

# **A Facile Depolymerization Reaction Enables Efficient Feedstock Recycle of Polymerized Small Molecule Acceptors in All-Polymer Solar Cells**

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## 1. Experimental Section

### 1.1 Materials

Monomer Y-ICBr, polymer donor JD40 and PJ2 were synthesized according to the procedures reported.<sup>1,2</sup> Compound 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile, 3-octylthiophene-2-carbaldehyde, isomer-mixed brominated 1,1-dicyanomethylene-3-indanone (IC-Br) and PZ1 are purchased from Solarmer Materials Inc. Compound 2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile was purified as the reported literature.<sup>3</sup> Other chemicals and solvents are purchased from Energy, J&K, Alfa Aesar and TCI Chemical Co., respectively.

### 1.2 Synthetic Procedures

**1.2.1 Poly[(2,2'-((2Z,2'Z)-((12,13-bis(2-decyldodecyl)-3,9-diundecyl-12,13-dihydro[1,2,5]thiadiazolo[3,4e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-j]thieno[2',3':4,5]thieno[3,2-b]-indole-2,10-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)) dialononitrile-alt-2,5-thiophene)] (PJ1)**

Monomer Y-ICBr (1986 mg, 1.0 mmol), 2,5-bis(trimethylstannyl)thiophene (409 mg, 1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (18 mg) and P (*o*-tol)<sub>3</sub> (27 mg) were combined in a 150 mL sealed tube. Dry chlorobenzene (CB) (50 mL) was added under an atmosphere argon. The mixture was stirred at 110°C for 72h. After cooled down to room temperature, the reactant mixture was poured into MeOH (500 mL). The precipitate was filtered and

Soxhlet extracted with methanol, hexane, dichloromethane and chloroform. The dichloromethane and chloroform ingredients were respectively collected, precipitated into 200 mL methanol, filtered and dried under vacuum to affording PJ1-DCM in 28% yield for dichloromethane batch ( $M_n = 6.5$  kDa,  $M_w = 14.0$  kDa) and PJ1-CF in 68% yield for chloroform batch ( $M_n = 15.5$  kDa,  $M_w = 29.2$  kDa).

### ***1.2.2 The universal procedures of the depolymerization reaction***

PSMA (0.1mmol), IC-Br (0.4 mmol) were combined in a round-bottom flask containing 20 mL chloroform. After stirring at 60 °C for 10 min, pyridine (1 mL) was added into the mixture under air atmosphere. The mixture was stirred at 50 °C for another 4 h and the reactant mixture was immediately purified by a fast column chromatography on silica gel to afford compound Y-ICBr (yield 90% for PJ1-CF, 92% for PJ1-DCM, and 86% for PJ2) or Z-ICBr (yield 85%). For the mass spectrum test, the terminal mixtures were collected from silical gel column after the Y-ICBr for PJ1-CF depolymerization with the eluent of DCM: CF (v/v, 3:1).

**Y-ICBr recovered from PJ1-CF:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.08 (s, 2H), 8.74–8.45 (m, 2H), 8.03–7.85 (m, 2H), 7.80–7.77 (m, 2H), 4.82 (m, 4H), 3.15 (m, 4H), 2.21 (m, 2H), 1.86–1.82 (m, 4H), 1.53 – 1.47 (m, 4H), 1.36 (m, 4H), 1.26 (m, 28H), 1.22 – 1.13 (m, 36H), 1.02 (m, 36H), 0.88 – 0.81(m, 22H). MALDI-TOF-MS (m/z):  $[\text{M}]^+$  calcd. for  $\text{C}_{114}\text{H}_{152}\text{Br}_2\text{N}_8\text{O}_2\text{S}_5$ , 1986.632; found, 1986.898.

**Y-ICBr recovered from light-soaked active-layer blends:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.17 (s, 2H), 8.83 (m, 1H), 8.56 (m, 1H), 8.03 (s, 1H), 7.88–7.84 (m, 2H), 7.80–7.78 (m, 1H), 4.77 (m, 4H), 3.22 (m, 4H), 2.13 (m, 2H), 1.91–1.85 (m, 4H), 1.55–

1.49 (m, 4H), 1.38 (m, 4H), 1.27 (m, 28H), 1.22 – 1.13 (m, 36H), 0.98 (m, 36H), 0.88 – 0.81(m, 22H). MALDI-TOF-MS (m/z): [M]<sup>+</sup> calcd. for C<sub>114</sub>H<sub>152</sub>Br<sub>2</sub>N<sub>8</sub>O<sub>2</sub>S<sub>5</sub>, 1986.632; found, 1986.902.

**Y-ICBr recovered from PJ1-DCM batch:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.15 (s, 2H), 8.81–8.53 (m, 2H), 8.03–7.87 (m, 2H), 7.87–7.78 (m, 2H), 4.78 (m, 4H), 3.19 (m, 4H), 2.15 (m, 2H), 1.86 (m, 4H), 1.53 – 1.48 (m, 4H), 1.37 (m, 4H), 1.26 (m, 28H), 1.19 – 1.10 (m, 36H), 0.98 (m, 36H), 0.88 – 0.80(m, 22H). MALDI-TOF-MS (m/z): [M]<sup>+</sup> calcd. for C<sub>114</sub>H<sub>152</sub>Br<sub>2</sub>N<sub>8</sub>O<sub>2</sub>S<sub>5</sub>, 1986.632; found, 1985.889.

**Y-ICBr recovered from PJ2:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.16 (s, 2H), 8.83–8.54 (m, 2H), 8.04–7.79 (m,4H), 4.47 (m, 4H), 3.21 (m, 4H), 2.14 (m, 2H), 1.89–1.86 (m, 4H), 1.52 (m, 4H), 1.37 (m, 4H), 1.26 (m, 28H), 1.20 – 1.12 (m, 36H), 0.98 (m, 36H), 0.88 – 0.82(m, 22H). MALDI-TOF-MS (m/z): [M]<sup>+</sup> calcd. for C<sub>114</sub>H<sub>152</sub>Br<sub>2</sub>N<sub>8</sub>O<sub>2</sub>S<sub>5</sub>, 1986.632; found, 1985.901.

**Z-ICBr recovered from PZ1:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.00 (s, 2H), 8.85–8.56 (m, 2H), 8.04–7.79 (m,4H), 7.74 (m,2H), 7.62 (m,2H), 2.10–2.05 (m,4H), 1.98–1.93 (m,4H), 1.27–1.11 (m, 104H), 0.87 – 0.79 (m, 20H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 187.23, 186.83, 161.06, 159.61, 159.05, 157.73, 156.83, 141.28, 141.22, 138.91, 138.26, 138.03, 137.81, 137.47, 135.44, 130.30, 129.75, 128.26, 126.91, 126.47, 124.76, 121.37, 121.28, 116.18, 114.65, 114.50, 114.30, 69.56, 54.35, 38.97, 31.91, 29.80, 29.72, 29.69, 29.67, 29.61, 29.56, 29.37, 29.28, 24.34, 22.69, 14.14. MALDI-TOF-MS (m/z): [M]<sup>+</sup> calcd. for C<sub>106</sub>H<sub>144</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>, 1729.911; found, 1729.903.

### ***1.2.3 The preparation of compound 8***

Compound 6 (449 mg, 2 mol), compound 7 (1552 mg, 8 mol) were combined in a two-neck flask with 50mL chloroform under nitrogen. Pyridine (1 mL) was then slowly added to the mixture and the reaction was stirred at 65 °C for 24 hours. After being cooled to room temperature, the crude mixture was purified with column chromatography on silica gel using PE /DCM (1/1.5, v/v) as the eluent to afford compound 8 as yellow flake crystal (712 mg, 89%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.05 (s, 1H), 8.70 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.80 – 7.69 (m, 2H), 7.13 (d, *J* = 5.1 Hz, 1H), 3.01 – 2.94 (m, 2H), 1.65 (m, 2H), 1.43 – 1.35 (m, 2H), 1.29 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 188.01, 161.37, 160.20, 139.90, 139.79, 137.04, 135.61, 135.15, 134.57, 131.80, 130.43, 125.34, 123.90, 122.30, 114.75, 114.55, 69.84, 31.96, 31.84, 30.06, 29.39, 29.19, 22.65, 14.11. MS (m/z): calcd. for C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>OS, 400.1609; found, 401.1682.

#### ***1.2.4 Model reaction between compound 8 and compound 9***

Compound 8 (0.3 mmol, 120.2mg), compound 9 (0.6 mmol, 163.8 mg) were combined in a round-bottom flask containing 15 mL chloroform. Pyridine (1 mL) was then added into the mixture under stirring at air atmosphere. The mixture was stirred at 50 °C for another 4 h and the raw product was purified by column chromatography on silica gel using PE /DCM (1/1, v/v) as the eluent to afford compound 10 (80.5mg, 56%). After the collection of compounds 8 and 10, the column chromatography was sequentially conducted using DCM eluent to obtain the mixed terminal for the MS analysis. Compound 10, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.08 (s, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 1.8 Hz, 1H), 7.93 (d, *J* = 5.1 Hz, 1H), 7.86 (dd, *J* = 8.5, 1.9 Hz,

1H), 7.15 (d,  $J = 5.1$  Hz, 1H), 3.03 – 2.89 (m, 2H), 1.69 – 1.63 (m, 2H), 1.43 – 1.34 (m, 2H), 1.32 – 1.26 (m, 8H), 0.87 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 186.56, 160.91, 160.38, 140.64, 138.39, 138.24, 137.90, 136.25, 131.92, 130.60, 129.92, 127.10, 126.57, 121.64, 114.61, 114.47, 70.03, 31.98, 31.83, 30.12, 29.39, 29.37, 29.18, 22.65, 14.10$ . MS ( $m/z$ ): calcd. for  $\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{OS}$ , 478.0714; found, 481.0771.

### ***1.2.5 The preparation of PJ1 from the repolymerization of recycled Y-ICBr monomer***

Monomer Y-ICBr (recovered from DCM batch or light-aging blends) (158.8 mg, 0.08 mmol), 2,5-bis(trimethylstannyl)thiophene (32.7 mg, 0.08 mmol),  $\text{Pd}_2(\text{dba})_3$  (1.8 mg) and  $\text{P}(o\text{-tol})_3$  (2.7 mg) were combined in a 10 mL sealed tube. Dry chlorobenzene (CB) (4 mL) was added under an atmosphere argon. The mixture was stirred at 110 °C for 72h. After cooled down to room temperature, the reactant mixture was poured into MeOH (300 mL). The precipitate was filtered and Soxhlet extracted with methanol, hexane, dichloromethane and chloroform. The dichloromethane and chloroform ingredients were respectively collected, precipitated into 200 mL methanol, filtered and dried under vacuum to affording different PJ1 batches (CF phase). PJ1-LS (repolymerized from monomer of light-soaking blends, yield 70%) ( $M_n = 14.0$  kDa,  $M_w = 36.8$  kDa) and PJ1-DM (repolymerized from monomer of dichloromethane extraction component, yield 67%) ( $M_n = 16.2$  kDa,  $M_w = 32.6$  kDa).

