# Supporting Information

## Contents

## 1. Materials and measurements

$^1$H-NMR and $^{13}$C-NMR spectra were recorded at 400 MHz and 100 MHz on a Bruker AVANCE spectrometer with tetramethylsilane (TMS) as the internal standard. The Molecular weight was determined with GPC at 150 °C on a PL-GPC 220 system using a PL-GEL 10 μm Olexis column and 1, 2, 4-trichlorobenzene as the eluent against polystyrene standards. Optical absorption spectra were recorded on a JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of 1000 nm min$^{-1}$. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V s$^{-1}$ 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. Thermogravimetric analysis data were obtained from a TGA8000 Thermogravimetric Analyzer (PerkinElmer), DSC measurement was performed on a DSC-250 apparatus.

Photovoltaic devices with inverted configuration were made by spin-coating a ZnO sol-gel at 4000 rpm for 60 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coating CB solution containing the polymer and the appropriate amount of DIO as processing additive. The thin films were then transferred into the N$_2$-filled glove box. MoO$_3$ (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ca. 7 × 10$^{-5}$ Pa as the back electrode. The thickness of the active layer is about 75 nm.

The active area of the cells was 0.040 cm$^2$. The $J$–$V$ curves were measured under AM1.5G illumination at 100 mW cm$^{-2}$ using an AAA solar simulator (XES-70S1, SAN-EI Electric 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).

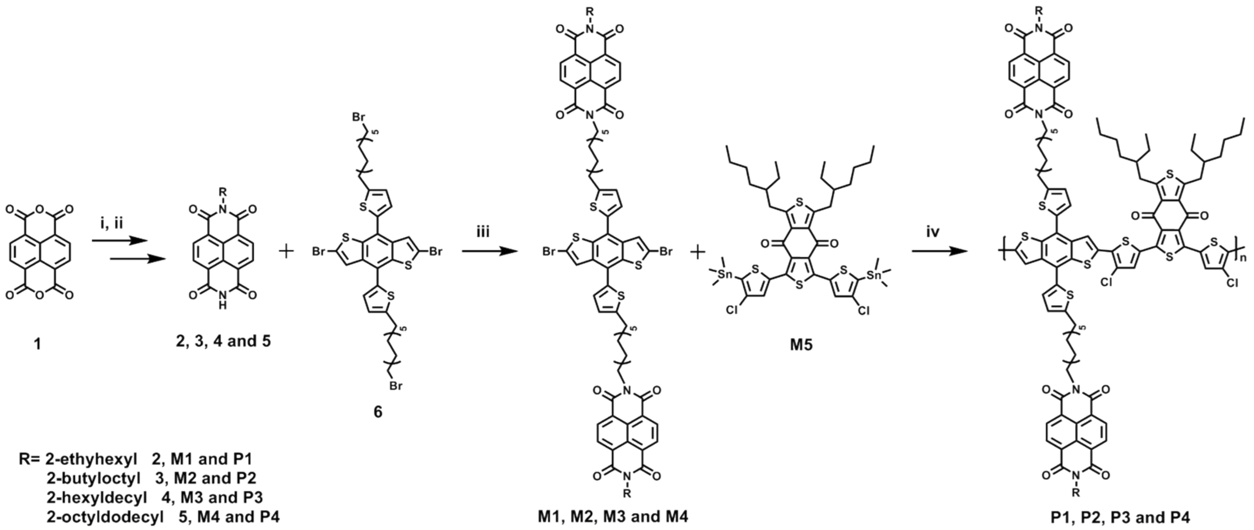
GIWAXS measurements were performed at SAXS/WAXS beamline, Australian Synchrotron ANSTO. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 15.2 keV X-ray beam was incident at a grazing angle of 0.08°-0.12°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nano scope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

The hole mobility of P1-P4 films in SCOSCs were measured by space charge limit current (SCLC) measurement with the device configuration of ITO/PEDOT:PSS/active layer/MoO$_3$/Ag. The electron mobilities were extracted from electron-only devices with the configuration of ITO/ZnO/active layer/Ca/Al. All film samples were prepared with the same measurement of the solar cell devices by spin-coating solutions in N$_2$-filled glove box and thermal annealed for 10 min. And the hole mobilities were calculated with the Mott-Gurney equation in the SCLC region (slope = 2 in log$J$ vs log$V$ plots):

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3} \qquad \textbf{(Equation S1)}$$

Where $\varepsilon_0$ is the permittivity of the vacuum, $\varepsilon_r$ is the dielectric constant of the polymer, and $L$ is the thickness of the polymer layer.

## 2. Synthesis of the monomers and polymers



**Scheme S1.** The chemical structures of the monomers, polymers and their synthetic routes. (i) 2-ethyhexan-1-amine, 2-butyloctan-1-amine, 2-hexyldecan-1-amine or 2-octyldodecan-1-amine in DMF at 120 °C, 12 h; (ii) $NH_4OAc$ in AcOH at 100 °C, 4 h; (iii) $K_2CO_3$ in DMF at 70 °C, 24 h; (iv) Stille polymerization, $Pd(PPh_3)_4$ in toluene/DMF (10:1, v/v) at 115 °C, 48 h.

The monomer **M5** were purchased from Solarmer Inc., Beijing. The compound **3**, **6** and the monomer **M2** were synthesized according to the literatures.[1, 2]

**2:** **1** (1.2 g, 4.5 mmol) was dissolved in 50 ml dry DMF under an inert atmosphere, 2-ethyhexan-1-amine (0.58 g, 4.5 mmol) was added. After the mixture was stirred at 120 °C for 12 h, the reactant quenched by brine, then extracted by dichloromethane (100 mL) and dried over anhydrous $MgSO_4$. After removing solvent, the crude product was dissolved in 50ml AcOH, $NH_4OAc$ (2.71 g, 0.045 mol) was added. After the mixture was stirred at 100 °C for 4 h, the reactant quenched by water, then extracted by chloroform (100 mL) and dried over anhydrous $MgSO_4$. After removing solvent, the crude product was purified by silica gel chromatography (chloroform : petroleum ether, v/v = 2:1 as eluent) to obtain **2** (0.81 g, yield 48% ) as off-white solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.75-8.82 (m, 4H), 8.56 (s, 1H), 4.13-4.17 (t, 2H), 1.94 (s, 1H), 1.24-1.40 (m, 8H), 0.88-0.96 (m, 6H). MS (MALDI-TOF) m/z: $[M+H]^+$, Calcd for $C_{22}H_{22}N_2O_4$: 378.2; found: 379.1.

