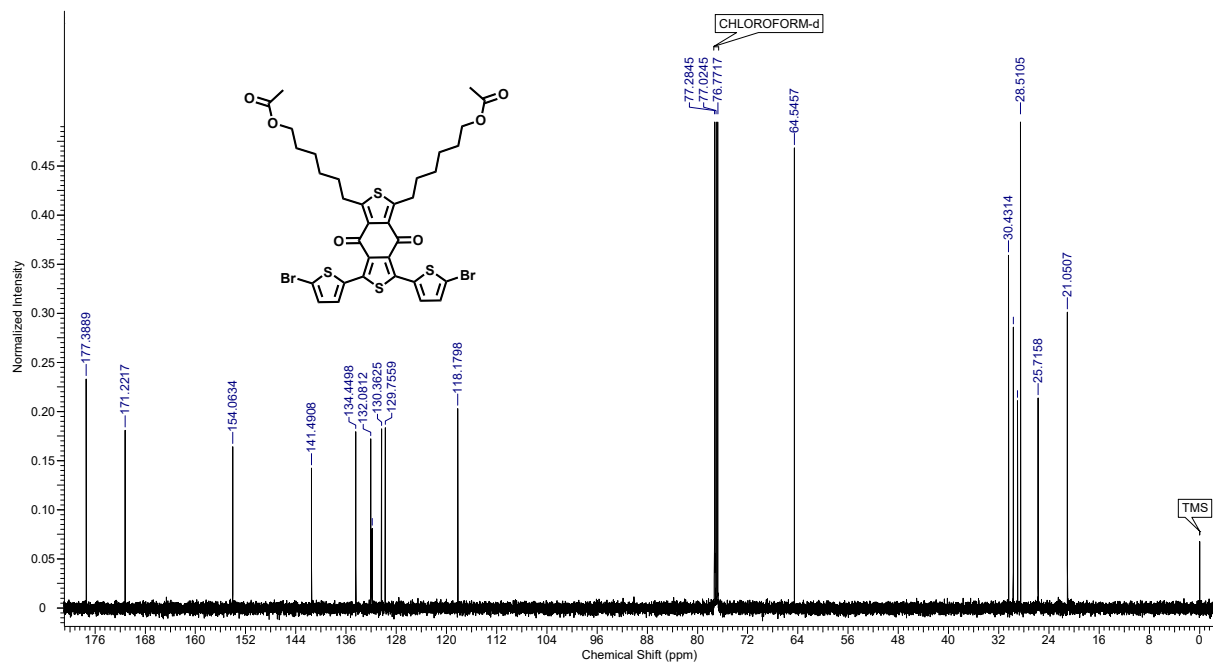


Fig. S13 ^{13}C NMR spectrum of compound 7

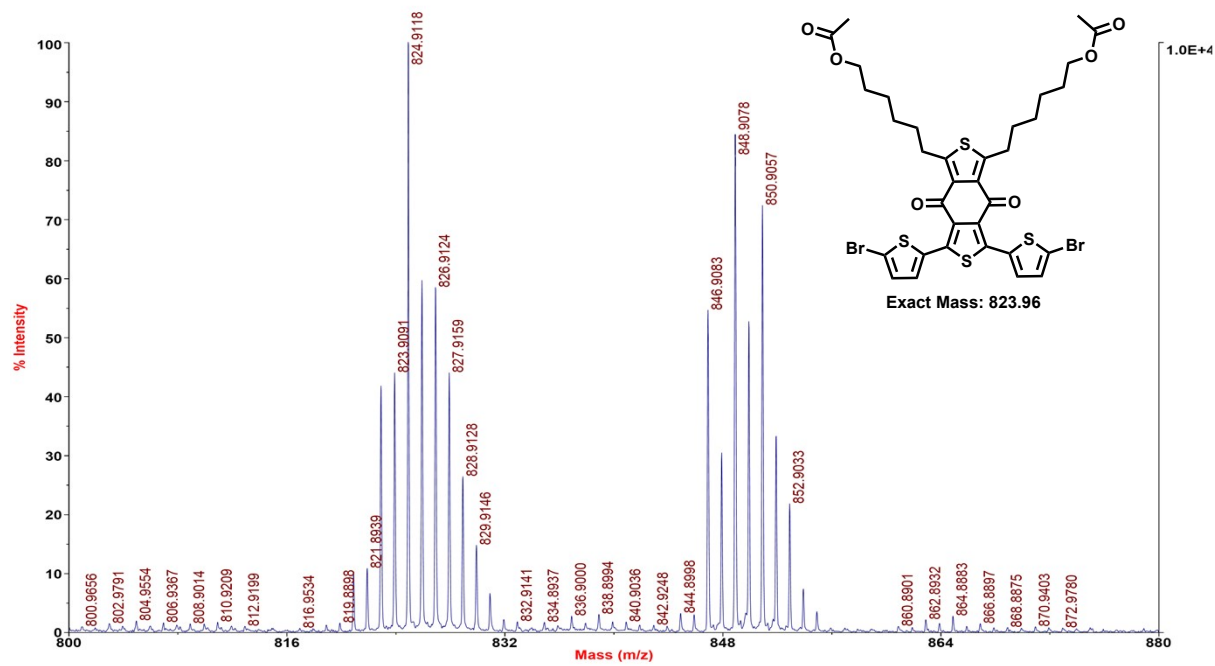


Fig. S14 Mass spectrum of compound 7

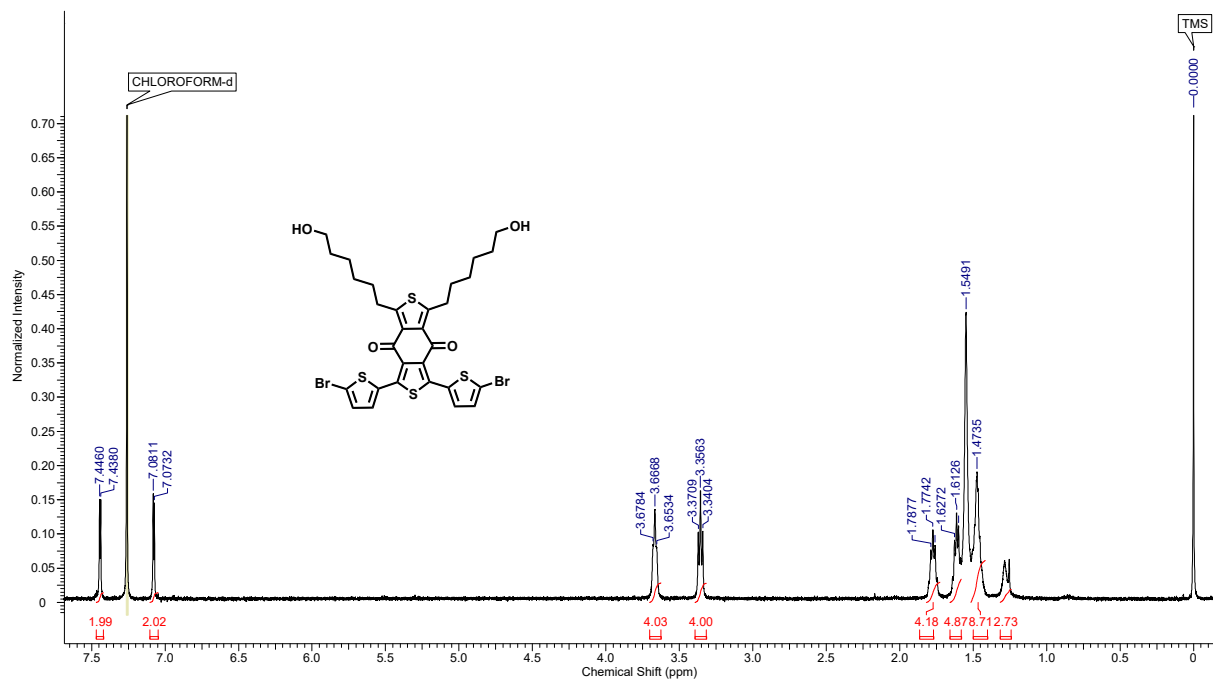


Fig. S15 ^1H NMR spectrum of compound 8

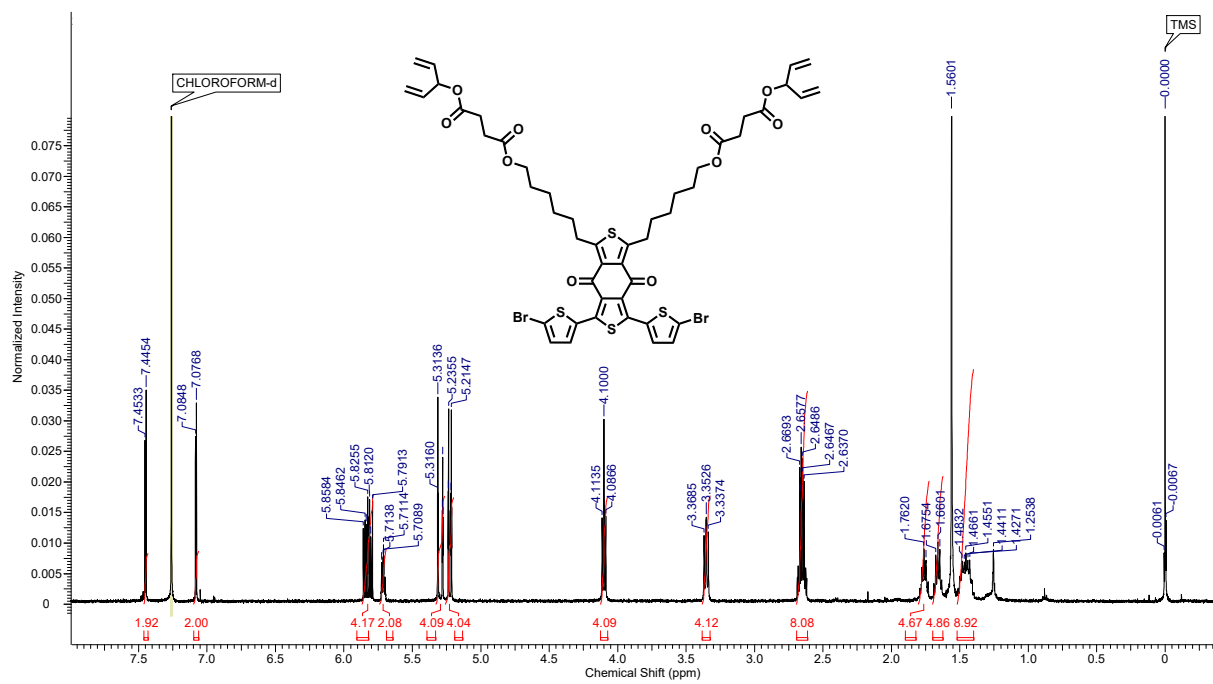