### **1.3 Instruments and Measurement**

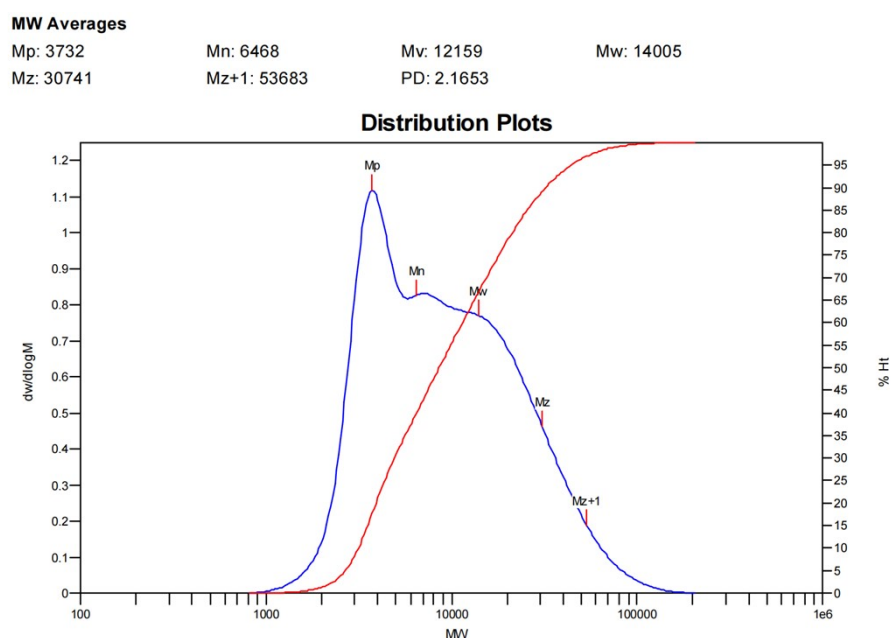
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AV-500 MHz

spectrometer with tetramethylsilane (TMS) as the internal reference. Mass spectra were measured on Bruker ultrafleXtreme or Bruker tims-TOF. The molecular weights of the polymers were obtained on an Acquity Advanced Polymer Chromatography (Waters) with high temperature chromatograph, using 1,2,4-trichlorobenzene as the eluent at 150 °C. UV-Vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer.

#### 1.4 Device Fabrication and characterization

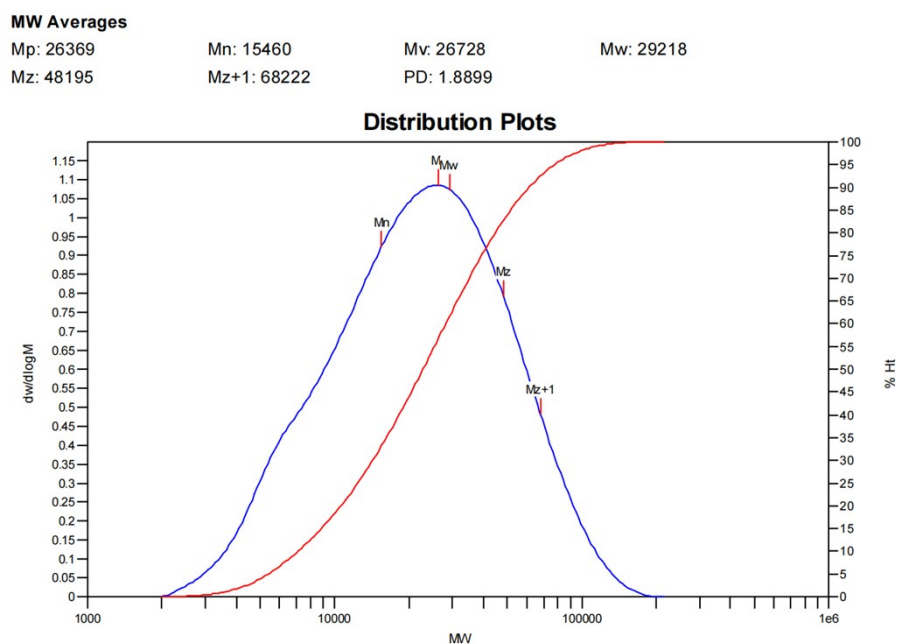
The conventional structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/JD40:PJ1/poly[(9,9-bis(3'-((N,N-dimethyl)-N-ethylammonium)propyl)-2,7-fluorene)-alt-5,5'-bis(2,2'-thiophene)-2,6-naphthalene-1,4,5,8-tetracarboxylic-N,N'-di(2-ethylhexyl)imide]dibromide (PNDIT-F3N-Br)/Ag was used to fabricate the all-PSCs devices. The indium tin oxide (ITO) substrates were cleaned by sequentially sonication with detergent, deionized water, and isopropanol. After dried in oven at 80 °C overnight, the substrates were treated with an oxygen plasma for 5 min and then coated with PEDOT:PSS (CLEVIOS PVP Al 4083) at 3500 rpm for 30 s. Annealing at 150 °C on a hot plate in air for 15 min gave a thin film of about ~40 nm. Then the substrates were transferred into a N<sub>2</sub> protected glove box. The active layers were obtained by spin-coating the chloroform solution of JD40:PJ1 blend with the total concentration of 8 mg mL<sup>-1</sup>. The optimal film thickness of ca. 100 nm was obtained by controlling the rotate speed of ~2300 rpm. All the active layers were thermal annealed in a hot plate for 10 min. Subsequently, ~10 nm PNDIT-F3N-Br was spin-coated onto the active layers as cathode interface. Finally, 100 nm Ag were

thermally deposited on top of the interface through a shadow mask in a vacuum chamber at a pressure of  $3 \times 10^{-7}$  torr. The effective area of the device was confined as  $0.04 \text{ cm}^2$  by a non-refractive mask to improve the accuracy of measurements. The current density–voltage ( $J$ – $V$ ) characteristics were measured under a computer controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The light intensity was calibrated by a standard silicon solar cell (certified by NREL) before the testing, giving a value of  $100 \text{ mW cm}^{-2}$  during the test of  $J$ – $V$  characteristics. The external quantum efficiency (EQE) spectra were recorded with a QE-R measurement system (Enlitech, QE-R3011, Taiwan). The light-aging test was conducted in Crysco P3000 apparatus, all the devices were tested at air atmosphere without cooling system.

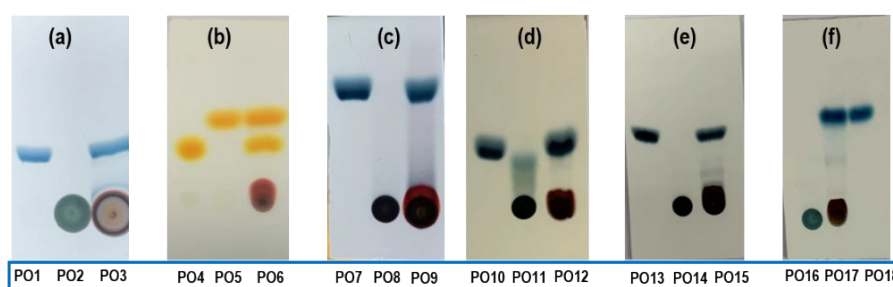


**Fig. S1.** High-temperature GPC measurements of PJ1-DCM batch.

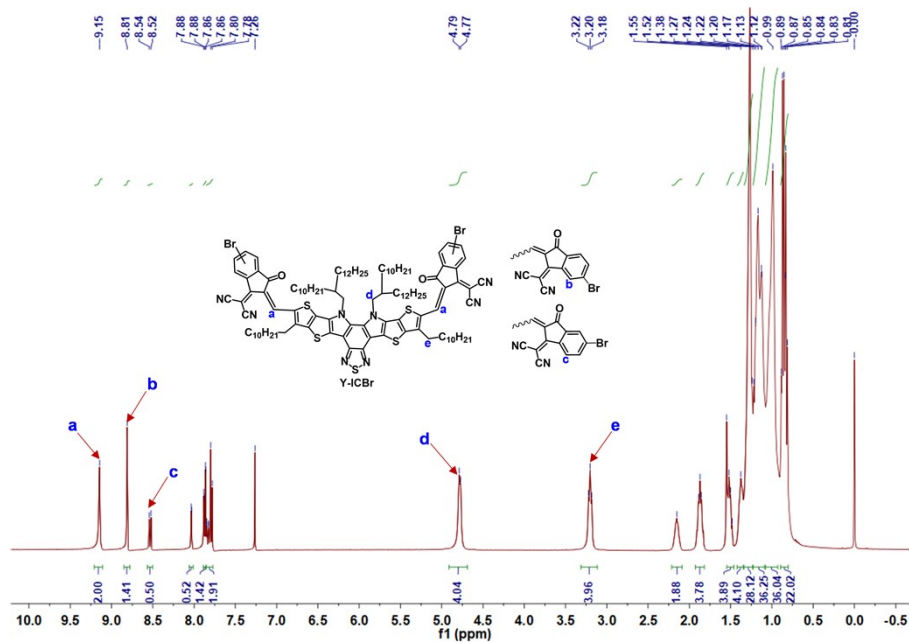




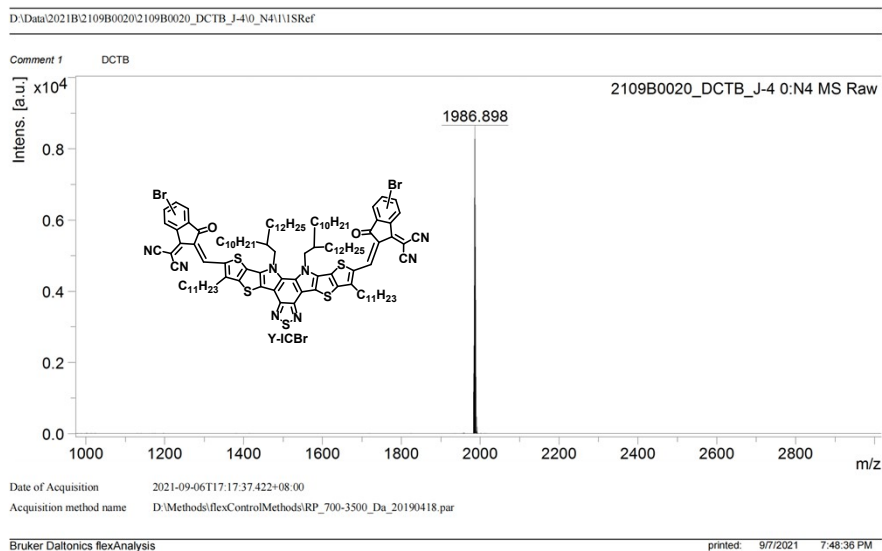
**Fig. S2.** High-temperature GPC measurements of PJ1-CF batch.