**4:** **1** (1.2 g, 4.5 mmol) was dissolved in 50 ml dry DMF under an inert atmosphere, 2-hexyldecan-1-amine (1.09 g, 4.5 mmol) was added. After the mixture was stirred at 120 °C for 12 h, the reactant quenched by brine, then extracted by dichloromethane (100 mL) and dried over anhydrous $MgSO_4$. After removing solvent, the crude product was dissolved in 50ml AcOH, $NH_4OAc$ (2.71 g, 0.045 mol) was added. After the mixture was stirred at 100 °C for 4 h, the reactant quenched by water, then extracted by chloroform (100 mL) and dried over anhydrous $MgSO_4$. After removing solvent, the crude product was purified by silica gel chromatography (chloroform : petroleum ether, v/v = 2:1 as eluent) to obtain **5** (1.12 g, yield 51% ) as white solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.87 (s, 1H), 8.76-8.80 (m, 4H), 4.13 (d, 2H), 1.98 (s, 1H), 1.24-1.38 (m, 24H), 0.83-0.86 (m, 6H). MS (MALDI-TOF) m/z: $[M+H]^+$, Calcd for $C_{30}H_{38}N_2O_4$: 490.3; found: 490.9.

**5:** **1** (1.2 g, 4.5 mmol) was dissolved in 50 ml dry DMF under an inert atmosphere, 2-octyldodecan-1-amine (1.34 g, 4.5 mmol) was added. After the mixture was stirred at 120 °C for 12 h, the reactant quenched by brine, then extracted by dichloromethane (100 mL) and dried over anhydrous $MgSO_4$. After removing solvent, the crude product was dissolved in 50ml AcOH, $NH_4OAc$ (2.71 g, 0.045 mol) was added. After the mixture was stirred at 100 °C for 4 h, the reactant quenched by water, then extracted by chloroform (100 mL) and dried over anhydrous $MgSO_4$. After removing solvent, the crude product was purified by silica gel chromatography (chloroform : petroleum ether, v/v = 2:1 as eluent) to obtain **5** (1.35 g, yield 55% ) as white solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.81 (s, 1H), 8.75 (d, 4H), 4.13 (d, 2H), 1.99 (s, 1H), 1.22-1.37 (m, 32H), 0.83-0.88 (m, 6H). MS (MALDI-TOF) m/z: $[M+H]^+$, Calcd for $C_{34}H_{46}N_2O_4$: 546.3; found: 548.0.

**M1:** **6** (122 mg, 0.12 mmol) was dissolved in 25 ml dry DMF, **2** (109.5 mg, 0.29 mmol) and potassium carbonate (83 mg, 0.6 mmol) were added. The mixture was stirred at 70 °C for 24 h, there were some creamy white solid separated out. The mixture was filtered and the creamy white solid was washed by hot water and hot acetone to obtain **M1** (140 mg, yield 72%). $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.74 (s, 8H), 7.56 (s, 2H), 7.19-7.20 (d, 2H), 6.88-6.89 (d, 2H), 4.16-4.20 (t, 4H), 4.12-4.16 (t, 4H), 2.88-2.91 (t, 4H), 1.92-1.95 (t, 2H), 1.73-1.78 (m, 8H), 1.30-1.43 (m, 48H), 0.92-0.95 (t, 6H), 0.85-0.88 (t, 6H). $^{13}$C NMR (400 MHz, CDCl3): $\delta$ (ppm) 163.2, 162.8, 147.8, 140.1, 135.9, 135.6, 130.9, 130.8, 127.9, 126.7, 126.6, 126.5, 126.0, 124.4, 122.4, 116.7, 44.6, 40.9, 37.9, 31.5, 30.6, 30.2, 29.5, 29.4, 29.3, 29.1, 28.6, 28.0, 27.0, 24.0, 23.0, 14.0, 10.5. MS (MALDI-TOF) m/z: $[M+H]^+$, Calcd for $C_{86}H_{96}Br_2N_4O_8S_4$: 1600.45; found: 1601.5.

**M3:** **6** (122 mg, 0.12 mmol) was dissolved in 25 ml dry DMF, **4** (142.3 mg, 0.29 mmol) and potassium carbonate (83 mg, 0.6 mmol) were added. The mixture was stirred at 70 °C for 24 h, there were some white solid separated out. The mixture was filtered and the white solid was washed by hot water and hot acetone to obtain **M3** (173.2 mg, yield 78%). $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.74 (s, 8H), 7.55 (s, 2H), 7.19-7.20 (d, 2H), 6.88 (s, 2H), 4.16-4.20 (t, 4H), 4.11-4.13 (d, 4H), 2.88-2.91 (t, 4H), 1.98(s, 2H), 1.75-1.76 (d, 8H), 1.23-1.41 (m, 80H), 0.83-0.85 (m, 12H). $^{13}$C NMR (400 MHz, CDCl3): *δ* (ppm) 163.1, 162.8, 147.7, 140.1, 135.8, 135.6, 130.9, 130.8, 127.9, 126.7, 126.6, 126.5, 126.0, 124.4, 122.4, 116.7, 44.9, 40.9, 36.5, 31.8, 31.7, 31.6, 31.6, 31.5, 30.2, 29.9, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.0, 27.0, 26.4, 26.3, 22.6, 22.5, 14.1, 14.0. MS (MALDI-TOF) m/z: $[M+H]^+$, Calcd for $C_{102}H_{128}Br_2N_4O_8S_4$: 1824.7; found: 1824.7.

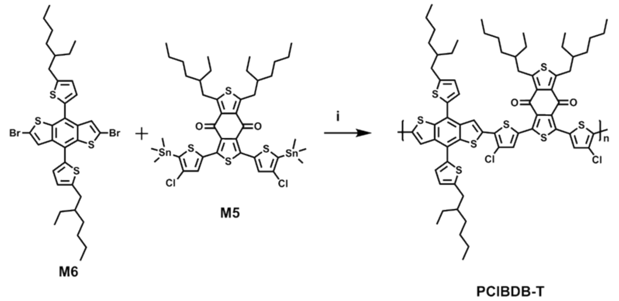
**M4:** **6** (122 mg, 0.12 mmol) was dissolved in 25 ml dry DMF, **5** (158.6 mg, 0.29 mmol) and potassium carbonate (83 mg, 0.6 mmol) were added. The mixture was stirred at 70 °C for 24 h, there were some white solid separated out. The mixture was filtered and the white solid was washed by hot water and hot acetone to obtain **M4** (176.8 mg, yield 75%). $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.74 (s, 8H), 7.55 (s, 2H), 7.19-7.20 (d, 2H), 6.88-6.89 (d, 2H), 4.16-4.20 (t, 4H), 4.11-4.13 (d, 4H), 2.87-2.91 (t, 4H), 1.98(s, 2H), 1.74-1.78 (t, 8H), 1.21-1.41 (m, 96H), 0.83-0.88 (m, 12H). $^{13}$C NMR (400 MHz, CDCl3): *δ* (ppm) 163.1, 162.8, 147.7, 140.1, 135.9, 135.6, 130.9, 130.8, 127.9, 126.7, 126.6, 126.5, 126.0, 124.4, 122.4, 116.7, 44.9, 40.9, 36.5, 31.8, 31.8, 31.6, 31.6, 31.5, 30.2, 29.9, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.0, 27.0, 26.4, 26.3, 22.6, 22.6, 14.0. MS (MALDI-TOF) m/z: $[M+H]^+$, Calcd for $C_{102}H_{128}Br_2N_4O_8S_4$: 1937.8; found: 1938.6.