Fig. S16 ^1H NMR spectrum of the monomer BDD-diene

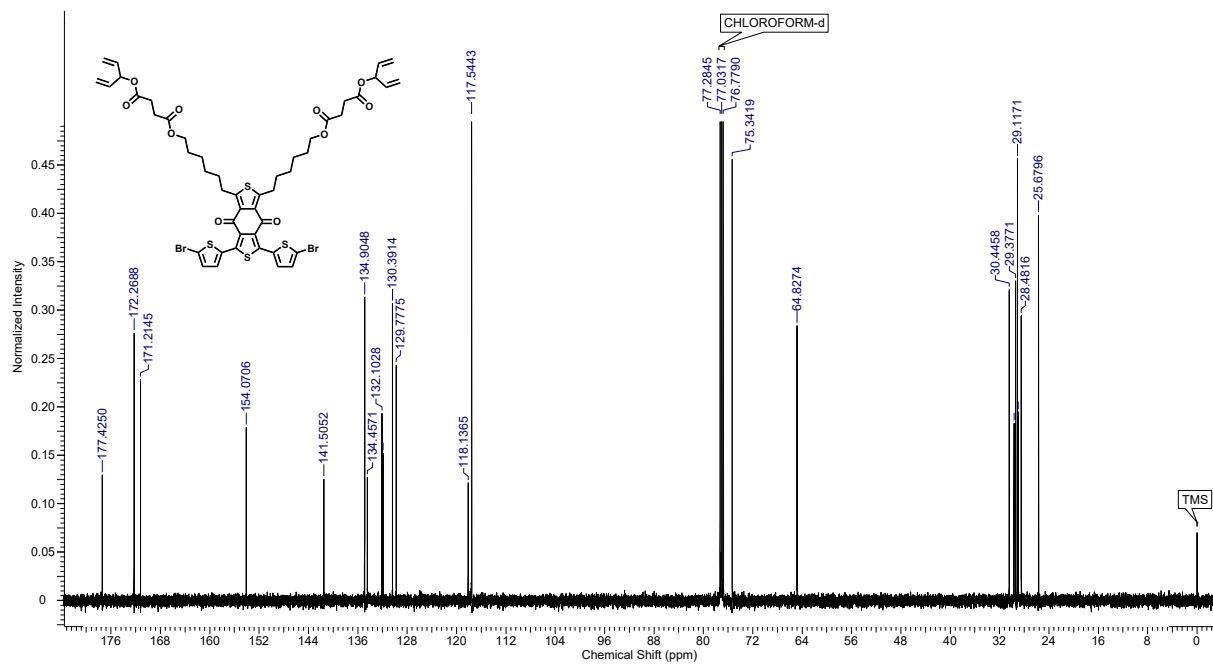


Fig. S17 ^{13}C NMR spectrum of the monomer BDD-diene

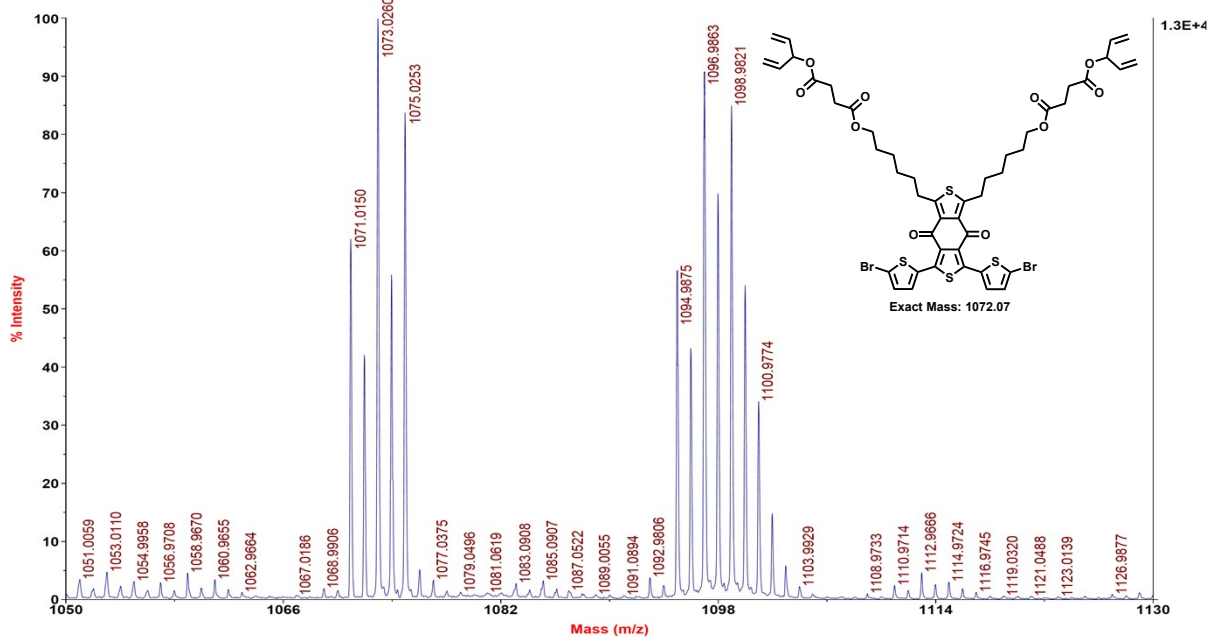


Fig. S18 Mass spectrum of the monomer BDD-diene

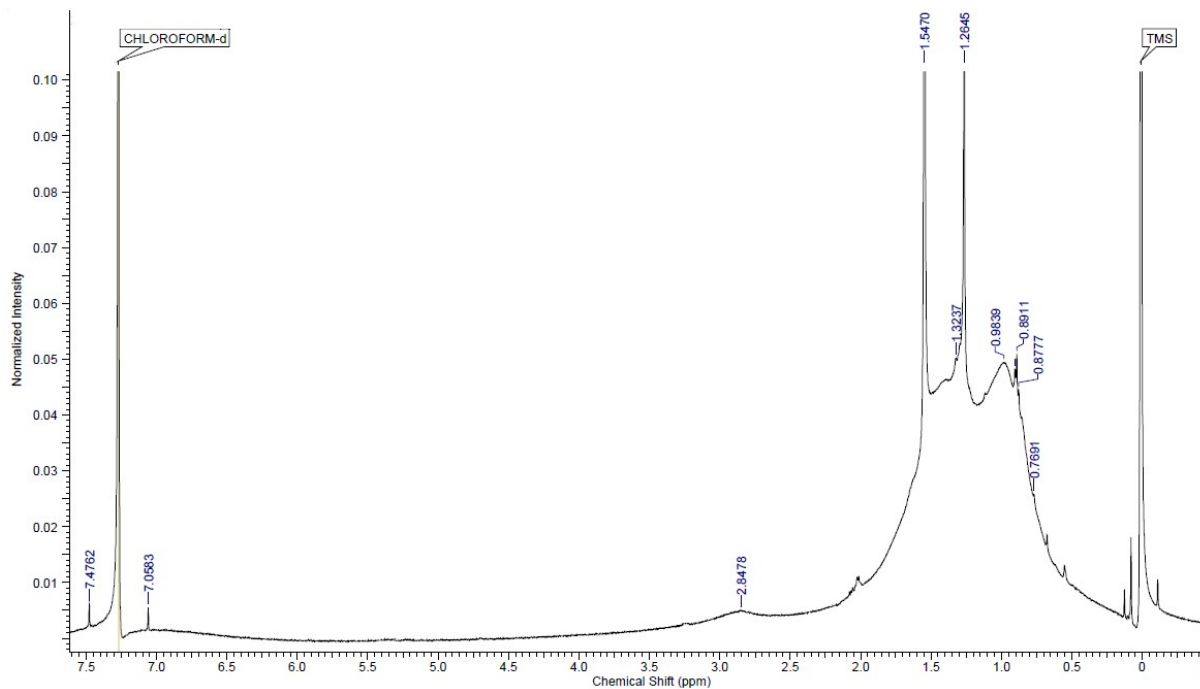