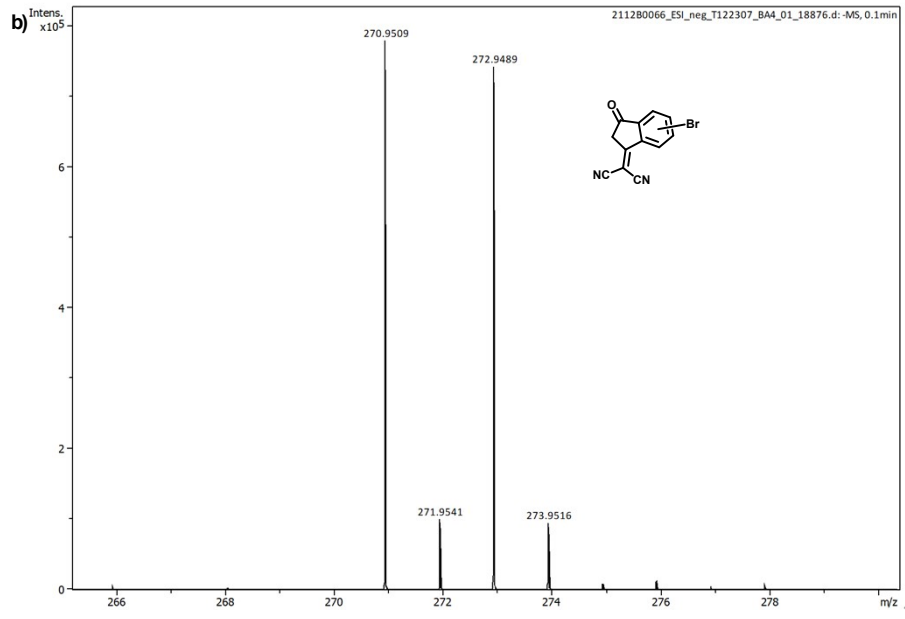
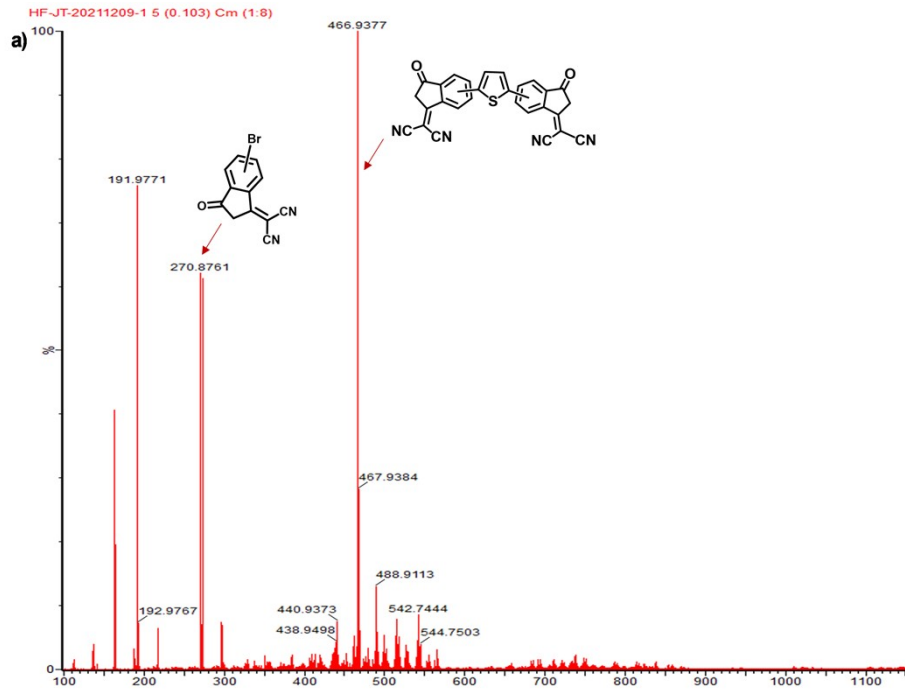
**Fig. S3.** The TLC results for the depolymerization and model reaction:(a) depolymerization reaction of PJ1-CF batch; PO1:Y-ICBr; PO2:PJ1-CF batch; PO3:depolymerization reaction mixture of PJ1-CF; (b) Model reaction from compound 8 to compound 10;PO4:compound 8; PO5:compound 10; PO6: model reaction mixture; (c) Depolymerization reaction of light-soaking active-layer blends; PO7:Y-ICBr; PO8:light-soaking blend;PO9: depolymerization reaction mixture of light-soaking blend; d) depolymerization reaction of PJ1-DCM batch;PO10:Y-ICBr;PO11:PJ1-DCM batch;PO12: PJ1-DCM batch depolymerization reaction mixture; (e) PJ2 depolymerization reaction; PO13:Y-ICBr; PO14:PJ2 solution; PO15: PJ2 depolymerization reaction mixture; (f) PZ1 depolymerization reaction; PO16:PZ1 solution; PO17:PZ1 depolymerization reaction mixture; PO18: Z-ICBr.

