Supplementary Information

(3*E*,7*E*)-3,7-Bis(2-oxoindolin-3-ylidene)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione based polymers for balanced ambipolar organic thin film transistors

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Contents

1. Materials and Characterization

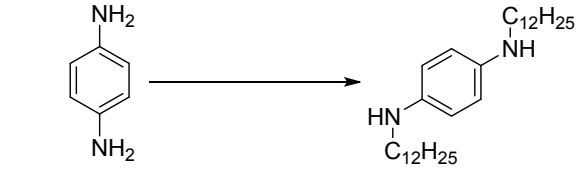
All chemicals were purchased from commercial sources and used without further purification unless specified. 6-Bromo-1-(2-decyltetradecyl)indoline-2,3-dione[1] and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene[2] were synthesized according to the literature. Computational simulations were performed using density function theory (DFT) calculation with the 6-311G+(d,p) basis set and all the orbital pictures were obtained using GaussView 5.0 software. GPC measurements were performed on a Waters SEC system using chlorobezene as eluent and polystyrene as standards at 80°C. TGA measurementss were carried out on a TA Instruments SDT 2960 at a scan rate of 10°C min^{-1} under nitrogen. The UV-Vis-IR absorption spectra of polymers were recorded on a Thermo Scientific model GENESYS™ 10S VIS spectrophotometer. Cyclic voltammetry (CV) data were obtained on a CHI600E electrochemical analyser using an Ag/AgCl reference

electrode and two Pt disk electrodes as the working and counter electrodes in a 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 100 mV s^{-1}. Ferrocene was used as the reference, which has a HOMO energy value of -4.8 eV.[3] NMR data was recorded with a Bruker DPX 300 MHz spectrometer with chemical shifts relative to tetramethylsilane (TMS, 0 ppm). Transmission XRD measurements were carried out on a Bruker Smart 6000 CCD 3-circle D8 diffractometer with a Cu RA (Rigaku) X-ray source (λ = 0.15406 nm) and the polymer flakes stacked between two Mylar substrates. Atomic force microscopy (AFM) images were taken on polymer thin films spin-coated on the dodecyltrichlorosilane (DDTS)-modified SiO_2/Si substrates with a Dimension 3100 scanning probe microscope.

2. Fabrication and characterization of OTFT devices

The bottom-contact, bottom-gate configuration was used for all OTFT devices. The preparation procedure of the substrate and device is as follows. A heavily n-doped SiO_2/Si wafer with ~300 nm-thick SiO_2 was patterned with gold source and drain pairs by conventional photolithography and thermal deposition. Then the substrate was treated with air plasma, followed by cleaning with acetone and isopropanol in an ultra-sonic bath. Subsequently, the substrate was placed in a solution of dodecyltrichlorosilane (DDTS) in toluene (3 % in toluene) at room temperature for 20 min. the substrate was washed with toluene and dried under a nitrogen flow. Then a polymer solution in chloroform (5 mg mL^{-1}) was spin-coated onto the substrate at 3000 rpm for 60s to give a polymer film (~40 nm), which was further subject to thermal annealing at different temperatures for 20 min in a glove box. All the OTFT devices have a channel length (L) of 30 μm and a channel width (W) of 1000 μm, and were characterized in the same glove box using an Agilent B2912A Semiconductor Analyser.

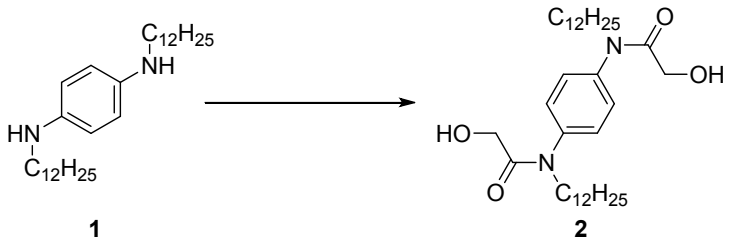
3. Synthetic procedures



p-phenylenediamine **1**

Synthesis of *N*,*N*'-didodecylbenzene-1,4-diamine (1)

To a solution of *p*-phenylenediamine (4.33 g, 40.0 mmol) in ethanol (120 mL), 1-bromododecane (19.94 g, 80.0 mmol) was added. The reaction mixture was stirred under reflux for 24 h. Upon cooling to room temperature, the reaction mixture was filtered. The filter cake was washed with ethanol and then dried in vacuo to give **1**. Yield: 4.45 g (25%). ^{1}H-NMR (300 MHz, DMSO-d_6) δ 6.90 (s, 4H), 3.07 (t, J = 7.0 Hz, 4H), 1.60 – 1.48 (m, 4H), 1.24 (br, 36H), 0.85 (t, J = 6.4 Hz, 6H).

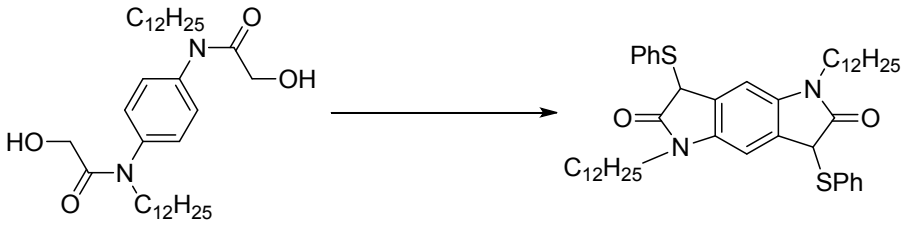


1 **2**

Synthesis of *N*,*N*'-(1,4-phenylene)bis(N-dodecyl-2-hydroxyacetamide) (2)

To a solution of **1** (4.45 g, 10.0 mmol) and triethylamine (5.2 mL) in CH_2Cl_2 (50 mL), acetoxyacetyl chloride (2.4 mL, 22.3 mmol) was added dropwise at 0°C. Then the reaction mixture was allowed to warm to room temperature and stirred for 15 h. Then the reaction was quenched with saturated $NaHCO_3$ aqueous solution. The organic phase was further washed with brine twice and dried over anhydrous Na_2SO_4. Upon removal of solvent in vacuo, the intermediate acetoxy amide was dissolved in a mixture solvent of THF (50 mL), methanol (45 mL), and water (5 mL) before K_2CO_3 (13.8 g, 100 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. The solid was then filtered off and washed with CH_2Cl_2. The combined filtrate was washed with brine, dried over Na_2SO_4 and concentrated in vacuo to give the crude product, which was further purified by silica gel column chromatography with hexane : ethyl acetate (1:1) to

give **2**. Yield: 3.04 g (54%). ^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.36 (s, 4H), 4.58 (t, J = 5.7 Hz, 2H), 3.71 (s, 4H), 3.63 (t, J = 7.0 Hz, 4H), 1.45 – 1.30 (m, 4H), 1.21 – 1.19 (m, 36H), 0.85 (t, J = 6.4 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.35, 140.12, 129.83, 60.57, 49.77, 31.89, 29.60, 29.54, 29.32, 27.72, 26.69, 22.67, 14.11.

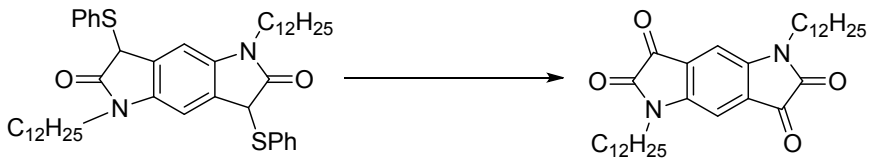


2 **3**

Synthesis of 1,5-didodecyl-3,7-bis(phenylthio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (3)

To a solution of oxalyl chloride (0.85 mL, 9.80 mmol) in CH_2Cl_2 (30 mL) at -78°C, was added dimethyl sulfoxide (DMSO) (1.3 mL, 18.3 mmol) in CH_2Cl_2 (10 mL) dropwise. After stirring for 30 min, a solution of **2** (2.50 g, 4.46 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred for another hour, and then triethylamine (6.0 mL, 43.0 mmol) was added and the solution was allowed to warm to room temperature. After stirring for another 1.5 h, CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ aqueous solution (150 mL) were added. The organic phase was separated and washed with saturated $NaHCO_3$ aqueous solution twice and dried over anhydrous Na_2SO_4. Upon removal of sovent, the crude gloyamide intermediate was used immediately without further purification. To a solution of the crude gloyamide in CH_2Cl_2 (50 mL), thiophenol (0.91 mL, 8.92 mmol) was added. After stirring at room temperature for 15 h, trifluoroacetic acid (TFAA) (5.7 mL, 40.2 mmol) was added. After stirring for another hour, $BF_3 \bullet Et_2O$ (2.8 mL, 22.0 mmol) was added. The reaction mixture was stirred for another 6 h and quenched by saturated $NaHCO_3$ aqueous solution cautiously. The organic phase was separated and washed with saturated $NaHCO_3$ aqueous solution three times and dried over anhydrous Na_2SO_4. Removing solvent in vacuo gave the crude product **3**, which was used for the next step without further purification. Yield: 1.59 g

(48%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 10H), 6.68 (s, 2H), 4.55 – 4.51 (m, 2H), 3.73 – 3.37 (m, 4H), 1.35 – 1.26 (br, 40H), 0.87 (t, J = 6.4 Hz, 6H).