Fig. S19 ^1H NMR spectrum of the polymer PM6-X0

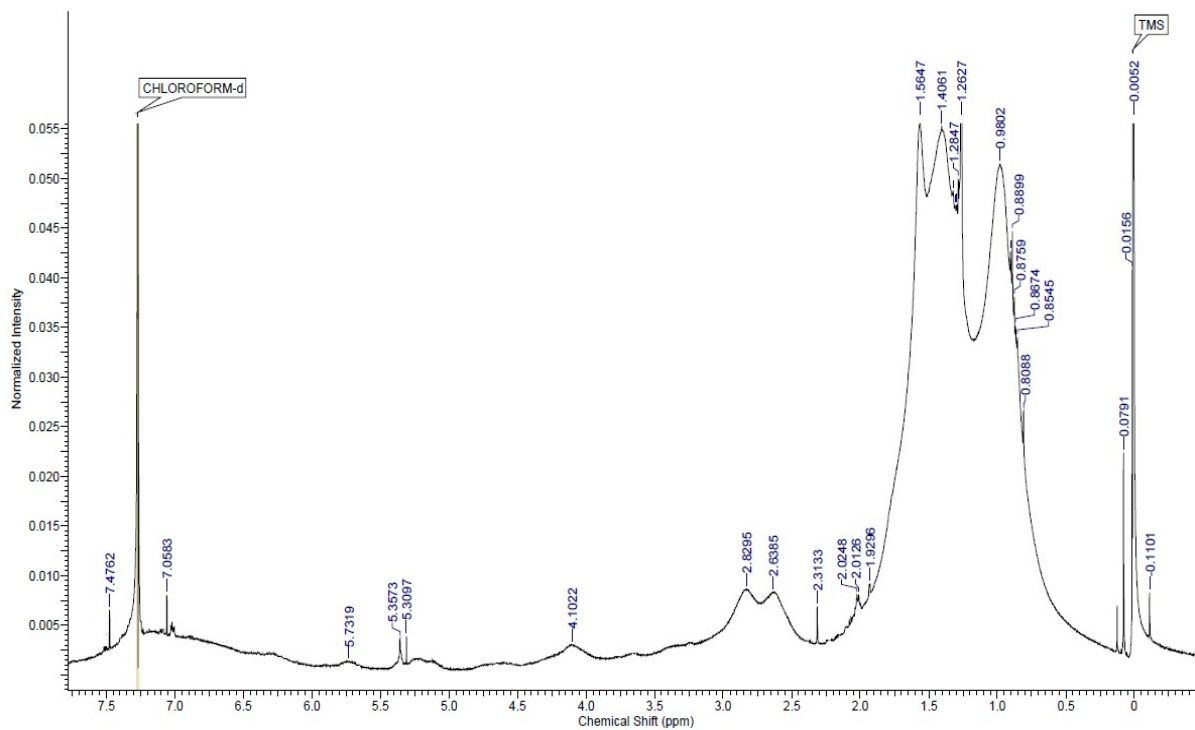


Fig. S20 ^1H NMR spectrum of the polymer PM6-X30

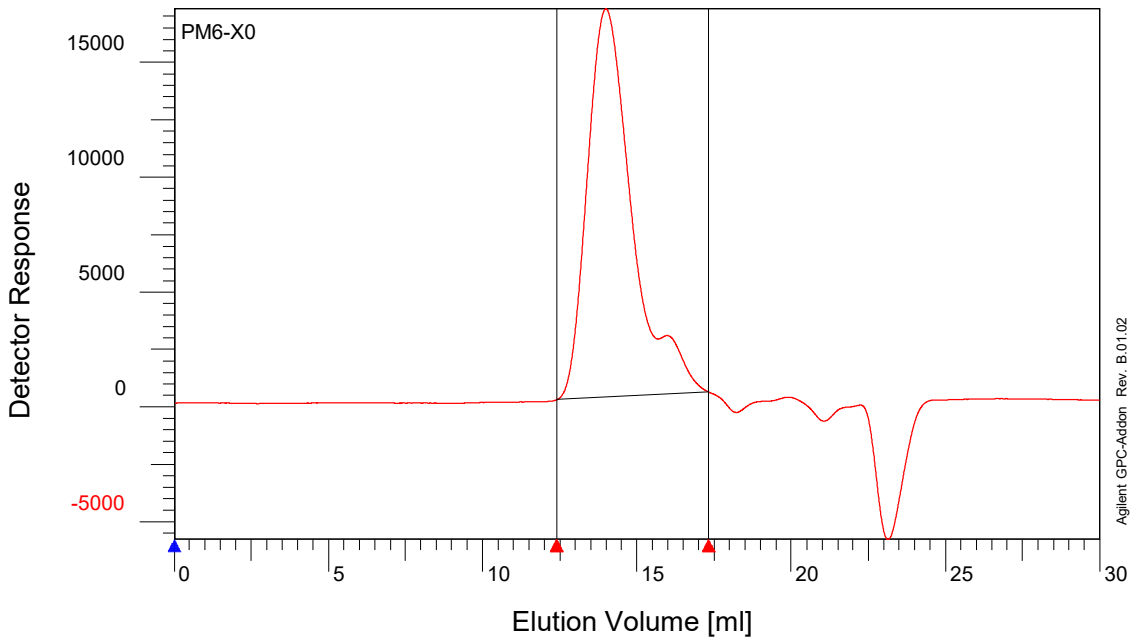


Fig. S21 GPC result of the polymer PM6-X0

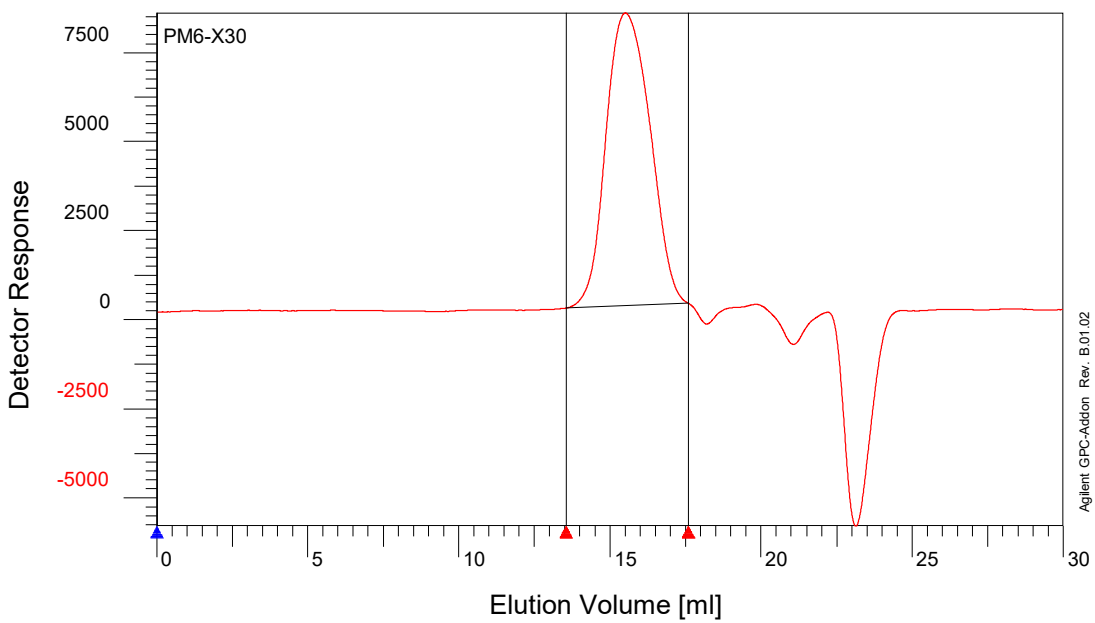


Fig. S22 GPC result of the polymer PM6-X30

