

Electronic Supplementary Information

Synergistic effect of side-chain engineering and terminal-group halogenation on naphthalenediimide-based non-fused ring electron acceptors for efficient organic solar cells

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Experimental Section

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. The materials of D18, PM6, Monomer (M1), 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-2Cl) were purchased from Derthon OPV Co Ltd. Monomer (M2) and Monomer (M3) was prepared according to the previously reported literature.¹

Measurements: ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ¹H NMR and ¹³C NMR spectra were referenced to tetramethylsilane (0 ppm) for CDCl₃. The molecular mass was confirmed using an Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF-MS). Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. DSC measurements were carried out with a NETZSCH (DSC 200 F3) apparatus at a heating/cooling rate of 10/10°C/min under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s⁻¹ against a platinum wire and saturated calomel electrodes (SCE) as reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The ferrocene/ferrocene (Fc/Fc⁺) pair was used as an internal reference and the potential was calculated to be 0.40 V. The deposition of a copolymer on the electrode was done by the evaporation of a chloroform solution. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument.

DFT Calculations. The geometries optimization and potential energy scan were computed with Density Functional Theory (DFT) using B3LYP hybrid functional with

basis set 6-31g*. Quantum-chemical calculation was performed with the Spartan 10 software. All of the alkyl side chains were replaced with methyl groups to simplify the calculation.²

Charge Carrier Mobility Measurements. The hole-only and electron-only devices were measured with device structures of ITO/PEDOT:PSS/PM6:Acceptor/MoO₃/Ag and ITO/ZnO/ PM6:Acceptor /PDIN/Ag, respectively. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the following equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \frac{V^2}{d^3}$$

where J is the current, μ_0 is the carrier mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), i.e., $V = V_{appl} - V_{bi} - V_s$. The carrier mobility can be calculated from the slope of the $J^{1/2}$ - V curves.

Fabrication of Polymer Solar Cells and Characterization: The indium tin oxide (ITO) glass substrates were cleaned sequentially under sonication for 30 min with acetone, detergent, deionized water and isopropyl alcohol and then dried at 80 °C in baking oven overnight, followed by a plasma treatment for 4 min. The pre-cleaned ITO substrate were coated with PEDOT:PSS (filtered through a 0.45 μm PES filter) by spin-coating (3000 rpm. for 30 s, thickness of ~40 nm) and then baked at 150 °C for 15 min in air. Then, the substrates were transferred into a nitrogen (N₂) protected glovebox. The device configuration was ITO/PEDOT:PSS/PM6:Acceptor/ PDIN /Ag, and the active layers were spin coated from CF solution containing PM6:acceptor (weight ratio 1:1.5) or D18:acceptor (weight ratio 1:1.5) to obtain thicknesses of ~100 nm. Thermal annealing of the blend films was carried out by placing them onto a hot plate in a nitrogen atmosphere. A 5 nm PDIN layer was then spin-coated from methanol solution

onto the active layer. The thin films were transferred into a vacuum evaporator connected to the glove box, and Ag (100 nm) was deposited sequentially through a shadow mask under 10^{-5} Pa, with an active area of the cells of 0.038 cm^2 .

The current–voltage (J – V) curves were measured on a computer-controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5 G spectra from a class solar simulator (Taiwan, Enlitech), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center certified reference monocrystal silicon cell (Enlitech). The EQE data were recorded with a QE-R3011 test system from Enli technology company (Taiwan).

Synthesis of the monomers

4,9-bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2,7-bis(2-hexyldecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (M4)³

A mixture of compound M1 (6.22 g, 11.00 mmol), M2 (4.36 g, 5.00 mmol), and Pd(PPh₃)₄ (231.11 mg, 0.20 mmol) in dry DMF (60 mL) was stirred at 120 °C under argon for 12 h. After cooling to room temperature, the mixture was poured into a solution of KF and extracted with DCM (50 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. The residue was purified via column chromatography on silica gel (petroleum ether/DCM, 3:1) to afford a purple dark oil (6.14 g, 4.05 mmol, 81%). ¹H NMR (400 MHz, CDCl₃): δ 8.80 (t, $J = 3.1\text{ Hz}$, 2H), 7.33 (t, $J = 14.7\text{ Hz}$, 2H), 7.24 (d, $J = 4.9\text{ Hz}$, 2H), 6.99 (dt, $J = 4.8, 1.4\text{ Hz}$, 2H), 4.10 (d, $J = 7.3\text{ Hz}$, 4H), 2.01 – 1.86 (m, 10H), 1.40 – 1.17 (m, 44H), 1.13 – 0.89 (m, 34H), 0.88 – 0.61 (m, 42H); ¹³C NMR (101 MHz, CDCl₃): δ 163.54, 162.85, 162.75, 158.84, 157.92, 156.16, 154.98, 141.28, 139.90, 136.95, 136.84, 136.55, 134.93, 127.54, 126.03, 125.28, 125.09, 124.04, 122.50, 122.47, 113.02, 106.01, 53.90, 44.98, 43.45, 36.57, 35.18, 35.10, 34.38, 34.14, 31.93, 31.89, 31.75, 30.17, 29.82, 29.63, 29.36, 28.74, 28.58, 27.52, 27.18, 27.15, 26.53, 22.86, 22.70, 14.14, 10.81, 10.60.

4,9-bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2,7-bis(2-octyldodecyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (M5)

It was synthesized similarly as described for **M4**. Starting with **M1** (6.22 g, 11.00 mmol), **M3** (4.93 g, 5.00 mmol), Pd(PPh₃)₄ (231.11 mg, 0.20 mmol). Yield: 6.18 g (76%). ¹H NMR (400 MHz, CDCl₃): δ 8.80 (t, *J* = 3.0 Hz, 2H), 7.39 – 7.27 (m, 2H), 7.24 (d, *J* = 4.9 Hz, 2H), 7.03 – 6.93 (m, 2H), 4.05 (d, *J* = 7.3 Hz, 4H), 2.06 – 1.84 (m, 10H), 1.43 – 1.15 (m, 68H), 1.17 – 0.91 (m, 34H), 0.90 – 0.57 (m, 42H); ¹³C NMR (101 MHz, CDCl₃): δ 162.87, 162.81, 162.75, 158.71, 158.62, 157.91, 143.02, 141.35, 139.90, 139.84, 139.78, 139.68, 136.90, 136.82, 136.55, 127.54, 126.03, 125.24, 125.11, 122.47, 121.36, 121.11, 53.94, 53.90, 53.86, 45.01, 43.45, 43.40, 43.33, 36.58, 35.18, 35.10, 34.39, 34.14, 34.11, 31.94, 31.76, 30.18, 29.69, 29.64, 29.39, 29.36, 28.75, 28.59, 28.56, 27.54, 27.18, 27.14, 26.55, 22.84, 22.72, 14.15, 10.83, 10.60.

6,6'-(2,7-bis(2-hexyldecyl)-1,3,6,8-tetraoxo-1,2,3,6,7,8 hexahydrobenzo [lmn][3,8]phenanthroline-4,9-diyl)bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (M6)

Under nitrogen atmosphere, compound **M4** (4.55 g, 3.00 mmol) was dissolved in anhydrous DMF (50 mL), Afterwards, the phosphorus oxychloride (2 mL) was dropwise added at 0°C, and the mixture was stirred at the room temperature for 30 min. Then, the mixture was heated to 80°C and stirred overnight. After cooling to room temperature, the mixture was poured into water to quench the reaction and extracted with extracted with DCM (50 mL × 3). The combined organic layer was dried over MgSO₄, filtered, and evaporated to dryness. The residue was purified via column chromatography on silica gel (petroleum ether/DCM, 1:1) to afford a black oil (4.01 g, 85%). ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 2H), 8.90 (t, *J* = 3.1 Hz, 2H), 7.43 (s, 2H), 7.05 (s, 2H), 4.32 (d, *J* = 7.3 Hz, 4H), 2.06 – 1.89 (m, 10H), 1.43 – 1.19 (m, 44H), 1.15 – 0.91 (m, 34H), 0.88 – 0.61 (m, 42H); ¹³C NMR (101 MHz, CDCl₃): δ 182.43, 164.67, 163.25, 162.97, 158.84, 158.21, 156.86, 155.47, 141.85, 140.31, 137.36, 136.95, 136.78, 135.12, 127.85, 126.64, 125.81, 125.37, 124.34, 122.79, 122.67, 113.42,

106.51, 53.95, 44.99, 43.48, 36.60, 35.23, 35.19, 34.41, 34.26, 31.97, 31.92, 31.82, 30.24, 29.89, 29.72, 29.39, 28.78, 28.62, 27.54, 27.19, 27.17, 26.56, 22.87, 22.72, 14.16, 10.82, 10.61.

6,6'-(2,7-bis(2-octyldodecyl)-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo [lmn] [3,8] phenanthroline-4,9-diyl) bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde) (M7)

It was synthesized similarly as described for **M6**. Starting with **M5** (4.88 g, 3.00 mmol), phosphorus oxychloride (2 mL). Yield: 3.99 g (79%). ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 2H), 8.90 (t, *J* = 3.0 Hz, 2H), 7.43 (s, 2H), 7.05 (s, 2H), 4.05 (d, *J* = 7.3 Hz, 4H), 2.06 – 1.84 (m, 10H), 1.43 – 1.15 (m, 68H), 1.17 – 0.91 (m, 34H), 0.90 – 0.57 (m, 42H); ¹³C NMR (101 MHz, CDCl₃): δ 182.43, 163.42, 163.16, 162.94, 159.11, 159.03, 158.06, 143.92, 141.85, 140.19, 140.06, 139.96, 139.84, 137.04, 136.98, 136.95, 127.92, 126.73, 125.68, 125.73, 122.83, 121.76, 121.61, 54.05, 53.98, 53.87, 45.03, 43.46, 43.42, 43.35, 36.59, 35.18, 35.12, 34.39, 34.15, 34.12, 31.94, 31.76, 30.19, 29.69, 29.65, 29.39, 29.36, 28.75, 28.60, 28.56, 27.54, 27.18, 27.14, 26.55, 22.84, 22.72, 14.15, 10.84, 10.61.

