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Electronic Supplementary Information (ESI)

Room-temperature Smectic Liquid Crystal Monolayers for Field-effect Transistors

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Experimental Section

Instruments and measurements

Nuclear magnetic resonance spectra were collected on a Bruker AVANCE 400 spectrometer using tetramethylsilane (TMS) as the internal standard. MALDI-TOF-MS spectra were measured on a Bruker BIFLEXIII mass spectrometer. UV–vis absorption spectra of the two samples in diluted chloroform solutions (1×10^{-5} M) and in thin films cast onto quartz glass were performed by using an Agilent Cary 60 UV-Vis. Cyclic voltammetry (CV) experiments of the two samples were carried out on an electrochemistry workstation (CHI660C, Chenhua Shanghai) using a conventional three-electrode configuration, including a glassy carbon working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode. The CV curves of the samples were collected in an anhydrous and N_2-saturated $CHCl_3$ solution in the presence of 0.1 M tetrabutylammonium hexafluorophosphate(n-Bu_4NPF_6) as the supporting electrolyte. Thermogravimetric analysis (TGA) was recorded on a Perkin–Elmer TGA-7 with a heating rate of 10 $^oCmin^{-1}$ under an argon atmosphere. Differential scanning calorimetry (DSC) was performed on a TA instrument 2920 at a heating/cooling rate of 10 $^oCmin^{-1}$ under nitrogen flow.

Modification of substrates

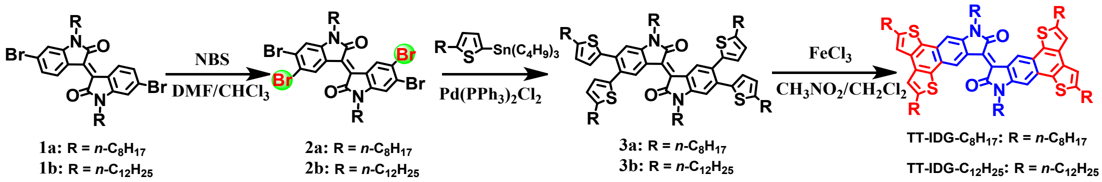
The heavily doped n-type Si wafers with a 300 nm thick SiO_2 layer were used as substrates of OFETs, which were cleaned with deionized water, piranha solution (70/30 vol./vol. H_2SO_4/H_2O_2), deionized water, isopropanol and blow-dried by N_2. Then, the substrates were treated with plasma for 5 min at 100 W.

Fabrication of liquid crystal monolayer transistors

Liquid crystal monolayers of TT-IDG-C8 and TT-IDG-C12 were grown on SiO_2/Si^{++} substrate by the drop-casting method. The thin film Au electrodes (about 100 nm) were pasted onto the crystals to fabricate the bottom-gate top-contact devices with the help of mechanical probes.[1] Devices were characterized by Agilent 1500A.

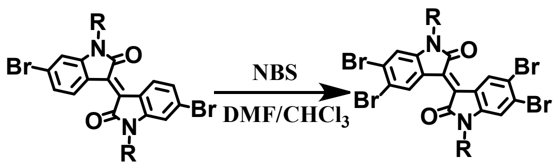
Material Synthesis

Synthesis of tetrathienyl-fused isoindigo derivative



All the chemical reagents were purchased from Chem Greatwall, Derthon, and Alfa Aesar, and used as received directly. Tributyl(5-octylthiophen-2-yl)stannane, tributyl(5-dodecylthiophen-2-yl)stannane, tributyl(thiophen-2-yl)stannane, (E)-6,6'-dibromo-1,1'-dioctyl-[3,3'-biindolinylidene]-2,2'-dione (1a) and (E)-6,6'-dibromo-1,1'-didodecyl-[3,3'-biindolinylidene]-2,2'-dione (1b) were synthesized according to the reported literature.[2, 3]

General procedure for the preparation of 2a and 2b

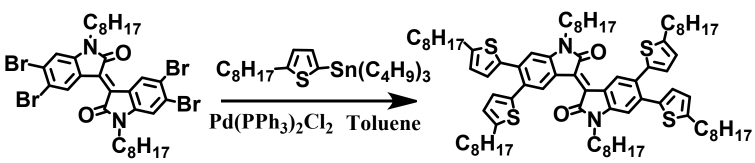


1a: R = n-C_8H_{17} **2a**: R = n-C_8H_{17}
1b: R = n-$C_{12}H_{25}$ **2b**: R = n-$C_{12}H_{25}$

A mixture solution of 1a or 1b (1.5 mmol), N-bromosuccinimide (NBS, 7.5 mmol), DMF (60 mL) and $CHCl_3$ (60 mL) was added to a 250 mL three-neck round-bottomed flask under a N_2 atmosphere. Then the mixture was stirred at 70 °C for 4 hours. After cooling to room temperature, the solid was collected and washed with water and methanol, the crude product was collected by filtration to yield a red brown solid. The crude product (2a or 2b) was directly used in the next step without further purification.

Synthesis of compound 3a

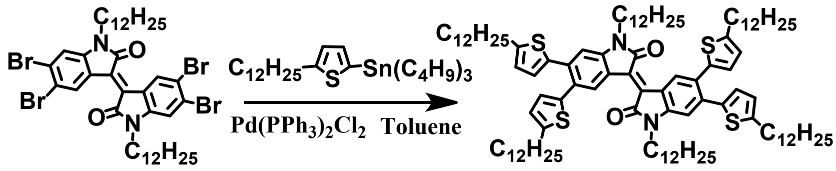
Under a N_2 atmosphere, a mixture of 2a (0.5 g, 0.6 mmol), tributyl(5-octylthiophen-2-yl)stannane (3.03 g, 6 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), and toluene (70 mL) was added to a 250 mL dried three-neck round-bottom flask. Then the mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was further purified by silica gel column chromatography (eluent: petroleum ether/dichloromethane, v/v = 3:1), affording a black solid (0.65 g, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.27 (s, 2H), 6.88 (s, 2H), 6.80–6.78 (t, 4H), 6.66–6.64 (t, 4H), 3.80–3.77 (t, 4H), 2.79–2.75 (t, 8H), 1.66–1.65 (m, 12H), 1.35–1.26 (m, 60H), 0.90–0.87 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 168.00, 167.92, 148.41, 147.93, 146.48, 144.74, 144.29, 140.24, 140.12, 138.19, 132.64, 132.46, 129.80, 127.80, 127.54, 127.42, 127.34, 126.99, 126.02, 124.46, 124.19, 123.85, 120.61, 108.95, 40.18, 40.11, 31.94, 31.91, 31.82, 31.76, 31.66, 31.64, 30.19, 29.71, 29.70, 29.68, 29.67, 29.65, 29.61, 29.55, 29.40, 29.38, 29.36, 29.33, 29.31, 29.28, 29.20, 29.15, 29.12, 27.54, 26.98, 22.72, 22.70, 22.65, 14.15, 14.12.