P1**:** To a degassed solution of monomer **M1** (40.04 mg, 25.0 μmol), **M5** (25.19 mg, 25.1 μmol) in toluene (3 mL) and DMF (0.3 mL), $Pd(PPh_3)_4$ (0.90 mg, 0.78 μmol) was added. The mixture was stirred at 115 °C for 48 h. after which it was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexane, dichloromethane and chlorobenzene. The chlorobenzene was evaporated and the polymer was precipitated in acetone. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield P1 (45.04 mg, 85.1%) as dark blue solid. GPC (*o*-DCB, 140 °C): $M_n$ = 28.2 kg mol$^{-1}$, $M_w$ = 72.6 kg mol$^{-1}$ and $Đ_M$ = 2.57.

P2**:** To a degassed solution of monomer **M2** (42.85 mg, 25.0 μmol), **M5** (25.11 mg, 25.0 μmol) in toluene (2.5 mL) and DMF (0.25 mL), Pd($PPh_3$)$_4$ (0.89 mg, 0.77 μmol) was added. The mixture was stirred at 115 °C for 48 h. after which it was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexane, dichloromethane and chlorobenzene. The chlorobenzene was evaporated and the polymer was precipitated in acetone. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield P2 (45.82 mg, 82.2%) as dark blue solid. GPC (*o*-DCB, 140 °C): $M_n$ = 51.5 kg mol$^{-1}$, $M_w$ = 106.5 kg mol$^{-1}$ and $Đ_M$ = 2.07.

P3**:** To a degassed solution of monomer **M3** (45.66 mg, 25.0 μmol), **M5** (25.13 mg, 25.0 μmol) in toluene (2.5 mL) and DMF (0.25 mL), Pd($PPh_3$)$_4$ (0.91 mg, 0.78 μmol) was added. The mixture was stirred at 115 °C for 48 h. after which it was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexane and trichloromethane. The trichloromethane was evaporated and the polymer was precipitated in acetone. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield P3 (48.61 mg, 82.8%) as dark blue solid. GPC (*o*-DCB, 140 °C): $M_n$ = 45.1 kg mol$^{-1}$, $M_w$ = 103.3 kg mol$^{-1}$ and $Đ_M$ = 2.29.

P4: Same procedure as for P3 was used, but now **M4** (44.58 mg, 23.0 μmol) and **M5** (23.08 mg, 23.0 μmol) were used as the monomers. Yield: 44.3mg (78.5%). GPC (*o*-DCB, 140 °C): $M_n$ = 27.8 kg mol$^{-1}$, $M_w$ = 56.3 kg mol$^{-1}$ and $Đ_M$ = 2.02.



**Scheme S2.** The chemical structures and synthetic routes of PClBDB-T. **M6** and PClBDB-T were synthesized according to the literatures.[3]

## 3. GPC curves

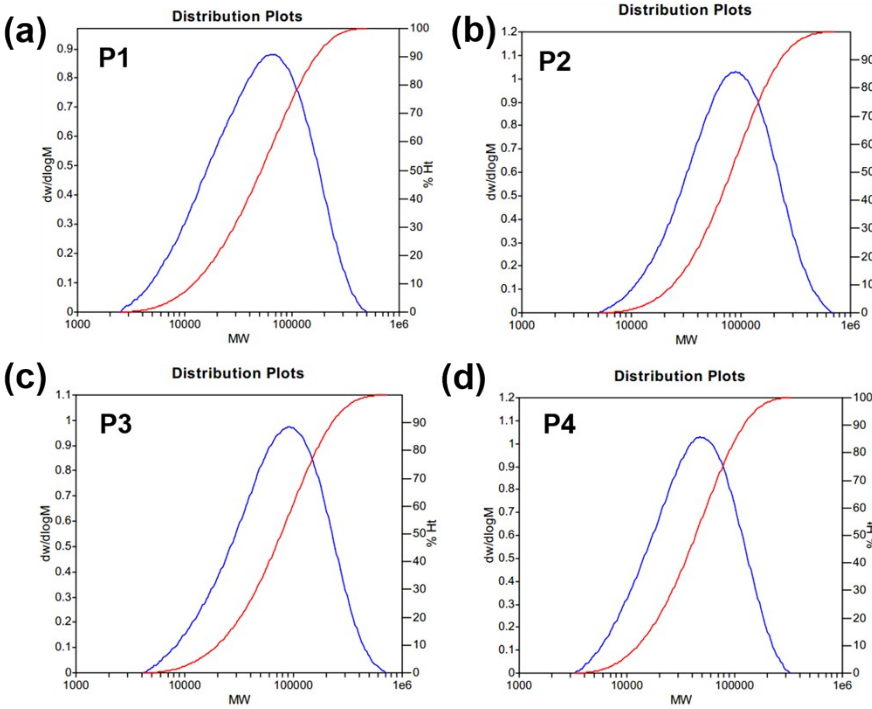


**Figure S1.** GPC curves recorded at 140 °C with *o*-DCB as eluent. (a) P1, (b) P2, (c) P3, (d) P4.

## 4. Optical and electrochemical properties

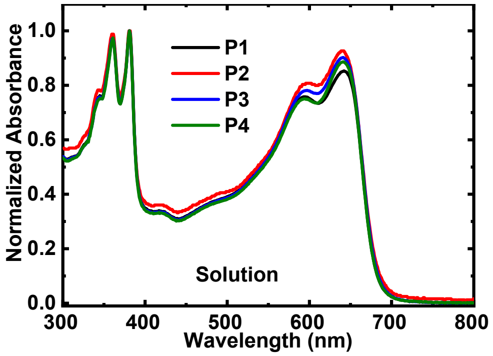


**Figure S2.** Optical absorption spectra of the polymers in $CHCl_3$ solution.

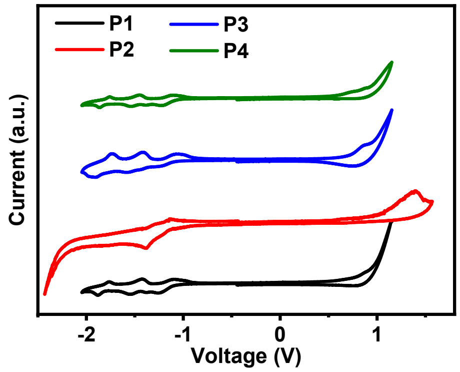


**Figure S3.** Cyclic voltammograms of the polymer thin films. Potential vs. Fc/Fc$^+$.

## 5. Solar cells performances

**Table S1.** Characteristics of P1-based solar cells spin coated from different solution and different thermal annealing temperature (10 min).