3 **4**

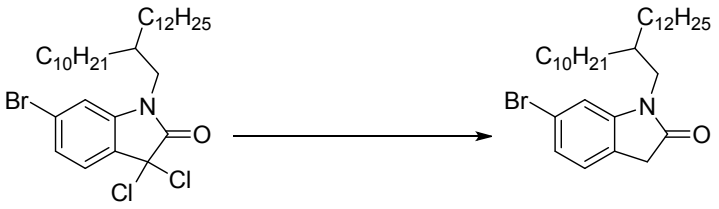
Synthesis of 1,5-didodecylpyrrolo[2,3-*f*]indole-2,3,6,7(1*H*,5*H*)-tetraone (4)

To a solution of **3** (1.40 g, 1.89 mmol) in a solvent of THF (50 mL) and water (8.5 mL), ammonium cerium nitrate (8.28 g, 15.1 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. The solution was then concentrated in vacuo and the residue was purified by silica gel column chromatography with hexane : ethyl acetate (2:1) to give **4**. Yield: 0.491 g (47%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 2H), 3.73 (t, J = 7.4 Hz, 4H), 1.70 – 1.66 (m, 4H), 0.88 (t, J = 6.3 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 183.35, 156.63, 147.33, 123.13, 106.81, 40.84, 31.92, 29.54, 29.48, 29.35, 29.20, 27.10, 26.88, 22.70, 14.14.

6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione **5**

Synthesis of 6-bromo-3,3-dichloro-1-(2-decyltetradecyl)indolin-2-one (5)

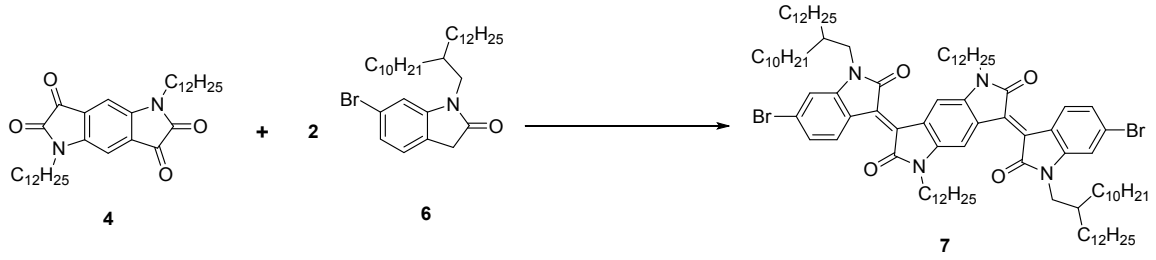
To a solution of 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione (1.13 g, 2.0 mmol) in toluene (15 mL), was added anhydrous PCl_5 (0.92 g, 4.4 mmol). The reaction mixture was stirred at room temperature for 24 h. Then a saturation $NaHCO_3$ aqueous solution was added to quench the reaction and the organic layer was washed with brine three times and dried over anhydrous Na_2SO_4. Removing solventin vacuo gave the unstable **5**, which was used for the next step without further purification.



5 6

Synthesis of 6-bromo-1-(2-decyltetradecyl)indolin-2-one (6)

To a solution of the intermediate in acetic acid (10 mL), zinc powder (0.29 g, 4.4 mmol) was added portionwise. After the resultant mixture was stirred at room temperature for 20 minutes the excess zinc powder was filtered off and washed with dichloromethane. The combined organics was washed brine and saturation $NaHCO_3$ aqueous solution. The solution was then concentrated in vacuo and purified by silica gel column chromatography with hexane : ethyl acetate (10:1) to give **5**. Yield: 0.86 g (78%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.07 (q, 2H), 6.92 (s, 2H), 3.54 (d, J = 7.5 Hz, 2H), 3.46 (s, 2H), 1.83 (m, 1H), 1.38 – 1.25 (br, 40H), 0.88 (t, J = 6.4 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 175.05, 146.47, 125.58, 124.80, 123.39, 121.29, 111.97, 44.63, 35.88, 35.34, 31.94, 31.48, 30.01, 29.67, 29.38, 26.38, 22.72, 14.15

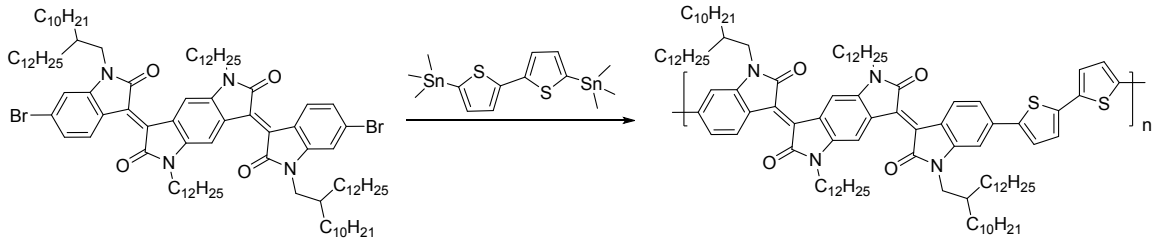


4 6 7

Synthesis of (3*E*,7*E*)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)-1,5-didodecyl-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (7)

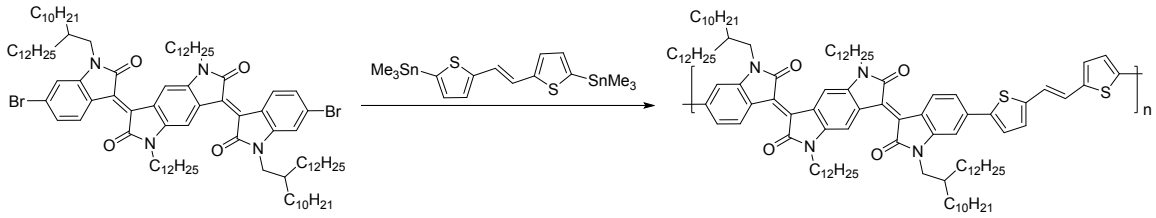
To a solution of **4** (0.25 g, 0.45 mmol) and **5** (0.50 g, 0.50 mmol) in acetic acid (6 mL), was added concentrated HCl aqueous solution (0.05 mL). The reaction mixture was heated to reflux and stirred for 24 h. Upon cooling to room temperature, the precipitate was filtered off from the reaction mixture and was further purified by silica gel column chromatography with chloroform : hexane (1:1) to give **6**. Yield: 0.232 g (32%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.14 (d, J = 8.4 Hz, 2H), 8.82 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.86 (s, 2H), 3.82 (t, J = 6.9 Hz, 2H), 3.62 (d, J = 6.9 Hz, 2H), 1.87 (m, 2H), 1.72

(m, 4H), 1.40 – 1.24 (m, 116H), 0.88 – 0.84 (m, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 168.16, 167.44, 146.57, 140.44, 133.82, 133.25, 131.54, 127.12, 125.20, 125.02, 120.65, 111.63, 109.71, 44.67, 40.44, 36.24, 32.08, 31.68, 31.67, 29.85, 29.51, 27.51, 27.38, 27.23, 26.54, 22.85, 14.28. HRMS $(M + H)^+$ calc. for $C_{98}H_{156}Br_2N_4O_4^+$: 1612.0572; found: 1612.0491.



