Supporting Information

for

Chlorination as a Useful Method to Modulate Conjugated Polymers: Balanced and Ambient-Stable High-Performance Ambipolar Field-Effect Transistors and Inverters Based on Chlorinated Isoindigo Polymers

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1. General procedures and experimental details

Chemical reagents and CYTOP were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene was distilled from sodium prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). ^{1}H NMR chemical shifts were referenced to TMS (0 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm). HR ESI-MS was recorded on a Bruker BIFLEX III mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer, and differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter. Gel permeation chromatography (GPC) was performed on Polymer Laboratories PL-GPC220 at 140 ^{o}C using 1,2,4-tricholorobenzene (TCB) as eluent. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-*vis* spectrometer. Cyclic voltammetry (CV) was performed on BASI Epsilon workstation. Thin film measurements were carried out in acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum wire as a counter electrode, and all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode (scan rate: 50 mV s^{-1}). Photo-electron spectra (PES) were performed on AC-2 photoelectron spectrometer (Riken-Keiki Co.). The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2398 Å. BL14B1 is a beamline based on bending magnet and a Si (111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope (Extended Multimode). All experiments were carried out in tapping mode under ambient conditions. A silicon nitride cantilever (Budget Sensors Tap300Al) was used with a resonant frequency around 300 kHz.

Device Fabrication and Characterization. Top-gate/bottom-contact FET devices and complementary inverters were fabricated using n^{++}-Si/SiO_2 (300 nm) substrates. The gold source and drain bottom electrodes (with Ti as the adhesion layer) were patterned by photolithography on the SiO_2 surface. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning agent, deionized water (twice), and *iso*-propanol. The cleaned substrates were dried under vacuum at 80 ^{o}C. The substrates were used directly in ambient or transferred into a glovebox. A thin film of the polymer was deposited on the treated substrates by spin-coating at 1500 rpm for 60s using a polymer solution (6 mg/mL), optionally followed by thermal annealing at 140 ℃, 160 ℃, 180 ℃ or 200 ℃ in ambient or in a glovebox for 5 min. After polymer thin film deposition, a CYTOP solution (CYTOP CTL809M:CT-solv180 = 3:1) was spin-coated onto the semiconducting layer at 2000 rpm for 60s resulting in a

dielectric layer of 500 nm thick. The CYTOP layer was then baked at 100 ^{o}C for 1 h under ambient conditions or in a glovebox. Gate electrodes comprising a layer of Al (50 nm) were then evaporated through a shadow mask onto the dielectric layer by thermal evaporation. The OTFT devices had a channel length (L) of 50 μm and a channel width (W) of 1000 μm.

The evaluations of the FETs and inverters were carried out in atmosphere (humidity 50-60%) on a probe stage using a Keithley 4200 SCS as parameter analyzer. The carrier mobility, μ, was calculated from the data in the saturated regime according to the equation $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$, where I_{SD} is the drain current in the saturated regime. W and L are, respectively, the semiconductor channel width and length, C_i (C_i = 3.7 nF) is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage. $V_G - V_T$ of the device was determined from the relationship between the square root of I_{SD} at the saturated regime.

2. Table S1 and Fig. S1-S13

Table S1. Thermal, Optical, and Electrochemical Properties of Three Polymers

Polymers	T_d (^{o}C)	λ_{max}^{sol} (nm)[a]	λ_{max}^{film} (nm)	E_g^{opt} (eV)[b]	E_{HOMO}^{CV} (eV)[c]	E_{LUMO}^{CV} (eV)[c]	E_{HOMO}^{PES} (eV)[d]	E_{LUMO}^{PES} (eV)[e]
PII2T	416	714, 667	718, 652	1.57	–5.42	–3.70	–5.31	–3.74
PCII2T	405	682	745, 682	1.53	–5.64	–3.86	–5.36	–3.83
PCII2Se	397	710	758, 703	1.51	–5.57	–3.84	–5.35	–3.84

[a] 10^{-5} M in chloroform. [b] Estimated from the onset of thin-film absorption. [c] Cyclic voltammetry determined with Fc/Fc^{+} (E_{HOMO} = –4.80 eV) as external reference. [d] Determined by UV-PES. [e] $E_{LUMO}^{PES} = E_{HOMO}^{PES} - E_g^{opt}$.

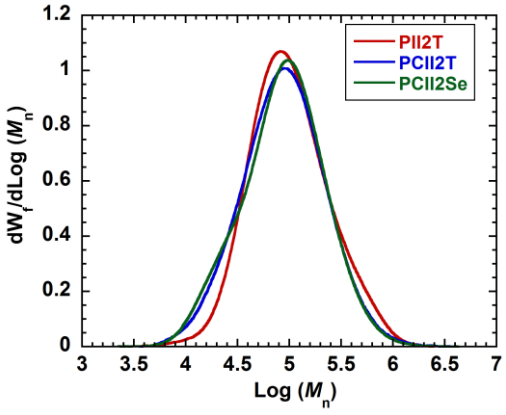


Fig. S1. Gel permeation chromatography (GPC) traces of the polymers. Molecular weights of polymers were evaluated with 1,2,4-tricholorobenzene (TCB) as eluent at 140 ^{o}C.