2a **3a**

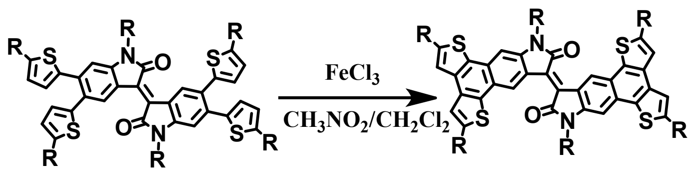
Synthesis of compound 3b

Under a N_2 atmosphere, a mixture of 2b (0.5 g, 0.6 mmol), tributyl(5-dodecylthiophen-2-yl)stannane (3.03 g, 6 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), and toluene (70 mL) was added to a 250 mL dried three-neck round-bottom flask. Then the mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was further purified by silica gel column chromatography (eluent: petroleum ether/dichloromethane, v/v = 3:1), affording a black solid (0.78 g, 89 %). ^{1}H NMR (400 MHz, $CDCl_3/CD_2Cl_2$), δ (ppm): 9.27 (s, 2H), 7.22-7.26 (d, 4H), 6.88 (s, 2H), 6.79–6.78 (t, 4H), 6.65–6.63 (t, 4H), 3.80–3.76 (t, 4H), 2.77–2.75 (t, 8H), 1.72–1.70 (m, 12H), 1.35–1.24 (m, 108H), 0.90–0.85 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 168.01, 147.94, 146.48, 144.30, 140.24, 140.12, 138.20, 132.62, 132.47, 127.41, 127.36, 124.17, 123.83, 120.62, 108.96, 31.94, 31.75, 31.66, 30.18, 29.73, 29.71, 29.69, 29.64, 29.62, 29.54, 29.44, 29.40, 29.37, 29.14, 27.56, 27.00, 22.71, 14.14.



2b 3b

General procedure for the preparation of TT-IDG-C8 and TT-IDG-C12



3a: R = n-C_8H_{17}
3b: R = n-$C_{12}H_{25}$
TT-IDG-C_8H_{17}: R = n-C_8H_{17}
TT-IDG-$C_{12}H_{25}$: R = n-$C_{12}H_{25}$

A solution of 3a or 3b (0.075 mmol) in 150 mL of dry dichloromethane was added to a solution of $FeCl_3$ (98 mg, 0.6 mmol) in CH_3NO_2 (1 mL) at 0 °C. After stirring for 15 min, 30 mL of methanol was added to quench the reaction. The mixture was washed with brine, aqueous saturated NH_4Cl, and then dried over Na_2SO_4. After removal of the solvents under vacuum, the crude product was further purified by silica gel column chromatography and recrystallized by ethanol to give TT-IDG-C8 or TT-IDG-C12.

TT-IDG-C8. Yield: 72 %, purple red solid. ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.99 (s, 2H), 7.25 (s, 2H), 7.19 (s, 2H), 6.87 (s, 2H), 3.84–3.81 (t, 4H), 3.03–3.01 (t, 4H), 2.92–2.88 (t, 4H), 1.90–1.87 (m, 4H), 1.77–1.75 (m, 8H), 1.34–1.25 (m, 60H), 0.91–0.87 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.66, 148.39, 145.32, 142.14, 135.46, 135.40, 133.67, 133.19, 132.03, 129.22, 122.53, 121.76, 120.62, 120.38, 119.30, 100.93, 31.92, 31.58, 31.07, 30.74, 29.43, 29.35, 29.31, 29.27, 29.21, 27.34, 27.19, 22.71, 22.68, 14.14, 14.12. HRMS: m/z $[M+H]^+$ calcd for ($C_{80}H_{110}N_2O_2S_4$): 1258.7455; found: 1258.7450.

TT-IDG-C12. Yield: 77 %, purple red solid. ^1H NMR (400 MHz, $CDCl_3/CD_2Cl_2$), δ (ppm): 9.27 (s, 2H), 7.22-7.26 (d, 4H), 6.88 (s, 2H), 6.79–6.78 (t, 4H), 6.65–6.63 (t, 4H), 3.80–3.76 (t, 4H), 2.77–2.75 (t, 8H), 1.72–1.70 (m, 12H), 1.35–1.24 (m, 108H), 0.90–0.85 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 167.59, 147.37, 144.96, 141.46, 136.47, 134.91, 132.90, 131.83, 131.58, 128.08, 127.62, 122.07, 121.54, 119.91, 119.42, 99.98, 40.06, 31.97, 31.72, 31.41, 31.03, 31.00, 29.76, 29.71, 29.69, 29.61, 29.53, 29.47, 29.41, 27.27, 27.17, 22.72, 22.70, 14.13, 14.11. HRMS: m/z $[M+H]^+$ calcd for ($C_{104}H_{158}N_2O_2S_4$): 1595.1211; found: 1585.1211; found: 1596.1199.

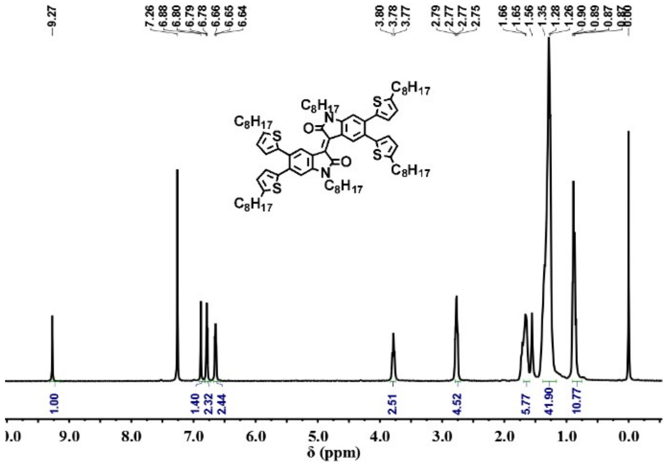


Fig. S1 ^1H NMR spectrum of 3a in $CDCl_3$ (a).