Synthesis of P1

To a 25 mL Schlenk flask, **6** (68.4 mg, 0.0424 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (20.8 mg, 0.0424 mmol) and tri(*o*-totyl)phosphine (1.0 mg, 0.00330 mmol, 8mol%) were charged. After degassing and refilling argon three times, chlorobenzene (5 mL) and tris(dibenzylideneacetone)-dipalladium (0.8 mg, 0.0008 mmol, 2mol%) were added. The reaction mixture was stirred at 120 °C for 72 h. Upon cooling to room temperature, the reaction mixture was poured into methanol (100 mL). The precipitate was collected by filtration and subject to Soxhlet extraction with acetone and hexanes successively. The residual was dissolved in chloroform and give **P1** upon removal of solvent in vacuo. Yield: 56.2 mg (82%).



Synthesis of P2

P2 was synthesized with **6** (67.0 mg, 0.0415 mmol) and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (21.6 mg, 0.0415 mmol), according to a similar synthetic procedure that was used for **P1**. Yield: 67.2 mg (98%).

4. Additional data

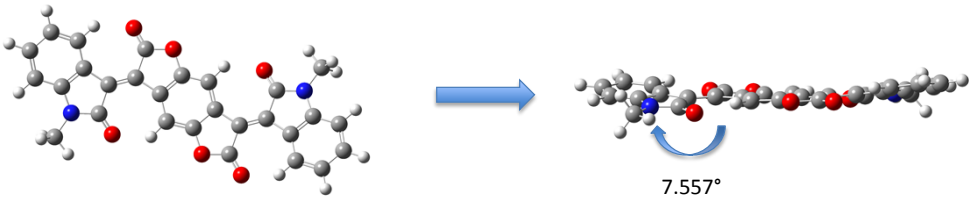


Fig. S1 The geometrical optimization of (3*E*,7*E*)-3,7-bis(1-methyl-2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (IBDF-Me) and the dihedral angle.

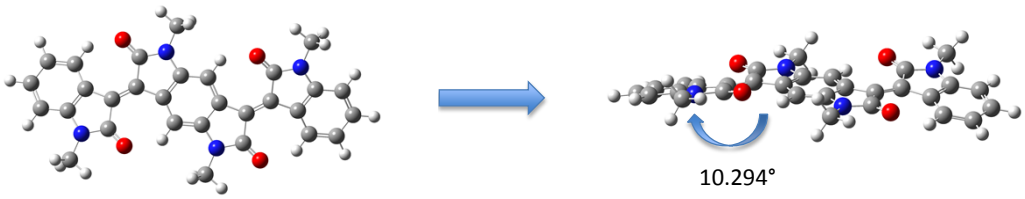


Fig. S2 The geometrical optimization of (3*E*,7*E*)-1,5-dimethyl-3,7-bis(1-methyl-2-oxoindolin-3-ylidene)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (IBDP-Me) and the dihedral angle.

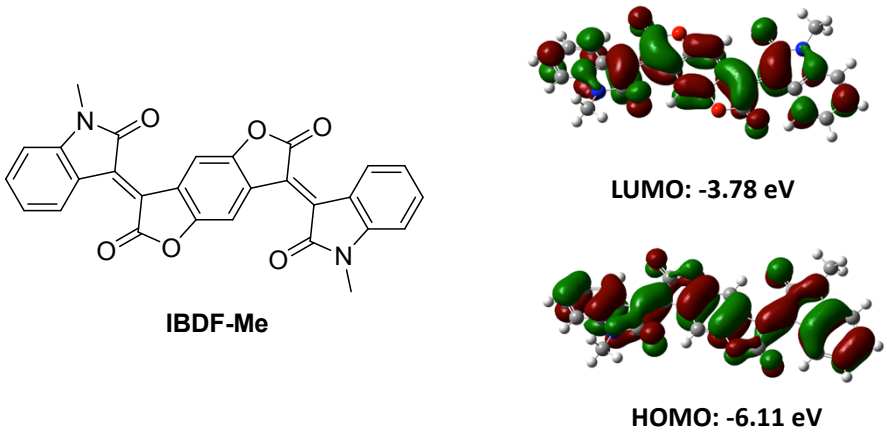


Fig. S3 Structure of IBDF-Me and its optimized LUMO and HOMO distribution.

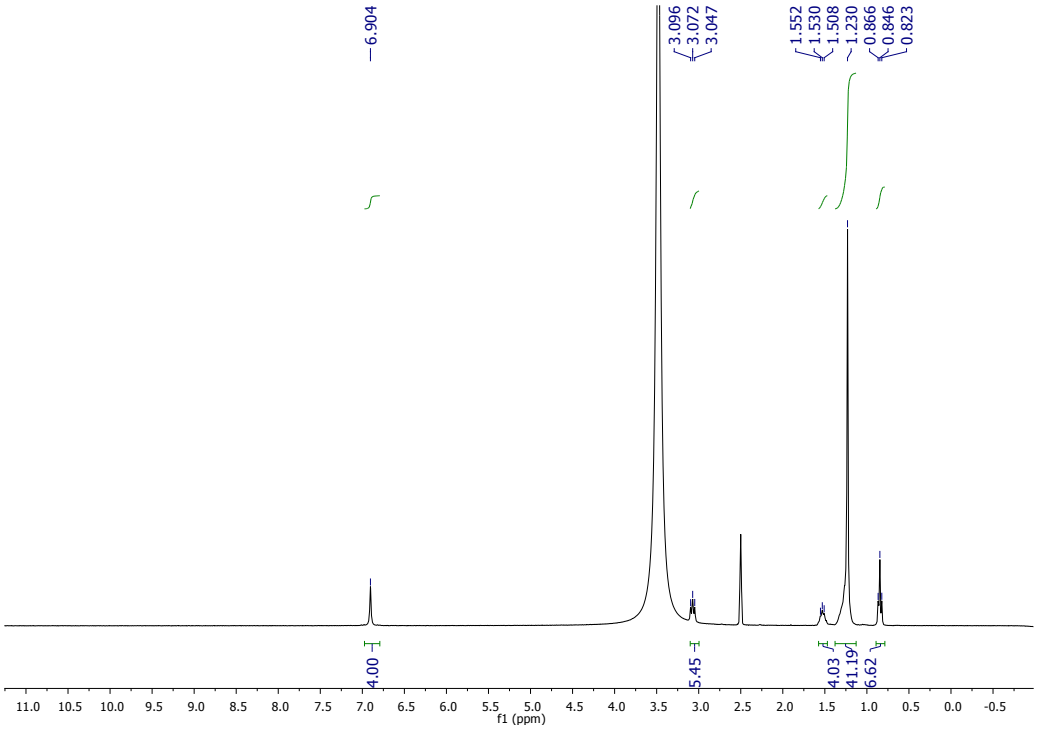


Fig. S4 300 MHz ^{1}H NMR spectrum for *N*,*N'*-didodecylbenzene-1,4-diamine (**1**) in DMSO-d6.

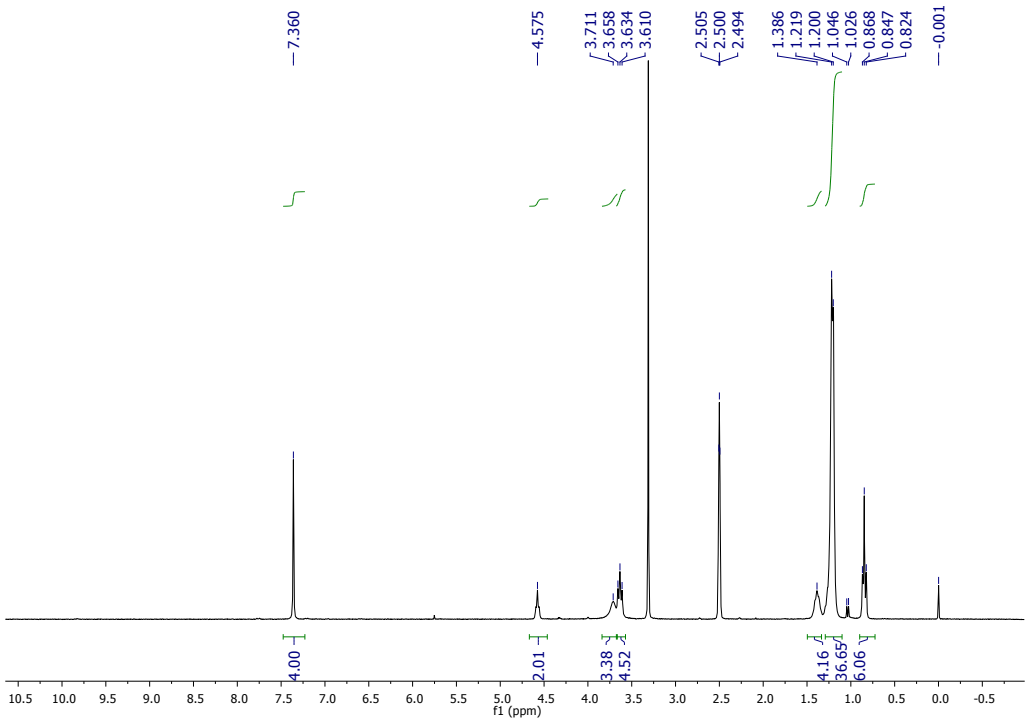


Fig. S5 300 MHz ^{1}H NMR spectrum for *N*,*N*'-(1,4-phenylene)bis(N-dodecyl-2-hydroxyacetamide) (**2)** in DMSO-d_6.