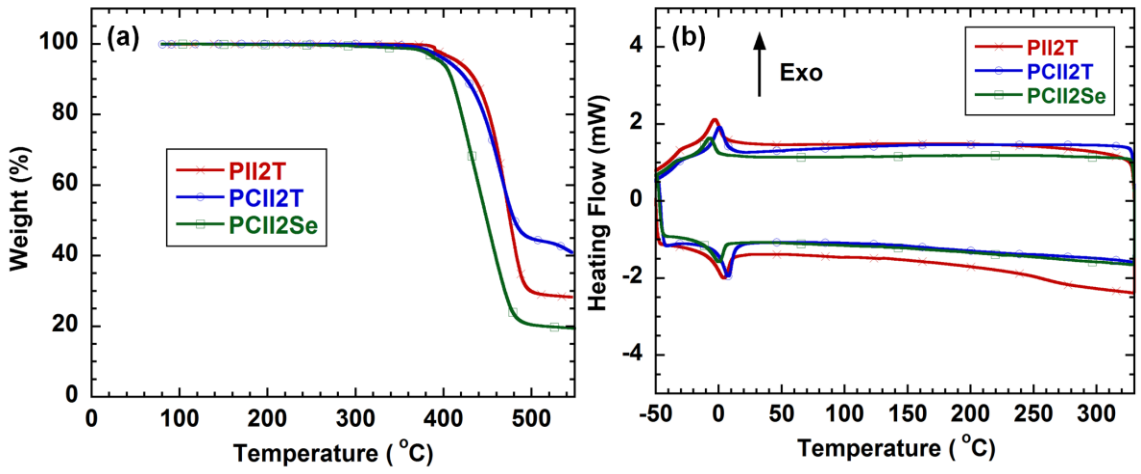


Fig. S2. (a) Thermal gravity analyses (TGA) of **PII2T** (5% loss, 416 °C), **PCII2T** (5% loss, 405 °C), and **PCII2Se** (5% loss, 397 °C). (b) Differential scanning calorimetry (DSC) traces of **PII2T** (T = 4 °C), **PCII2T** (T = 7 °C), and **PCII2Se** (T = 1 °C) (T is the phase transition temperature).

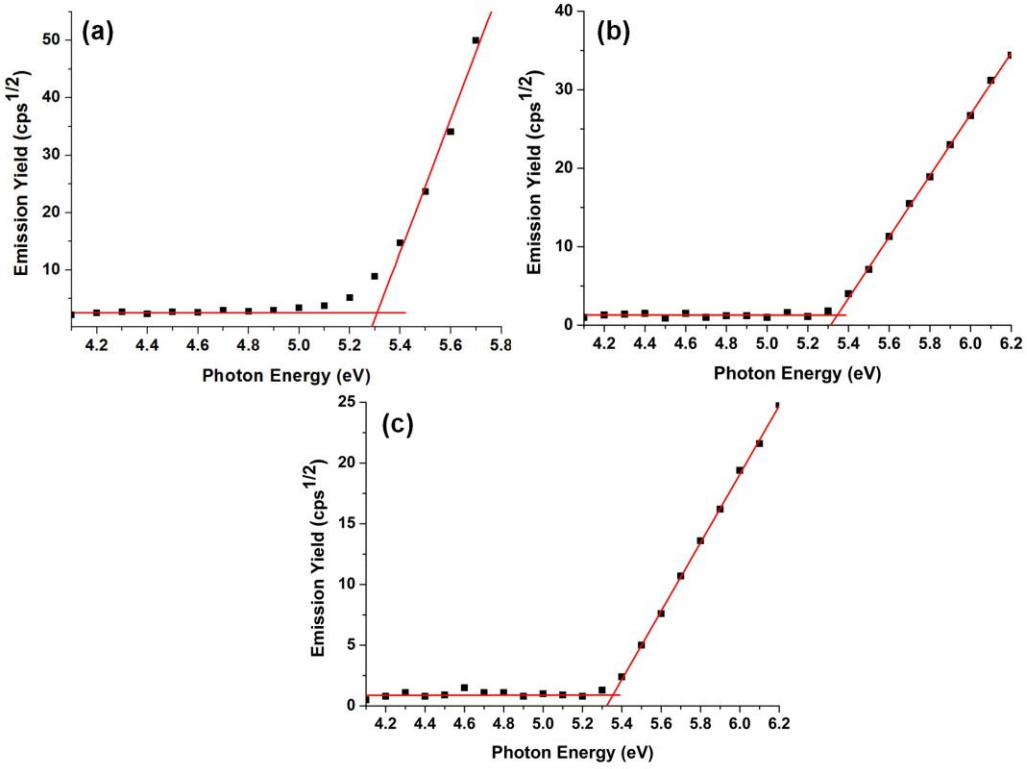


Fig. S3. Photo-electron spectra (PES) of (a) **PII2T**, (b) **PCII2T** and (c) **PCII2Se** in thin films.

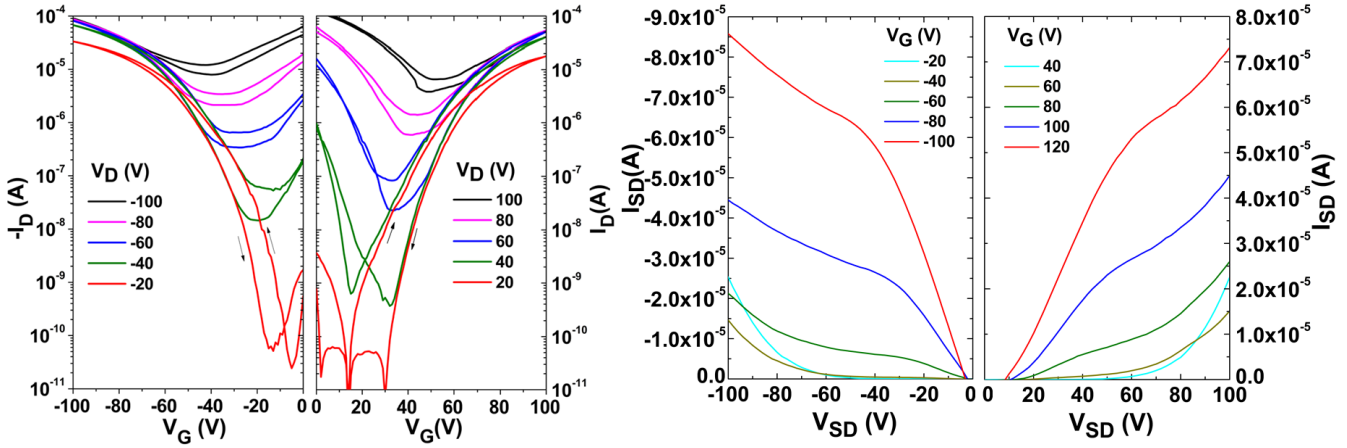


Fig. S4. The transfer and output characteristics of **PCII2T** devices fabricated and tested in ambient (L = 50 μm, W = 1000 μm, C_i = 3.7 nF cm^{-2}).