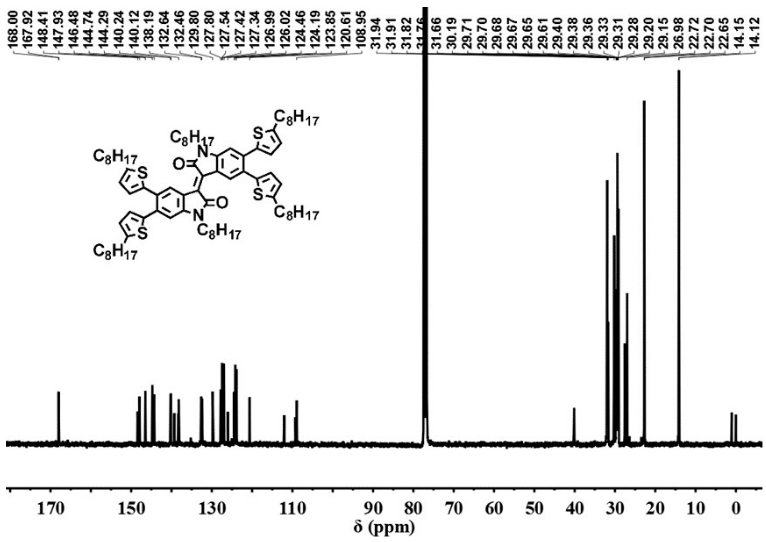


Fig. S2 ^{13}C NMR spectrum of 3a in $CDCl_3$.

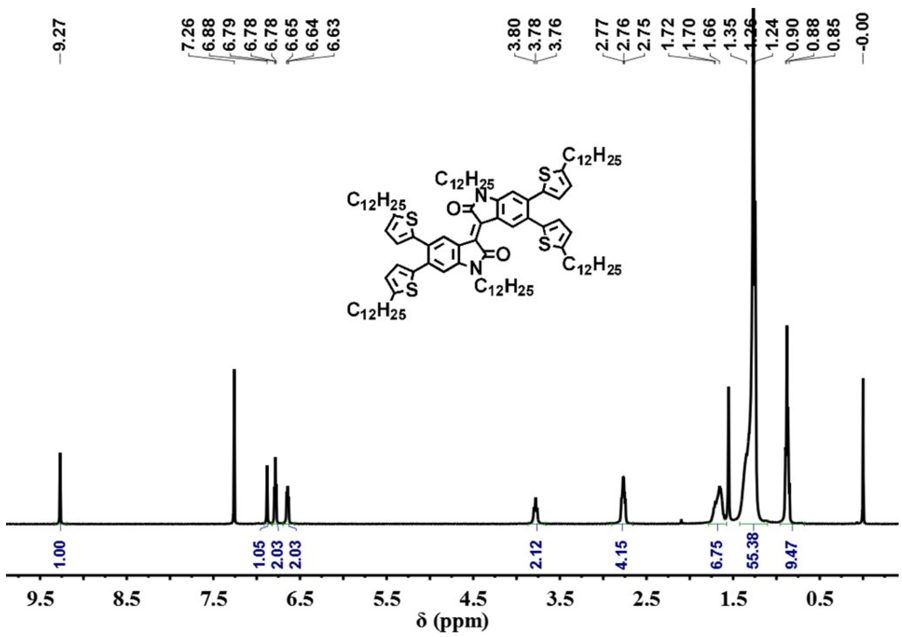


Fig. S3 ^{1}H NMR spectrum of 3b in $CDCl_3$.

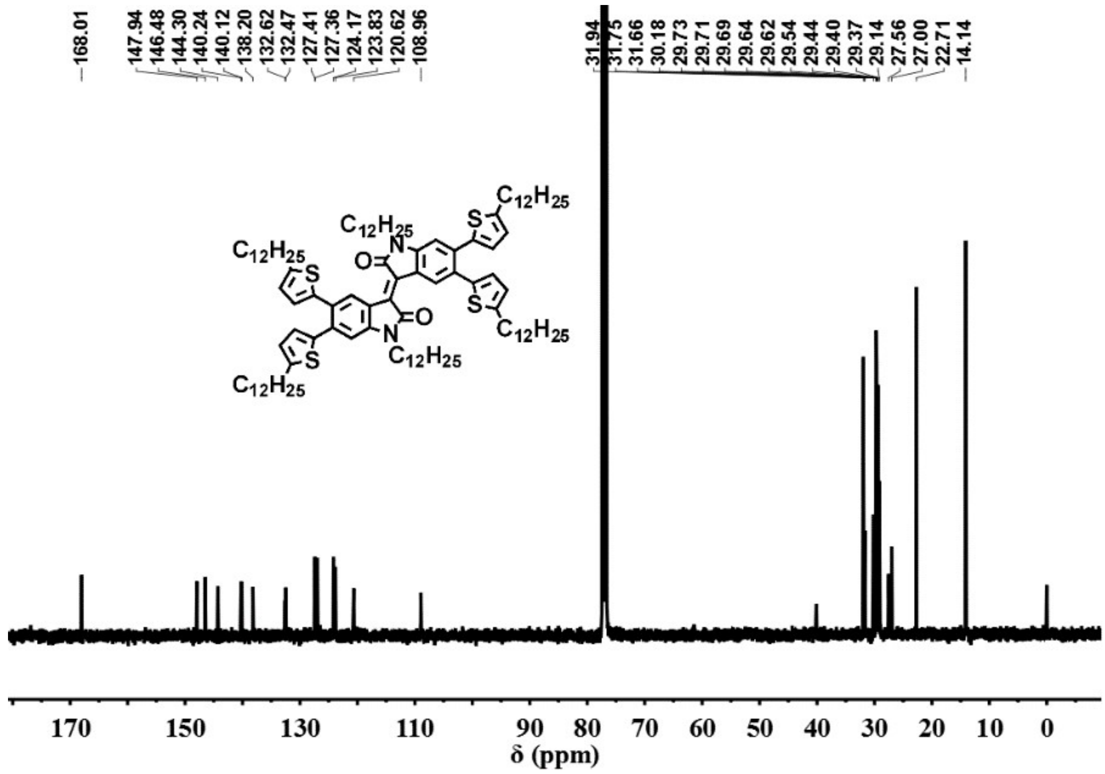


Fig. S4 ^{13}C NMR spectrum of 3b in $CDCl_3$.