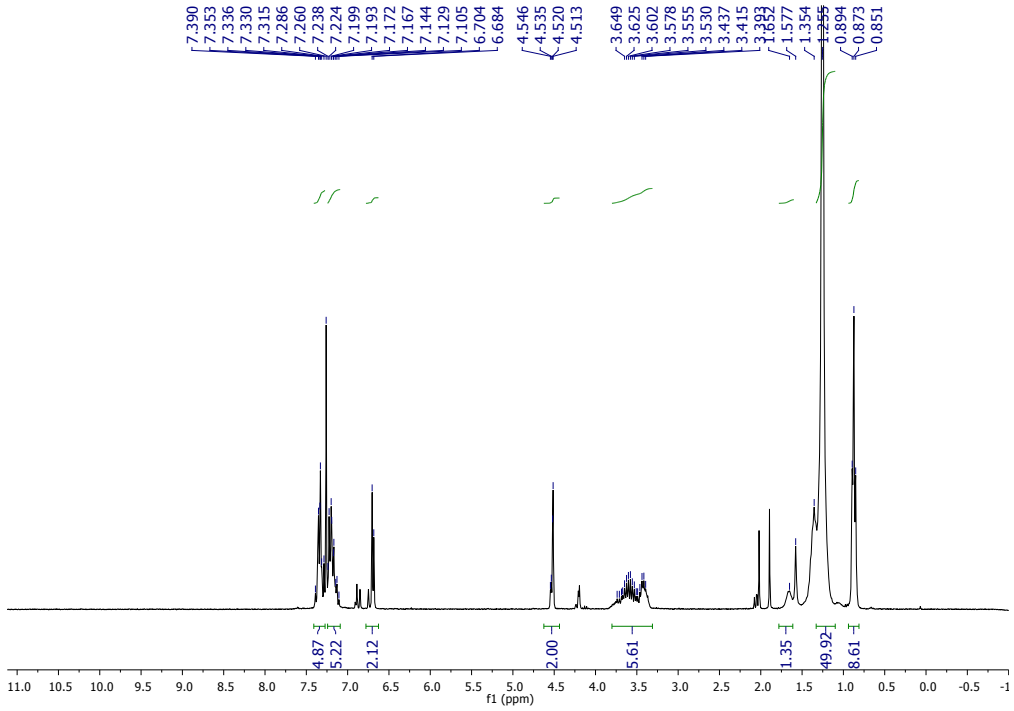


Fig. 6 300 MHz ^{1}H NMR spectrum for 1,5-didodecyl-3,7-bis(phenylthio)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (**3**) in chloroform-d.

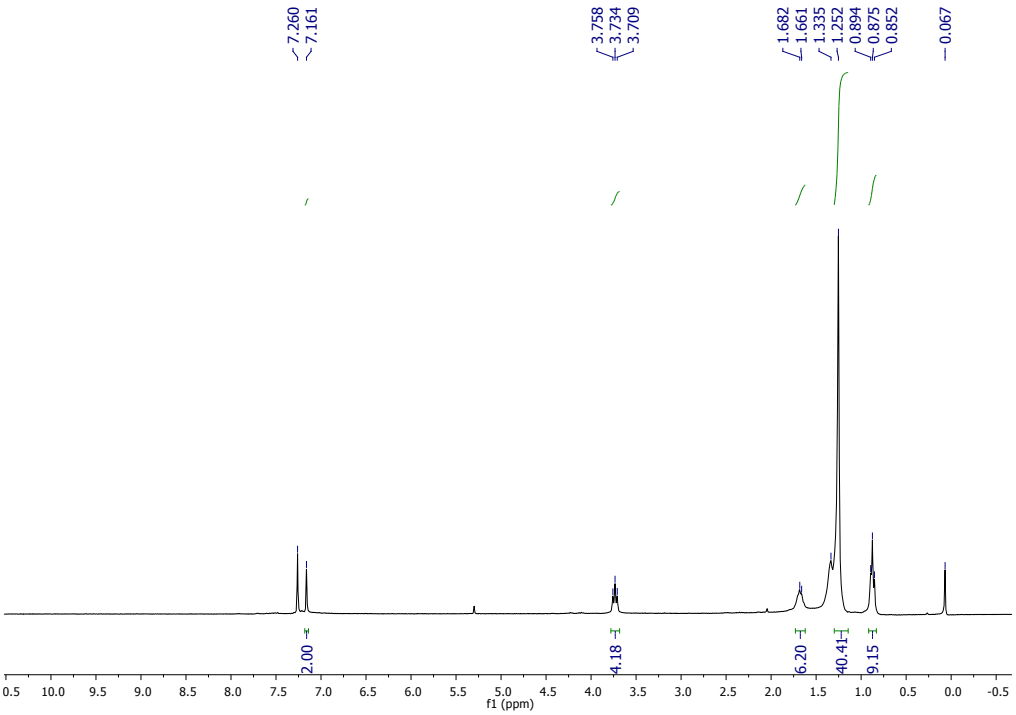


Fig. S7 300 MHz ^{1}H NMR spectrum for 1,5-didodecylpyrrolo[2,3-*f*]indole-2,3,6,7(1*H*,5*H*)-tetraone (**4**) in chloroform-d.

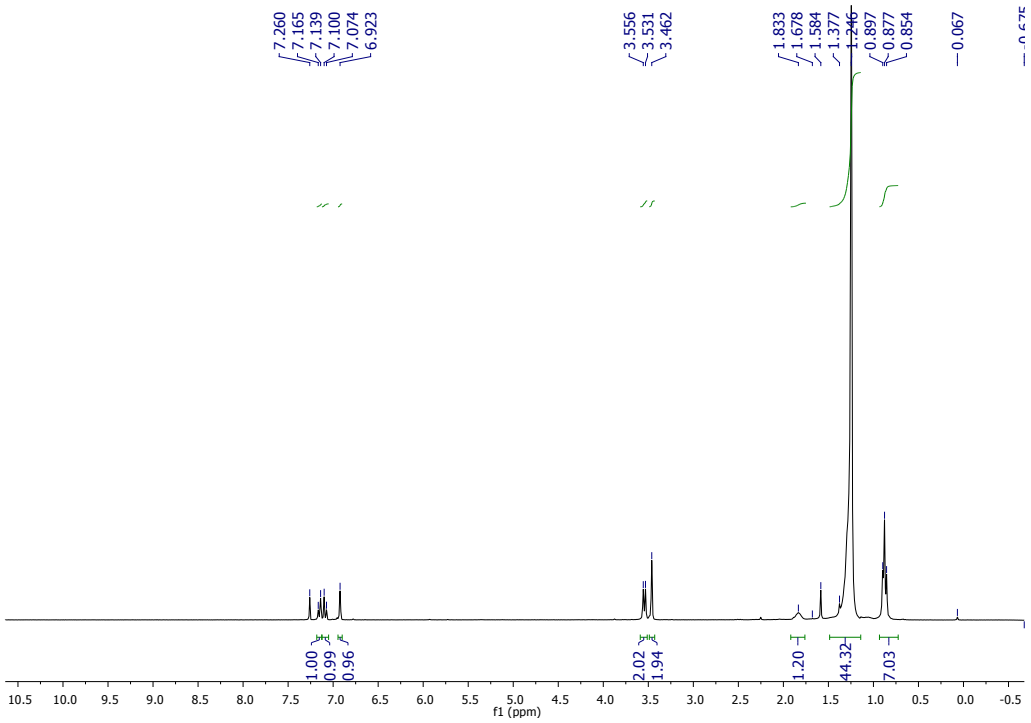


Fig. S8 300 MHz ^{1}H NMR spectrum for 6-bromo-1-(2-decyltetradecyl)indolin-2-one (**6**) in chloroform-d.