| Solvent | Thermal Anneal [ºC] | Thickness [nm] | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|---|---|
| CB | 150 | 75 | 10.93 | 0.97 | 0.52 | 5.48 |
| CB/DIO (1%) | 150 | 75 | 11.32 | 0.97 | 0.54 | 5.89 |
| **CB/DIO (2%)** | **150** | **75** | **11.49** | **0.97** | **0.57** | **6.30** |
| CB/DIO (3%) | 150 | 75 | 11.49 | 0.96 | 0.54 | 5.94 |
| | | | | | | |
| CB/DIO (2%) | 150 | 55 | 10.49 | 0.96 | 0.51 | 5.11 |
| **CB/DIO (2%)** | **150** | **75** | **11.05** | **0.98** | **0.57** | **6.20** |
| CB/DIO (2%) | 150 | 95 | 10.75 | 0.95 | 0.51 | 5.16 |
| | | | | | | |
| CB/DIO (2%) | RT | 75 | 9.93 | 0.97 | 0.44 | 4.19 |
| **CB/DIO (2%)** | **150** | **75** | **11.49** | **0.97** | **0.57** | **6.30** |
| CB/DIO (2%) | 200 | 75 | 11.25 | 0.91 | 0.55 | 5.59 |

**Table S2.** Characteristics of P2-based solar cells spin coated from different solution and different thermal annealing temperature (10 min).

| Solvent | Thermal Anneal [ºC] | Thickness [nm] | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|---|---|
| CB | 150 | 75 | 12.83 | 0.96 | 0.58 | 7.08 |
| CB/DIO (1%) | 150 | 75 | 12.31 | 0.96 | 0.65 | 7.59 |
| **CB/DIO (2%)** | **150** | **75** | **12.84** | **0.94** | **0.66** | **7.97** |
| CB/DIO (3%) | 150 | 75 | 12.19 | 0.94 | 0.68 | 7.80 |
| | | | | | | |
| CB/DIO (2%) | 150 | 55 | 10.77 | 0.95 | 0.70 | 7.04 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **CB/DIO (2%)** | **150** | **75** | **12.84** | **0.94** | **0.66** | **7.97** |
| CB/DIO (2%) | 150 | 95 | 12.89 | 0.93 | 0.62 | 7.45 |
| CB/DIO (2%) | RT | 75 | 10.98 | 0.96 | 0.49 | 5.14 |
| **CB/DIO (2%)** | **150** | **75** | **12.84** | **0.94** | **0.66** | **7.97** |
| CB/DIO (2%) | 200 | 75 | 13.06 | 0.91 | 0.65 | 7.80 |

**Table S3.** Characteristics of P3-based solar cells spin coated from different solution and different thermal annealing temperature (10 min).

| Solvent | Thermal Anneal [ºC] | Thickness [nm] | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|---|---|
| CB | 150 | 75 | 11.51 | 0.97 | 0.61 | 6.83 |
| CB/DIO (1%) | 150 | 75 | 11.68 | 0.96 | 0.64 | 7.15 |
| **CB/DIO (2%)** | **150** | **75** | **11.76** | **0.96** | **0.64** | **7.23** |
| CB/DIO (3%) | 150 | 75 | 11.27 | 0.96 | 0.64 | 6.90 |
| CB/DIO (2%) | 150 | 55 | 10.73 | 0.95 | 0.64 | 6.50 |
| **CB/DIO (2%)** | **150** | **75** | **11.76** | **0.96** | **0.64** | **7.23** |
| CB/DIO (2%) | 150 | 95 | 11.72 | 0.95 | 0.62 | 6.90 |
| CB/DIO (2%) | RT | 75 | 9.91 | 0.98 | 0.45 | 4.34 |
| **CB/DIO (2%)** | **150** | **75** | **11.76** | **0.96** | **0.64** | **7.23** |
| CB/DIO (2%) | 200 | 75 | 11.44 | 0.93 | 0.63 | 6.69 |

**Table S4.** Characteristics of P4-based solar cells spin coated from different solution and different thermal annealing temperature (10 min).

| Solvent | Thermal Anneal [ºC] | Thickness [nm] | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|---|---|
| CB | 150 | 75 | 7.91 | 0.93 | 0.70 | 5.10 |
| CB/DIO (1%) | 150 | 75 | 7.94 | 0.92 | 0.69 | 5.06 |
| **CB/DIO (2%)** | **150** | **75** | **8.60** | **0.93** | **0.66** | **5.24** |
| CB/DIO (3%) | 150 | 75 | 8.44 | 0.92 | 0.66 | 5.12 |
| CB/DIO (2%) | 150 | 55 | 7.49 | 0.92 | 0.68 | 4.73 |
| **CB/DIO (2%)** | **150** | **75** | **8.59** | **0.93** | **0.66** | **5.24** |
| CB/DIO (2%) | 150 | 95 | 8.45 | 0.92 | 0.64 | 4.95 |
| CB/DIO (2%) | RT | 75 | 7.13 | 0.99 | 0.44 | 3.07 |
| **CB/DIO (2%)** | **150** | **75** | **8.59** | **0.93** | **0.66** | **5.24** |
| CB/DIO (2%) | 200 | 75 | 7.99 | 0.91 | 0.61 | 4.42 |

**Table S5**. Photovoltaic performances of 6 devices based on P1 fabricated from CB/DIO (2%) annealed at 150 ºC for 10 min.

| No. | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|
| 1 | 11.49 | 0.97 | 0.57 | 6.30 |
| 2 | 11.19 | 0.97 | 0.58 | 6.27 |
| 3 | 10.85 | 0.96 | 0.60 | 6.27 |
| 4 | 11.81 | 0.96 | 0.55 | 6.24 |
| 5 | 11.70 | 0.96 | 0.55 | 6.18 |
| 6 | 11.72 | 0.96 | 0.54 | 6.08 |
| average | 11.46±0.34 | 0.96±0.01 | 0.57±0.02 | 6.22±0.07 |

**Table S6**. Photovoltaic performances of 6 devices based on P2 fabricated from CB/DIO (2%) annealed at 150 ºC for 10 min.

| No. | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|
| 1 | 12.84 | 0.94 | 0.66 | 7.97 |
| 2 | 12.41 | 0.95 | 0.67 | 7.92 |
| 3 | 12.42 | 0.94 | 0.68 | 7.92 |
| 4 | 12.46 | 0.94 | 0.67 | 7.87 |
| 5 | 11.88 | 0.94 | 0.70 | 7.79 |
| 6 | 12.32 | 0.93 | 0.67 | 7.73 |
| average | 12.39±0.28 | 0.94±0.01 | 0.68±0.01 | 7.87±0.08 |

**Table S7**. Photovoltaic performances of 6 devices based on P3 fabricated from CB/DIO (2%) annealed at 150 ºC for 10 min.

| No. | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|
| 1 | 11.76 | 0.96 | 0.64 | 7.23 |
| 2 | 12.03 | 0.96 | 0.63 | 7.21 |
| 3 | 11.97 | 0.96 | 0.62 | 7.16 |
| 4 | 12.03 | 0.96 | 0.61 | 7.14 |
| 5 | 11.45 | 0.96 | 0.65 | 7.11 |
| 6 | 11.67 | 0.96 | 0.63 | 7.09 |
| average | 11.82±0.21 | 0.96±0.01 | 0.63±0.01 | 7.16±0.05 |