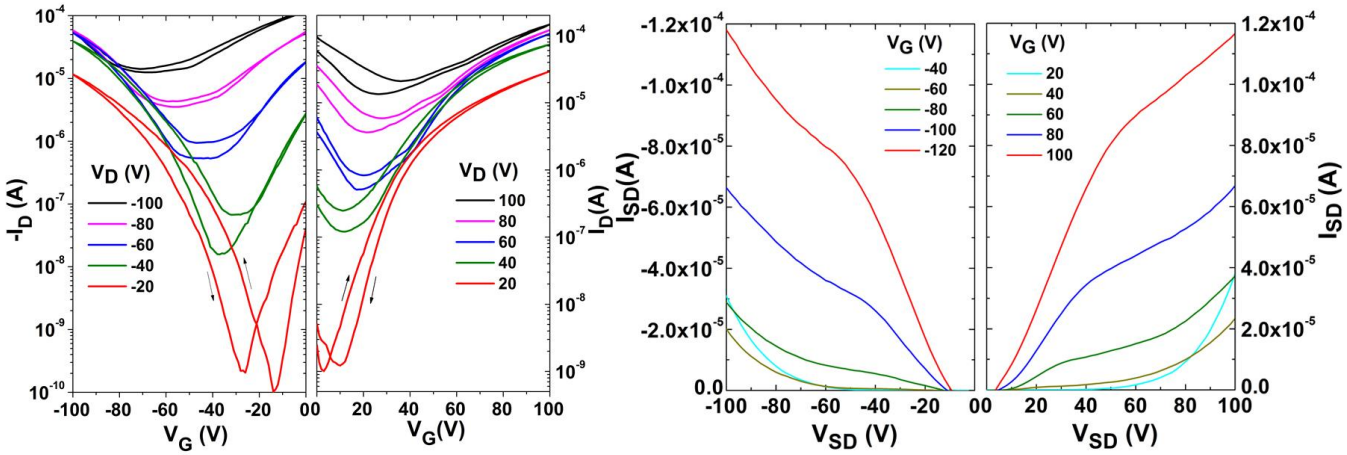


Fig. S5. The transfer and output characteristics of **PCII2Se** devices fabricated in glovebox and tested under ambient conditions (L = 50 μm, W = 1000 μm, C_i = 3.7 nF cm^{-2}).

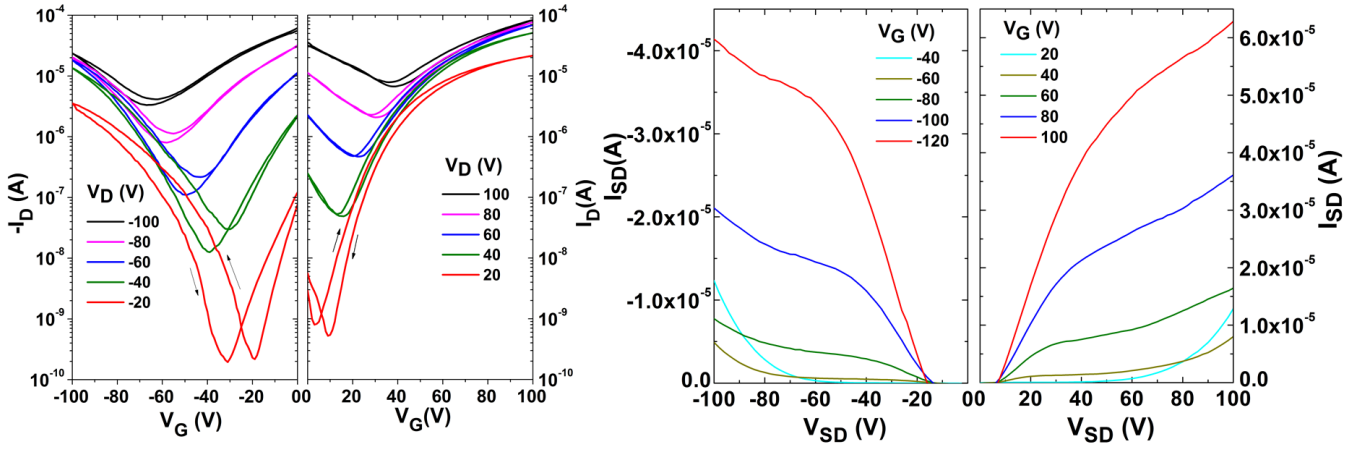


Fig. S6. The transfer and output characteristics of **PCII2T** devices fabricated in glovebox and tested under ambient conditions (L = 50 μm, W = 1000 μm, C_i = 3.7 nF cm^{-2}).

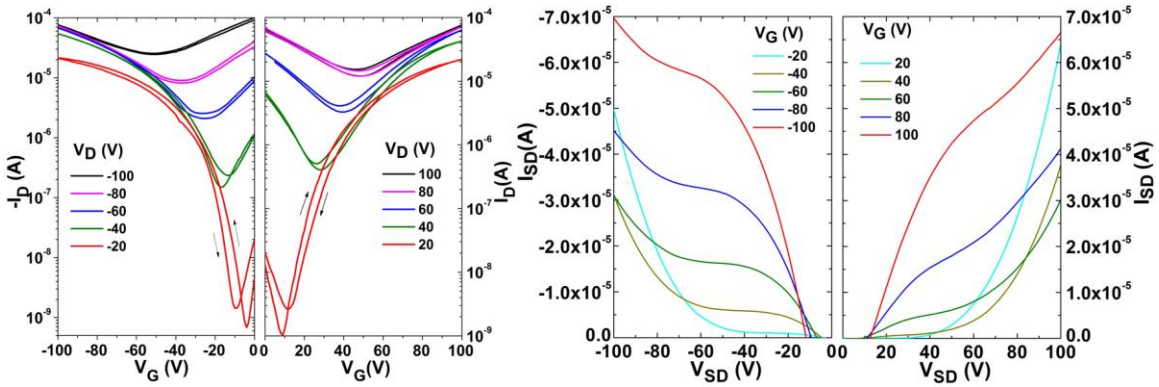


Fig. S7. The transfer and output characteristics of **PCII2T** devices fabricated and tested in ambient (L = 50 μm, W = 1000 μm, C_i = 3.7 nF cm^{-2}).