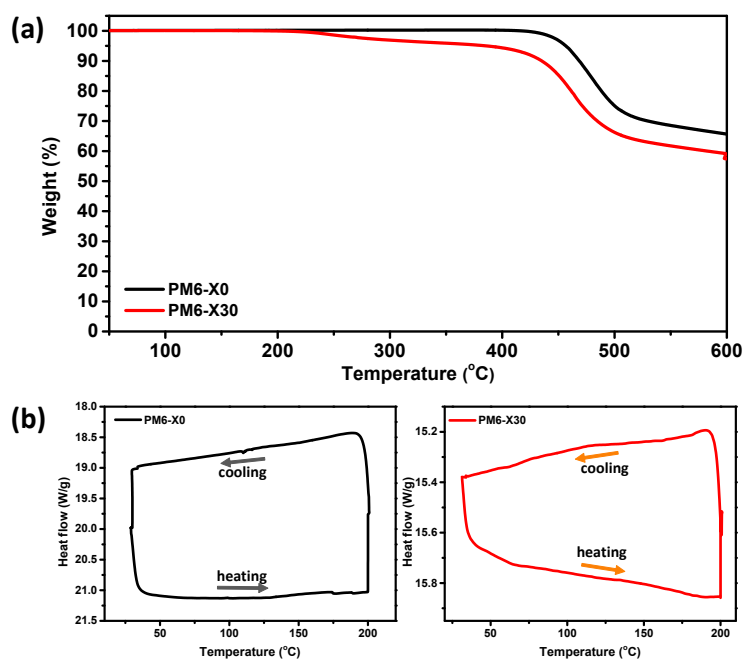


Fig. S23 (a) TGA curves and (b) DSC thermograms of PM6-X0 and PM6-X30 measured at a scan rate of 10 °C per minute.

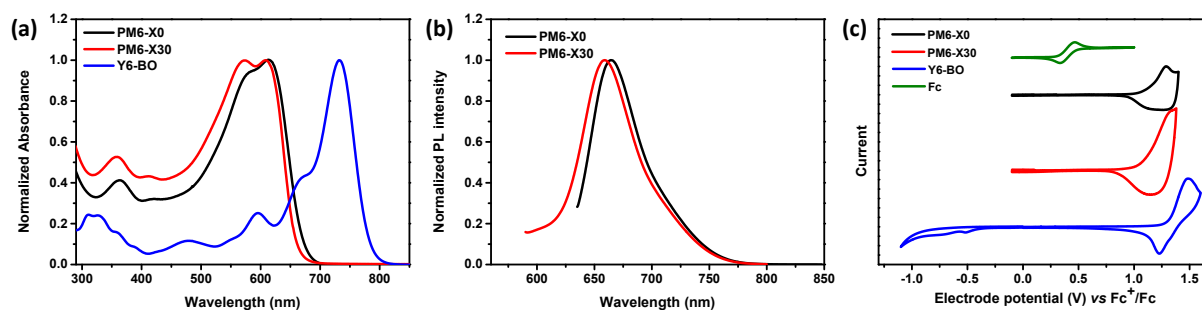


Fig. S24 (a) UV-Vis absorption spectra and (b) PL emission spectra in CF