**Table S8**. Photovoltaic performances of 6 devices based on P4 fabricated from CB/DIO (2%) annealed at 150 ºC for 10 min.

| No. | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | FF | PCE [%] |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | 8.59 | 0.93 | 0.66 | 5.24 |
| 2 | 8.08 | 0.93 | 0.69 | 5.20 |
| 3 | 8.15 | 0.93 | 0.67 | 5.11 |
| 4 | 7.97 | 0.94 | 0.68 | 5.10 |
| 5 | 7.95 | 0.93 | 0.69 | 5.09 |
| 6 | 8.54 | 0.92 | 0.65 | 5.08 |
| average | 8.21±0.26 | 0.93±0.01 | 0.67±0.01 | 5.14±0.06 |

## 6. SCLC measurements

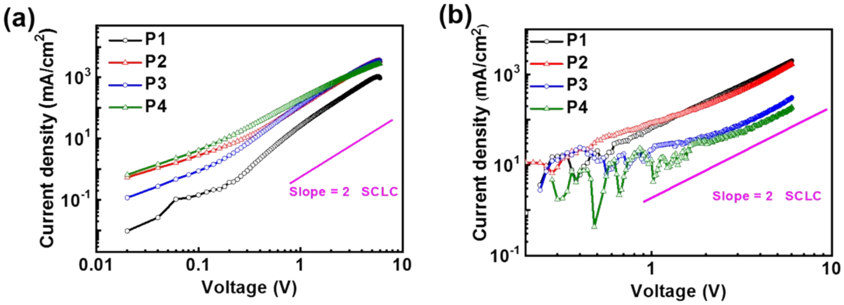


**Figure S4.** (a) Hole mobility extracted from SCLC measurement with hole-only devices (ITO/PEDOT:PSS/polymers/$MoO_3$/Ag) based on P1 **-** P4 films with the thickness of 138 nm, 141 nm, 115 nm and 110 nm (b) Electron mobility extracted from SCLC measurement with electron-only devices (ITO/ZnO/active layer/Ca/Al) based on P1 - P4 films with the thickness of 212 nm, 163 nm, 162 nm and 101 nm, respectively.