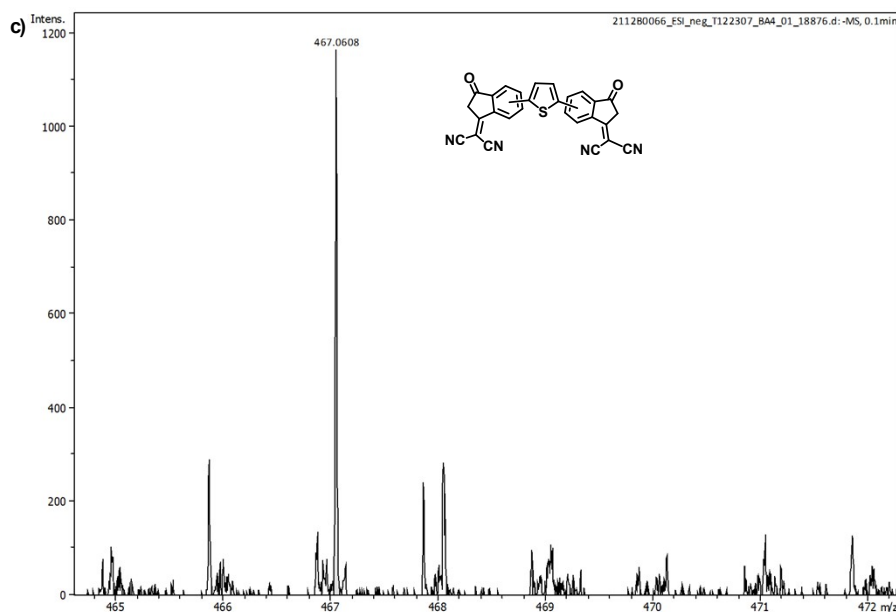


**Fig. S4.**  $^1\text{H}$  NMR spectrum of Y-ICBr recycled from PJ1-CF batch in  $\text{CDCl}_3$ .

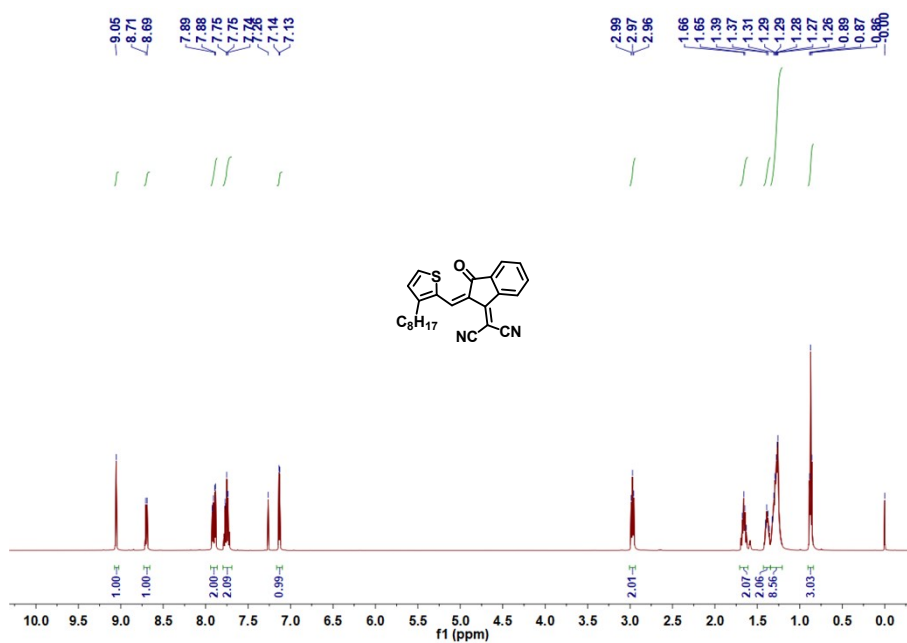


**Fig. S5.** MALDI-TOF-MS of Y-ICBr recycled from PJ1-CF batch.

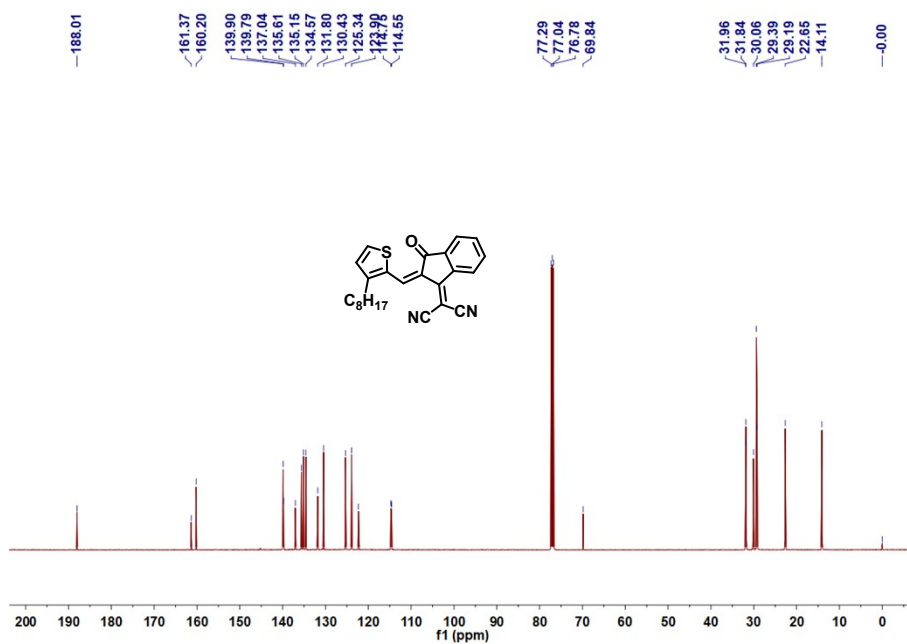




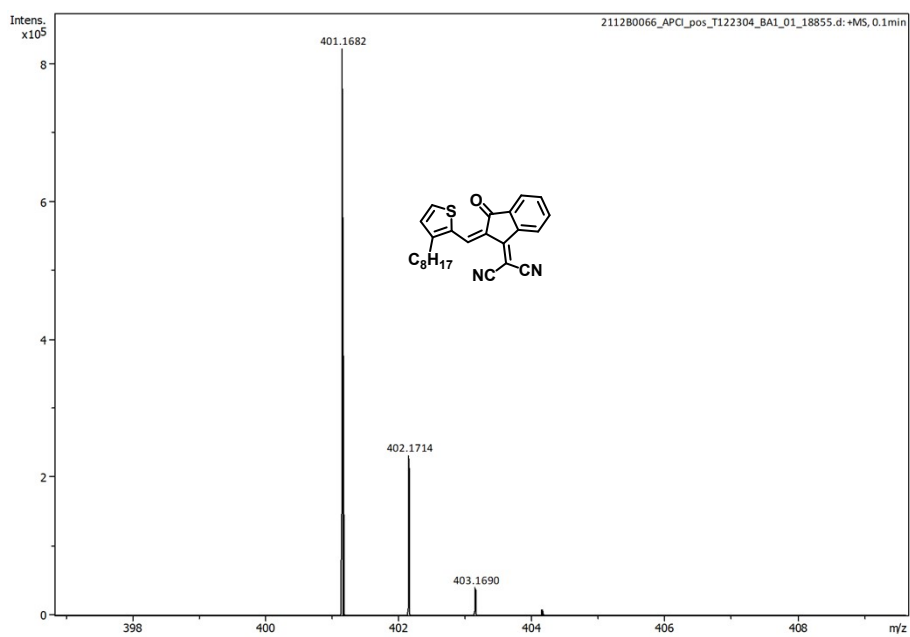
**Fig. S6.** MALDI-TOF-MS (a) and ESI-MS (b,c) tests of recovered terminal unit (containing compound 5 and excess IC-Br) after column chromatography.



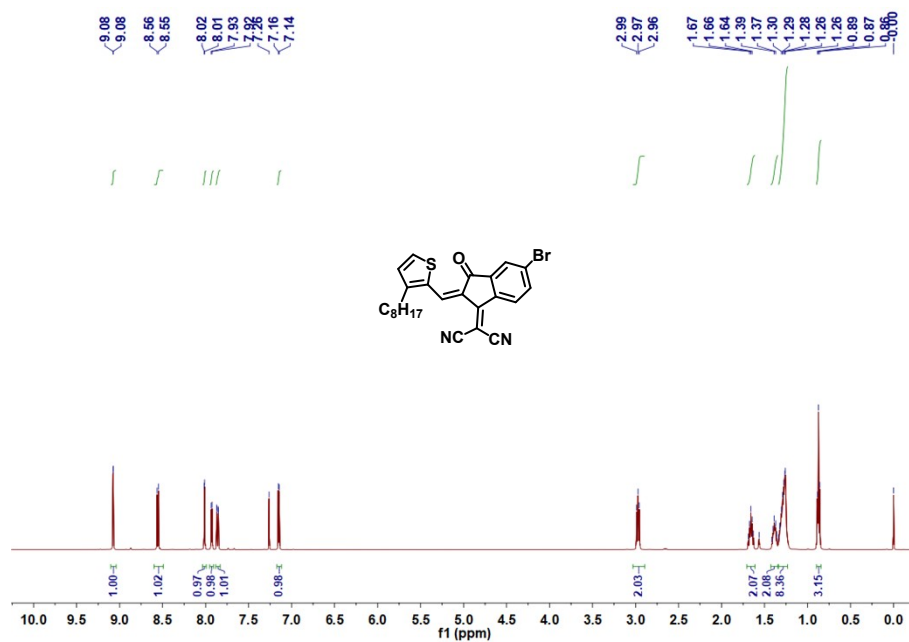
**Fig. S7.** <sup>1</sup>H NMR spectrum of compound 8 in CDCl<sub>3</sub>.



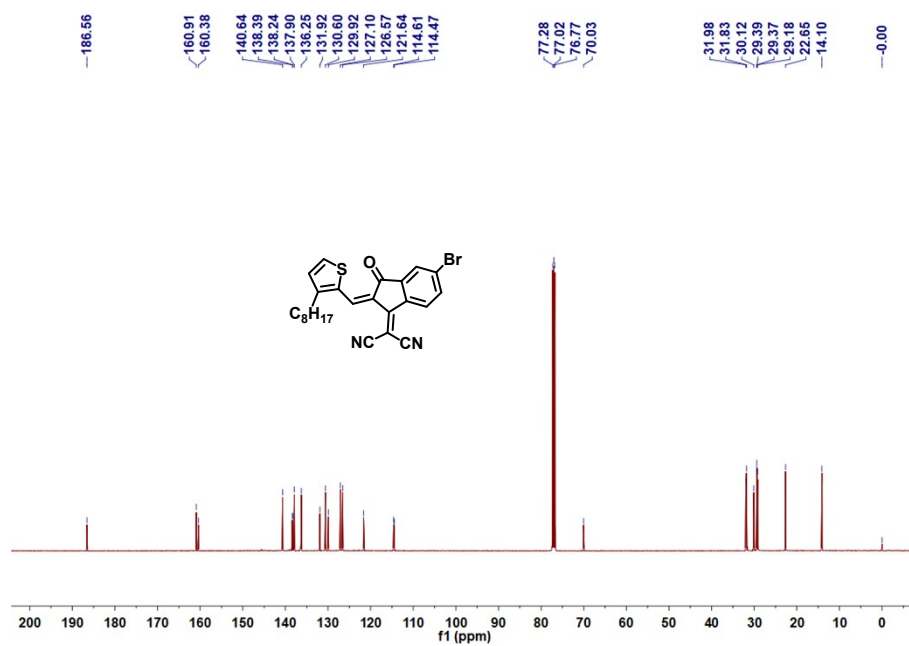
**Fig. S8.**  $^{13}\text{C}$  NMR spectrum of compound 8 in  $\text{CDCl}_3$ .



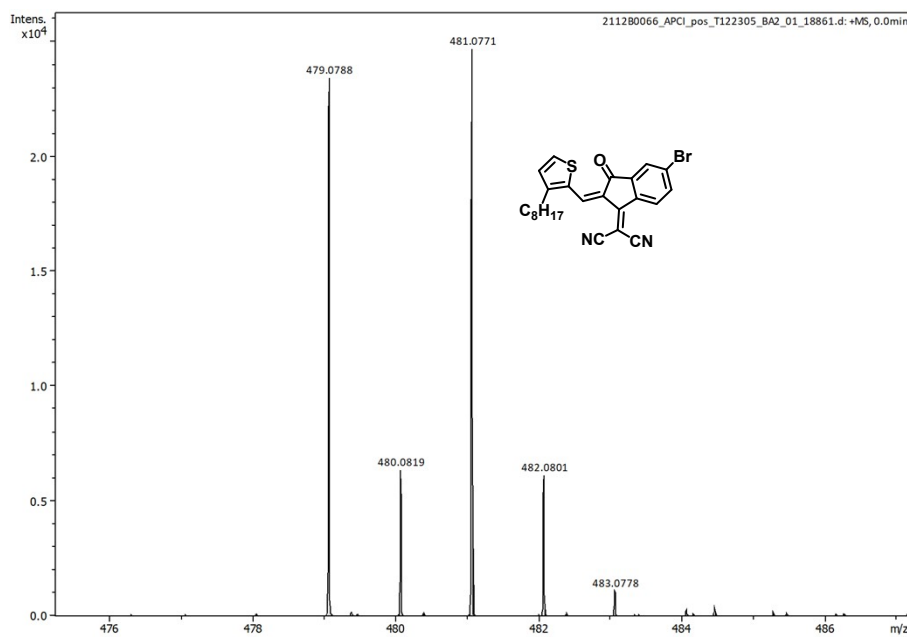
**Fig. S9.** APCI-MS test of compound 8.



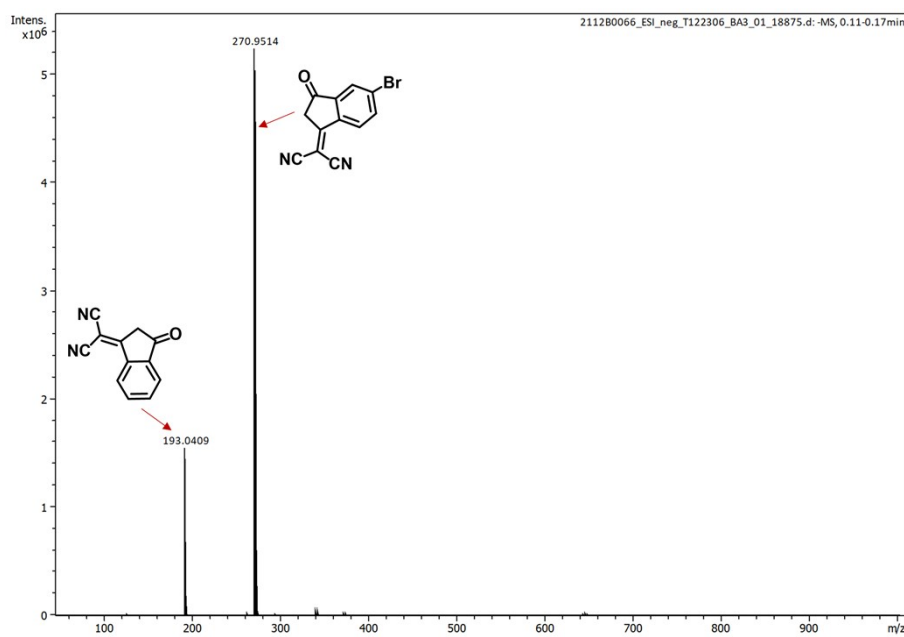
**Fig. S10.** <sup>1</sup>H NMR spectrum of compound 10 in CDCl<sub>3</sub>