NDI610-H:

Compound **M6** (314.49 mg, 0.20 mmol) and **IC** (116.51 mg, 0.60 mmol) were dissolved in the mixture of chloroform (40 mL) and anhydrous pyridine (0.3 mL) in a degassed two-neck round-bottom flask. The reaction was carried out at 60 °C for 24 hours. After removal of solvent under vacuum, the residue was purified via column chromatography on silica gel (petroleum ether/DCM, 1:1) to obtain a black solid (327.21 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.97 (s, 2H), 8.78 (t, *J* = 2.2 Hz, 2H), 8.74 – 8.61 (m, 2H), 7.92 (dt, *J* = 8.1, 3.6 Hz, 2H), 7.83 – 7.65 (m, 6H), 7.29 (dd, *J* = 18.0, 7.0 Hz, 2H), 4.09 (d, *J* = 7.1 Hz, 4H), 2.14 – 1.89 (m, 10H), 1.29 (d, *J* = 32.0 Hz, 44H), 1.14 – 0.95 (m, 32H), 0.92 – 0.60 (m, 44H). ¹³C NMR (101 MHz, CDCl₃) δ 188.49, 164.51, 162.31, 162.11, 160.68, 160.64, 159.39, 147.62, 140.59, 140.00, 139.44, 138.99, 137.98, 136.94, 136.24, 136.21, 134.94, 134.28, 132.85, 127.83, 125.65, 125.23,

123.61, 123.00, 120.88, 115.02, 68.14, 54.34, 45.25, 43.54, 36.57, 35.48, 34.25, 31.93, 31.87, 31.75, 30.16, 29.74, 29.63, 29.35, 28.72, 28.43, 27.48, 27.26, 26.49, 22.89, 22.86, 22.69, 14.15, 10.86, 10.83, 10.49, 10.46. MS (MALDI-TOF): calcd. for $C_{122}H_{150}N_6O_6S_4$ (M^+): 1924.82, Found: 1925.0924.

NDI610-Cl:

It was synthesized similarly as described for **NDI610-H**. Starting with M6 (314.49 mg, 0.20 mmol) and IC-2Cl (157.85 mg, 0.60 mmol). Yield: 338.26 mg (82%). 1H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 2H), 8.91 – 8.61 (m, 4H), 7.94 (s, 2H), 7.73 (s, 2H), 7.46 – 7.25 (m, 4H), 4.08 (d, $J = 6.9$ Hz, 4H), 2.15 – 1.93 (m, 10H), 1.20 (d, $J = 38.6$ Hz, 46H), 1.15 – 0.94 (m, 38H), 0.90 – 0.65 (m, 38H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.76, 170.60, 168.72, 167.22, 165.32, 162.05, 160.17, 158.78, 158.49, 158.46, 148.70, 148.67, 148.66, 148.64, 139.60, 139.41, 139.15, 138.98, 138.70, 136.22, 136.16, 136.11, 132.16, 127.88, 126.92, 125.68, 125.03, 124.62, 114.62, 68.58, 54.40, 45.22, 43.48, 43.34, 43.29, 41.51, 36.57, 35.51, 34.25, 34.17, 31.93, 31.87, 31.72, 30.15, 29.81, 29.63, 29.35, 28.72, 28.45, 27.46, 27.26, 26.52, 22.85, 22.69, 14.15, 10.85, 10.46.

MS (MALDI-TOF): calcd. for $C_{122}H_{146}Cl_4N_6O_6S_4$ (M^+): 2062.59, Found: 2062.8926.

NDI812-H:

It was synthesized similarly as described for **NDI610-H**. Starting with M7 (336.94 mg, 0.20 mmol) and IC (116.51 mg, 0.60 mmol). Yield: 325.92 mg (80%). 1H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 2H), 8.82 – 8.75 (m, 2H), 8.70 (d, $J = 6.9$ Hz, 2H), 7.93 (dd, $J = 5.6, 1.5$ Hz, 2H), 7.81 – 7.68 (m, 6H), 7.35 – 7.27 (m, 2H), 4.08 (d, $J = 6.7$ Hz, 4H), 2.11 – 1.92 (m, 10H), 1.21 (t, $J = 20.5$ Hz, 60H), 1.14 – 0.96 (m, 34H), 0.92 – 0.64 (m, 42H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.55, 164.49, 162.43, 162.30, 162.16, 162.11, 160.76, 160.24, 156.82, 155.76, 147.62, 140.00, 139.45, 138.38, 136.94, 136.20, 134.94, 134.28, 125.59, 125.23, 123.61, 121.34, 120.91, 115.22, 68.14, 54.39, 54.34, 45.18, 36.59, 35.46, 35.28, 34.25, 31.94, 31.73, 30.16, 29.70, 29.63, 29.38, 29.36, 28.73, 28.46, 28.43, 27.50, 27.26, 26.74, 26.51, 22.89, 22.86, 22.82, 22.71, 22.70,

14.15, 10.87, 10.84, 10.61, 10.58, 10.49, 10.47. MS (MALDI-TOF): calcd. for $C_{130}H_{166}N_6O_6S_4$ (M^+): 2037.03, Found: 2036.9702.

NDI812-Cl:

It was synthesized similarly as described for **NDI610-H**. Starting with M7 (336.94 mg, 0.20 mmol) and IC-2Cl (157.85 mg, 0.60 mmol). Yield: 338.26 mg (82%). 1H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 2H), 8.78 (d, $J = 4.4$ Hz, 4H), 7.94 (s, 2H), 7.74 (s, 2H), 7.34 – 7.27 (m, 2H), 4.08 (d, $J = 6.8$ Hz, 4H), 2.08 – 1.94 (m, 10H), 1.26 – 1.19 (m, 60H), 1.12 – 0.96 (m, 36H), 0.85 – 0.68 (m, 40H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.29, 165.32, 165.30, 162.23, 162.19, 162.05, 158.63, 158.42, 148.69, 139.61, 139.40, 139.15, 138.58, 138.26, 136.22, 127.84, 126.99, 125.68, 125.07, 124.64, 123.22, 119.92, 119.89, 114.67, 114.61, 68.64, 54.40, 45.32, 43.54, 43.37, 36.59, 35.51, 34.25, 34.22, 34.16, 31.72, 30.17, 29.70, 29.63, 29.38, 29.36, 28.74, 28.72, 28.45, 28.42, 27.47, 27.26, 27.20, 26.52, 22.89, 22.86, 22.71, 22.70, 14.15, 10.86, 10.84, 10.49, 10.46.

MS (MALDI-TOF): calcd. for $C_{130}H_{162}Cl_4N_6O_6S_4$ (M^+): 2174.80, Found: 2174.8096.

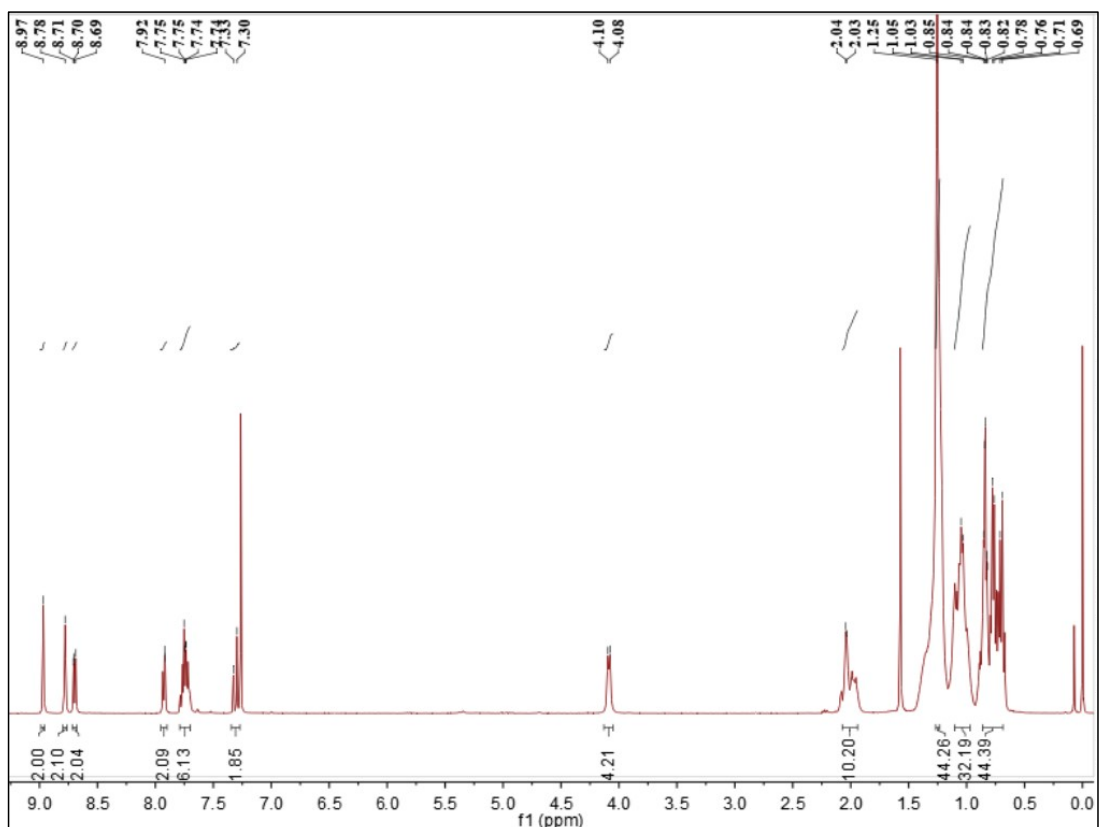


Fig. S1. ^1H NMR spectrum of NDI610-H.