solution; (c) cyclic voltammograms of the active layer materials in this work.

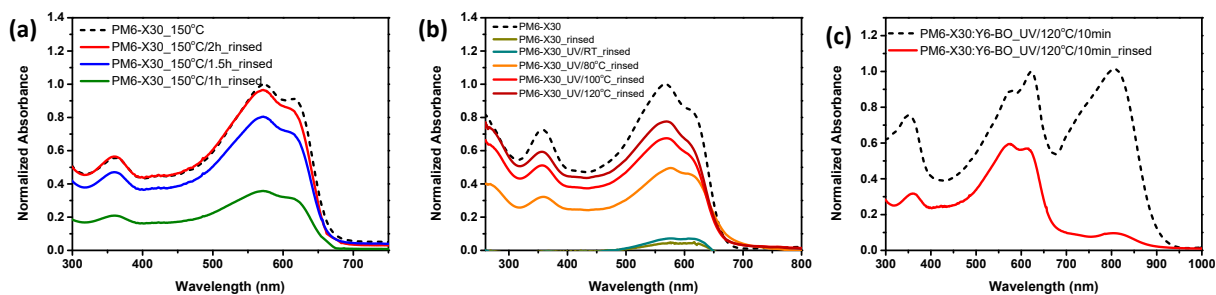


Fig. S25 UV-vis absorption spectra of (a) PM6-X30 film annealed at 150°C (b) UV irradiated PM6-X30 (c) UV irradiated PM6-X30:Y6-BO film before and after rinsing with CF.