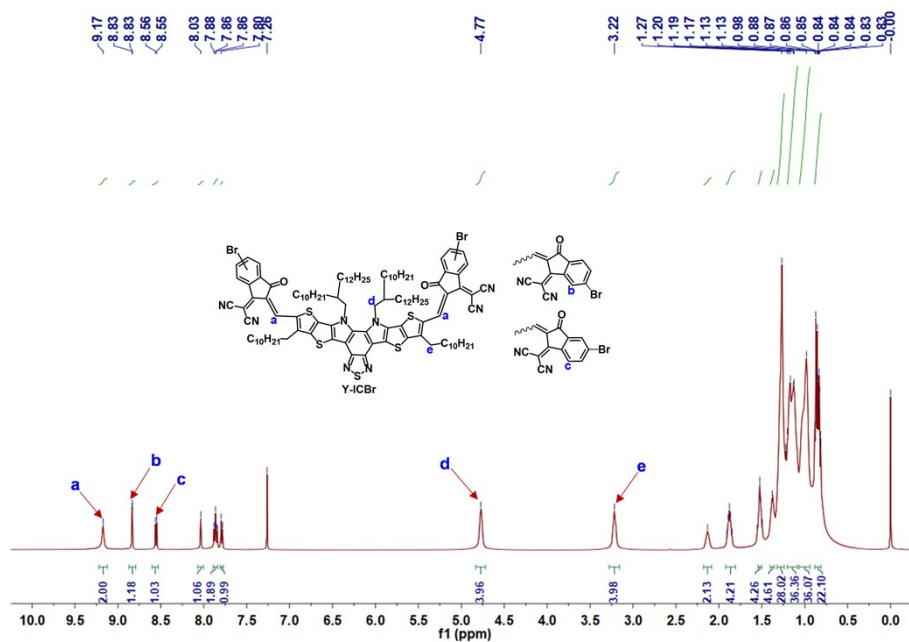
**Fig. S11.** <sup>13</sup>C NMR spectrum of compound 10 in CDCl<sub>3</sub>



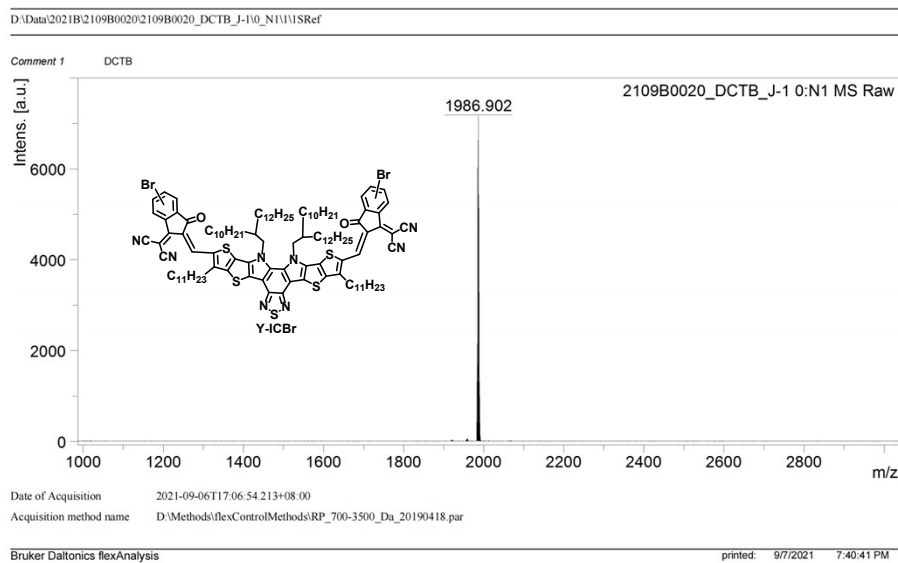
**Fig. S12.** APCI-MS of compound 10.



**Fig. S13.** ESI-MS of recovered terminals (containing compound 7 and 9) for model reaction.



**Fig. S14.**  $^1\text{H}$  NMR spectrum of Y-ICBr recycled from light-soaked active-layer blends.



**Fig. S15.** MALDI-TOF-MS of Y-ICBr recycled from light-soaked active layer blends.



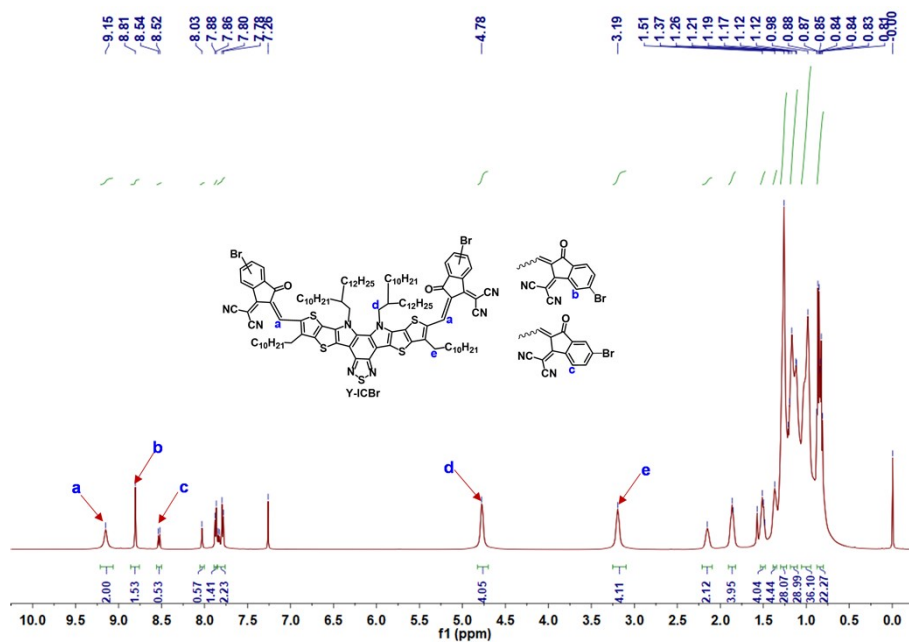


Fig. S16.  $^1\text{H}$  NMR spectrum of Y-ICBr recycled from PJ1-DCM batch in  $\text{CDCl}_3$ .

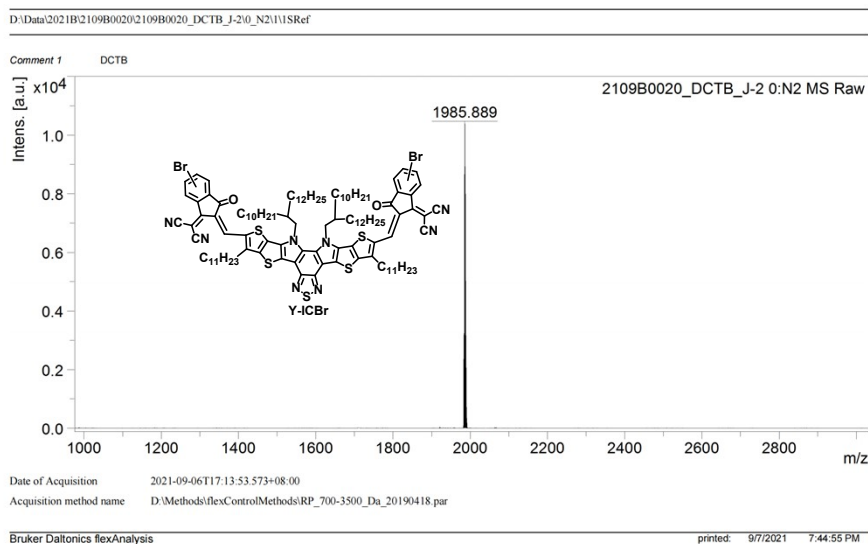
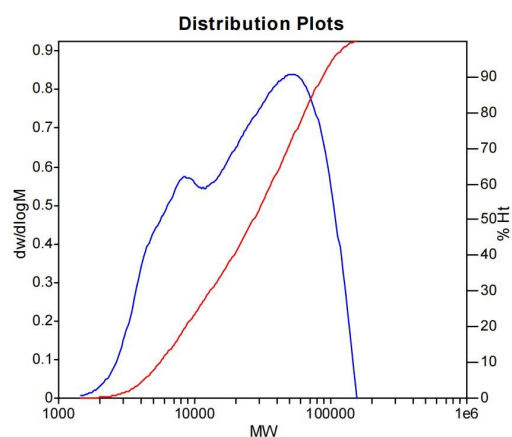


Fig. S17. MALDI-TOF-MS of Y-ICBr recycled from PJ1-DCM batch.

### MW Averages

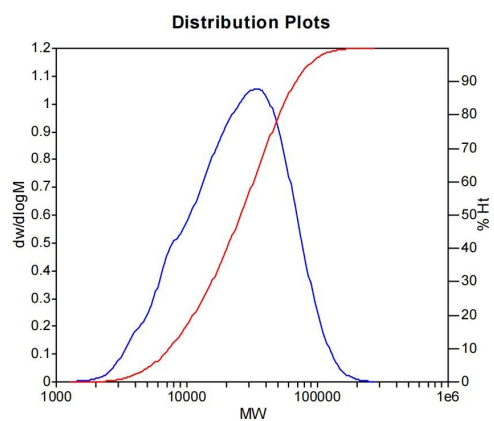
| Peak No | Mp    | Mn    | Mw    | Mz    | Mz+1  | Mv    | PD      |
|---------|-------|-------|-------|-------|-------|-------|---------|
| 1       | 51239 | 14012 | 36807 | 64585 | 83728 | 32430 | 2.62682 |



**Fig. S18.** High-temperature GPC measurement of repolymerized PJ1 based on monomer recycled from light-soaking blends.

### MW Averages

| Peak No | Mp    | Mn    | Mw    | Mz    | Mz+1  | Mv    | PD      |
|---------|-------|-------|-------|-------|-------|-------|---------|
| 1       | 34093 | 16220 | 32570 | 53873 | 76217 | 29801 | 2.00801 |



**Fig. S19.** High-temperature GPC measurement of repolymerized PJ1 based on recycled monomers from dichloromethane extraction component.

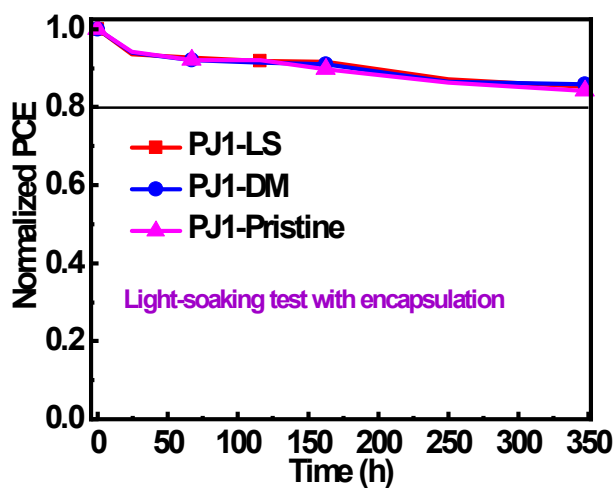


Fig. S20. The photostability of encapsulated all-PSC devices with different PJ1 batches.