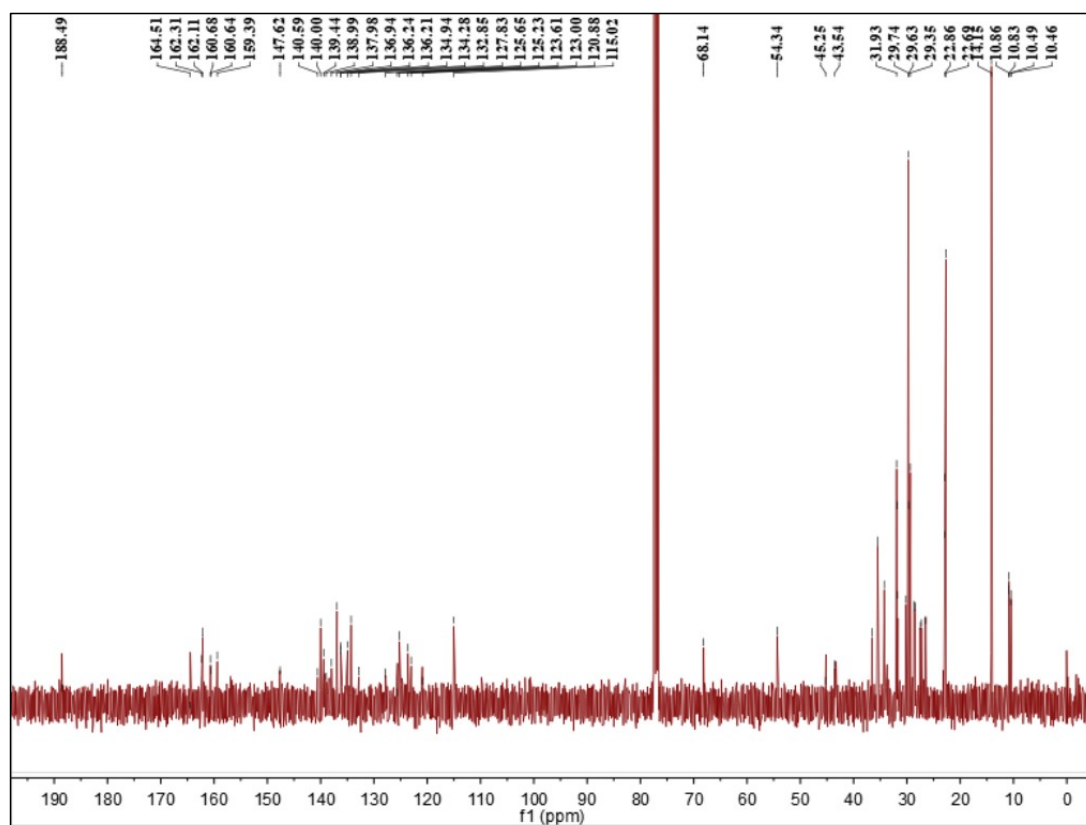


Fig. S2. ^{13}C NMR spectrum of NDI610-H.

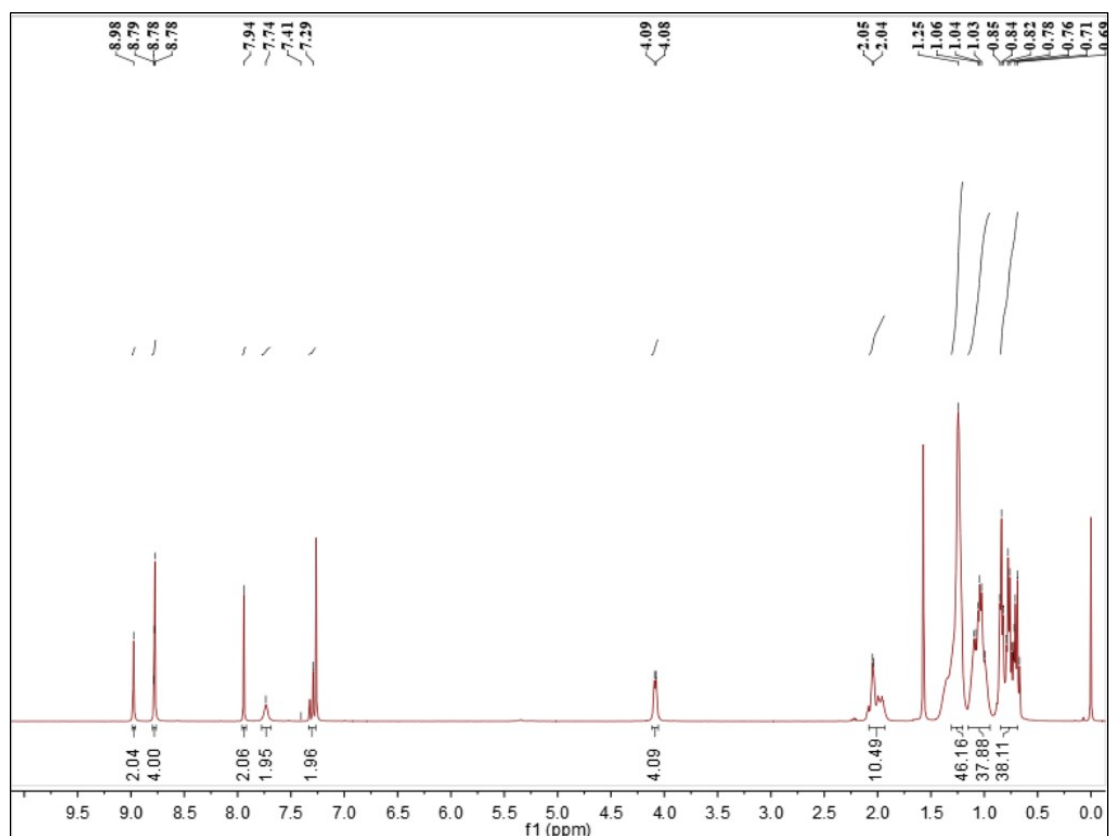


Fig. S3. ^1H NMR spectrum of NDI610-Cl.

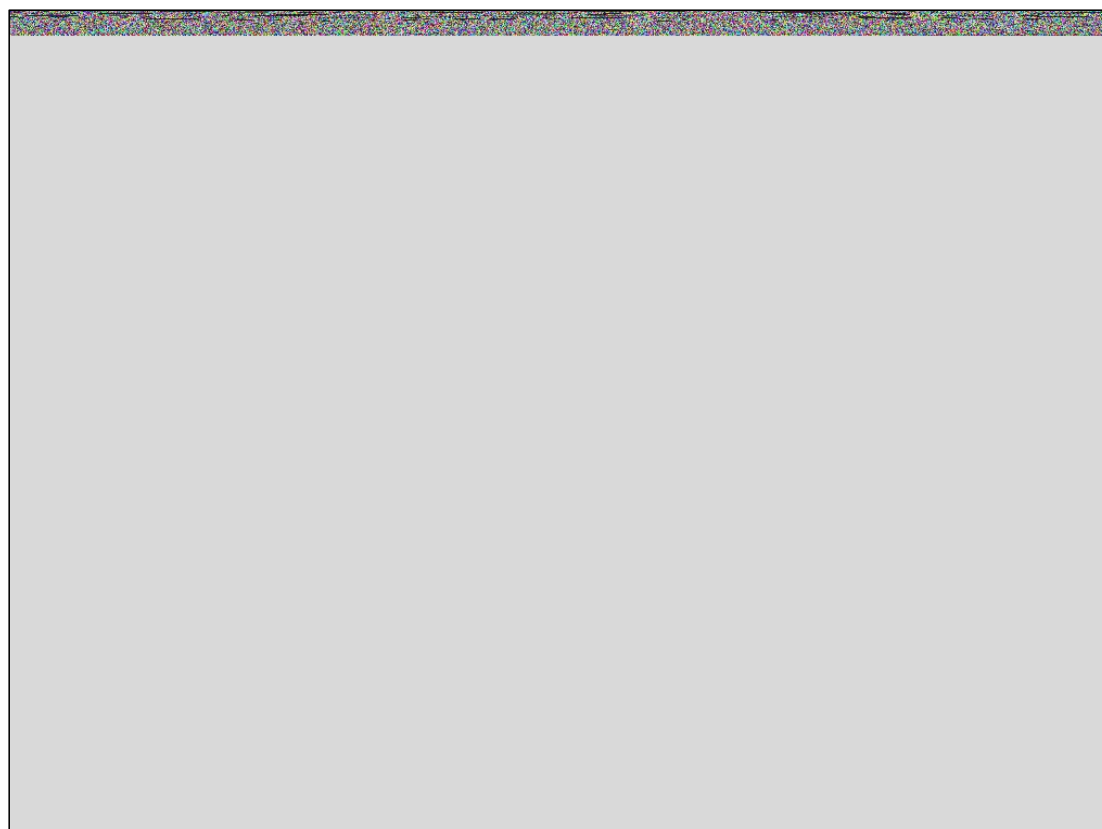


Fig. S4. ^{13}C NMR spectrum of NDI610-Cl.