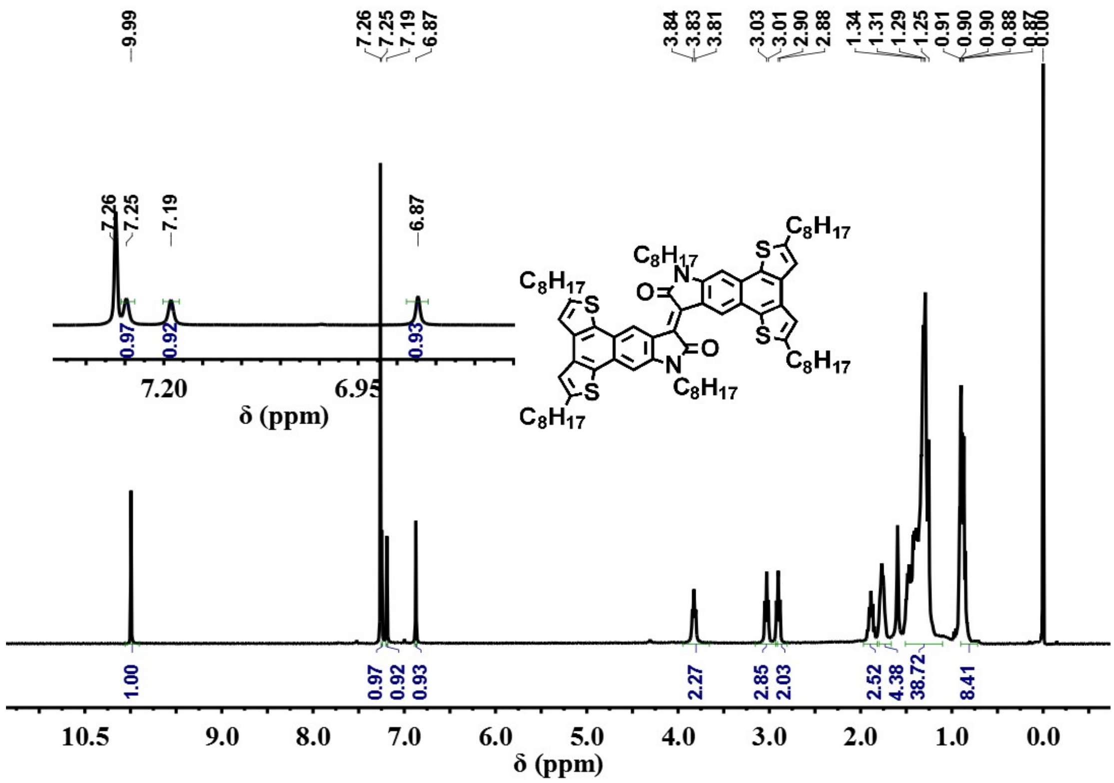


Fig. S5 ^{1}H NMR spectrum of TT-IDG-C8 in $CDCl_3$.

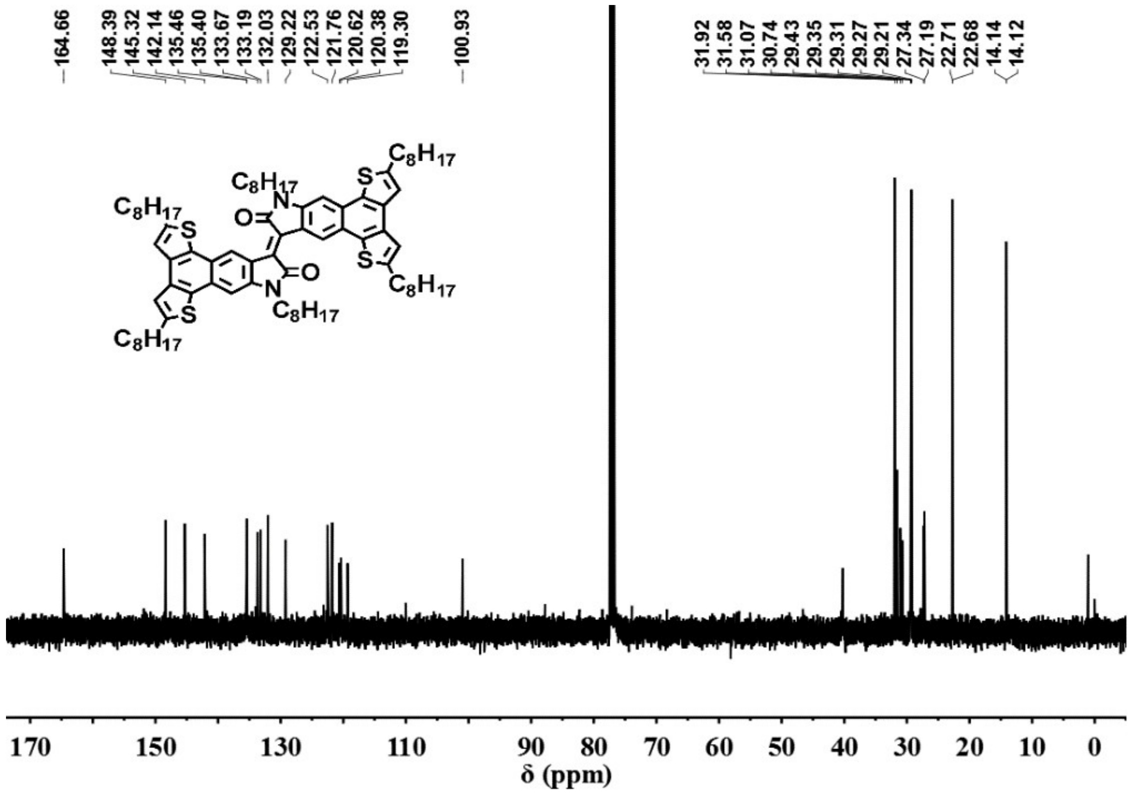


Fig. S6 ^{13}C NMR spectrum of TT-IDG-C8 in $CDCl_3$.