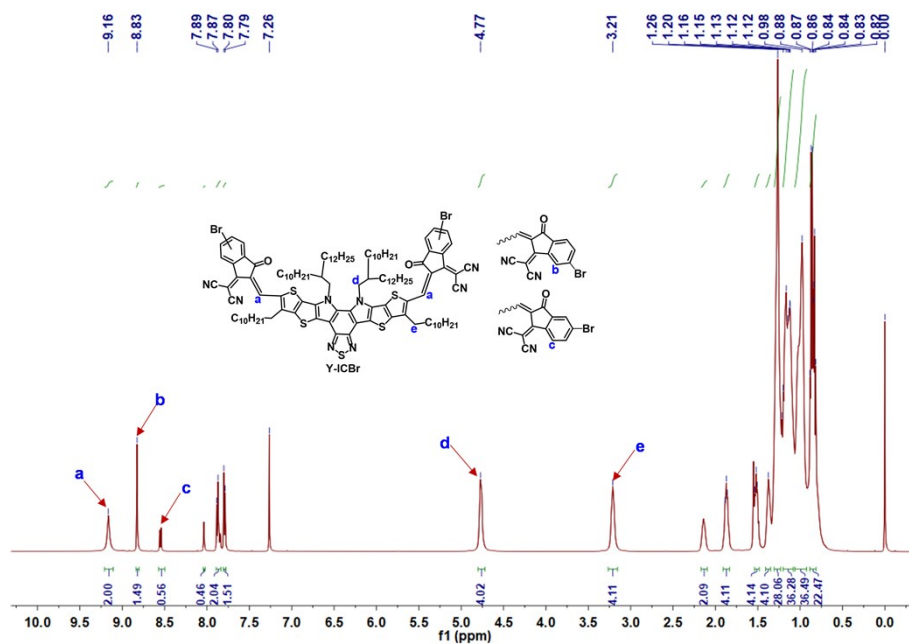


Fig. S21.  $^1\text{H}$  NMR spectrum of Y-ICBr recycled from PJ2 in  $\text{CDCl}_3$ .

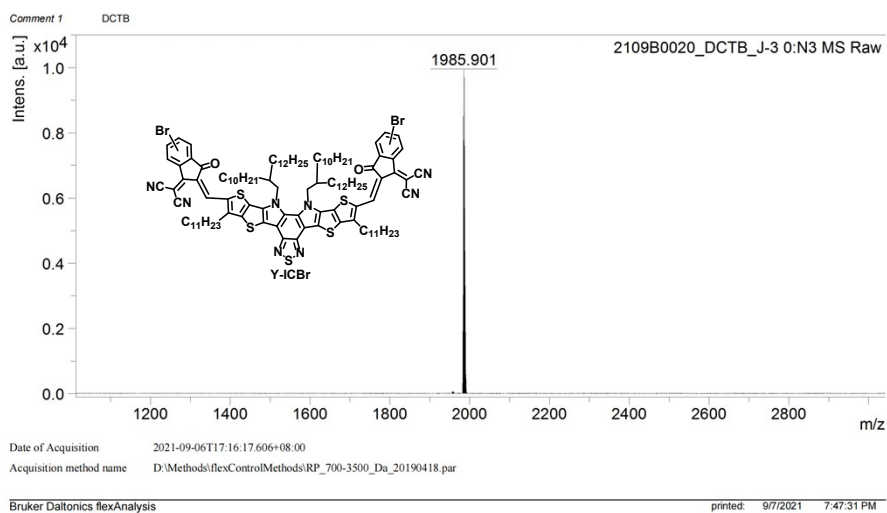


Fig. S22. MALDI-TOF-MS of Y-ICBr recycled from PJ2.

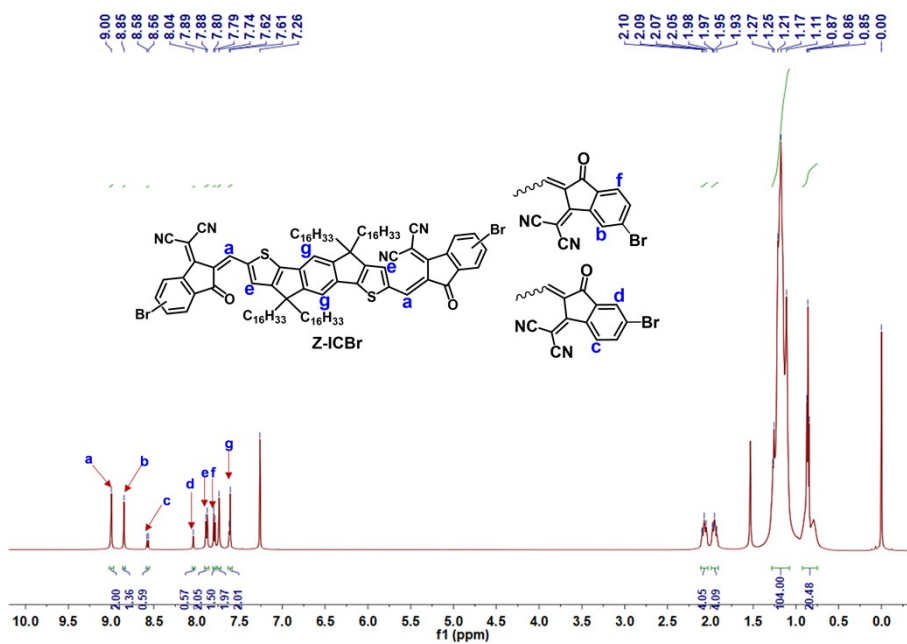
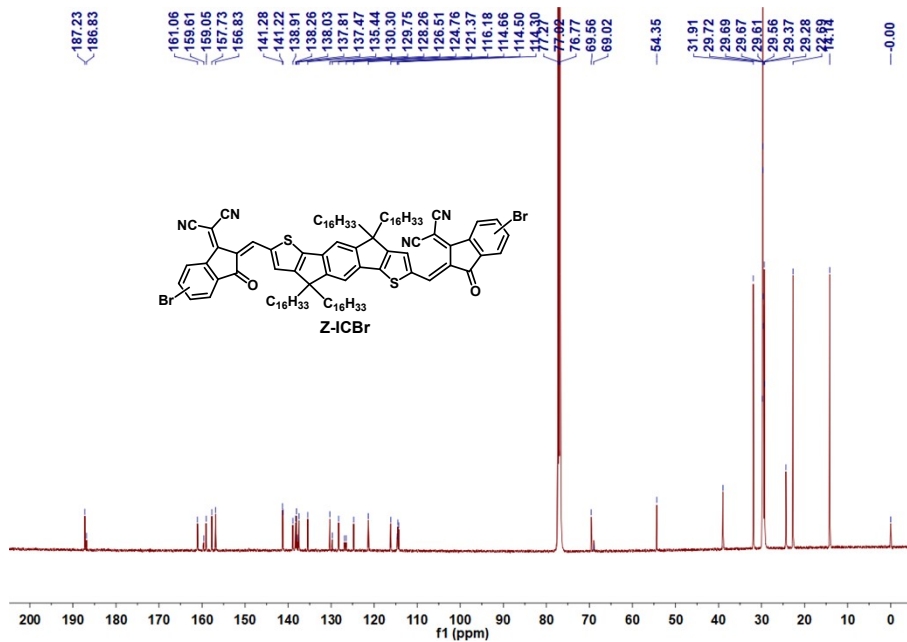
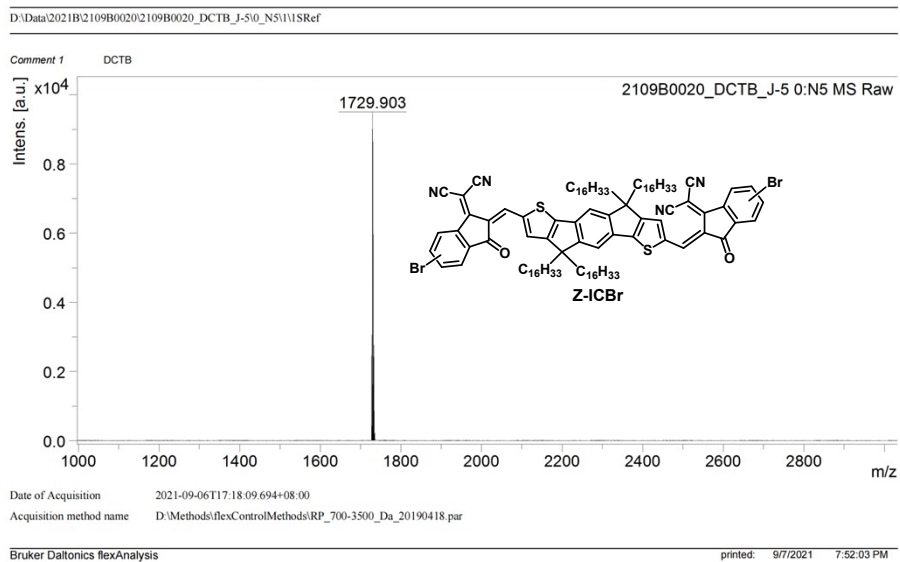


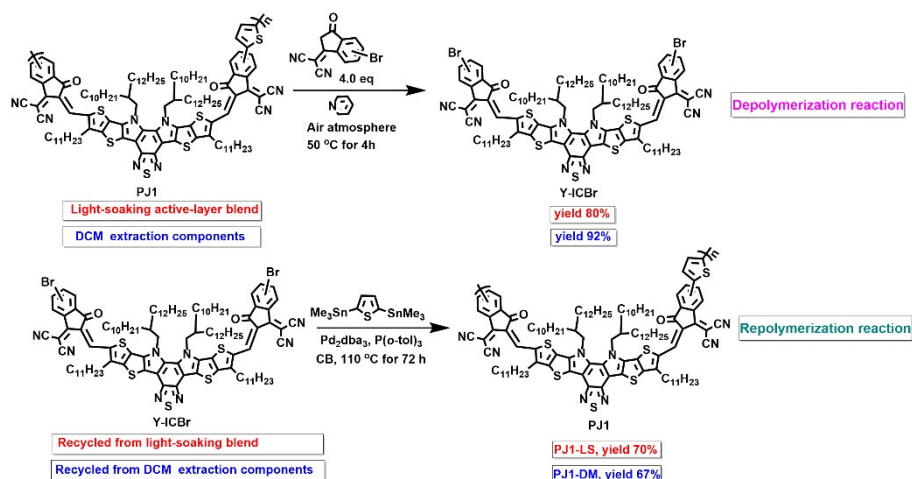
Fig. S23. <sup>1</sup>H NMR spectrum of Z-ICBr recycled from PZ1 in CDCl<sub>3</sub>.