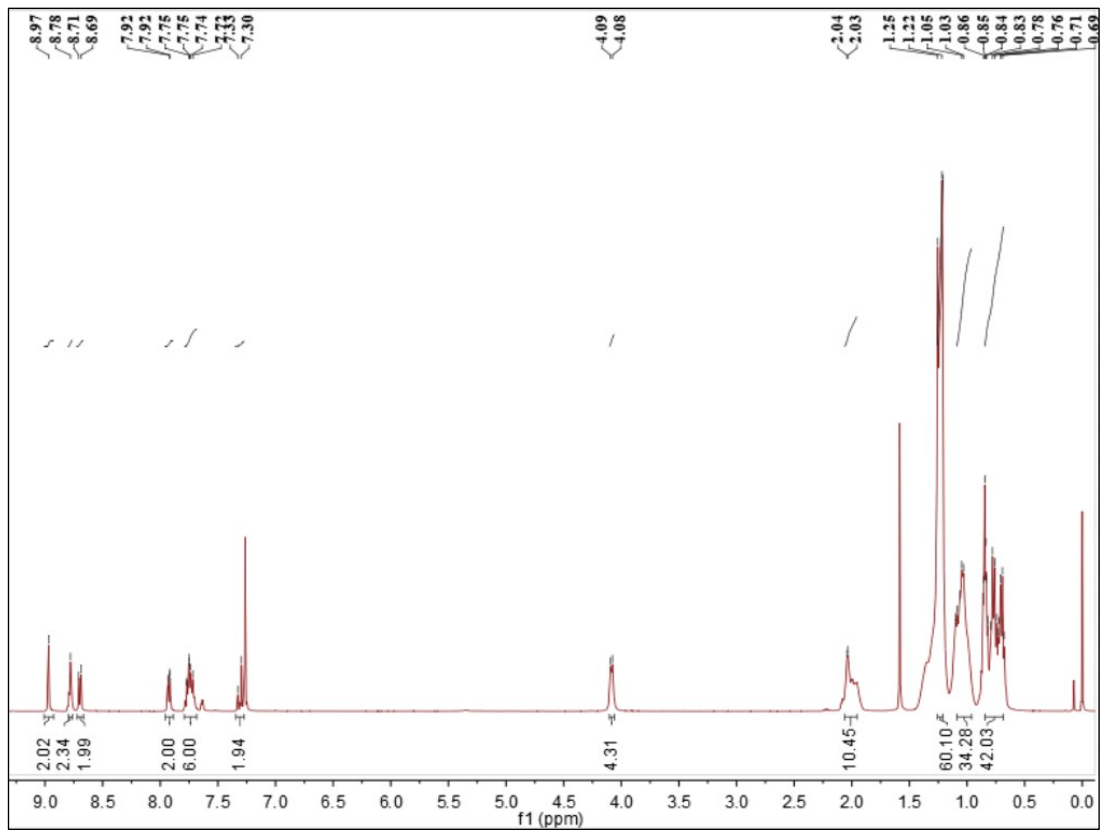


Fig. S5. ^1H NMR spectrum of NDI812-H.

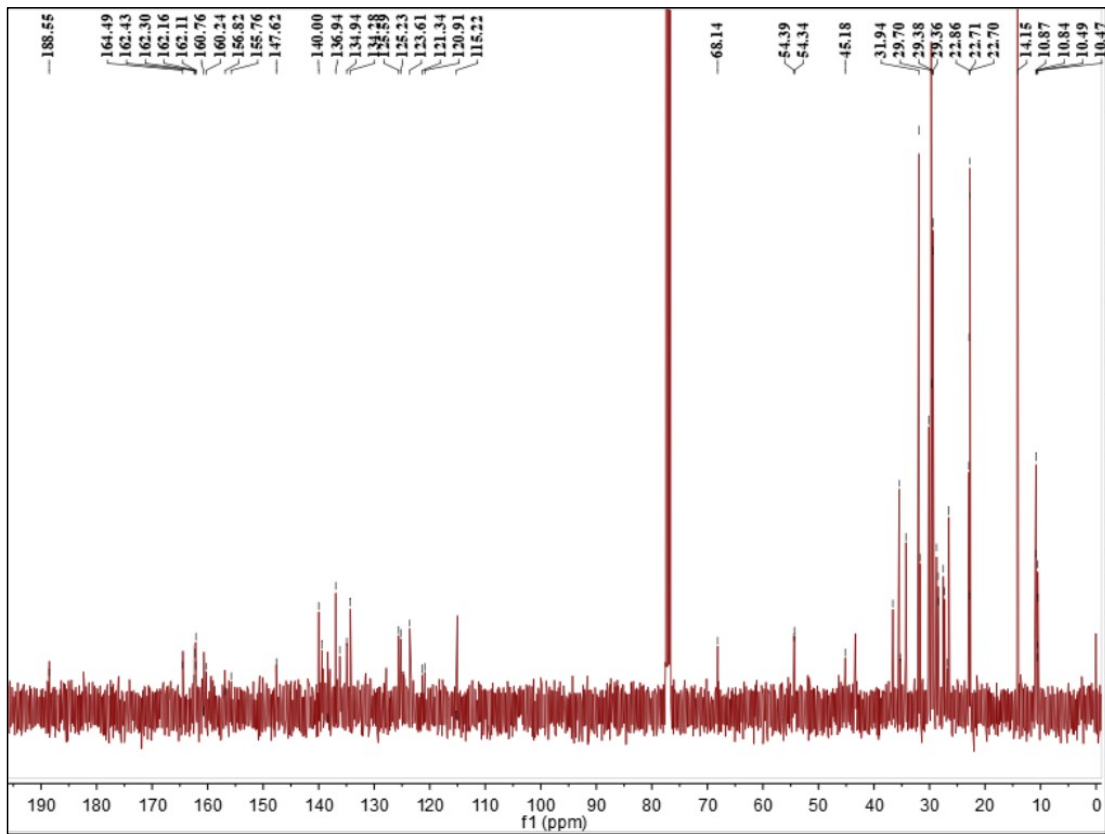


Fig. S6. ^{13}C NMR spectrum of NDI812-H.

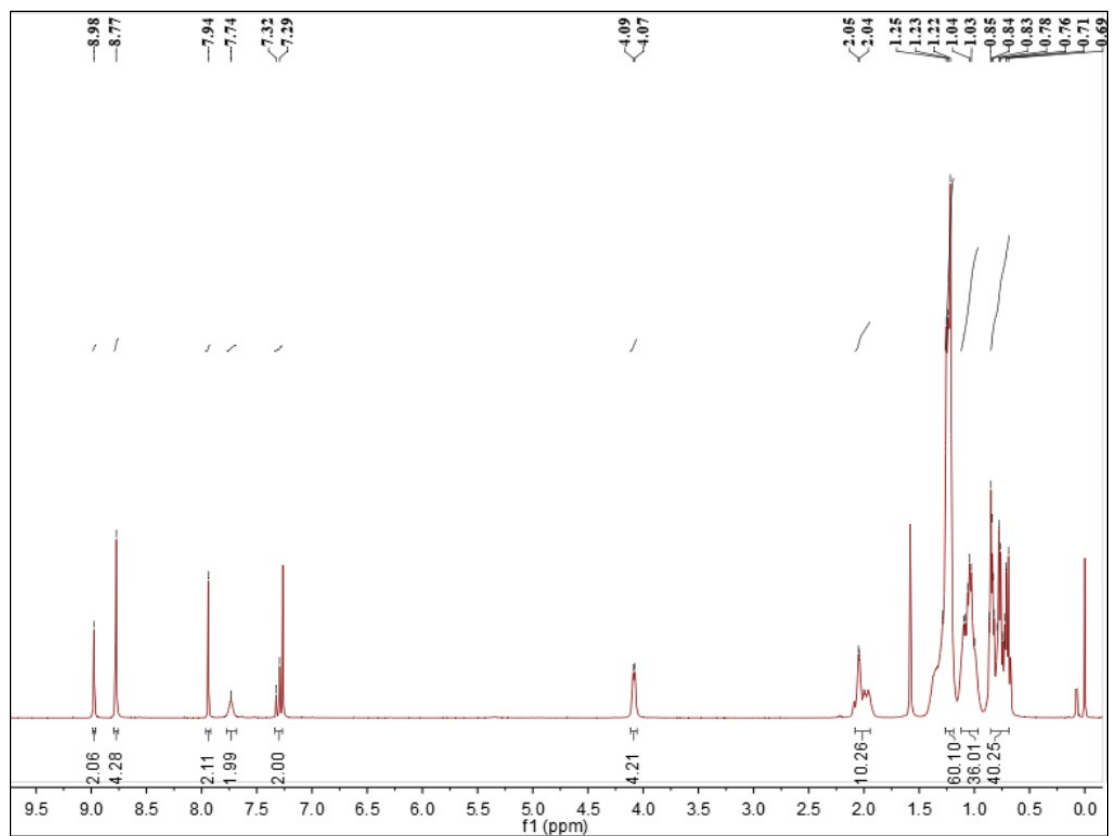


Fig. S7. ^1H NMR spectrum of NDI812-Cl.