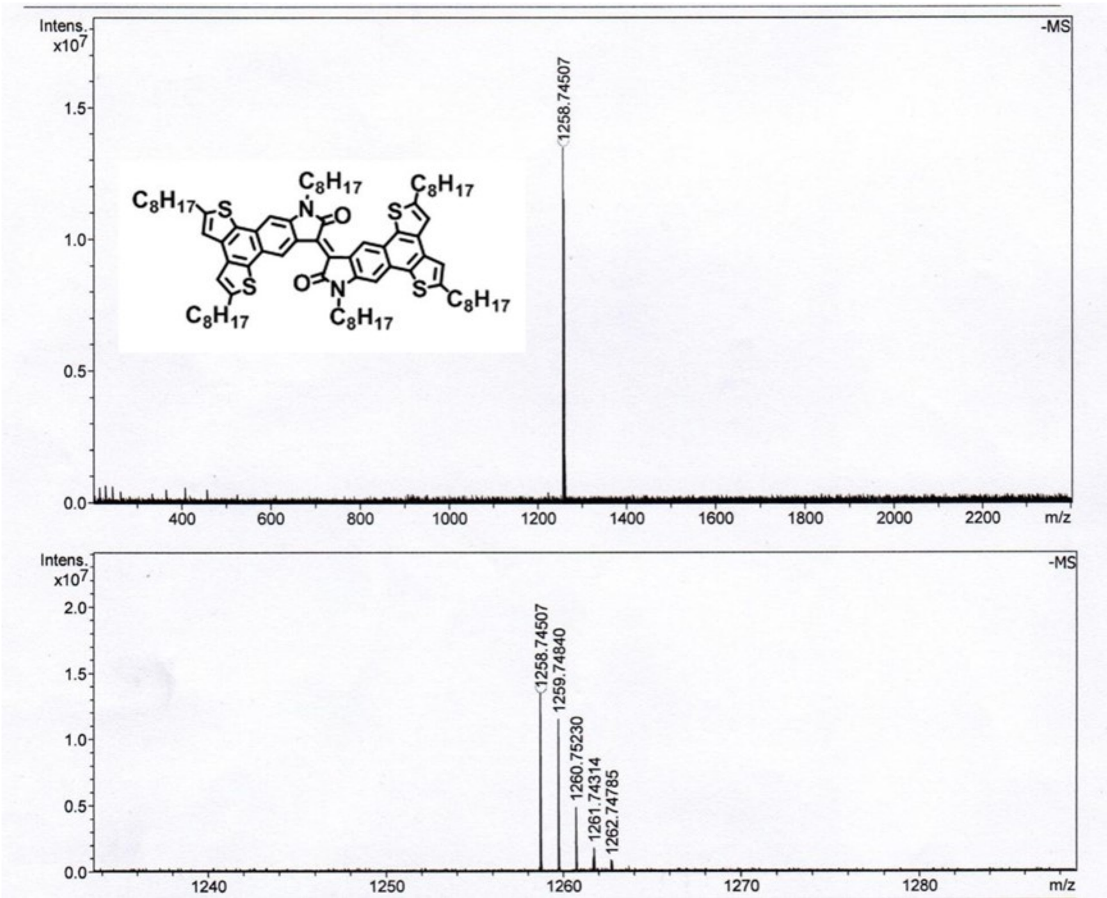


Fig. S7 HRMS spectrum of TT-IDG-C8.

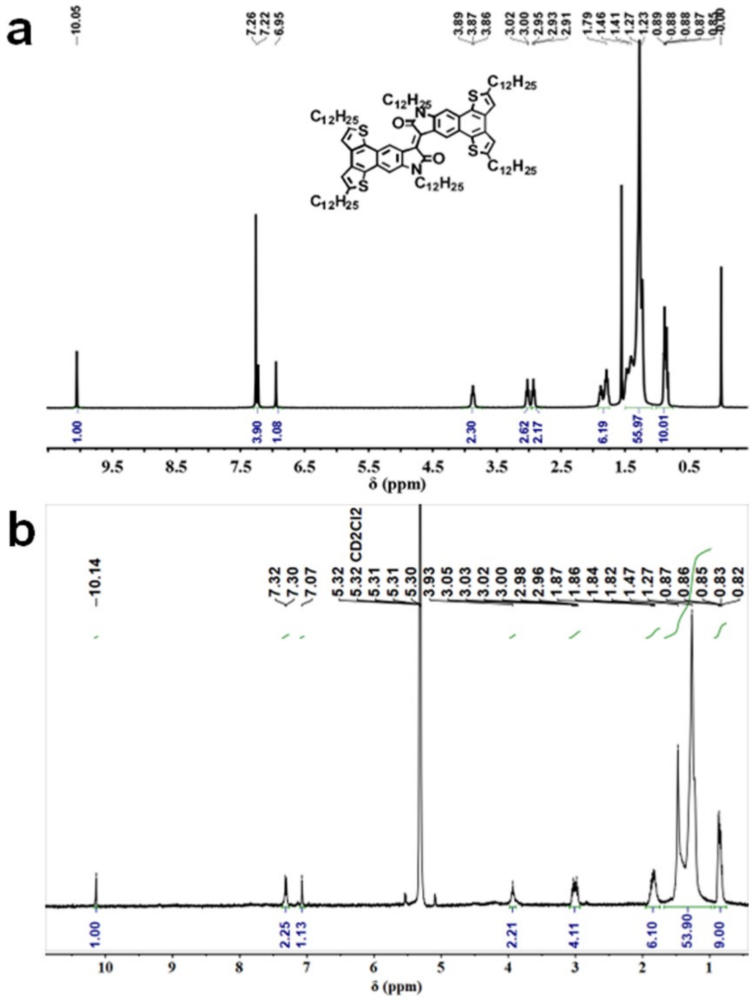


Fig. S8 ^1H NMR spectrum of TT-IDG-C12 in $CDCl_3$ (a) and CD_2Cl_2 (b).

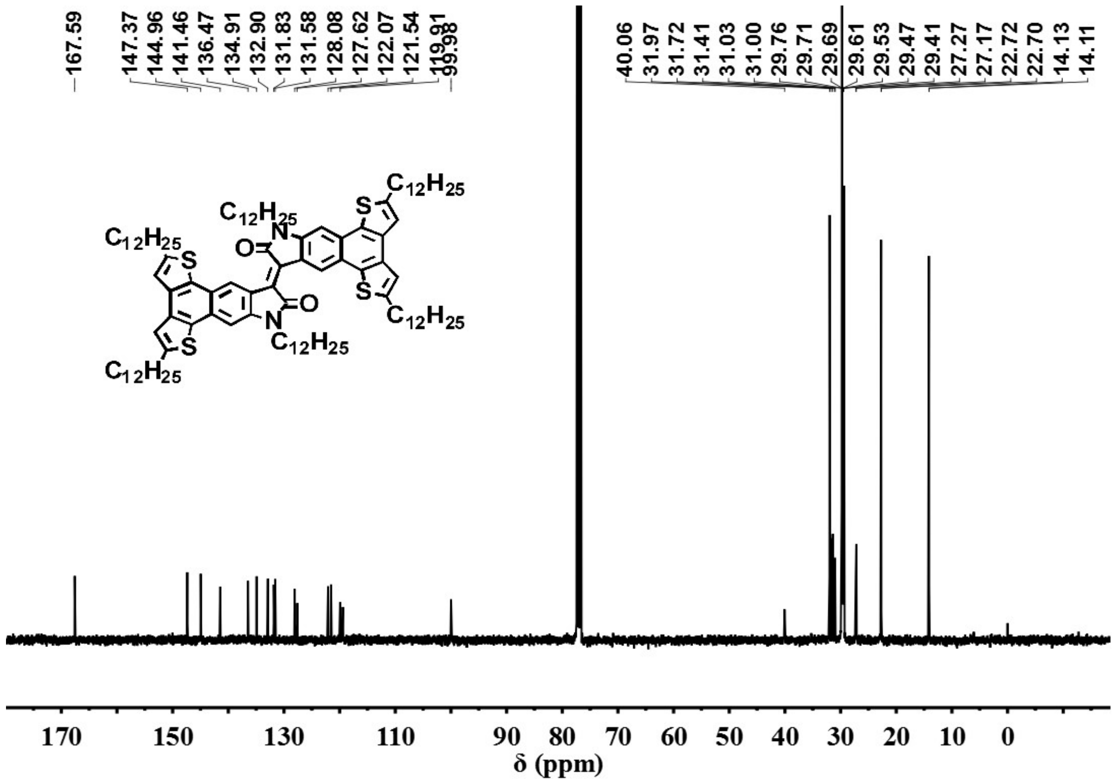


Fig. S9 ^{13}C NMR spectrum of TT-IDG-C12 in $CDCl_3$.