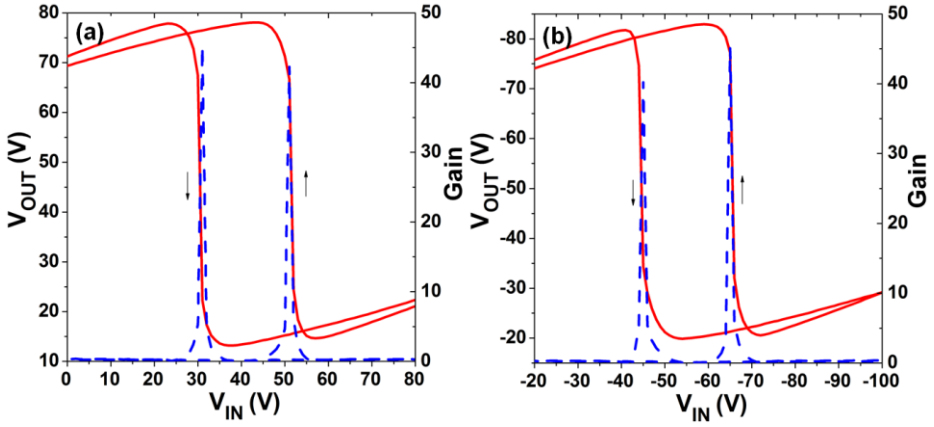


Fig. S8. The VTC and gain of **PCII2Se** inverter devices fabricated in glovebox and tested in ambient (a) V_{DD} = +100 V and (b) V_{DD} = –100 V (L = 50 μm, W = 4 mm). The highest gain is 46.

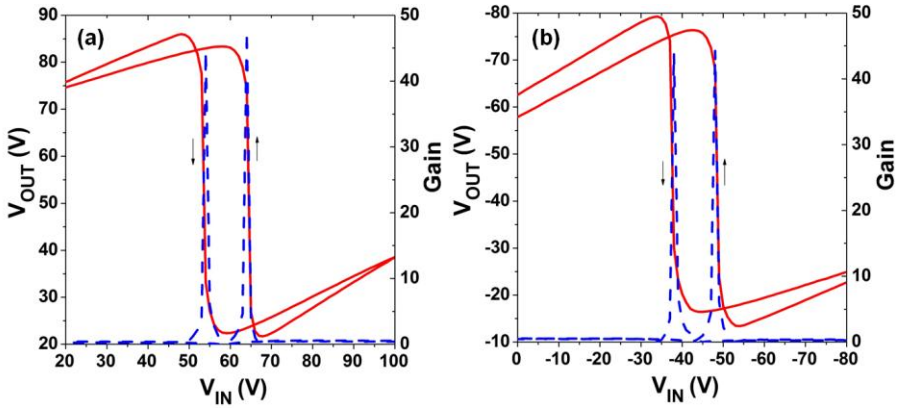


Fig. S9. The voltage transfer characteristic (VTC) and gain of **PCII2Se** inverter devices fabricated and tested in ambient (a) V_{DD} = +100 V and (b) V_{DD} = –100 V (L = 50 μm, W = 4 mm). The highest gain is 48. The threshold voltage difference of forward and reverse scan become obviously smaller than those devices fabricated in nitrogen (Fig. S8), presumably due to the more balanced threshold voltages in the *p*- and *n*- channel modes.

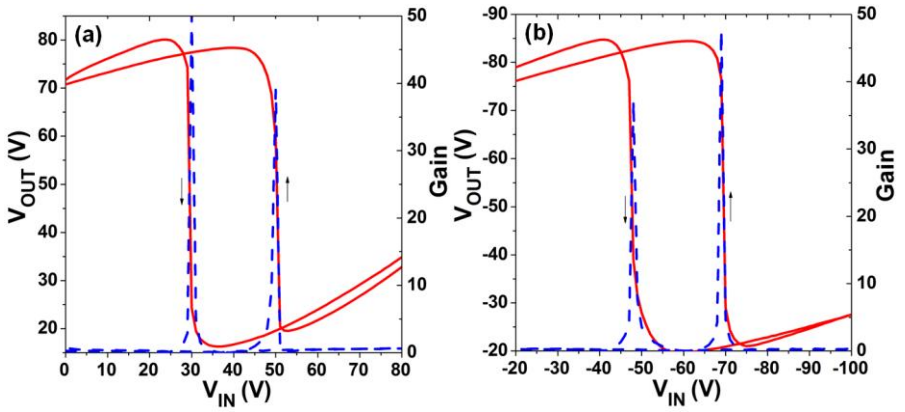


Fig. S10. The VTC and gain of **PCII2T** inverter devices fabricated in glovebox and tested in ambient (a) V_{DD} = +100 V and (b) V_{DD} = –100 V (L = 50 μm, W = 4 mm). The highest gain is 50.

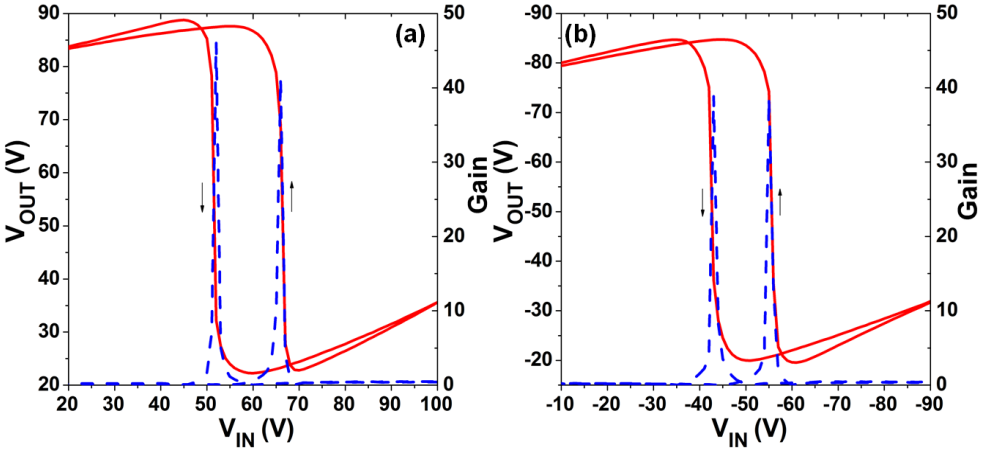


Fig. S11. The VTC and gain of **PCII2T** inverter devices fabricated and tested in ambient (a) V_{DD} = +100 V and (b) V_{DD} = –100 V (L = 50 μm, W = 4 mm). The highest gain is 46. The threshold voltage difference of forward and reverse scan become obviously smaller than those devices fabricated in nitrogen (Fig. S10).