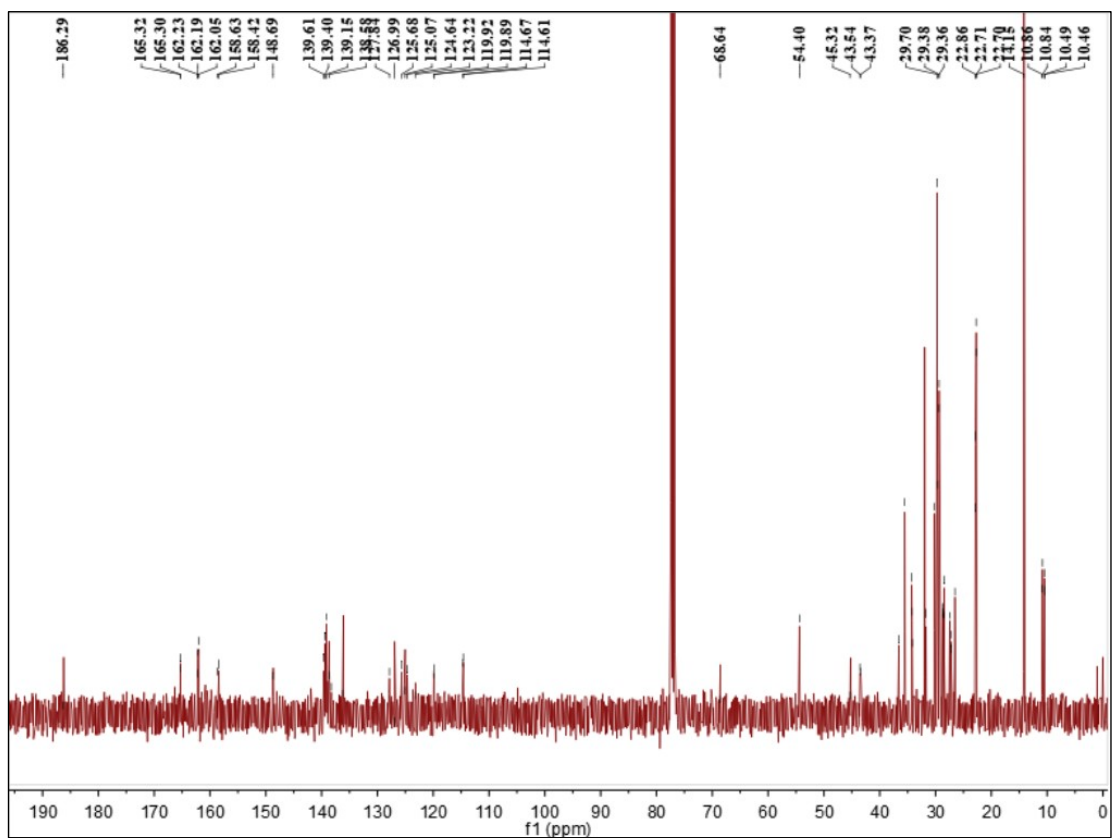


Fig. S8. ^{13}C NMR spectrum of NDI812-Cl.

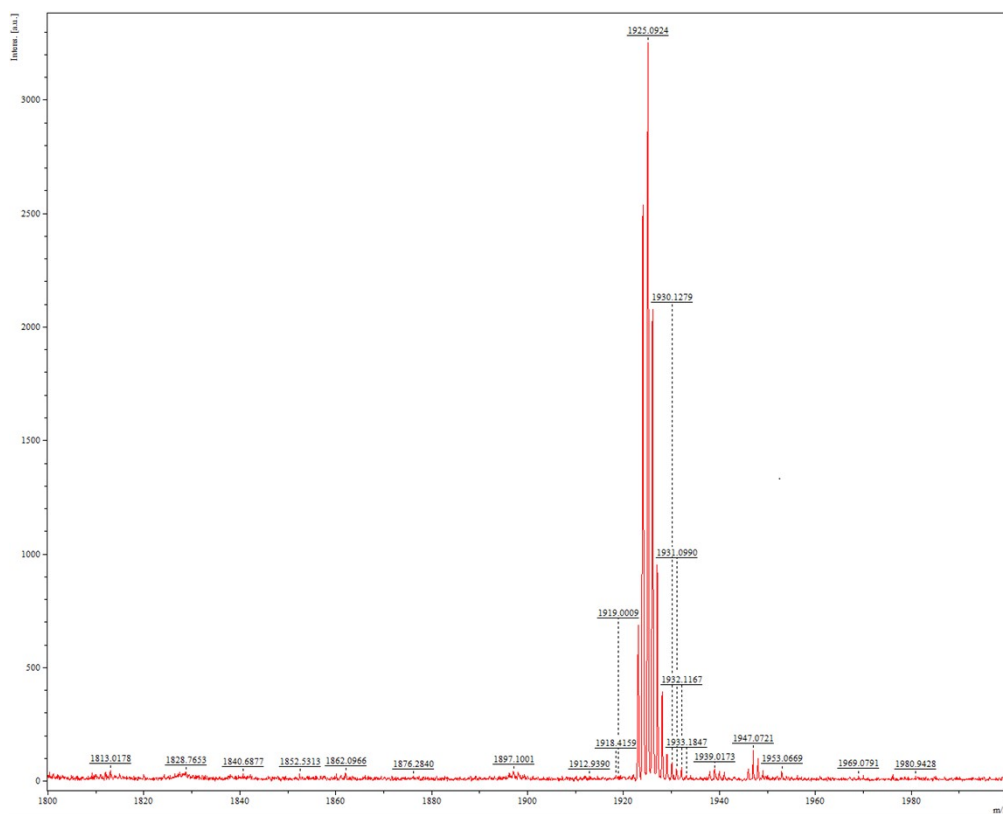


Fig. S9 MS spectrum (MALDI-TOF) of compound NDI610-H.

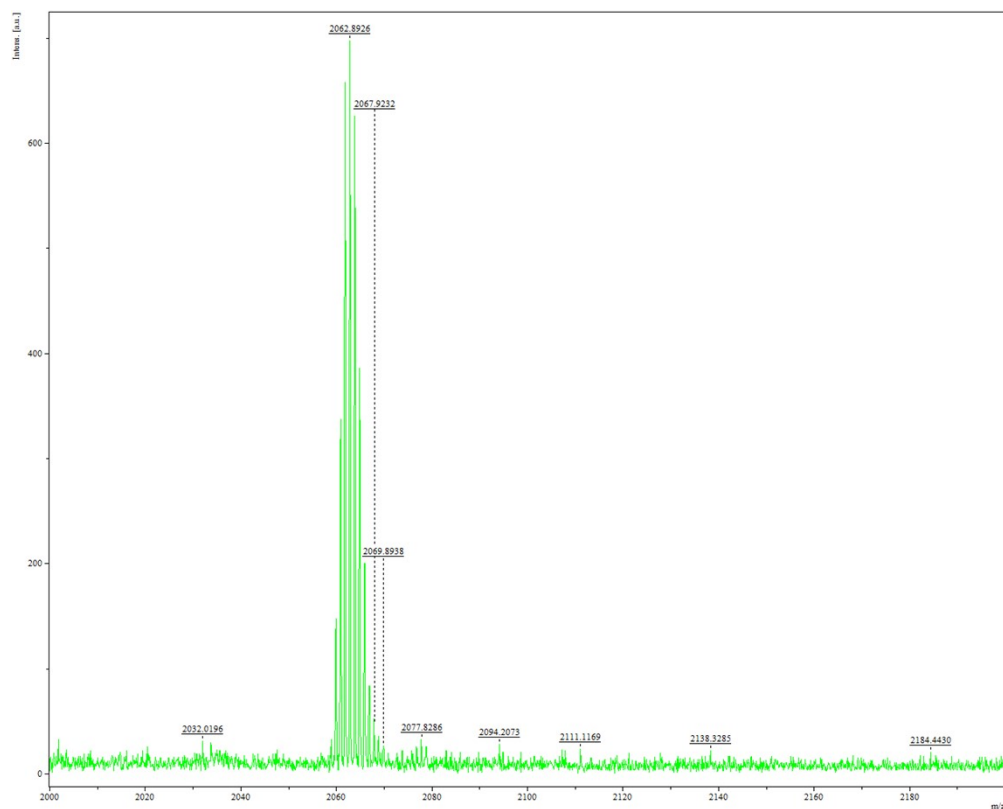


Fig. S10 MS spectrum (MALDI-TOF) of compound NDI610-Cl.

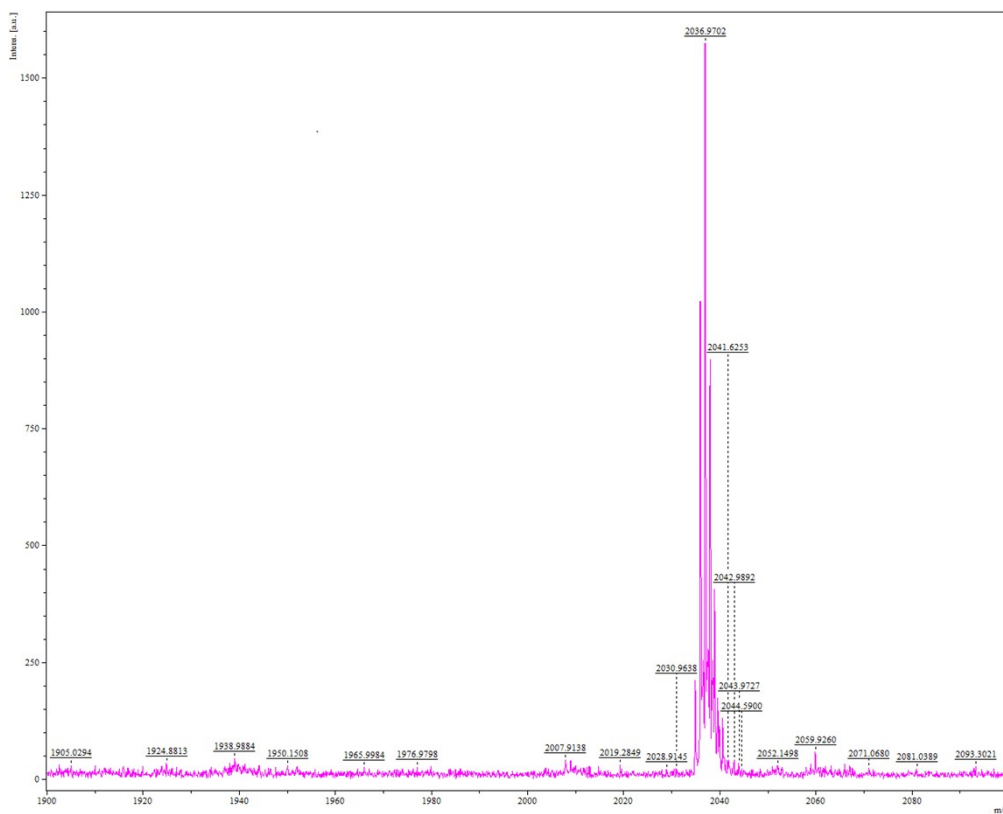


Fig. S11 MS spectrum (MALDI-TOF) of compound NDI812-H.