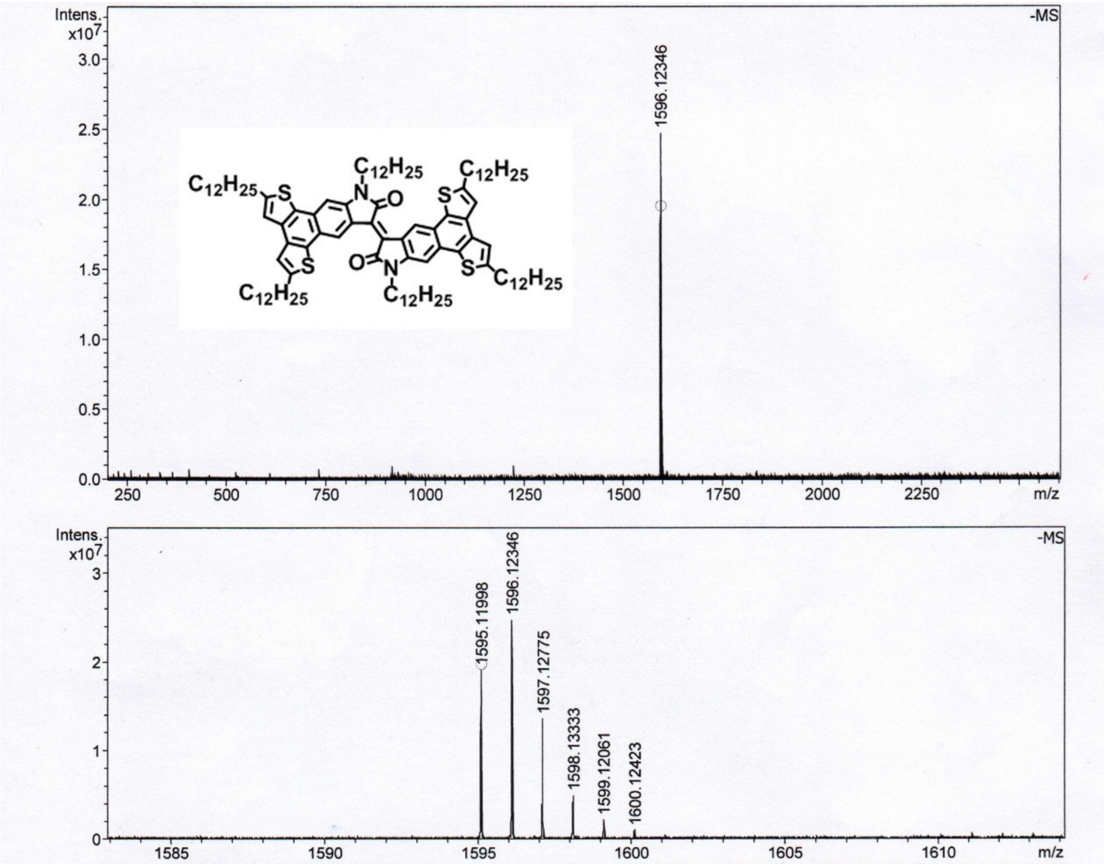


Fig. S10 HRMS spectrum of TT-IDG-C12.

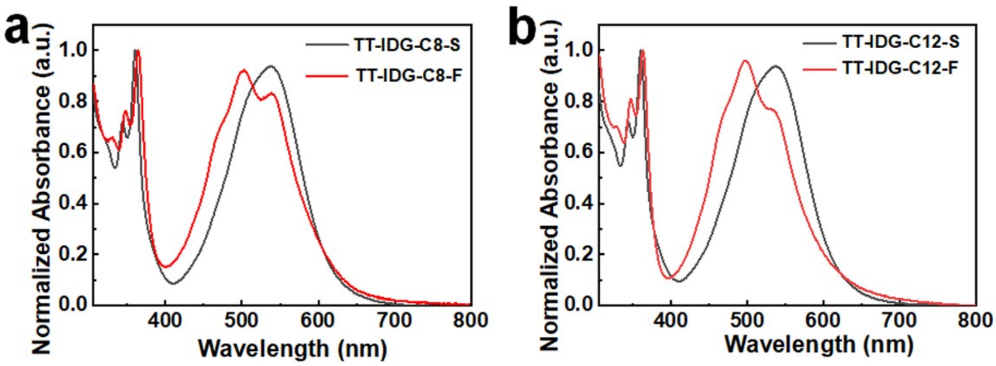


Fig. S11 Normalized UV–vis absorption spectra of TT-IDG-C8 and TT-IDG-C12 in solution and films, respectively.

Table S1. Normalized UV–vis absorption spectra data of TT-IDG-C8 and TT-IDG-C12 in solution and films, respectively.

Sample	λ_{sol}^{max} [nm]	λ_{film}^{max} [nm]	λ_{sol}^{onset} [nm]
TT-IDG-C8	**344,360,537**	**347,364,502,539**	**618**
TT-IDG-C12	**344,360,538**	**347,363,498,534**	**617**

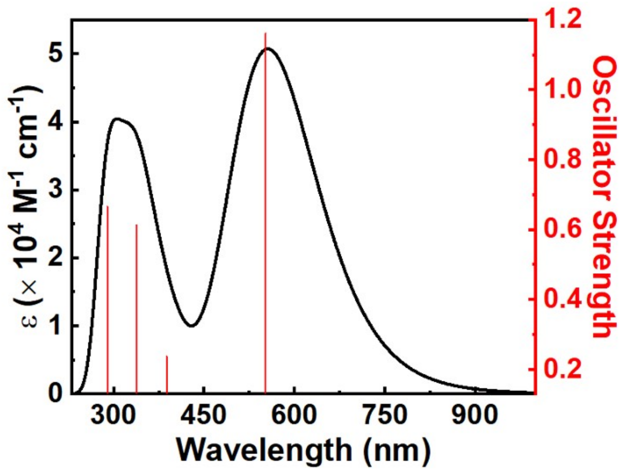


Fig. S12 Calculated absorption spectra and oscillator strength of π-extended isoindigo derivative at DFT/B3LYP/6-31G(d), the alkyl side chains were replaced by $-CH_3$ groups to simplify the calculations.