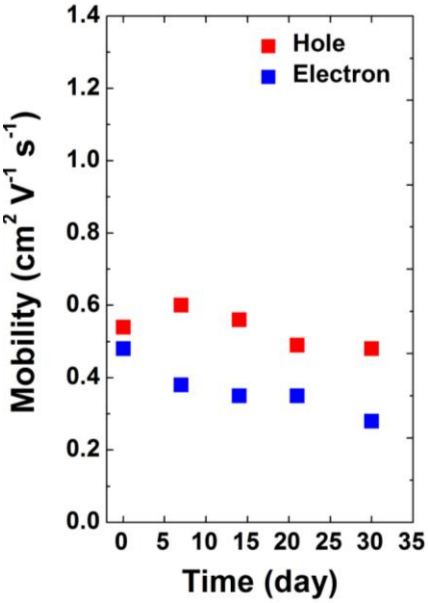


Fig. S12. Time-dependent decay of device performance of **PCII2T** under ambient condition.

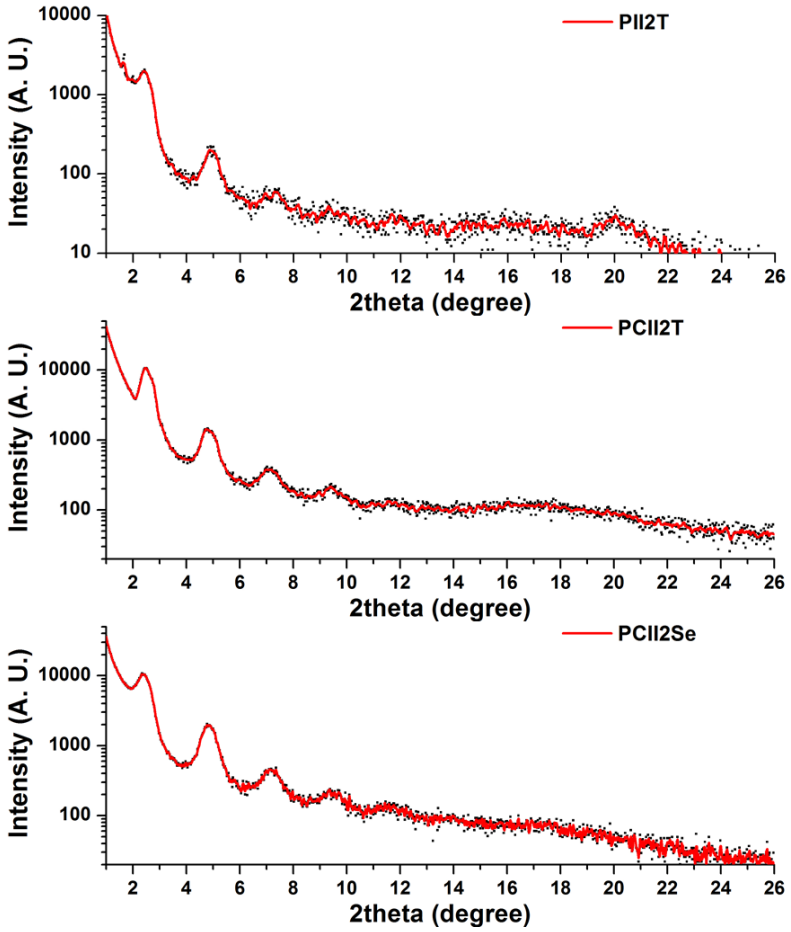
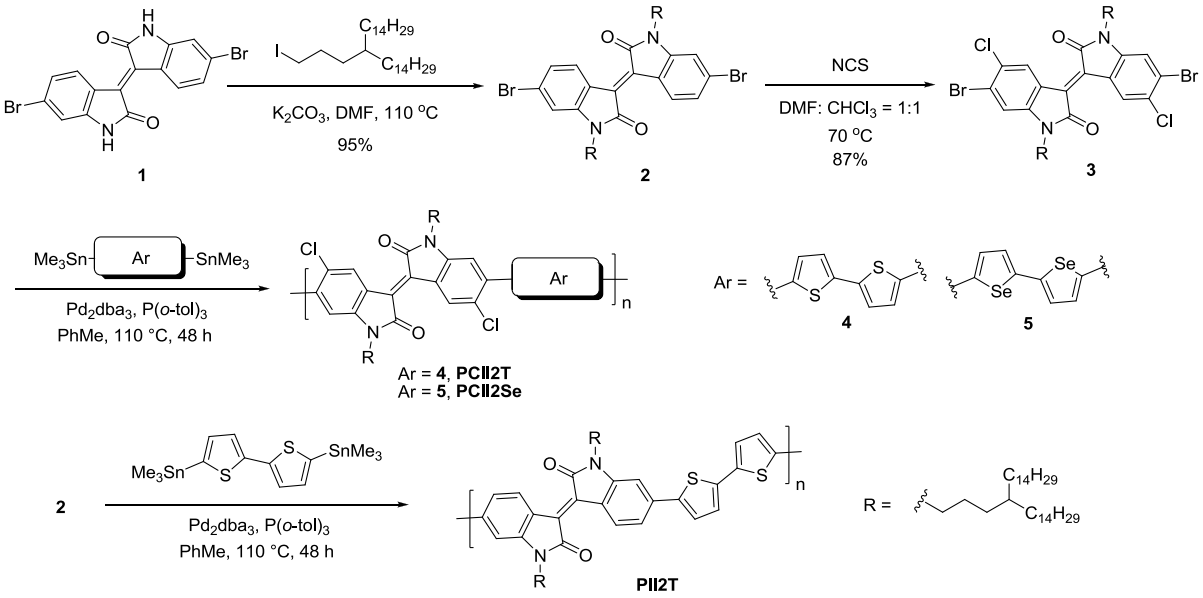
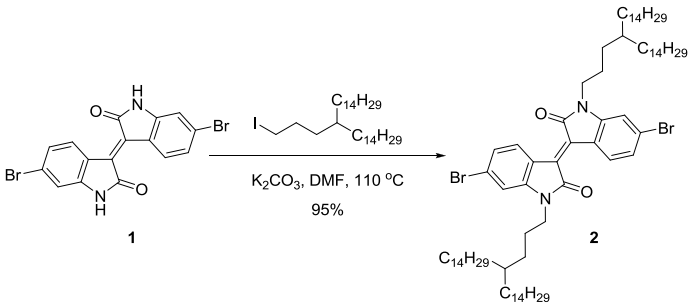


Fig. S13. Out-of-plane GIXD plots of **PII2T**, **PCII2T** and **PCII2Se** films obtained from a point detector in beamline BL14B1 (SSRF).