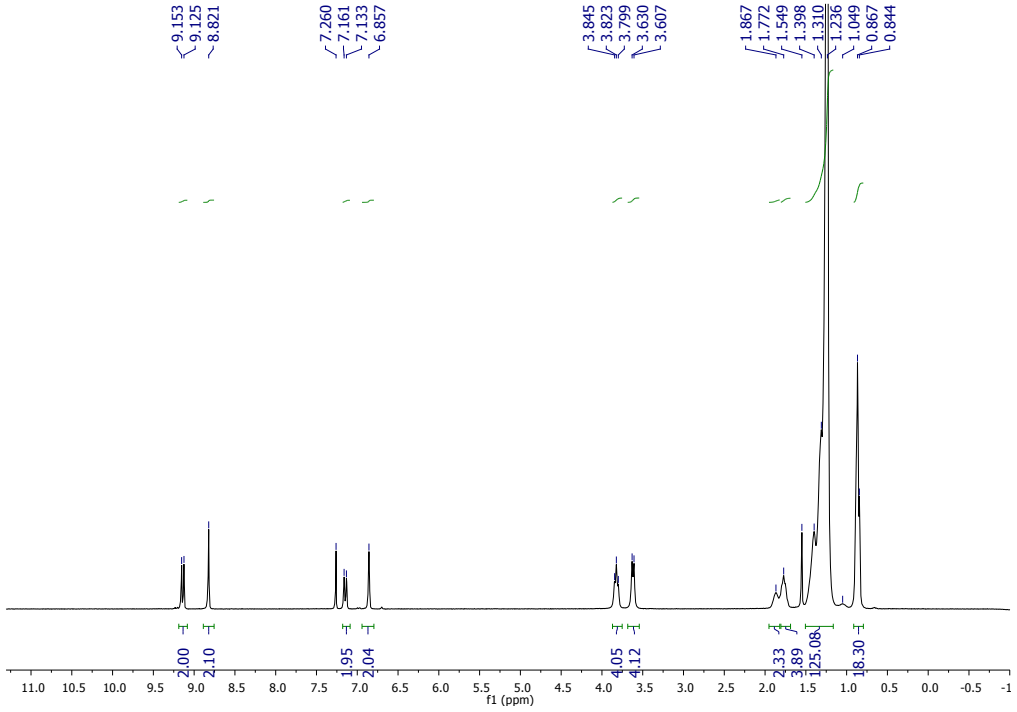


Fig. S9 300 MHz ^{1}H NMR spectrum for (3*E*,7*E*)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)-1,5-didodecyl-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (7) in chloroform-d.

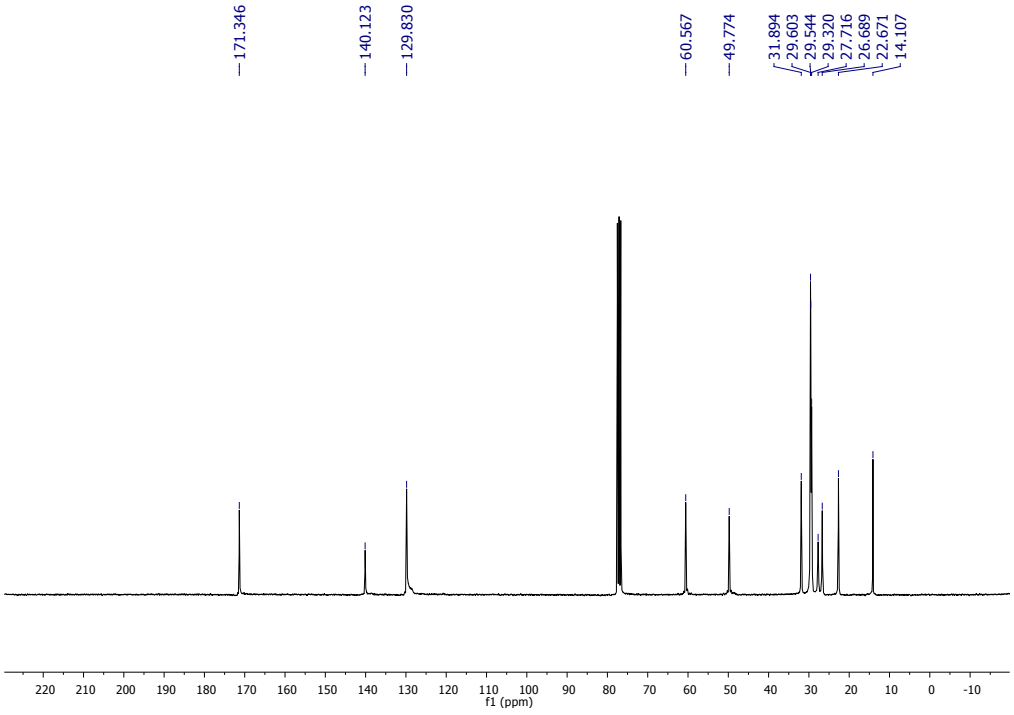


Fig. S10 75 MHz ^{13}C NMR spectrum for *N*,*N*'-(1,4-phenylene)bis(N-dodecyl-2-hydroxyacetamide) (**2)** in chloroform-d.

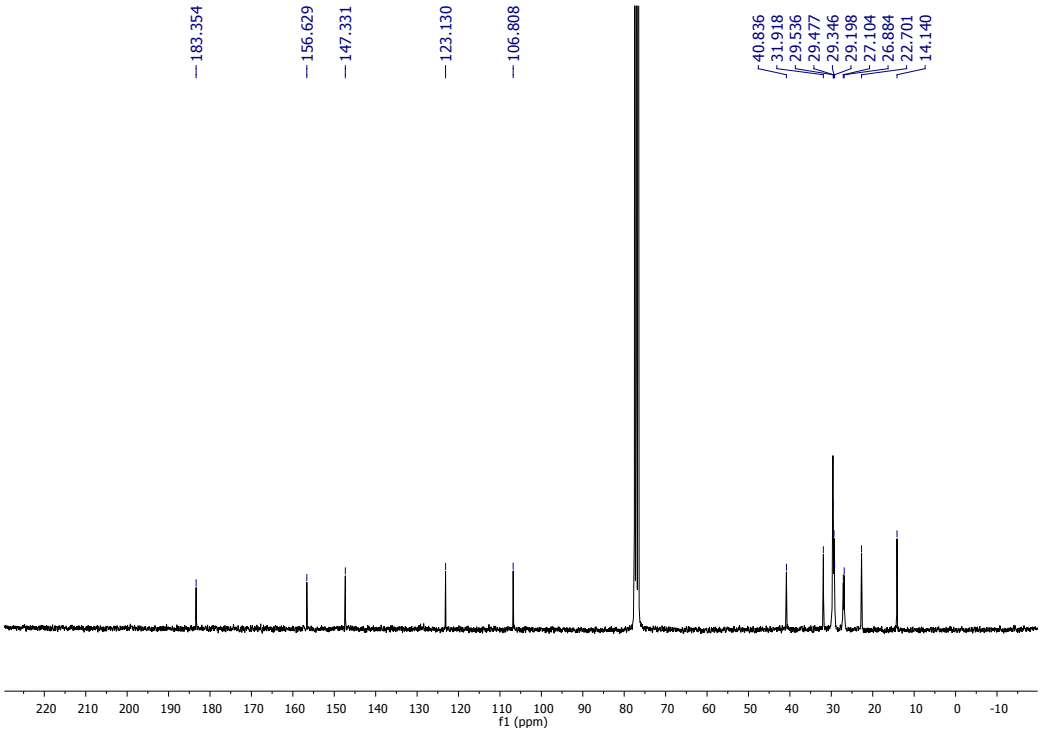


Fig. S11 75 MHz ^{13}C NMR spectrum for 1,5-didodecylpyrrolo[2,3-*f*]indole-2,3,6,7(1*H*,5*H*)-tetraone (**4**) in chloroform-d.