Table S2. The calculated key parameters of π-extended isoindigo derivative.

Compound	Excited States	Energy (eV)	Wavelength (nm)	Osc. Strength	Main contributions
TT-IDG	3	2.2450	552.27	1.1617	HOMO−2 → LUMO 84.1%
	5	3.1950	388.06	0.2382	HOMO−4 → LUMO 95.7%
	10	3.6677	338.04	0.6125	HOMO → LUMO+1 52.3%
	19	4.2834	289.45	0.6665	HOMO−1 → LUMO+3 43.5%

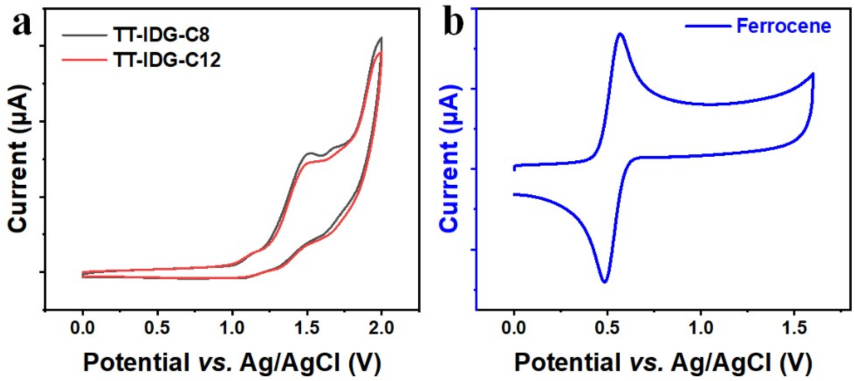


Fig. S13 Cyclic voltammetry results of (a) TT-IDG-C8 and TT-IDG-C12, (b) ferrocene.

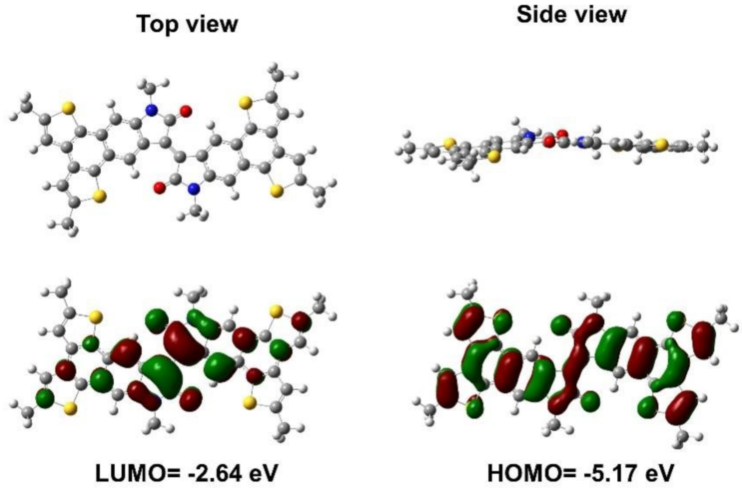


Fig. S14 Optimized conformation of π-extended isoindigo derivative. HOMO and LUMO orbital distributions and energy levels calculated by DFT/B3LYP/6-31G(d), the alkyl side chains were replaced by $-CH_3$ groups to simplify the calculations.

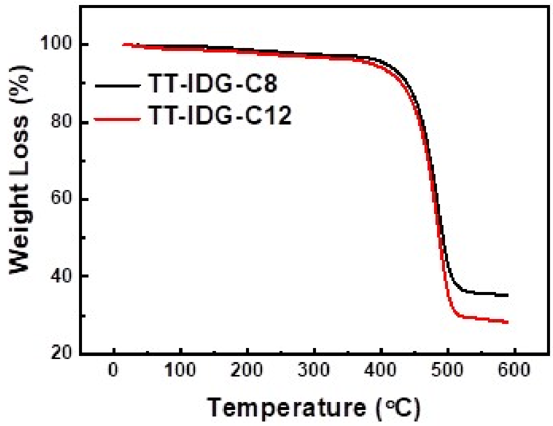


Fig. S15 TGA curves of TT-IDG-C8 and TT-IDG-C12 measured under N_2 atmosphere.

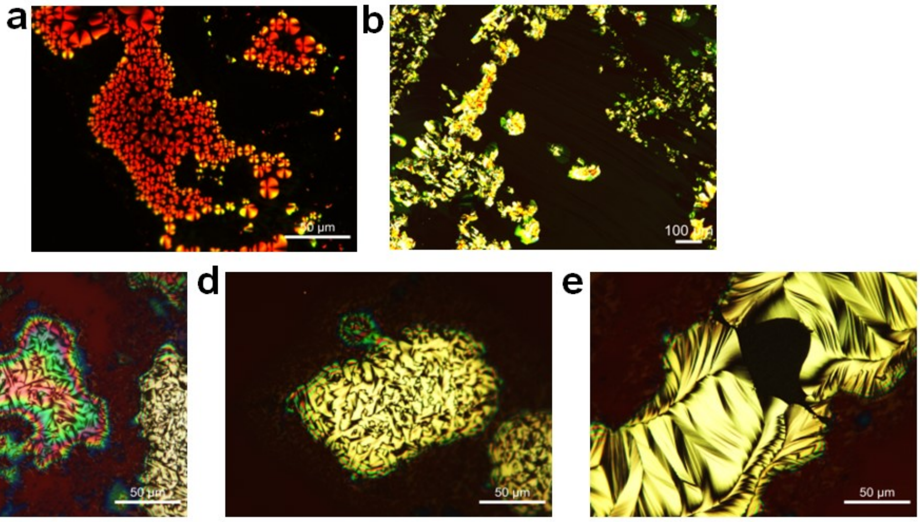


Fig. S16 The polarized optical images of TT-IDG-C8 (a, b) films cooling from 250 °C to 100 °C (a), 25 °C (b) and TT-IDG-C12 (c-e) films cooling from 280 °C to 25 °C (c), 50 °C (d) and 100 °C (e).