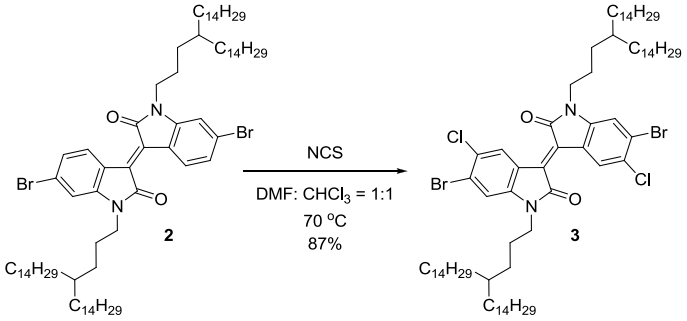
3、**Synthetic procedures and characterization**



6,6'-Dibromoisoindigo (**1**) were synthesized according to our previous work.[1]



Compound 2. To a solution of 6,6'-dibromoisoindigo (2.00 g, 4.76 mmol) and potassium carbonate (1.97 g, 14.3 mmol) in *N,N'*-dimethylformamide (DMF) (100 mL), 15-(3-iodopropyl)nonacosane (6.0 g, 10.4 mmol) was added under nitrogen. The mixture was stirred for 15 h at 100 °C and then the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL) and washed with water. The combined organic phase was washed with brine and dired over with Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by silica gel chromatography with eluent (PE:CH_2Cl_2 = 5:1) to give **2** as a deep-red solid. (6.0 g, 95 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 9.09-9.07 (d, J = 8.6 Hz, 2H), 7.16-7.14 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 2H), 6.90-6.89 (d, J = 1.8 Hz, 2H), 3.71-3.67 (t, J = 7.5 Hz, 4H), 1.67-1.57 (m, 4H), 1.42-1.26 (m, 110H), 0.89-0.86 (t, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.6, 145.7, 132. 6, 131.2, 126.7, 125.1, 120.4, 111.3, 40.6, 37.1, 33.5, 31.9, 30.8, 30.1, 29.7, 29.7, 29.4, 26.7, 24.5, 22.7, 14.1. Elemental Anal. calcd. for $C_{80}H_{136}Br_2N_2O_2$: C, 72.92; H, 10.40; N, 2.13; Found: C, 72.75; H, 10.27; N, 2.06. ESI-HRMS calcd. for $[M + H]^+$: 1315.9041; Found: 1315.9067.



Compound 3. To a solution of **2** (2.00 g, 1.52 mmol) in the mixed solvent of $CHCl_3$ (70 mL) and *N,N'*-dimethylformamide (DMF) (70 mL), *N*-chlorosuccinimide (1.00 g, 7.59 mmol) was added at 70 °C under nitrogen. The mixture was stirred at 70 °C for 3 h and then the solvents were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL) and washed with water. The combined organic phase was washed with brine and dired over with Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified by silica gel chromatography with eluent (PE:CH_2Cl_2 = 5:1) to give **3** as a dark-red solid (1.82 g, 87 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.43 (s, 2H), 7.02 (s, 2H), 3.73-3.69 (t, *J* = 7.4 Hz, 4H), 1.69-1.55 (m, 4H), 1.30-1.22 (m, 110H), 0.89-0.86 (t, *J* = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.2, 144.0, 132.6, 131.4, 127.8, 126.7, 121.5, 112.7, 40.8, 37.1, 33.5, 31.9, 30.7, 30.1, 29.7, 29.7, 29.4, 26.7, 24.4, 22.7, 14.1. Elemental Anal. Calcd. for $C_{80}H_{134}Br_2Cl_2N_2O_2$: C, 69.29; H, 9.74; N, 2.02; Found: C, 69.34; H, 9.42; N, 1.96. ESI-HRMS calcd. for $[M + H]^+$: 1383.8262; Found: 1383.8282.

General Procedures for the Stille Polymerization and Polymer Purification.

PCII2T. **3** (150 mg, 0.108 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (53.1 mg, 0.108 mmol), $Pd_2(dba)_3$ (2.0 mg, 2 mol%.), P(*o*-tol)$_3$ (2.6 mg, 8 mol%), and toluene (10 mL) were added to a Schlenk tube. The tube was charge with nitrogen through a *freeze-pump-thaw* cycle for three times. The mixture was stirred for 48 h at 120 ℃. *N,N'*-Diethylphenylazothioformamide (10 mg) was added and then the mixture was stirred for 1 h to remove any residual catalyst before precipitation from CH_3OH (200 mL). The precipitate was filtered through a nylon filter and purified by Soxhlet extraction for 8 h with acetone, 12 h with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL) and filtered off to afford a dark brown solid (99.1 mg, 97%). Elemental Anal. calcd for $(C_{88}H_{138}Cl_2N_2O_2S_2)_n$: C, 75.98; H, 10.00; N, 2.01; Found: C, 75.22; H, 9.91; N, 1.93.