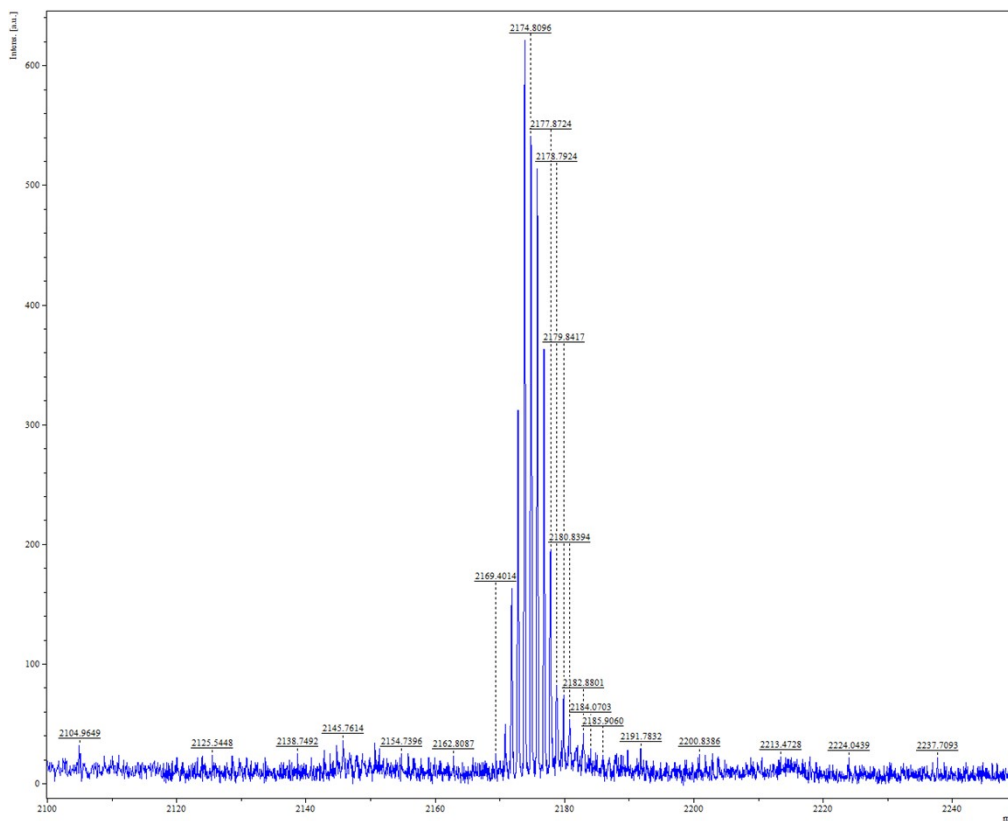


Fig. S12 MS spectrum (MALDI-TOF) of compound NDI812-Cl.

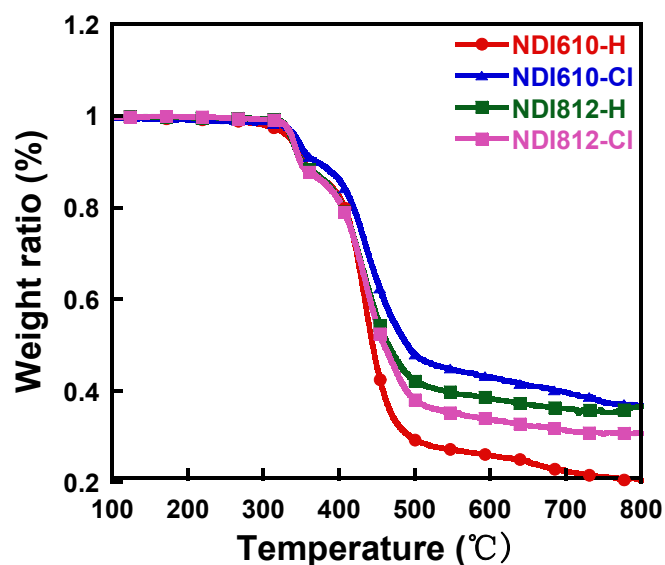


Fig. S13 TGA plot of NFREAs at a heating rate of 20°C/min under a nitrogen atmosphere.

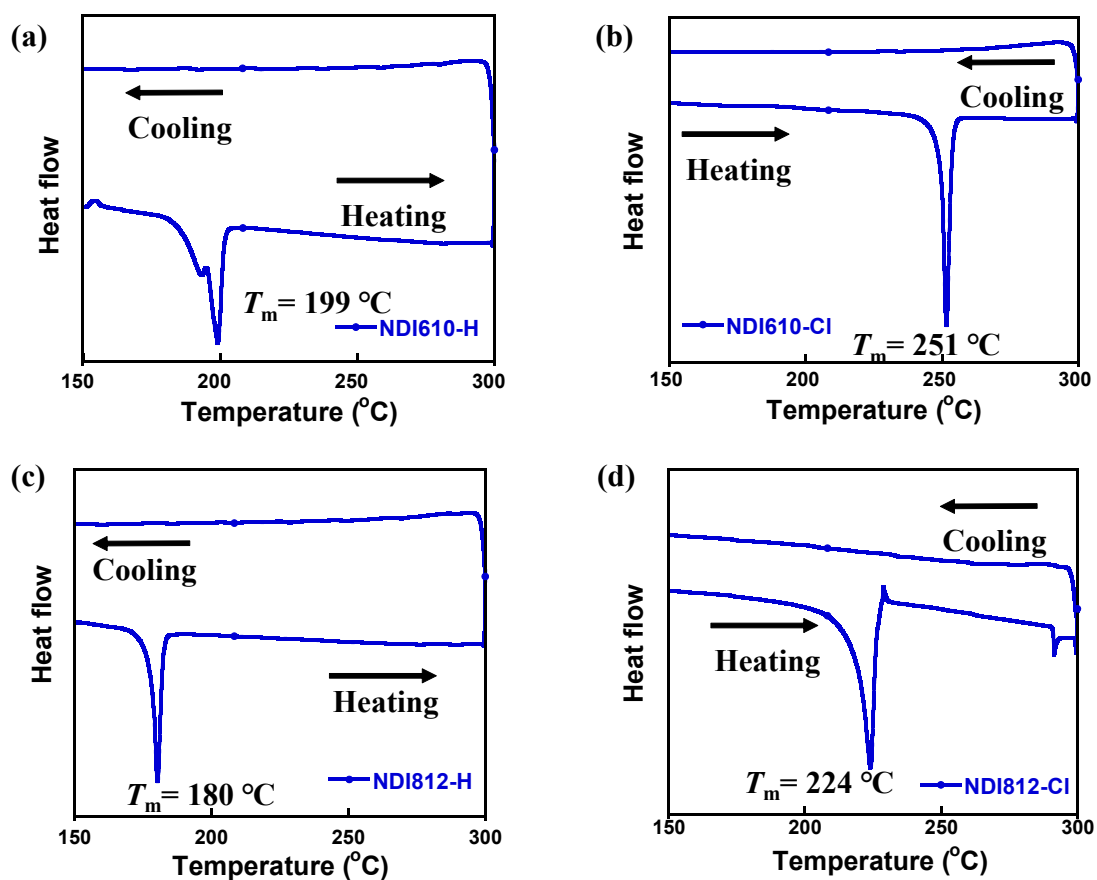


Fig. S14 DSC curves of NFREAs at a heating/cooling rate of 10/10°C/min under a nitrogen atmosphere.

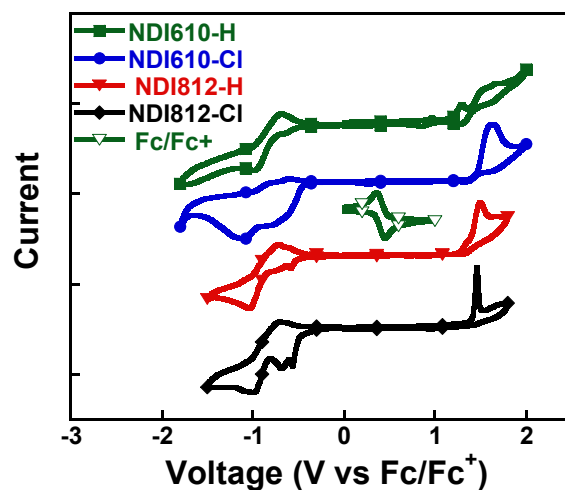


Fig. S15 CV curves of NFREAs with Fc/Fc⁺ as the reference, using platinum electrodes as the working electrode, platinum wire as the counter electrode and SCE as the reference electrode, scan one cycle at the potential scanning rate of 50 mV•s⁻¹ in 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution.