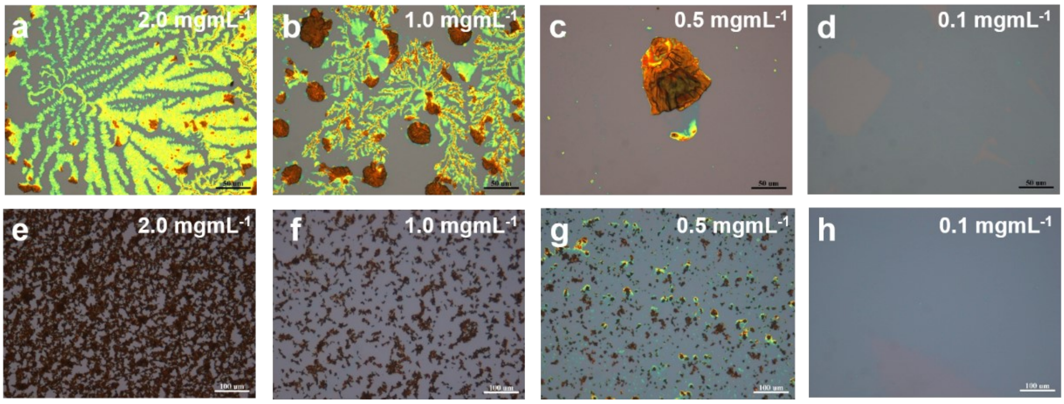


Fig. S17 The optical images of TT-IDG-C8 films fabricated by a varied concentration of chlorobenzene and methylbenzene as (a, e) 2.0, (b, f) 1.0, (c, g) 0.5 and (d, h) 0.1 mgmL^{-1}, respectively.

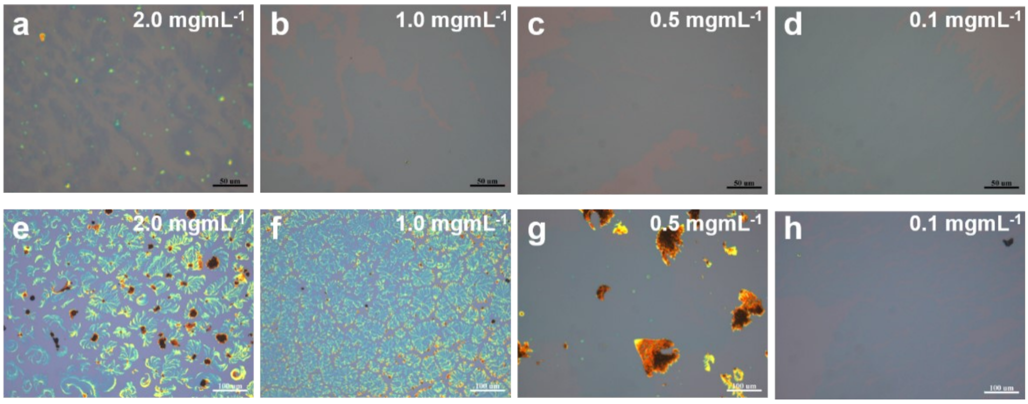


Fig. S18 The optical images of TT-IDG-C12 films fabricated by a varied concentration of chlorobenzene and methylbenzene as (a, e) 2.0, (b, f) 1.0, (c, g) 0.5 and (d, h) 0.1 mgmL^{-1}, respectively.

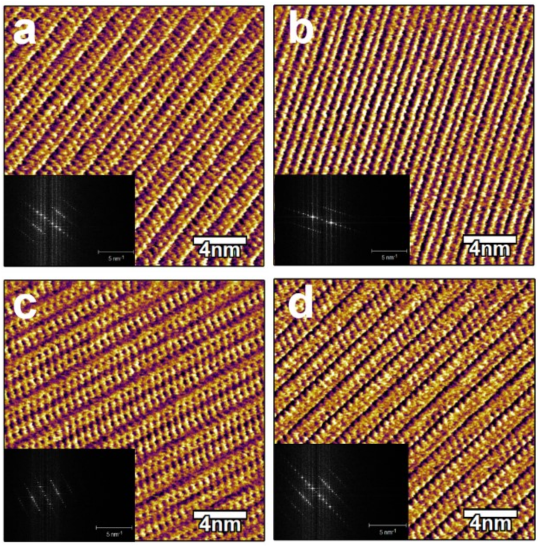


Fig. S19 HRAFM of liquid crystal bilayer and trilayer for TT-IDG-C8 (a, b) and TT-IDG-C12 (c, d), the insert pictures were the corresponding FFT images.

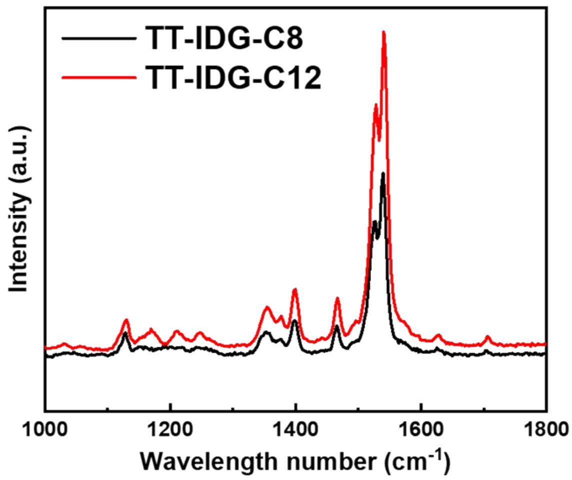


Fig. S20 Raman spectra of liquid crystal monolayer for TT-IDG-C8 and TT-IDG-C12.

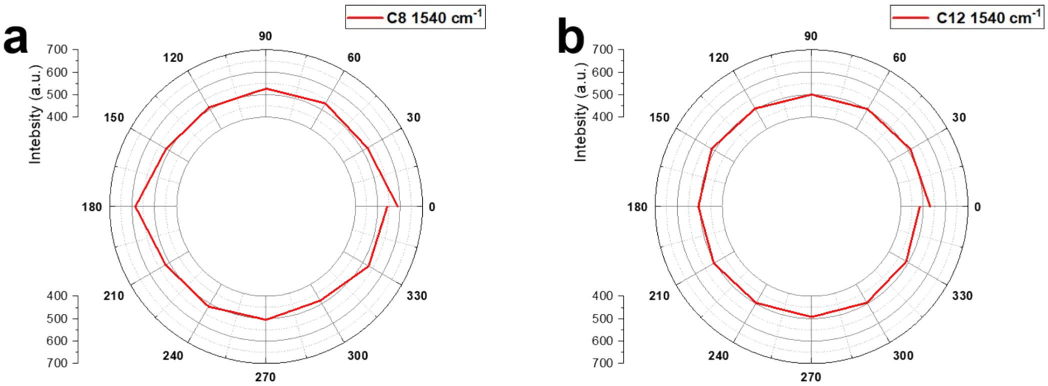


Fig. S21 Radar graphs of Raman intensity at 1540 cm^{-1} on different directions of liquid crystal monolayer of TT-IDG-C8 (a) and TT-IDG-C12 (b).

Reference

1. Q. Tang, L. Jiang, Y. Tong, H. Li, Y. Liu, Z. Wang, W. Hu, Y. Liu and D. Zhu, *Adv. Mater.*, 2008, **20**, 2947-2951.
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