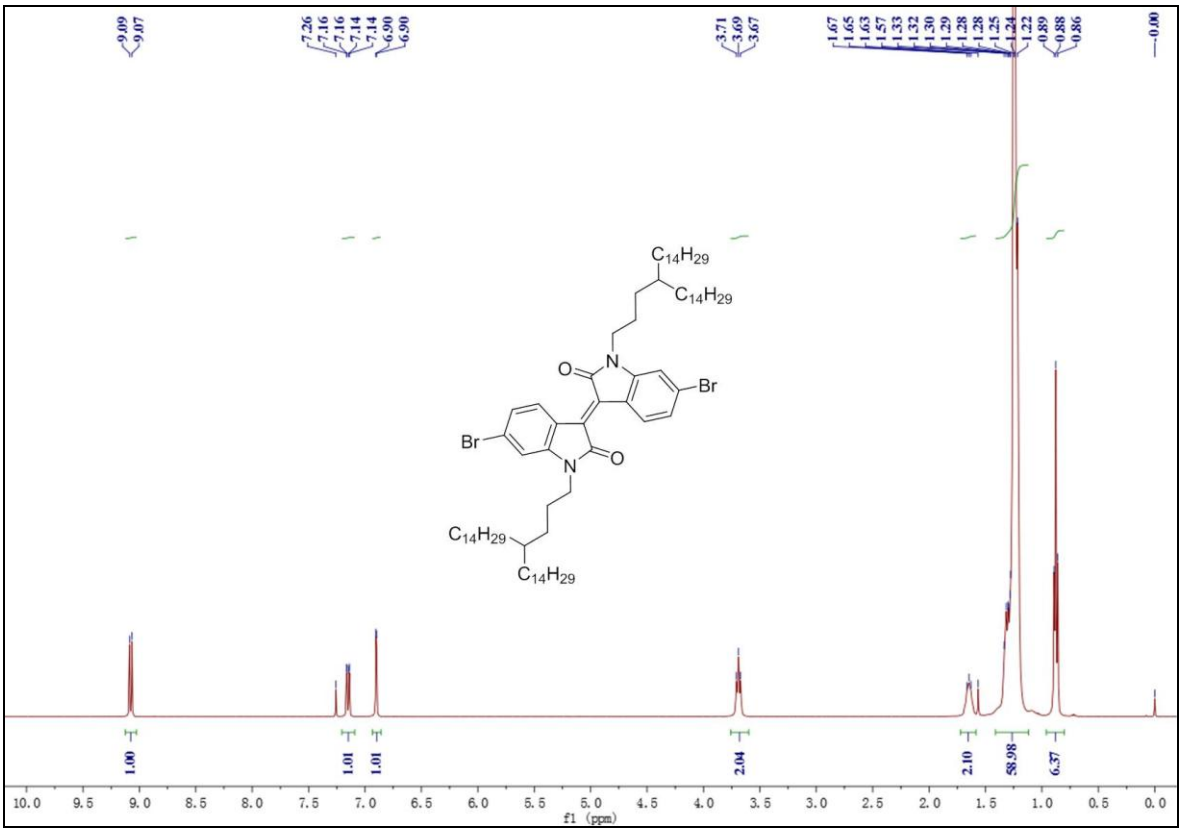
PCII2Se. yield: 98%. Elemental Anal. calcd. for $(C_{88}H_{138}Cl_2N_2O_2Se_2)_n$: C, 71.13; H, 9.43; N, 1.89; Found: C, 70.09; H, 9.14; N, 1.81.

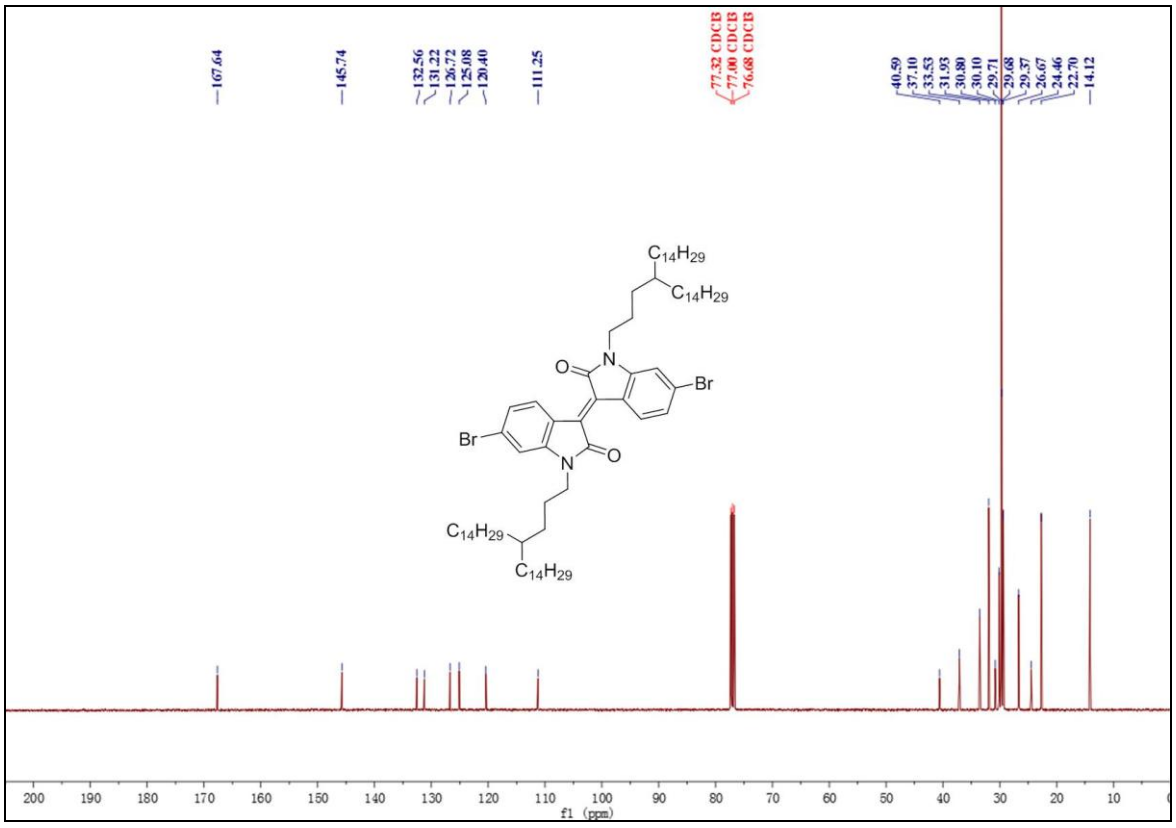
PII2T. yield: 94%. Elemental Anal. calcd. for $(C_{88}H_{140}N_2O_2S_2)_n$: C, 79.94; H, 10.67; N, 2.12; Found: C, 78.88; H, 10.12; N, 2.07.