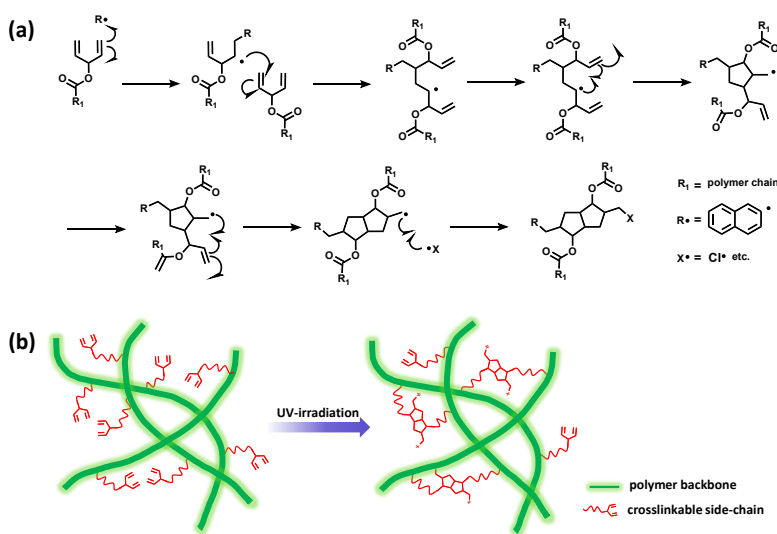


Fig. S26 a) Proposed mechanism of the cycloaddition reaction of 1,4-diene under UV irradiation. b) Possible crosslinking process between polymer (PM6-X30) chains under UV irradiation

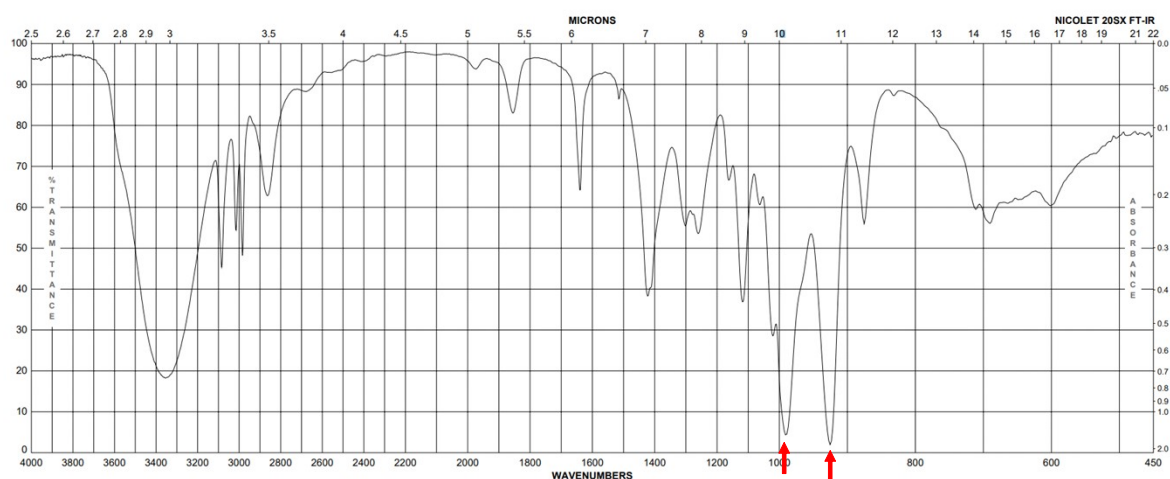


Fig. S27 Reference FT-IT spectra of 1,4-pentadien-3-ol (Sigma-Aldrich). The C=C-H bending mode we used in this spectrum image file is indicated by the arrows.

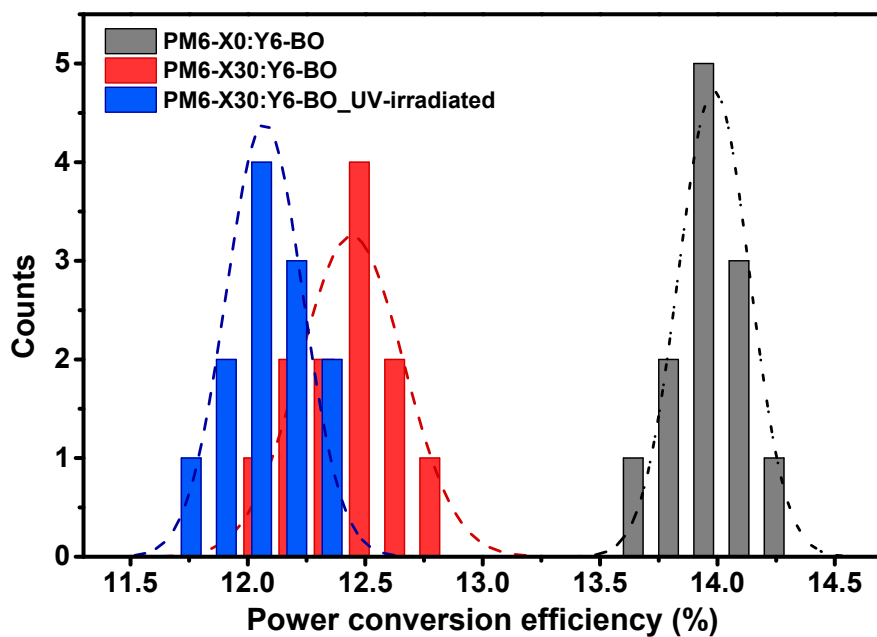


Fig. S28 Histogram of PCE values of the PSCs based on PM6-X0:Y6-BO, PM6-X30:Y6-BO and UV-irradiated PM6-X30:Y6-BO.