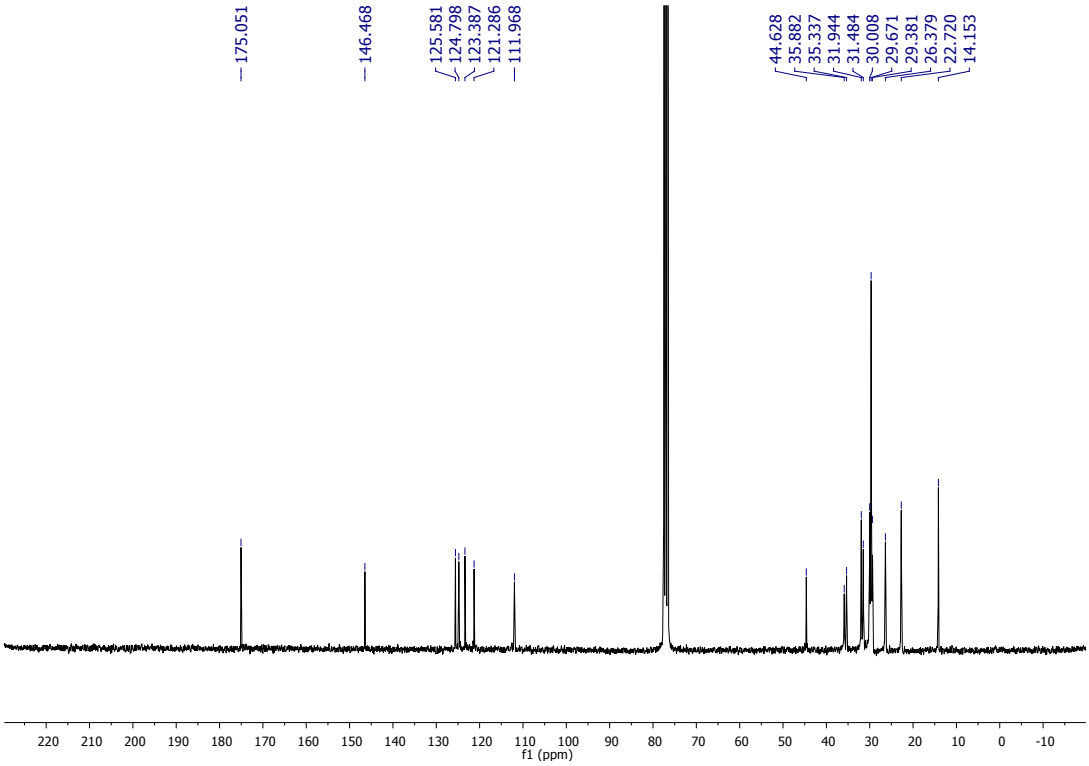


Fig. S12 75 MHz ^{13}C NMR spectrum for 6-bromo-1-(2-decyltetradecyl)indolin-2-one (**6**) in chloroform-d.

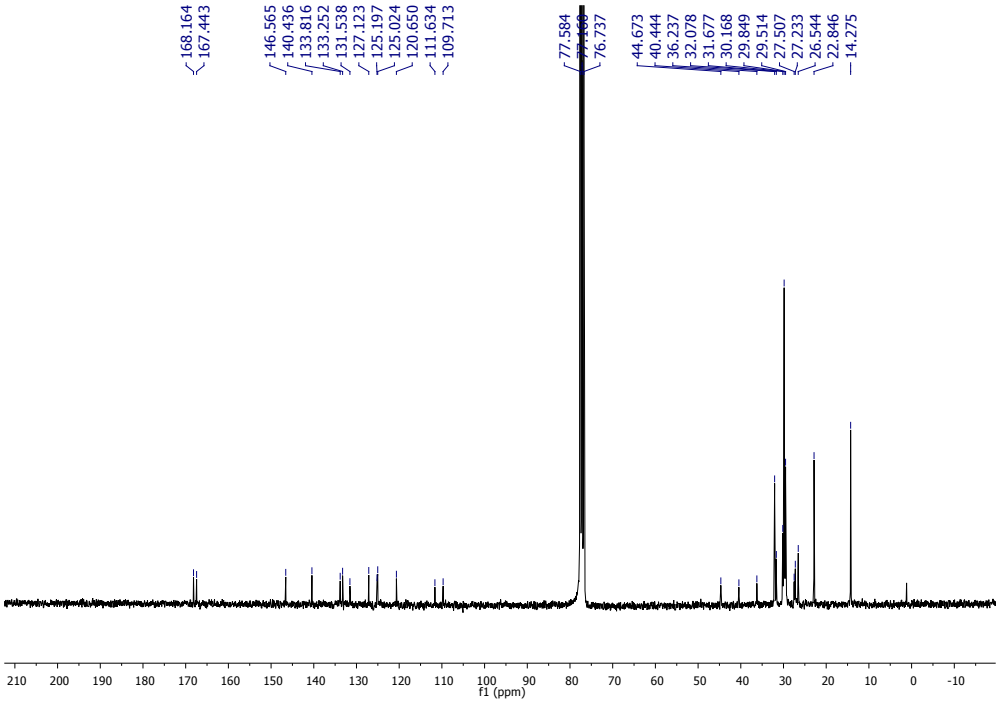


Fig. S13 75 MHz ^{13}C NMR spectrum for (3*E*,7*E*)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)-1,5-didodecyl-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (**7**) in chloroform-d.

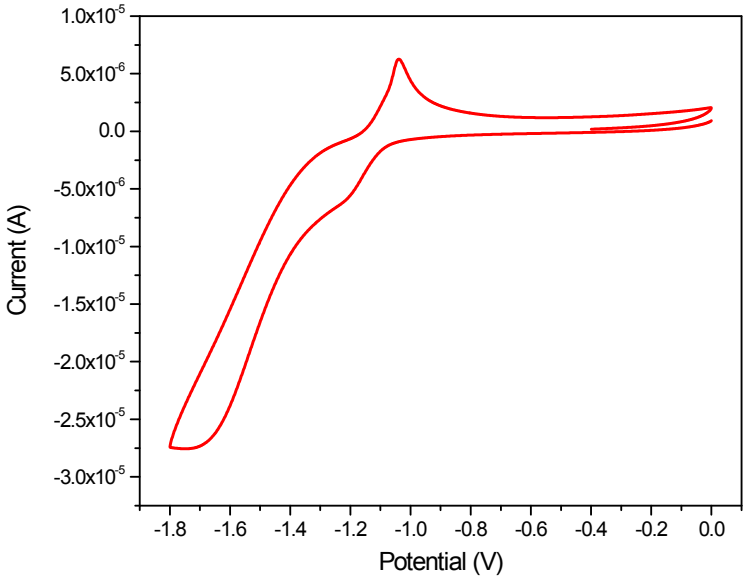


Fig. S14 The reduction cyclic voltammogram of a **P1** thin film at a scan rate of 0.100 V s^{-1}.

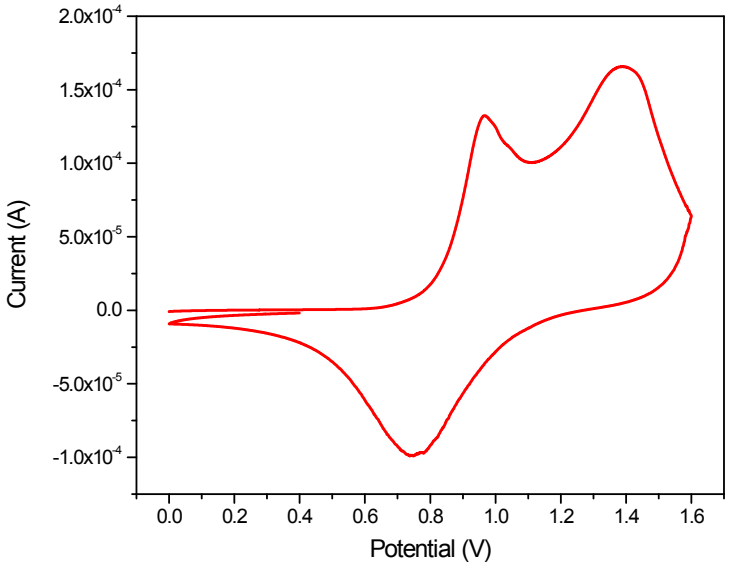


Fig. S15 The oxidation cyclic voltammogram of a **P1** thin film at a scan rate of 0.100 V s^{-1}.