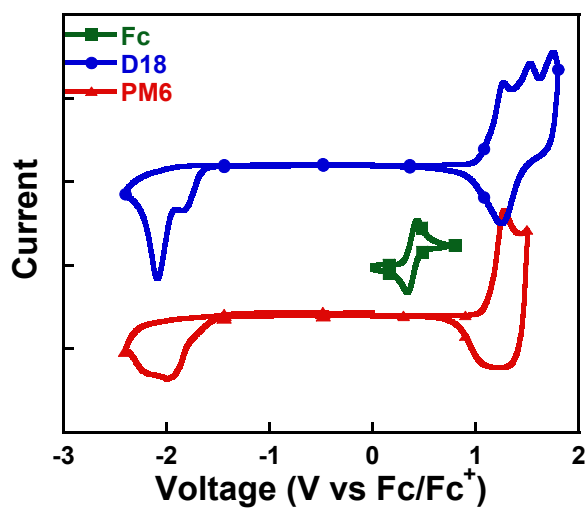


Fig. S16 CV curves of D18 and PM6.

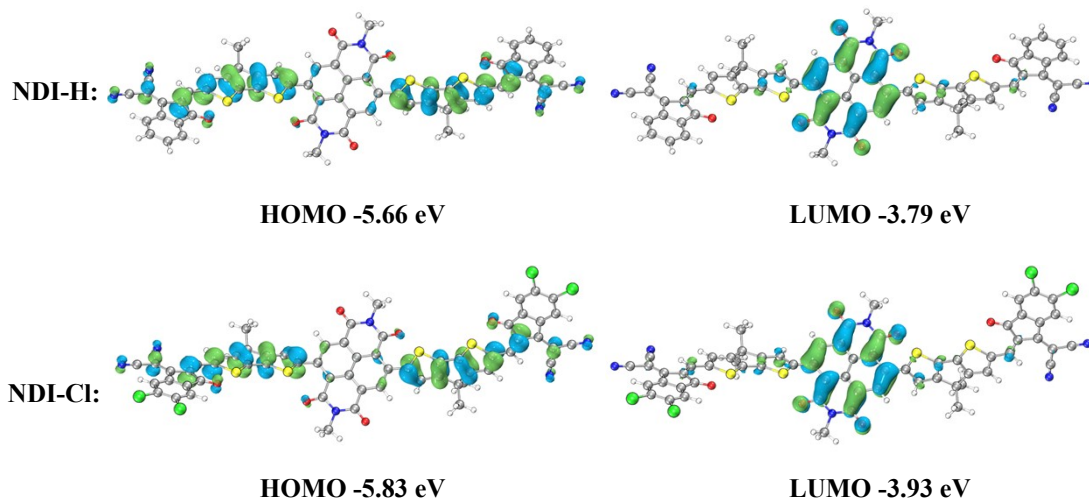


Fig. S17 The HOMO and LUMO energy levels of optimized geometries of NDI-H and NDI-Cl.

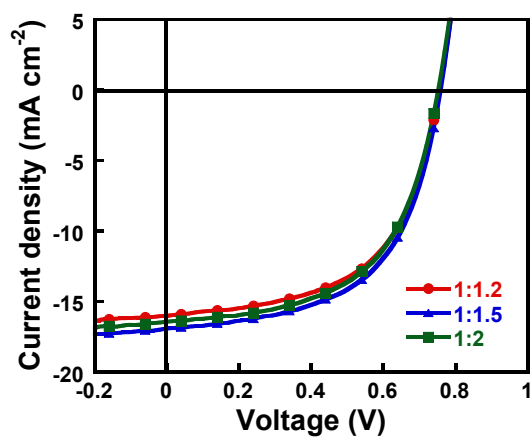


Fig. S18 J - V curves of OSCs under AM1.5 Illumination at 100 mW cm^{-2} with the PM6:NDI610-Cl processed with different weight ratios.

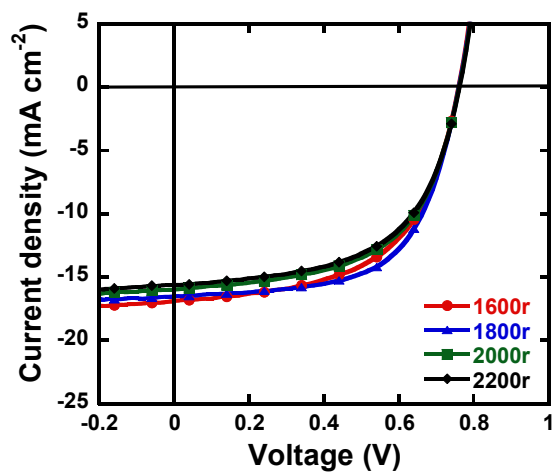


Fig. S19 J - V curves of OSCs under AM1.5 Illumination at 100 mW cm^{-2} with different speeding-coating rate of PM6:NDI610-Cl.

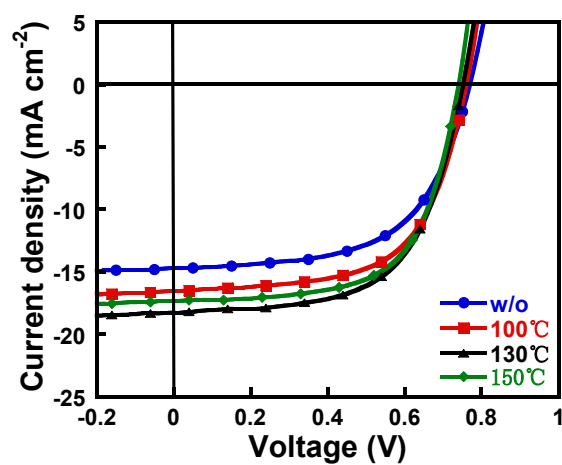


Fig. S20 J - V curves of OSCs under AM1.5 Illumination at 100 mW cm^{-2} with the PM6:NDI610-Cl processed with different thermal annealing temperature.

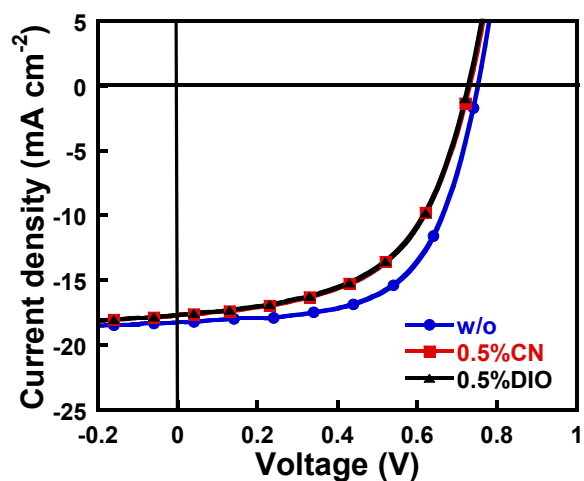


Fig. S21 J - V curves of OSCs under AM1.5 Illumination at 100 mW cm^{-2} with the PM6:NDI610-Cl processed with various solvent additive.

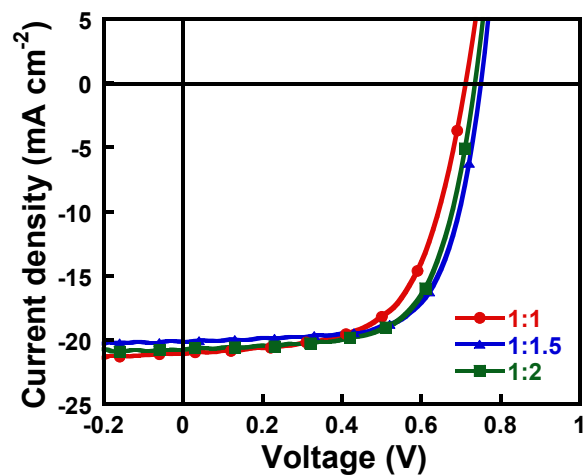


Fig. S22 J - V curves of OSCs under AM1.5 Illumination at 100 mW cm^{-2} with the D18:NDI610-Cl processed with different weight ratios.

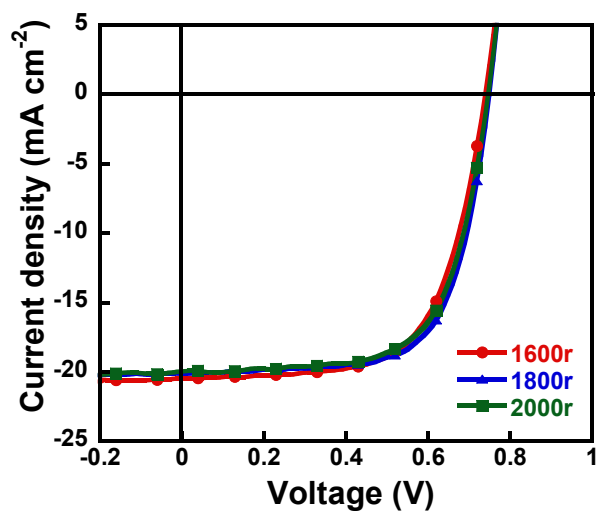


Fig. S23 J - V curves of OSCs under AM1.5 Illumination at 100 mW cm^{-2} with different speeding-coating rate of D18:NDI610-Cl.