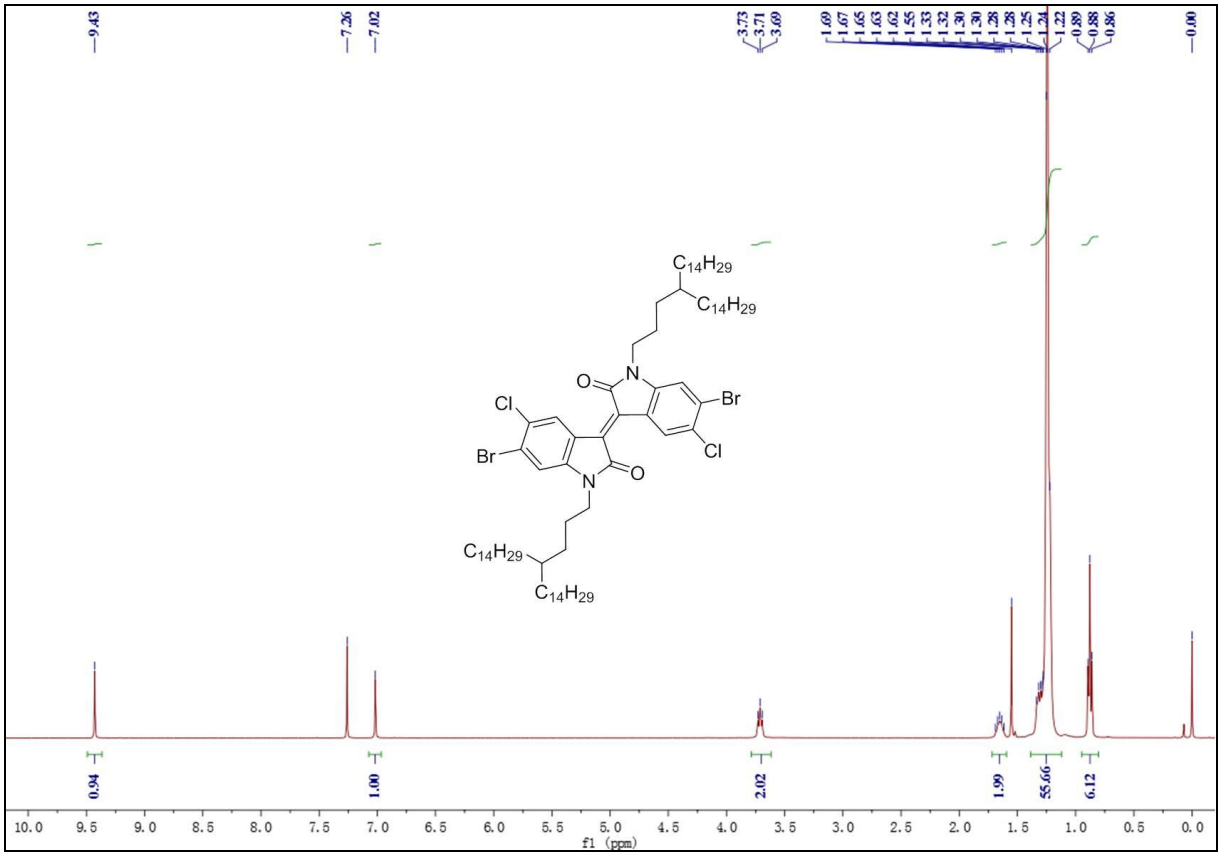
References:

1. Lei, T.; Cao, Y.; Fan, Y.; Liu C.-J.; Yuan, S.-C.; Pei, J. *J. Am. Chem. Soc.* **2011**, *133*, 6099.

4. ^{1}H and ^{13}C NMR spectra



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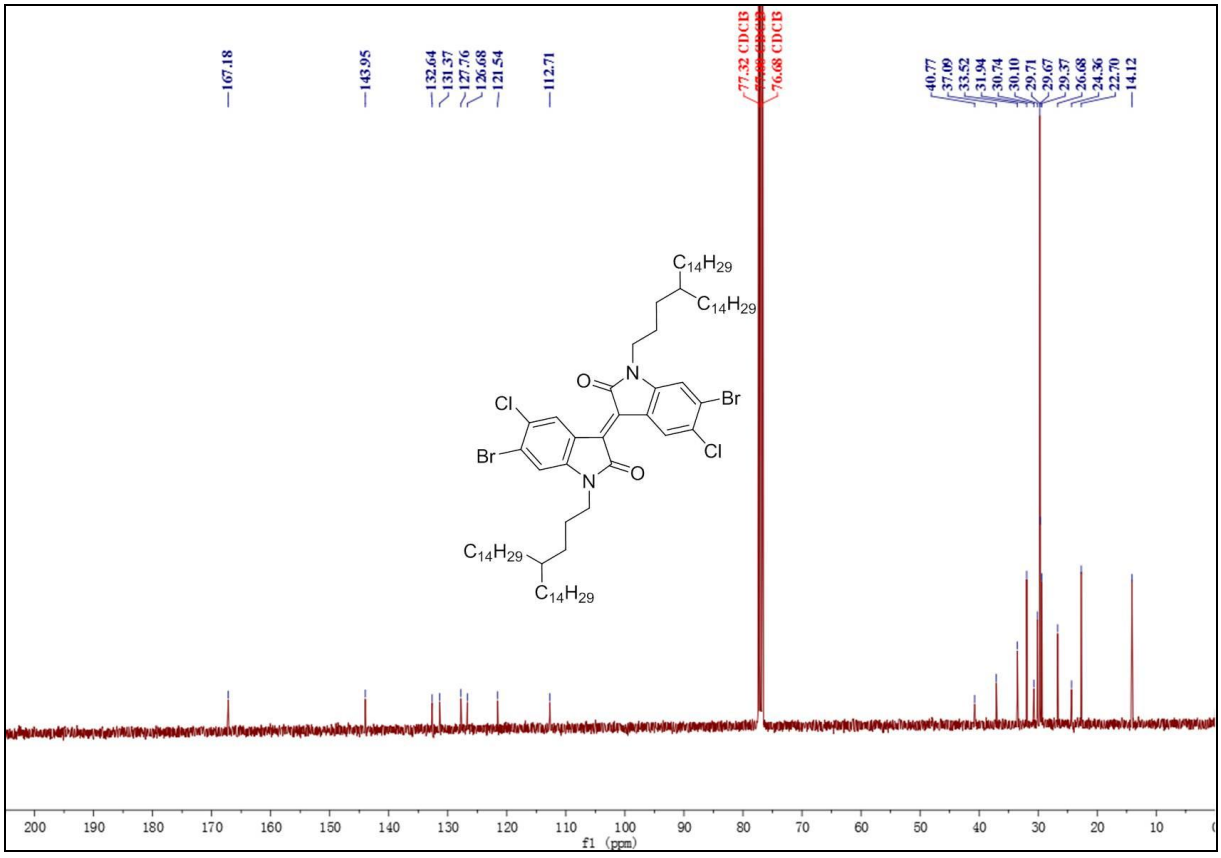
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C14H29
f1 (ppm)