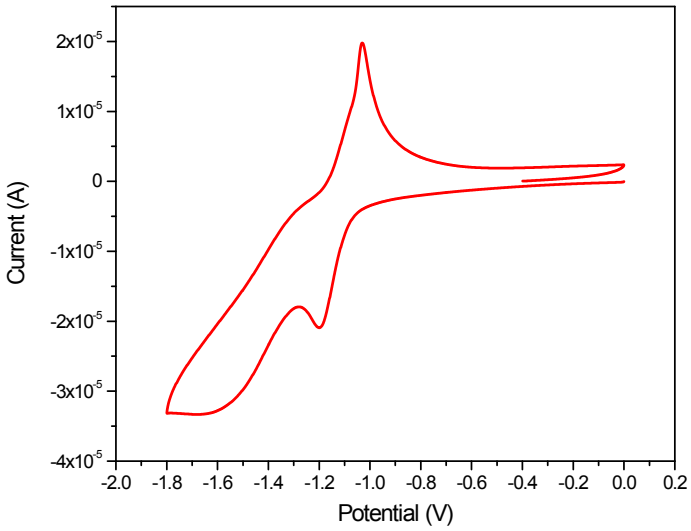


Fig. S16 The reduction cyclic voltammogram of a **P2** thin film at a scan rate of 0.100 V s^{-1}.

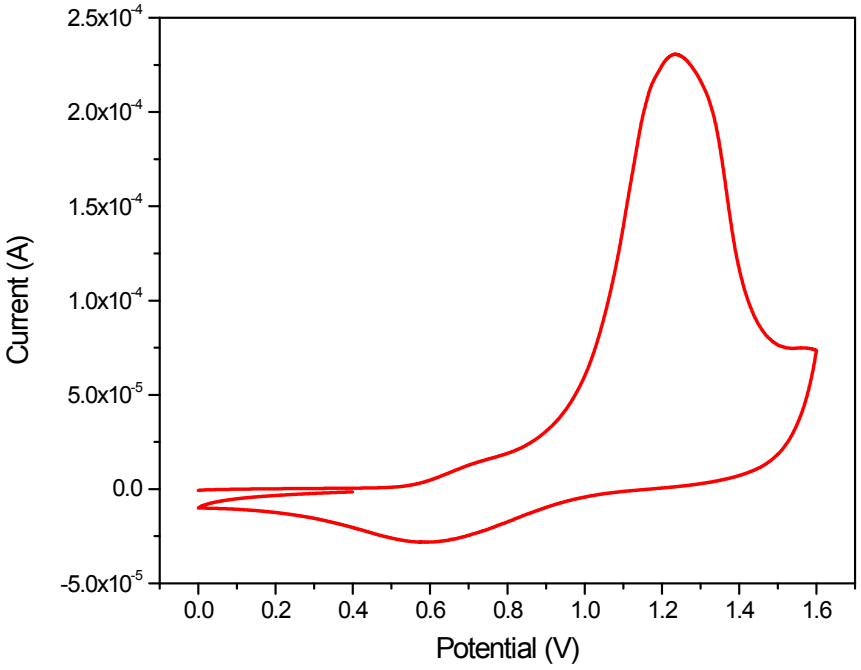


Fig. S17 The oxidation cyclic voltammogram of a **P2** thin film at a scan rate of 0.100 V s^{-1}.

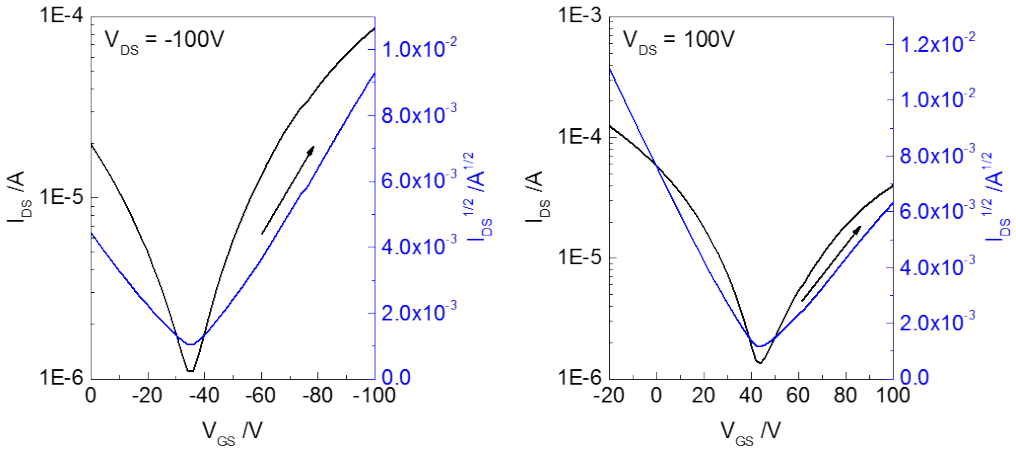


Fig. S13 Transfer curve of an OTFT device based on a thin film of **P2** annealed at 200 °C

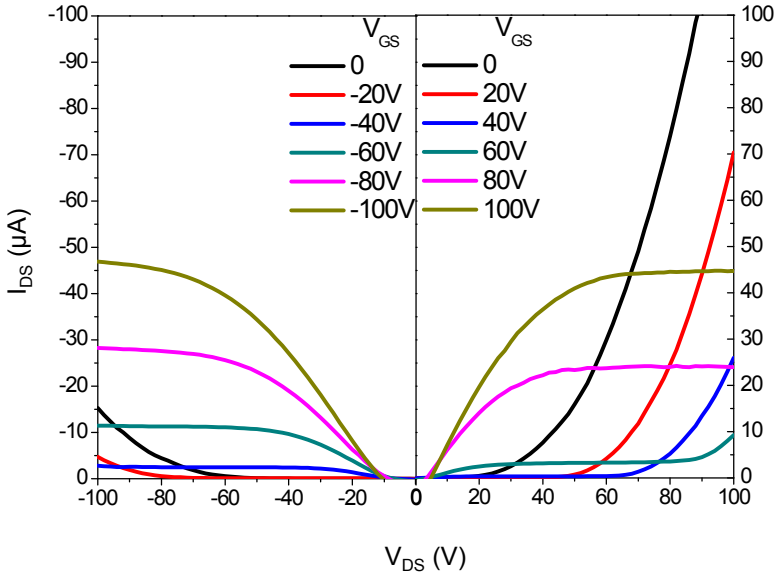


Fig. S14 Output curve of an OTFT device based on a thin film of **P2** annealed at 200 °C.

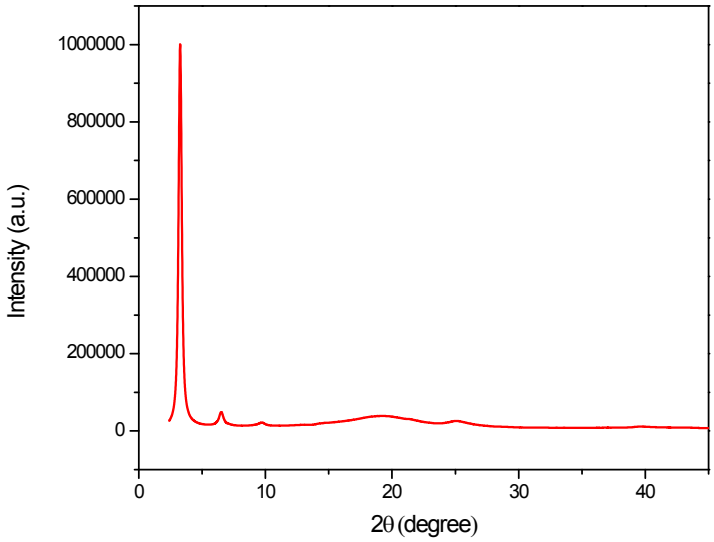


Fig. S15 Transmission XRD pattern of **P1** flakes stacked between two Mylar substrates.