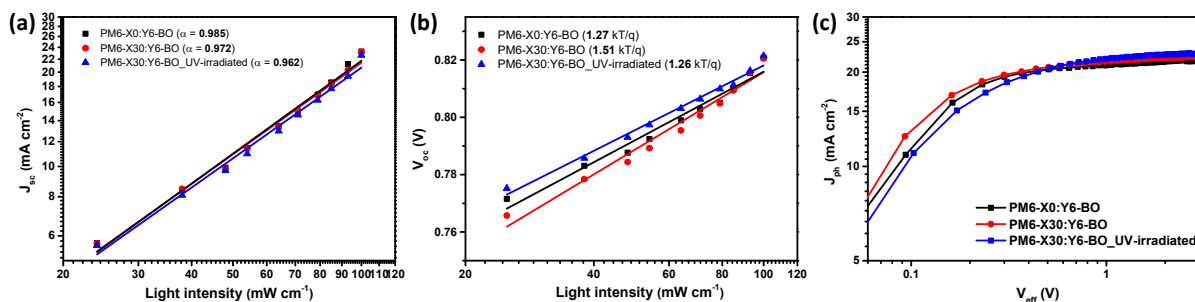


Fig. S29 (a) Light intensity dependence of J_{sc} , (b) light intensity dependence of V_{oc} and (c) photocurrent density versus effective voltage characteristics of the PSCs based on PM6-X0:Y6-BO, PM6-X30:Y6-BO and UV-irradiated PM6-X30:Y6-BO.

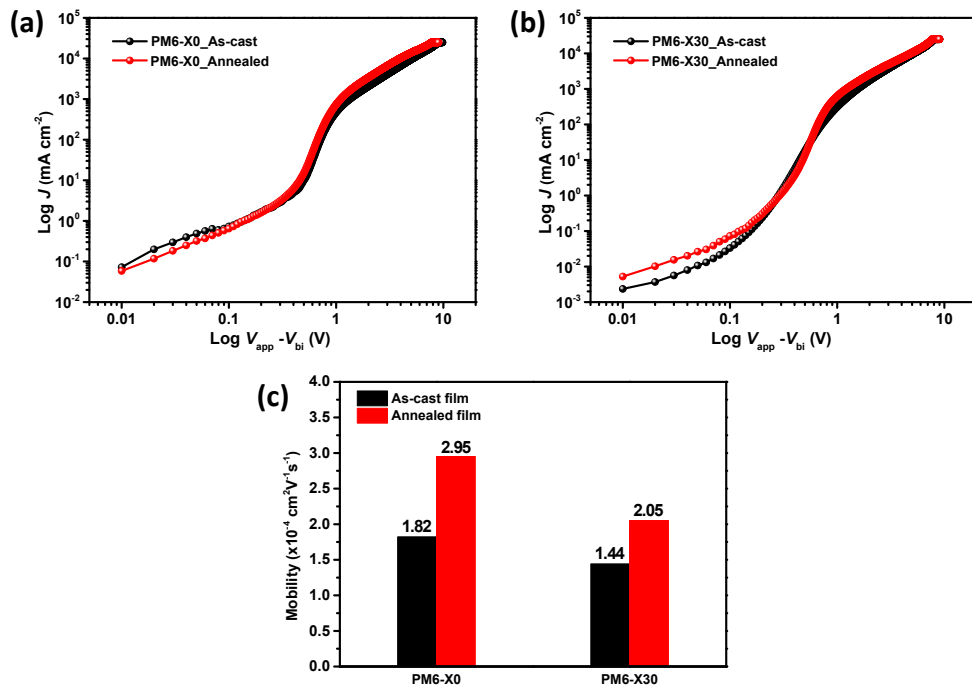


Fig. S30 J - V characteristics of the hole-only device based on a) PM6-X0 and b) PM6-X30 films under dark conditions. c) Hole mobility of the PM6-X0 and PM6-X30 films. Annealing condition: 120 °C for 10 min.

We measured the hole mobility of two polymers using the space charge limited current (SCLC) method. Specifically, we conducted a comparison of the hole mobility of PM6-X30 and PM6-X0 films in their as-cast and annealed (120 °C/10 min) states, utilizing a hole-only device (ITO/PEDOT:PSS/polymer/Au). Our findings indicate that the as-cast PM6-X30 films demonstrated a slightly reduced mobility ($1.44 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) compared to PM6-X0 ($1.82 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), but not to a significant extent. Both polymer films exhibited improved hole mobility after thermal annealing, which can be attributed to an increase in crystallinity and molecular packing.

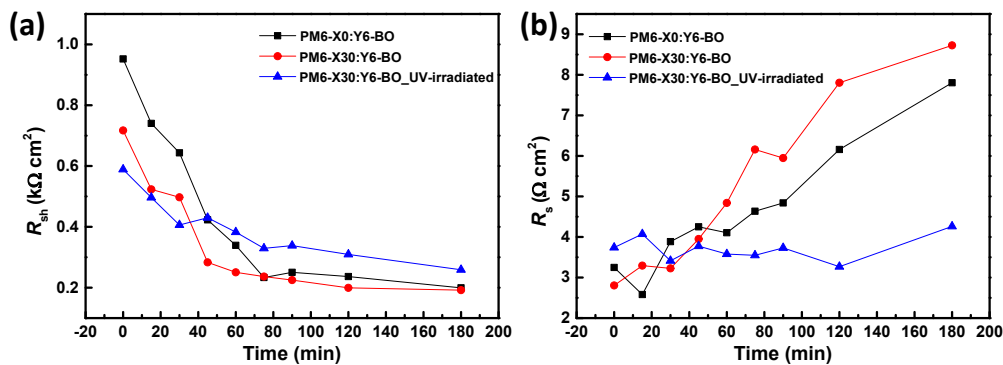


Fig. S31 (a) Shunt resistance (R_{sh}) and (b) series resistance (R_s) of the PSCs based on PM6-X0:Y6-BO, PM6-X30:Y6-BO, and UV-irradiated PM6-X30:Y6-BO during thermal aging at 80 °C in ambient conditions for 180 min.