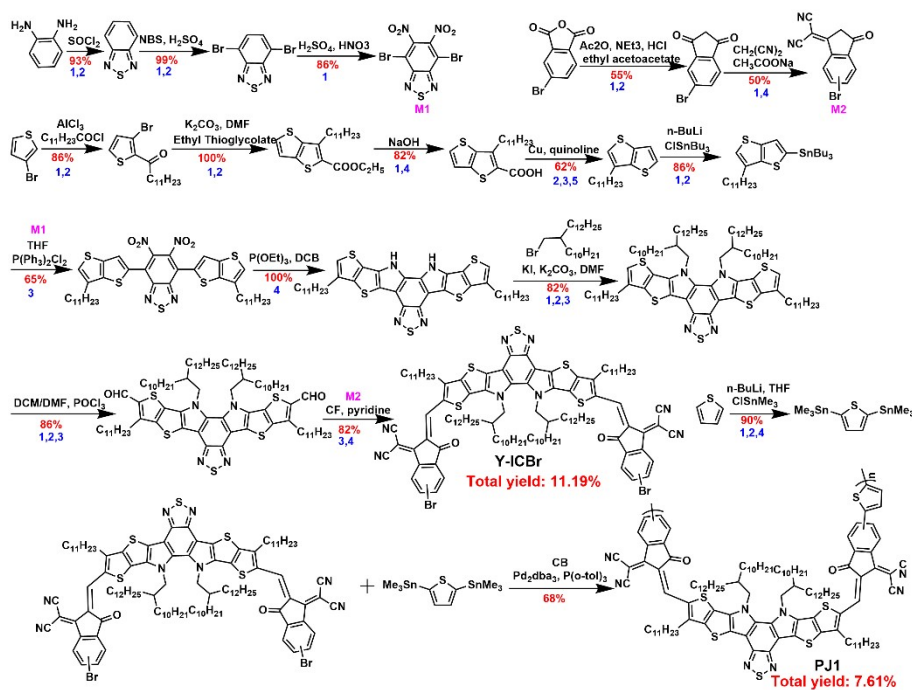
**Fig. S24.** <sup>13</sup>C NMR spectrum of Z-ICBr recycled from PZ1 in CDCl<sub>3</sub>.



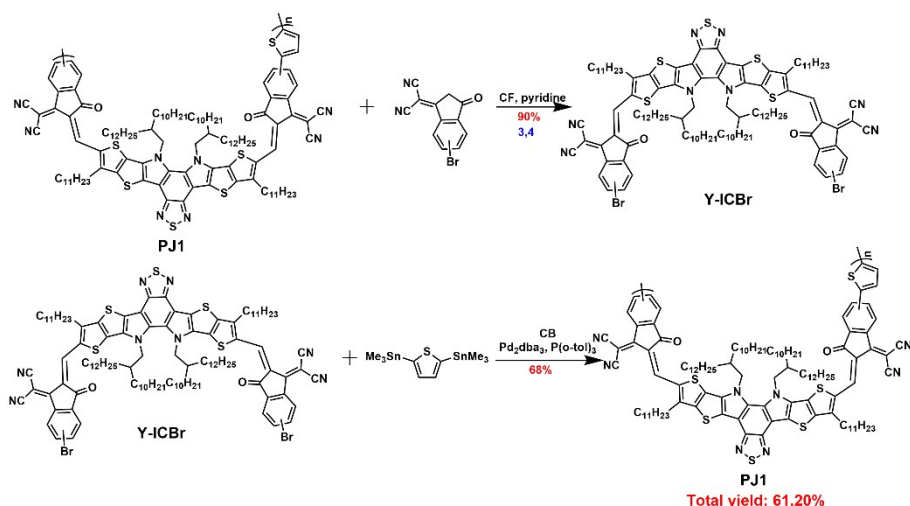
**Fig. S25.** MALDI-TOF-MS of Z-ICBr recycled from PZ1.



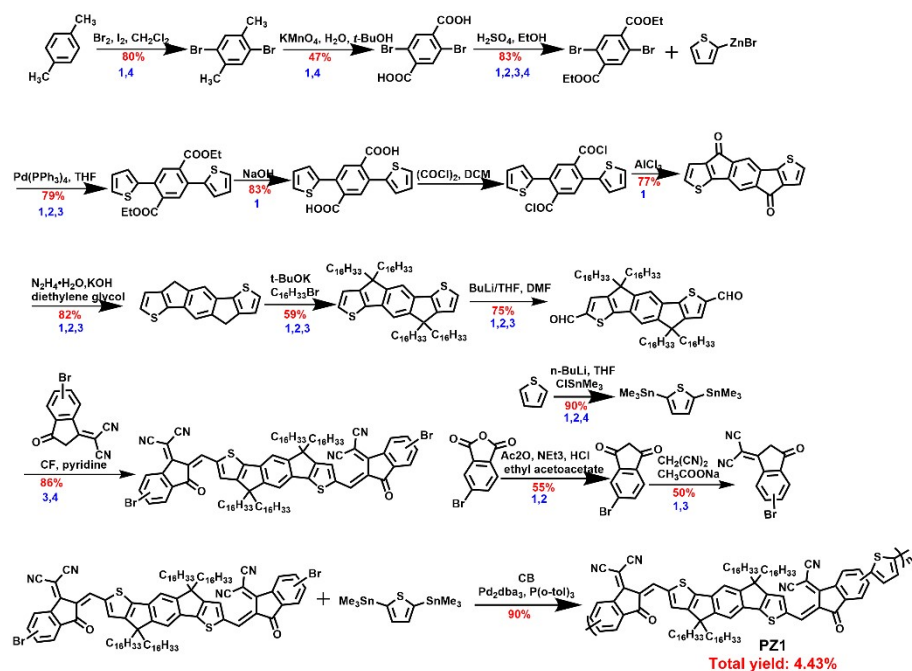
**Scheme S1.** The synthetic routes of depolymerization and repolymerization reactions.



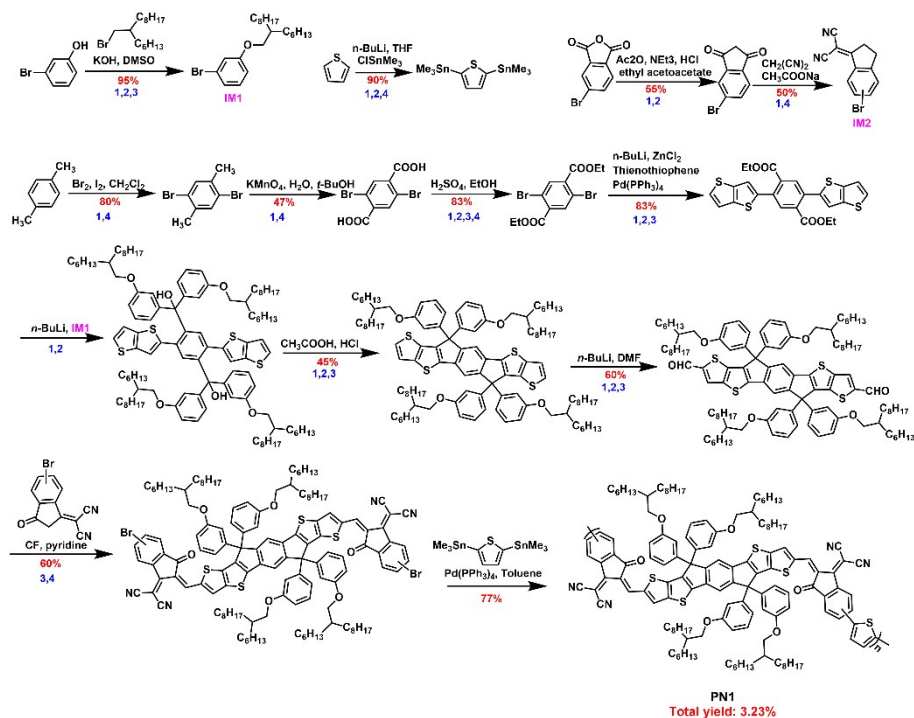
**Scheme S2.** The detailed synthetic routes of PJ1 (The unit operations are represented by codes: 1 = Quenching/neutralization, 2 = Extraction, 3 = Column chromatography, 4 = Recrystallization, 5 = Distillation/sublimation).



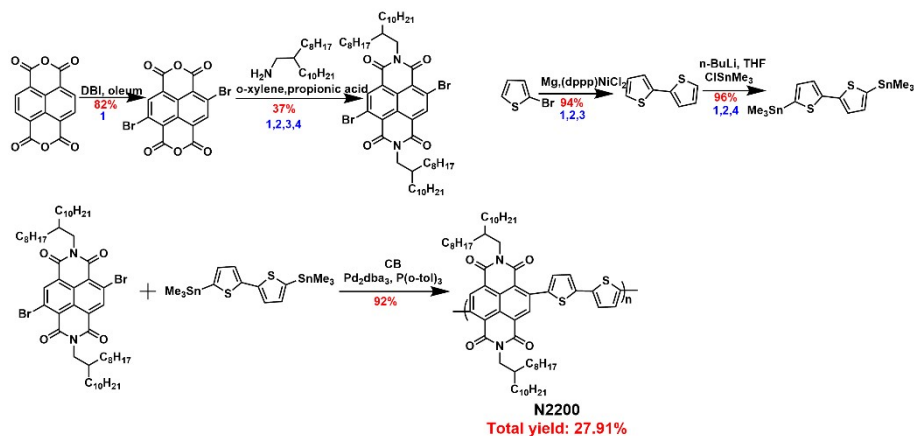
**Scheme S3.** The depolymerization and repolymerization routes of PJ1 (The unit operations are represented by codes: 1 = Quenching/neutralization, 2 = Extraction, 3 = Column chromatography, 4 = Recrystallization, 5 = Distillation/sublimation).



**Scheme S4.** The detailed synthetic routes of PZ1 (The unit operations are represented by codes: 1 = Quenching/neutralization, 2 = Extraction, 3 = Column chromatography, 4 = Recrystallization, 5 = Distillation/sublimation).

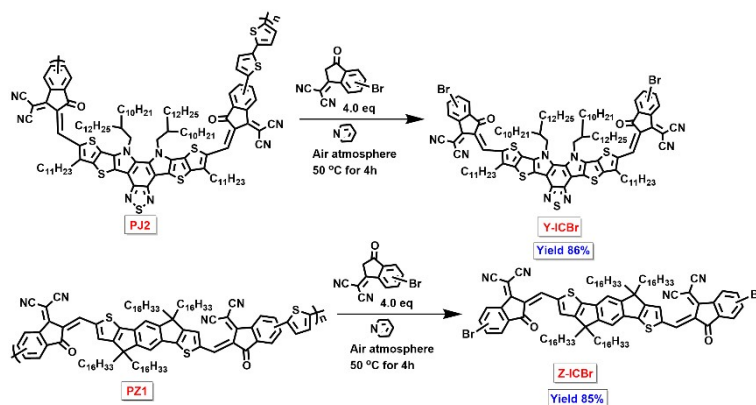


**Scheme S5.** The detailed synthetic routes of PN1 (The unit operations are represented by codes: 1 = Quenching/neutralization, 2 = Extraction, 3 = Column chromatography, 4 = Recrystallization, 5 = Distillation/sublimation).



**Scheme S6.** The detailed synthetic routes of N2200 (The unit operations are represented by codes: 1 = Quenching/neutralization, 2 = Extraction, 3 = Column chromatography, 4 = Recrystallization, 5 = Distillation/sublimation).