## 7. NMR of the compounds

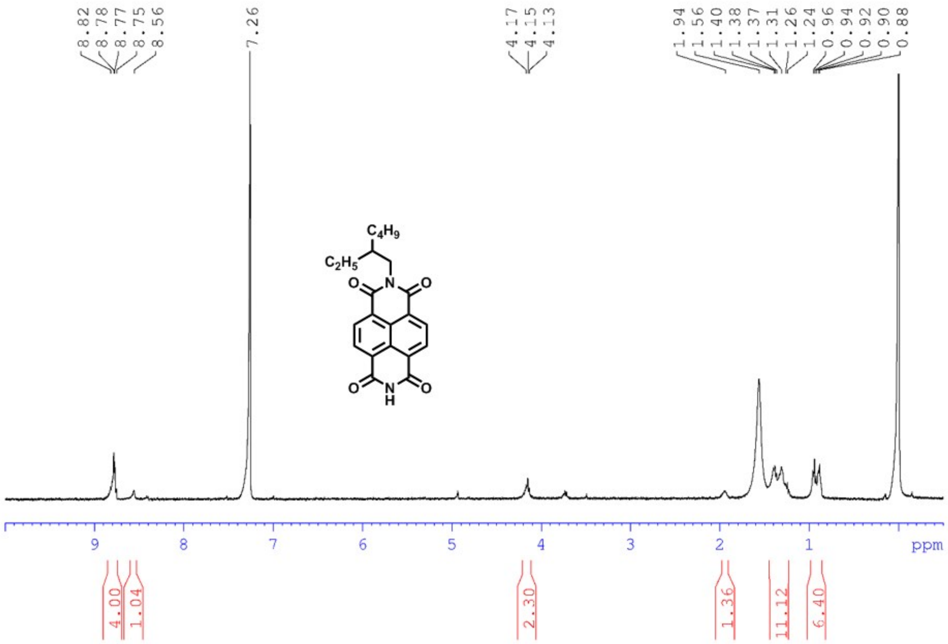


**Figure S5**. $^1$H-NMR of the compound **2** recorded in $CDCl_3$.

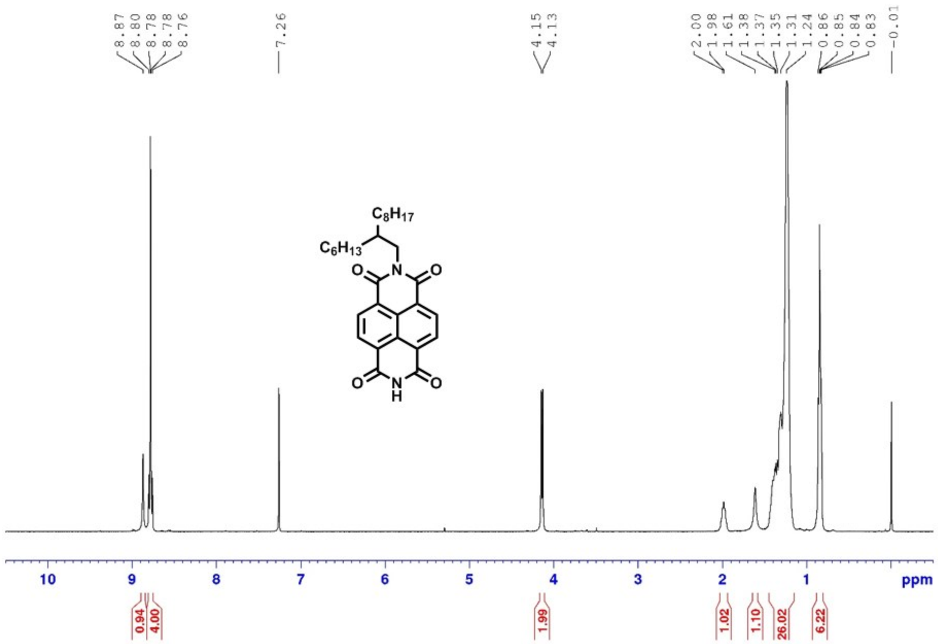


**Figure S6**. $^1$H-NMR of the compound **4** recorded in $CDCl_3$.

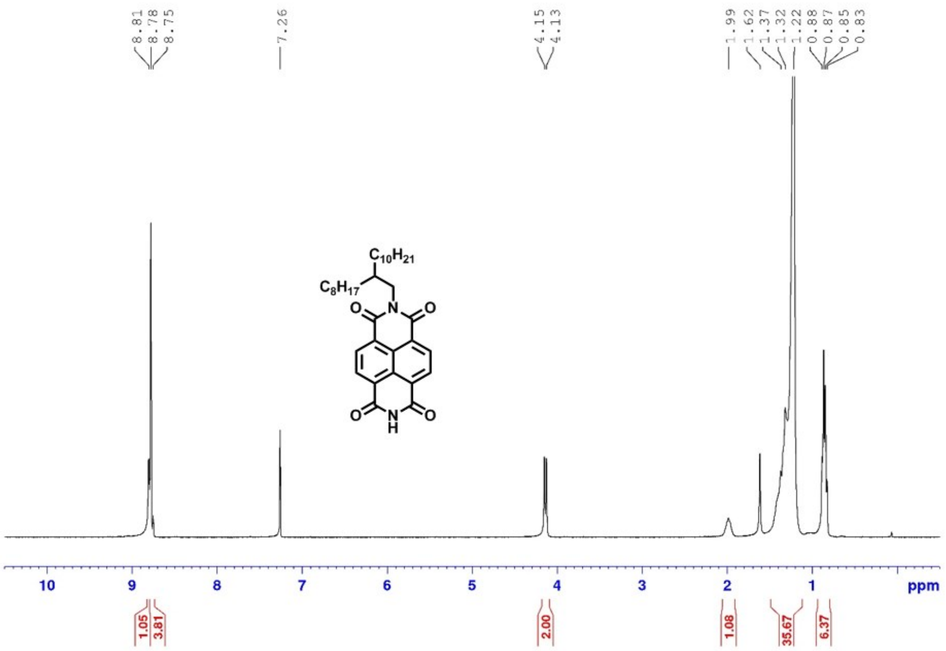


**Figure S7**. $^1$H-NMR of the compound **5** recorded in $CDCl_3$.

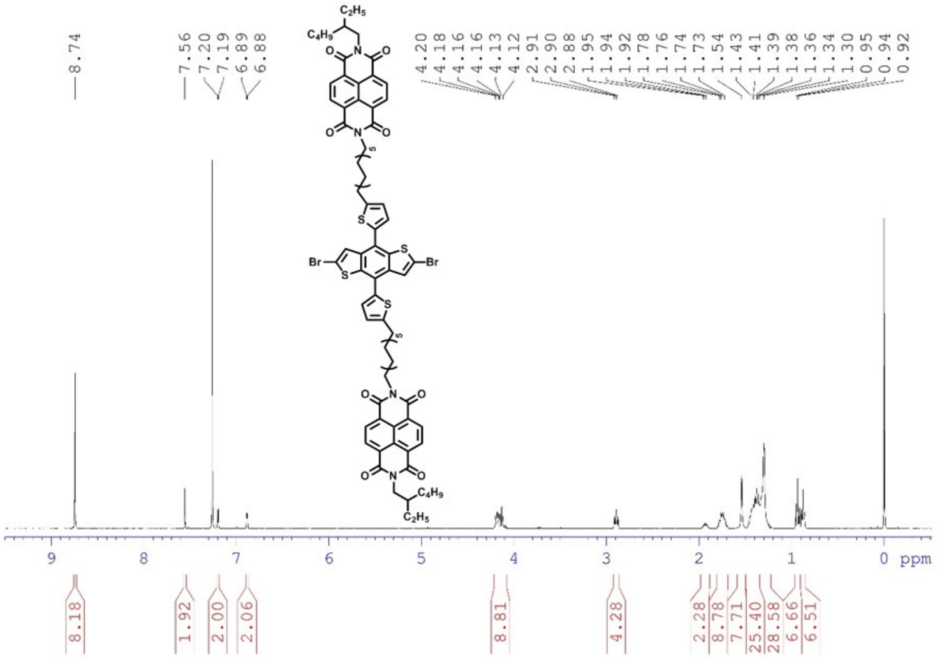


**Figure S8**. $^1$H-NMR of the compound **M1** recorded in $CDCl_3$.

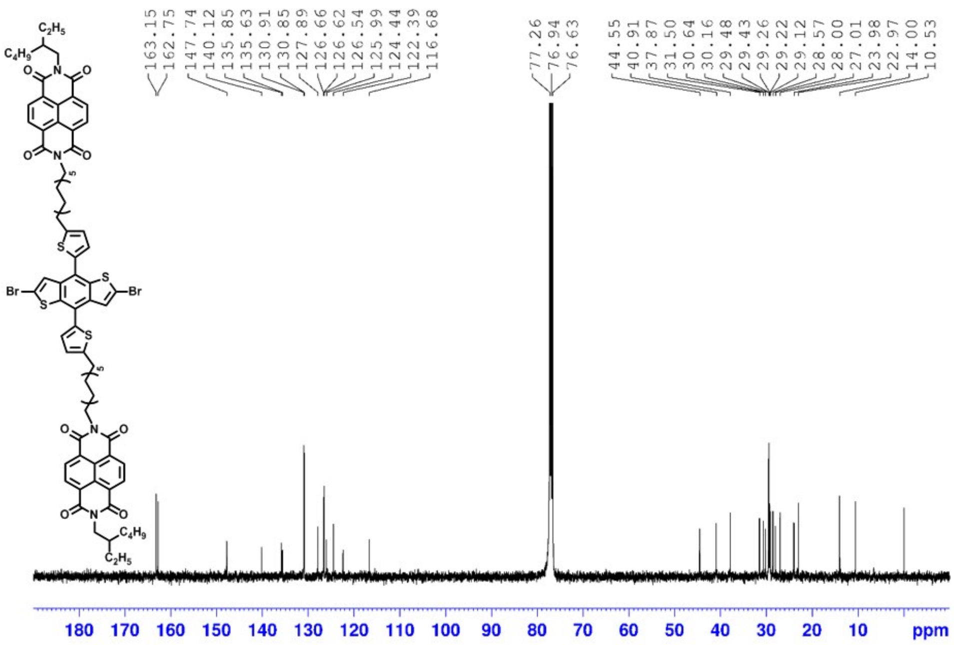


**Figure S9**. $^{13}$C-NMR of the compound **M1** recorded in CDCl$_3$.

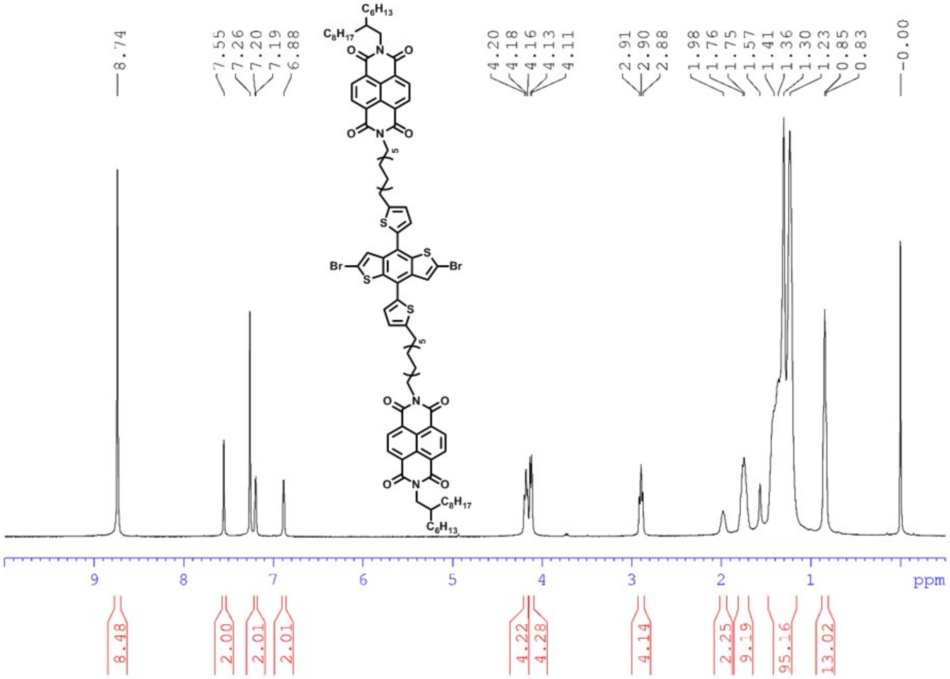