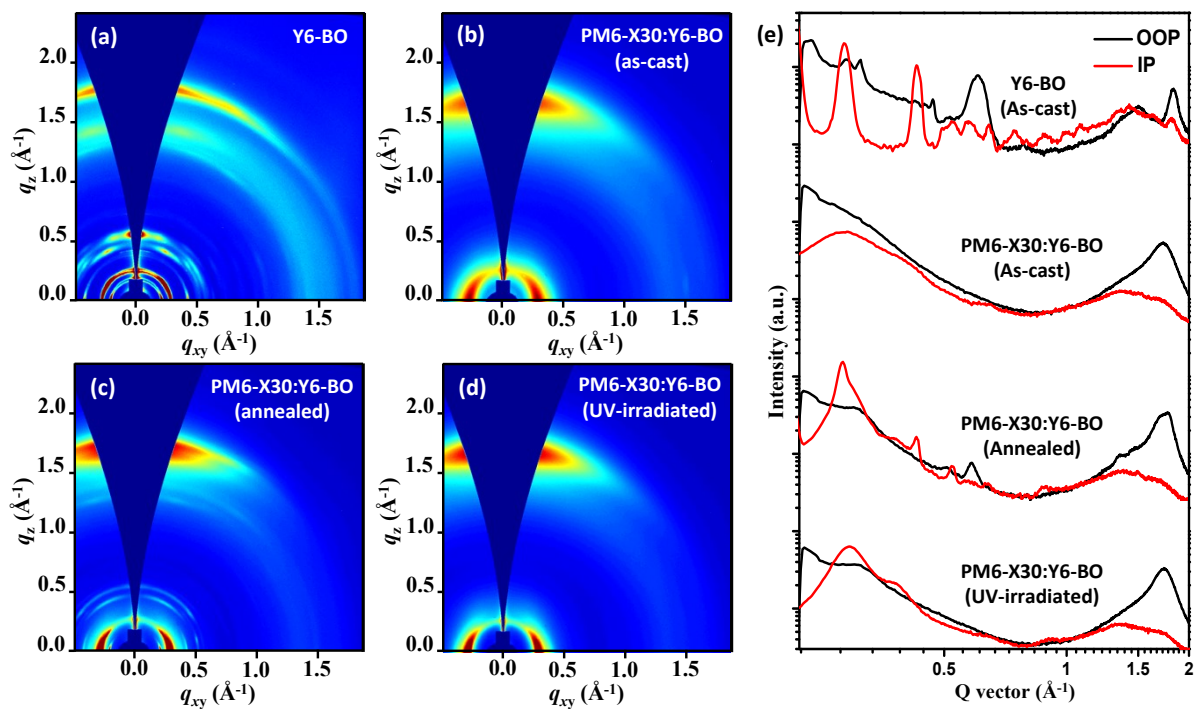


Fig. S32 GIWAXD 2D diffraction pattern of the (a) Y6-BO, (b) as-cast PM6-X30:Y6-BO, (c) annealed PM6-X30:Y6-BO and (d) UV irradiated PM6-X30:Y6-BO films. (e) Line cut profiles of the films.

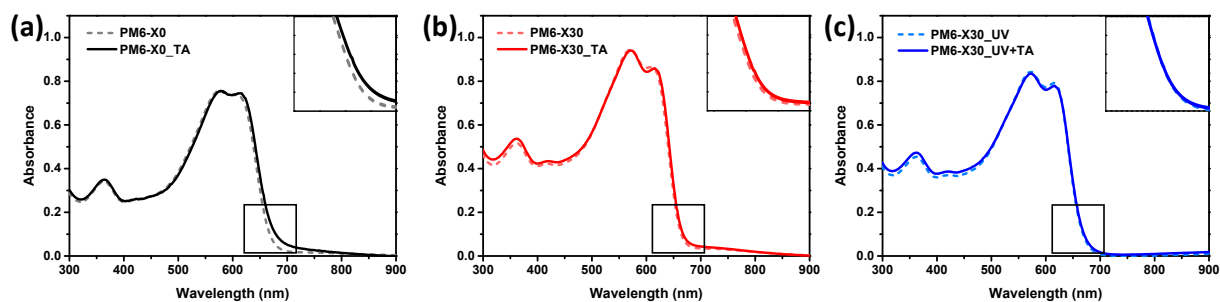


Fig. S33 UV -Vis absorption spectra of the (a) PM6-X30, (b) PM6-X30, and (c) crosslinked PM6-X30 film before (dotted-lines) and after (solid lines) thermal aging (TA) at 80 °C for 180 min.

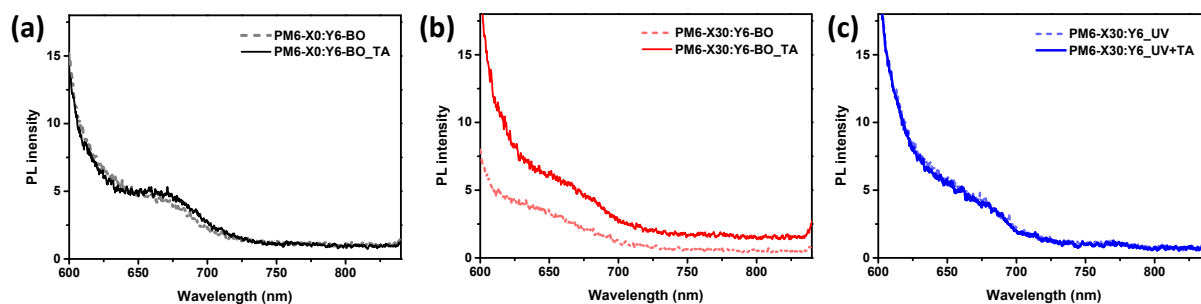


Fig. S34 PL spectra of the (a) PM6-X30:Y6-BO, (b) PM6-X30:Y6-BO, and (c) crosslinked PM6-X30:Y6-BO blend film before (dotted-lines) and after (solid lines) thermal aging (TA) at 80°C for 180 min.

4. References

- S1. N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, Oxford University Press, London, 1940.
- S2. G. Brotas, C. Costa, S. I. G. Dias, P. M. M. Costa, R. E. D. Paolo, J. Martins, J. Farinhas, L. Alcácer, J. Morgado, M. Matos and A. Charas, *Macromol. Chem. Phys.*, 2015, **216**, 519–529.
- S3. C. Cui, H. Fan, X. Guo, M. Zhang, Y. He, X. Zhan and Y. Li, *Polym. Chem.*, 2012, **3**, 99–104.
- S4. E. E. Nagy, I. F. D. Hyatt, K. E. Gettys, S. T. Yeazell, S. K. Frempong, Jr., and M. P. Croatt, *Org. Lett.*, 2013, **15**, 586–589.