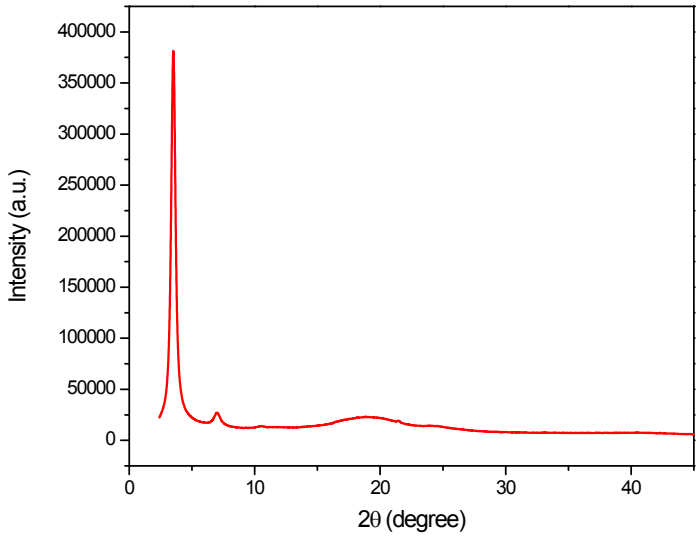


Fig. S16 Transmission XRD pattern of **P2** flakes stacked between two Mylar substrates.

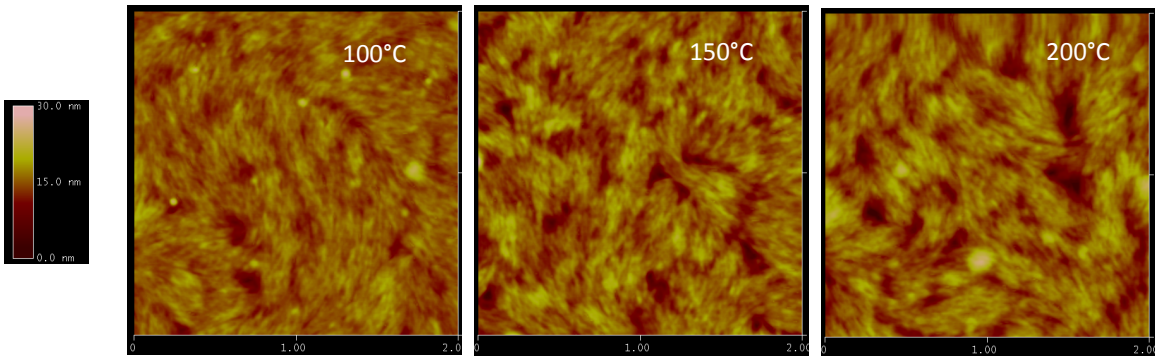


Fig. S17 AFM images (2μm × 2μm each) of **P1** thin films on SiO_2/Si substrates annealed at different temperatures.

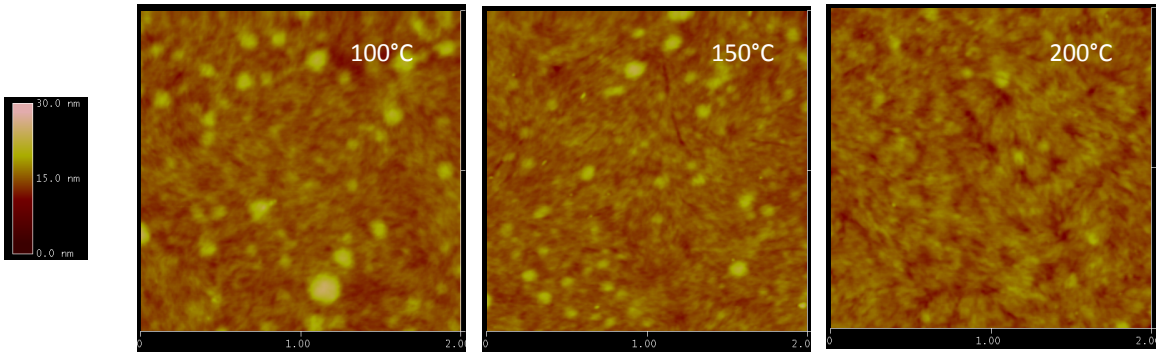


Fig. S18 AFM images (2μm × 2μm each) of **P2** thin films on SiO_2/Si substrates annealed at different temperatures.

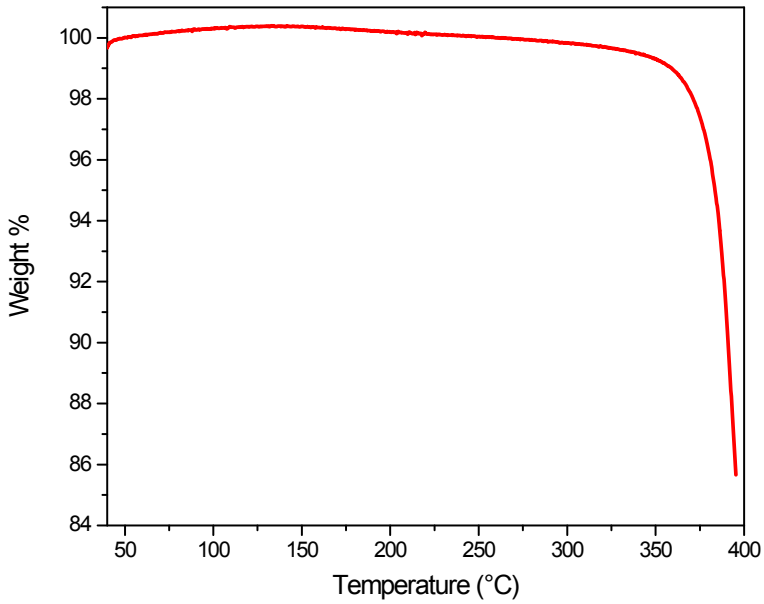


Fig. S19 TGA curve of **P1** under nitrogen at a heating rate of 10 °C min^{-1}.

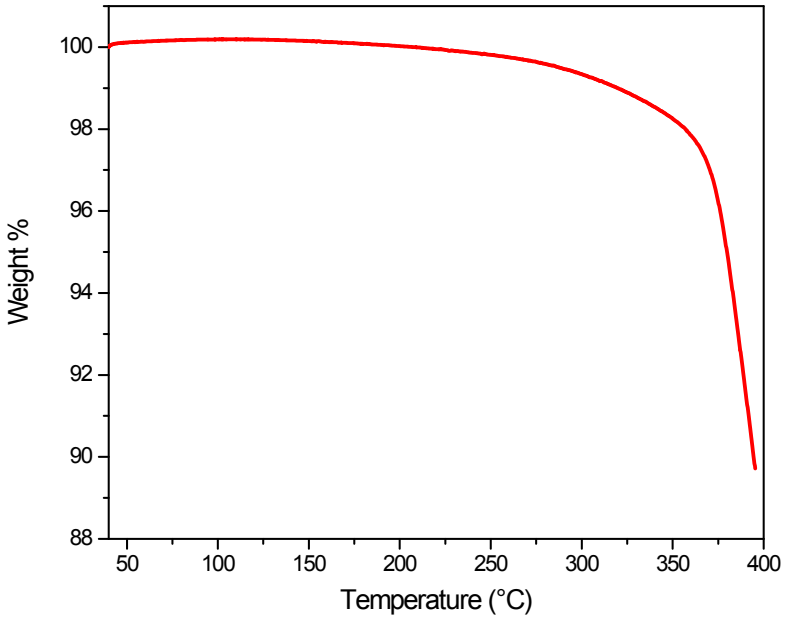


Fig. S20 TGA curve of **P2** under nitrogen at a heating rate of 10 °C min^{-1}.

Table S1 the summary of OTFT performance of **P1** and **P2**

Polymer	Annealing temperature (°C)	Hole mobility[a] (cm^2 V^{-1} s^{-1})	Electron mobility[a] (cm^2 V^{-1} s^{-1})
P1	100	0.15 (0.17)	0.063 (0.071)
	150	0.16 (0.19)	0.064 (0.088)
	200	0.040 (0.057)	0.073 (0.089)
P2	100	0.055 (0.062)	0.023 (0.027)
	150	0.081 (0.093)	0.037 (0.045)
	200	0.10 (0.10)	0.055 (0.075)
	250	0.091 (0.11)	0.055 (0.067)

[a] The average (maximum) mobility was calculated from the saturation region

5. References

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2. R. Kim, P. S. K. Amegadze, I. Kang, H.-J. Yun, Y.-Y. Noh, S.-K. Kwon and Y.-H. Kim, *Adv. Funct. Mater.*, 2013, **23**, 5719–5727.
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