**Figure S10**. $^{1}$H-NMR of the compound **M3** recorded in CDCl$_3$.

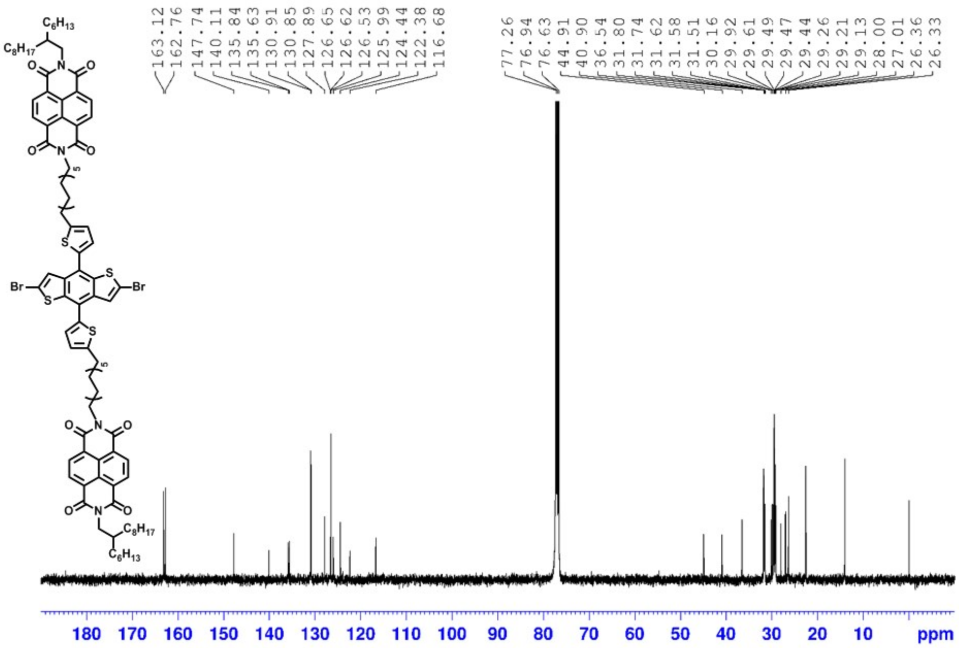


**Figure S11**. $^{13}$C-NMR of the compound **M3** recorded in CDCl$_3$.

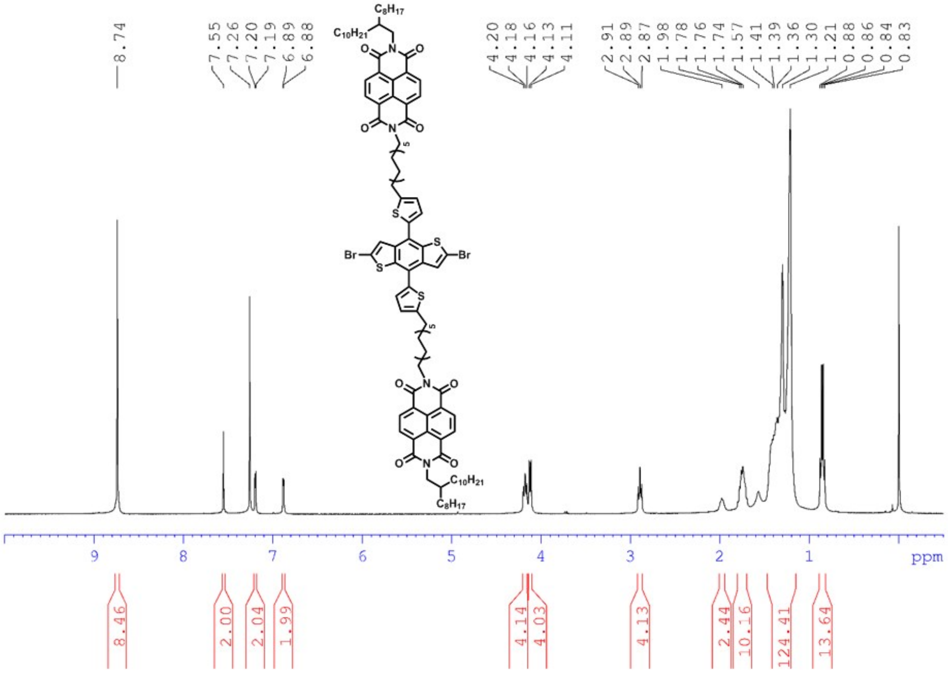


**Figure S12**. $^{1}$H-NMR of the compound **M4** recorded in CDCl$_3$.

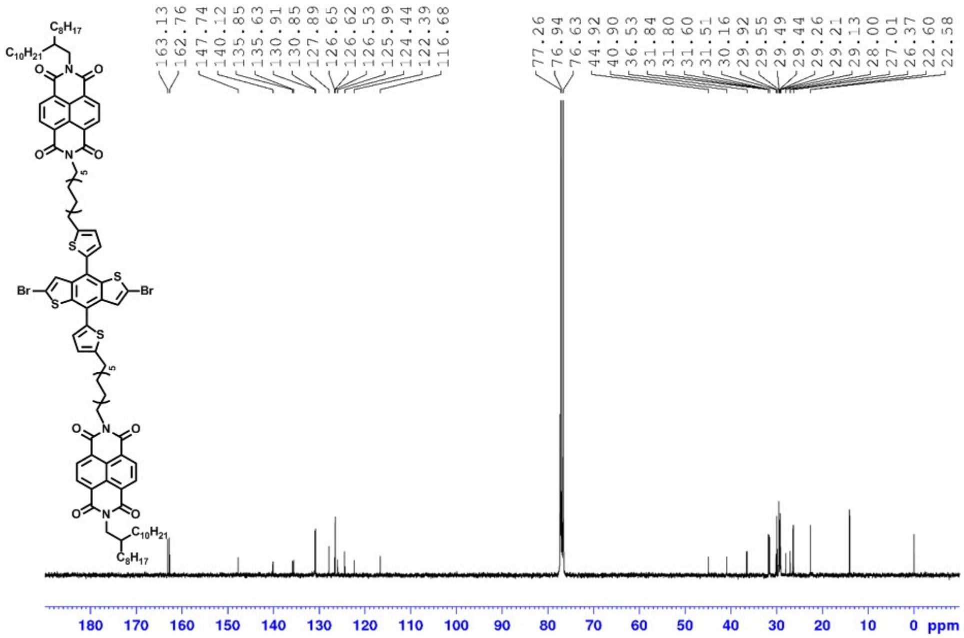


**Figure S13**. ${}^{13}$C-NMR of the compound **M4** recorded in CDCl$_3$.

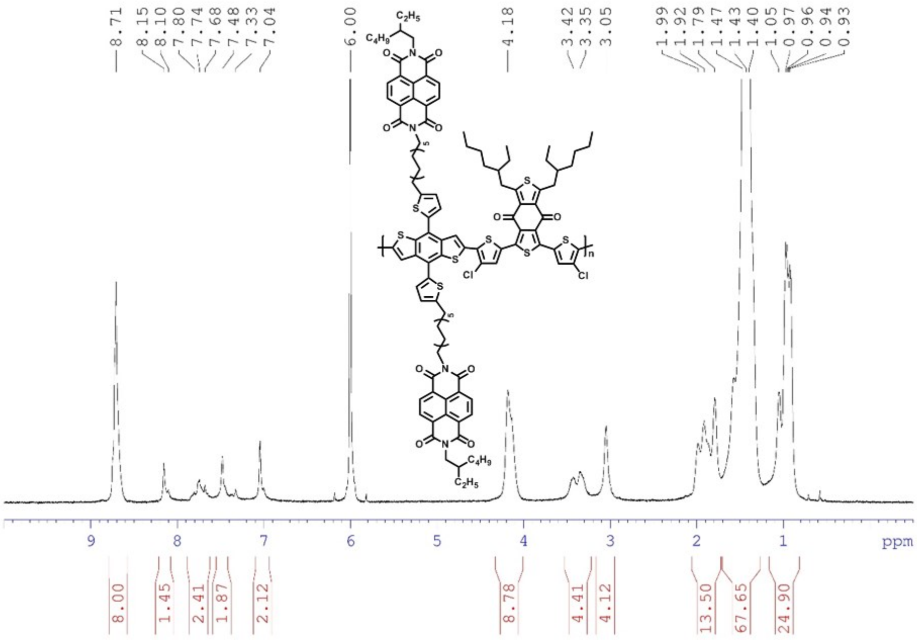