**Scheme S7.** The depolymerization reaction routes of PJ2 and PZ1.

**Table S1.** Starting materials, number of synthetic steps (NSS), reciprocal yield (RY), number of operation units for the isolation/purification (NUO), number of column chromatography for the isolation/purification (NCC) and number of hazardous chemicals (NHC) for polymer acceptor materials.

| Materials           | NSS | Yield (%) | RY <sup>b</sup> | NUO | NCC | NHC |
|---------------------|-----|-----------|-----------------|-----|-----|-----|
| Y-ICBr              | 16  | 11.19     | 8.9             | 33  | 5   | 32  |
| PJ1                 | 17  | 7.61      | 13.1            | 33  | 5   | 33  |
| PJ1- R <sup>a</sup> | 2   | 61.20     | 1.6             | 2   | 1   | 3   |
| PZ1                 | 15  | 4.43      | 22.6            | 31  | 6   | 31  |
| PN1                 | 13  | 3.23      | 31.0            | 31  | 6   | 30  |
| N2200               | 5   | 27.91     | 3.6             | 11  | 2   | 10  |

<sup>a</sup> PJ1 from the recycling monomer; <sup>b</sup> Reciprocal yields (RY) are calculated as the reciprocal of the overall yields of the final products from the key starting materials.

**Table S2.** The normalization of the synthetic parameters was made, using the following maximum values:  $NSS_{\max} = 17$ ;  $RY_{\max} = 31.0$ ;  $NUO_{\max} = 33$ ;  $NCC_{\max} = 6$ ;  $NHC_{\max} = 32$ .

| Materials | Norm. NSS | Norm. $\log_{10}(RY)$ | Norm. NUO | Norm. NCC | Norm. NHC | SC index <sup>c</sup> (%) | PCE (%) | FOM <sup>e</sup> |
|-----------|-----------|-----------------------|-----------|-----------|-----------|---------------------------|---------|------------------|
| Y-ICBr    | 0.94      | 0.64                  | 1.00      | 0.83      | 0.97      | 86.09                     | —       | —                |

|                      |      |      |      |      |      |                    |      |      |
|----------------------|------|------|------|------|------|--------------------|------|------|
| PJ1                  | 1.00 | 0.75 | 1.00 | 0.83 | 1.00 | 91.26              | 15.8 | 5.78 |
| PJ1- R <sup>a</sup>  | 0.12 | 0.14 | 0.06 | 0.17 | 0.09 | 12.01              | 15.8 | —    |
| PJ1- R1 <sup>b</sup> | —    | —    | —    | —    | —    | 55.99 <sup>d</sup> | 15.8 | 3.54 |
| PJ1- R2 <sup>c</sup> | —    | —    | —    | —    | —    | 44.42 <sup>d</sup> | 15.8 | 2.81 |
| PJ1- R3 <sup>b</sup> | —    | —    | —    | —    | —    | 38.77 <sup>d</sup> | 15.8 | 2.45 |
| PJ1- R4 <sup>b</sup> | —    | —    | —    | —    | —    | 35.49 <sup>d</sup> | 15.8 | 2.25 |
| PJ1- R5 <sup>b</sup> | —    | —    | —    | —    | —    | 33.39 <sup>d</sup> | 15.8 | 2.11 |
| PZ1                  | 0.88 | 0.91 | 0.94 | 1.00 | 0.94 | 92.07              | 11.2 | 8.22 |
| PN1                  | 0.76 | 1.00 | 0.94 | 1.00 | 0.91 | 89.95              | 10.5 | 8.57 |
| N2200                | 0.29 | 0.37 | 0.33 | 0.33 | 0.30 | 32.62              | 11.8 | 2.76 |

<sup>a</sup> PJ1-R represents one recycling and repolymerization process; <sup>b</sup> PJ1-R1, PJ1-R2, PJ1-R3, PJ1-R4, PJ1-R5 severally represent PJ1 preparation process when considering different times of recycling; <sup>c</sup>SC index=  $35*N\_NSS+25*N\_log_{10}(RY)+15*N\_NUO+15*N\_NCC+10*N\_NHC$ ; <sup>d</sup>  $SC(PJ1-Rn) = (91.26*0.68+12.01*0.68*0.802+12.01*0.68*0.802^2+\dots 12.01*0.68*0.802^n) / (0.68+0.68*0.802+0.68*0.802^2+\dots 0.68*0.802^n)$ , where 0.68 and 0.802 are respectively derived from the polymerization yield and total recycling yields calculated from light-aging devices(0.68\*0.80) and dichloromethane extraction(0.28\*0.92), here we assume all the PJ1 used for device fabrication can be 100% collected and then recycled with 80% yield; the dichloromethane extraction proportion remains 28% and can be recycled with 92% yield; <sup>e</sup> FOM=SC/PCE.

**Table S3.** Cost analysis of PJ1 before and after feedstock recycling based on 10 mmol Y-ICBr monomer.

| Materials                        | Primary material consumption               |   | Quantities | Cost (¥) |
|----------------------------------|--|---|------------|----------|
| PJ1                              | Reagents                                   | 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole | 10.22 g    | 817.6    |
|                                  |  | 3-undecylthieno[3,2-b]thiophene                   | 27.19 g    | 3262.8   |
|                                  |  | n-butyllithium(2.5M)                              | 100 mL     | 80       |
|                                  |  | chlorotributyltin                                 | 100 g      | 119      |
|                                  |  | triethyl phosphite                                | 250 g      | 44       |
|                                  |  | DMF(extra dry)                                    | 500 g      | 80       |
|                                  |  | phosphorus oxychloride                            | 100 g      | 134      |
|                                  |  | 11-(bromomethyl)tricosane                         | 29.6 g     | 798.2    |
|                                  |  | potassium carbonate                               | 500 g      | 30       |
|                                  |  | Pd(PPh) <sub>3</sub> Cl <sub>2</sub>              | 2 g        | 360      |
|                                  |  | potassium iodide                                  | 25g        | 30       |
|                                  |  | Pd <sub>2</sub> (dba) <sub>3</sub>                | 180 mg     | 172.8    |
|                                  |  | P( <i>o</i> -tol) <sub>3</sub>                    | 270 mg     | 48.6     |
|                                  |  | pyridine  | 100 mL     | 11.6     |
|                                  | brominated 1,1-dicyanomethylene-3-indanone | 13.65g  | 2730       |          |
|                                  | 2,5-bis(trimethylstannyl)thiophene         | 4.1g  | 820        |          |
|                                  | Solvents                                   | THF (extra dry)                                   | 1 L        | 136      |
|                                  |  | chlorobenzene                                     | 500 mL     | 35       |
|                                  |  | <i>o</i> -dichlorobenzene                         | 1 L        | 116      |
|                                  |  | methanol  | 20 L       | 520      |
|                                  |  | <i>n</i> -hexane                                  | 10 L       | 1032     |
|                                  |  | dichloromethane                                   | 10L        | 552      |
|                                  |  | chloroform  | 6L         | 468      |
|                                  |  | THF   | 1L         | 70       |
|                                  | dichloromethane (extra Dry)                | 200 mL  | 60         |          |
|                                  | Purification                               | potassium fluoride                                | 500 g      | 58       |
|                                  |  | MgSO <sub>4</sub>                                 | 1 Kg       | 15       |
| silica gel                       |  | 10 Kg   | 380        |          |
| petroleum ether                  |  | 50 L  | 790        |          |
| dichloromethane                  |  | 50 L  | 780        |          |
| chloroform                       |  | 10L   | 780        |          |
| quartz sand                      |  | 1 Kg  | 25         |          |
| Total cost (¥)                   |  |   | 15355.6    |          |
| Total PJ1- mass (g) <sup>a</sup> |  |   | 12.97g     |          |
| Unit Cost (¥)/g                  |  |   | 1183.6     |          |
| Depolymerization reaction        | Pyridine                                   | 20 mL   | 2.3        |          |
|                                  | chloroform                                 | 700 mL  | 39         |          |
|                                  | brominated 1,1-dicyanomethylene-3-indanone | 5.90g   | 1180       |          |
|                                  | petroleum ether                            | 2L  | 31.2       |          |
|                                  | dichloromethane                            | 1 L   | 15.6       |          |
|                                  | quartz sand                                | 500 g   | 12.5       |          |
|                                  | silica gel                                 | 1 Kg  | 38         |          |
|                                  | 2,5-bis(trimethylstannyl)thiophene         | 2.95g   | 590.4      |          |
| PJ1-R1 <sup>b</sup>              |  |   |            |          |

|                      |  |                                    |         |       |
|----------------------|--|------------------------------------|---------|-------|
|                      |  | Pd <sub>2</sub> (dba) <sub>3</sub> | 130 mg  | 124.8 |
|                      |  | P( <i>o</i> -tol) <sub>3</sub>     | 195 mg  | 35.1  |
|                      |  | chlorobenzene                      | 300 mL  | 21    |
|                      |  | methanol                           | 3L      | 78    |
|                      |  | n-hexane                           | 1 L     | 103.2 |
|                      |  | dichloromethane                    | 1.5 L   | 82.8  |
|                      |  | chloroform                         | 1 L     | 78    |
|                      |  | Recycling cost (¥)                 | 2431.9  |       |
|                      |  | Total cost (¥)                     | 17787.5 |       |
|                      |  | Total PJ1- mass (g)                | 22.5g   |       |
|                      |  | Unit Cost (¥)/g                    | 789.9   |       |
| PJ1-R2 <sup>b)</sup> |  | Recycling cost (¥)                 | 1789.9  |       |
|                      |  | Total cost (¥)                     | 19577.4 |       |
|                      |  | Total PJ1- mass (g)                | 29.55g  |       |
|                      |  | Unit Cost (¥)/g                    | 662.5   |       |
| PJ1-R3 <sup>b)</sup> |  | Recycling cost (¥)                 | 1317.4  |       |
|                      |  | Total cost (¥)                     | 20894.8 |       |
|                      |  | Total PJ1- mass (g)                | 34.72   |       |
|                      |  | Unit Cost (¥)/g                    | 601.8   |       |
| PJ1-R4 <sup>b)</sup> |  | Recycling cost (¥)                 | 969.6   |       |
|                      |  | Total cost (¥)                     | 21864.4 |       |
|                      |  | Total PJ1- mass (g)                | 38.5    |       |
|                      |  | Unit Cost (¥)/g                    | 567.5   |       |
| PJ1-R5 <sup>b)</sup> |  | Recycling cost (¥)                 | 713.6   |       |
|                      |  | Total cost (¥)                     | 22578.0 |       |
|                      |  | Total PJ1- mass (g)                | 41.3    |       |
|                      |  | Unit Cost (¥)/g                    | 546.3   |       |

<sup>a)</sup>Calculated from 68% polymerization yield. <sup>b)</sup>The depolymerization and reuse of active-layer materials and DCM batch was considered for the recycling process.

## Reference

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