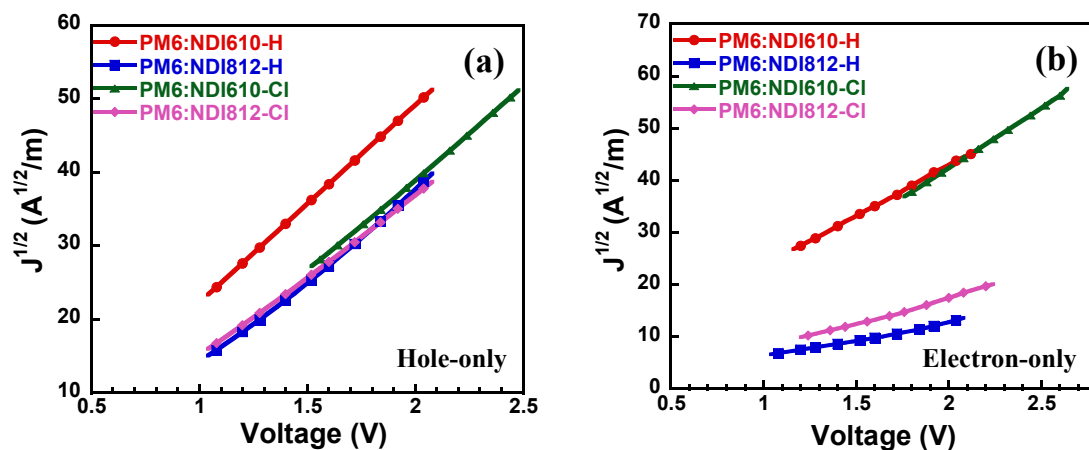


Fig. S24 $J^{1/2} \sim (V_{\text{appl}} - V_{\text{bi}} - V_{\text{s}})$ characteristics of hole-only (a) and electron-only (b)

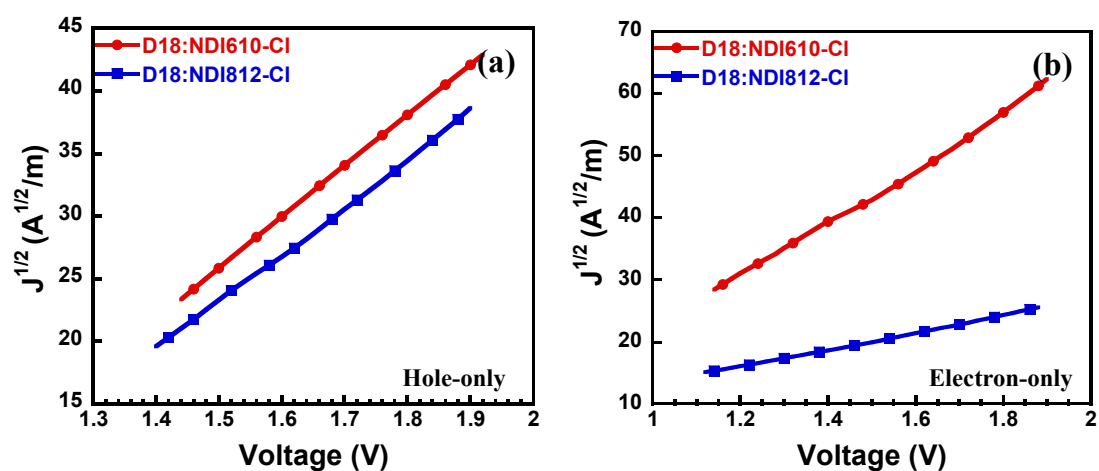


Fig. S25 $J^{1/2} \sim (V_{\text{appl}} - V_{\text{bi}} - V_{\text{s}})$ characteristics of hole-only (a) and electron-only (b)

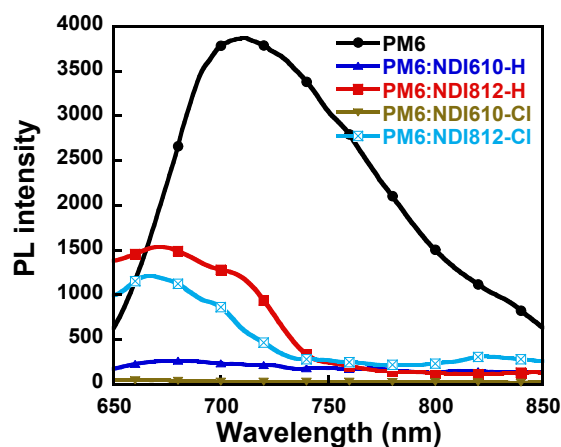


Fig. S26 Photoluminescence spectra of neat PM6, PM6:NDI610-H-, PM6:NDI812-H-, PM6:NDI610-Cl-, and PM6:NDI812-Cl-based blended films.

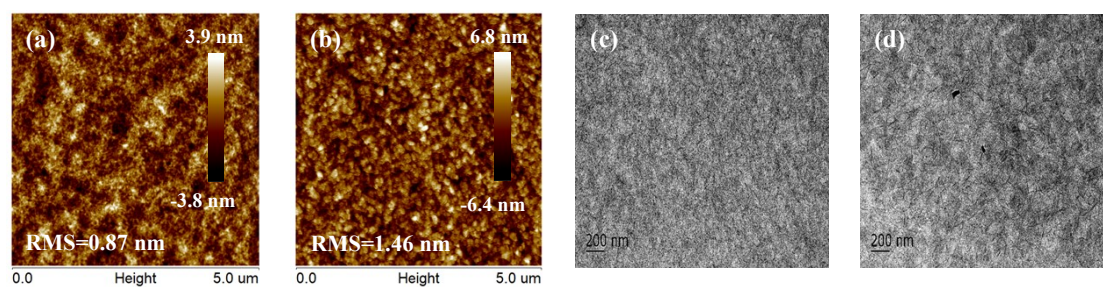


Fig. S27. (a, b) AFM height images and (c, d) TEM images of (a, c) D18:NDI610-Cl, and (b, d) D18:NDI812-Cl blended films.

Table S1 Device performance of the OSCs based on PM6: NDI610-Cl with different D/A ratios under AM1.5 Illumination at 100 mW cm^{-2} .

Blended film	D/A (wt/wt)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:NDI610- Cl	1:1.2	0.756	15.98	56.67	6.85
	1:1.5	0.759	16.89	56.84	7.28
	1:2	0.752	16.40	56.30	6.95

Table S2 Device performance of the OSCs based on PM6: NDI610-Cl with different spin coating speed under AM1.5 Illumination at 100 mW cm⁻².

Blended film	Speed (rpm)	Thickness [nm]	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:NDI610- Cl	1600	112	0.759	16.89	56.84	7.28
	1800	100	0.760	16.53	61.65	7.75
	2000	89	0.761	16.00	57.32	6.98
	2200	80	0.762	15.63	57.46	6.84

Table S3 Device performance of the OSCs based on PM6: NDI610-Cl with different thermal annealing under AM1.5 Illumination at 100 mW cm⁻².

Blended film	thermal annealing	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:NDI610- Cl	NO	0.769	14.70	59.03	5.20
	100°C	0.760	16.53	61.65	7.75
	130°C	0.751	18.26	60.87	8.35
	150°C	0.740	17.34	63.46	8.15

Table S4 Device performance of the OSCs based on PM6: NDI610-Cl processed with different additive under AM1.5 Illumination at 100 mW cm⁻².

Blended film ^a	Additive	V_{OC}	J_{SC}	FF	PCE
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		(V)	(mA cm ⁻²)	(%)	(%)
PM6:NDI610- Cl	w/o	0.751	18.26	60.87	8.35
	0.5% CN	0.731	17.69	54.72	7.08
	0.5% DIO	0.728	17.70	54.84	7.06

Table S5 Device performance of the OSCs based on D18: NDI610-Cl with different D/A ratios under AM1.5 Illumination at 100 mW cm⁻².

Blended film	D/A (wt/wt)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
D18:NDI610- Cl	1:1	0.711	21.10	61.64	9.25
	1:1.5	0.750	20.14	67.82	10.25
	1:2	0.735	20.76	66.16	10.09

Table S6 Device performance of the OSCs based on D18: NDI610-Cl with different spin coating speed under AM1.5 Illumination at 100 mW cm⁻².

Blended film	Speed (rpm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
D18:NDI610- Cl	1600	0.740	20.49	65.08	9.87
	1800	0.750	20.14	67.82	10.25
	2000	0.747	19.98	66.47	9.92

Table S7 Relevant parameters obtained from $J_{ph}-V_{eff}$ curves.

Blended films ^a	V_0 (V)	J_{ph}^b (mA cm ⁻²)	J_{sat} (mA cm ⁻²)	$P(E,T)^b$	L (nm)
PM6: NDI610- H	0.81	14.59	15.77	88.0%	100
PM6: NDI812- H	0.73	9.81	11.26	92.6%	100

PM6: NDI610- Cl	0.85	15.33	16.18	96.0%	100
PM6: NDI812- Cl	0.79	12.95	16.75	77.31%	100

^a Donor : Acceptor =1:1.2; all of the blend films are processed by CF with 0.25 vol% CN. ^b At the condition of $V_{\text{eff}} = V_0 - V_{\text{appl}}$ ($V_{\text{appl}} = 0$, under short-circuit condition).

Table S8 Relevant parameters obtained from $J_{\text{ph}}-V_{\text{eff}}$ curves.

Blended films ^a	V_0 (V)	J_{ph}^b (mA cm ⁻²)	J_{sat} (mA cm ⁻²)	P (E,T) ^b	L (nm)
D18: NDI610- Cl	0.99	20.13	20.39	98.72%	100
D18: NDI812- Cl	0.65	18.82	20.14	93.45%	100

^a Donor : Acceptor =1:1.5; all of the blend films are processed by CF and thermal annealing at 130°C. ^b At the condition of $V_{\text{eff}} = V_0 - V_{\text{appl}}$ ($V_{\text{appl}} = 0$, under short-circuit condition).

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