**Figure S14**. ${}^{1}$H-NMR of the polymer P1 recorded at 100 ºC with 1,1,2,2-tetrachloroethane-d$_2$ as the solvent.

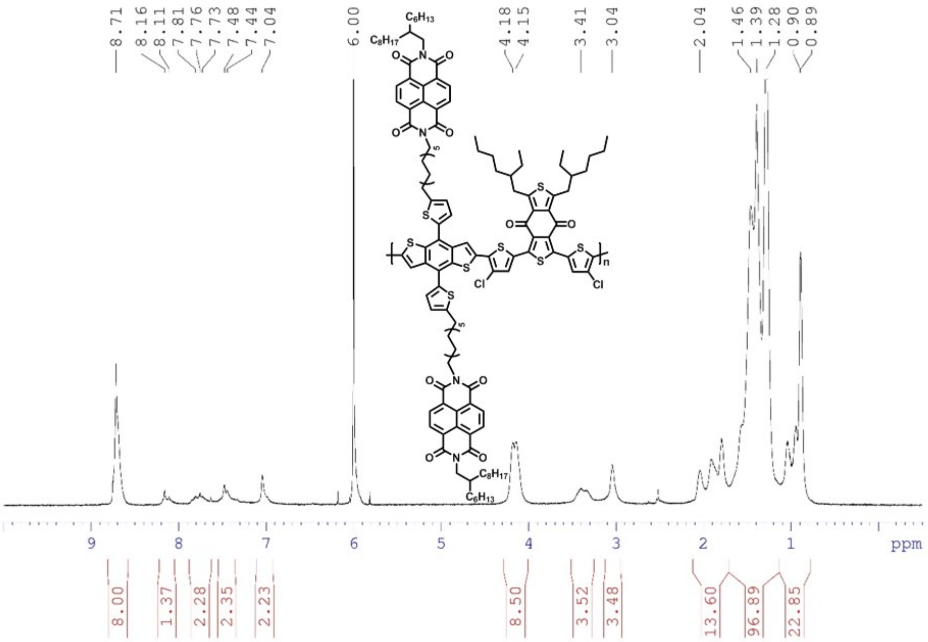


**Figure S15**. $^1$H-NMR of the polymer P3 recorded at 100 ºC with 1,1,2,2-tetrachloroethane-$d_2$ as the solvent.

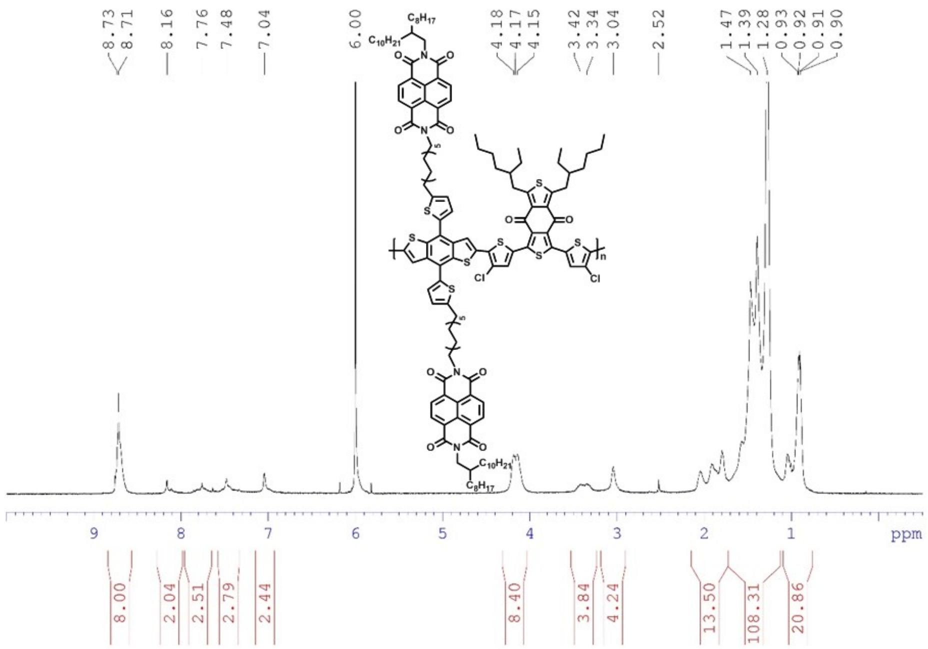


**Figure S16**. $^1$H-NMR of the polymer P4 recorded at 100 ºC with 1,1,2,2-tetrachloroethane-$d_2$ as the solvent.

## 8. References

1. X. Jiang, J. Yang, S. Karuthedath, J. Li, W. Lai, C. Li, C. Xiao, L. Ye, Z. Ma, Z. Tang, F. Laquai and W. Li, *Angew Chem Int Ed Engl*, 2020, **59**, 21683-21692.
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