

Supplementary Information

**A new n-type polymer based on *N,N'*-dialkoxynaphthalenediimide (NDIO)
for organic thin-film transistors and all-polymer solar cells**

Yinghui He^{a‡}, Xu Li^{b‡}, Haitao Liu^b, Han Meng^a, Guan Ying Wang^a, Bo Cui^c, Jinliang Wang^{b*}
and Yuning Li^{a*}

^aDepartment of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN),
University of Waterloo, 200 University Ave West, Waterloo, N2L 3G1, Canada.

^bInstitute of Chemistry, Henan Academy of Sciences, 56 Hongzhuan Road, Jinshui
District, Zhengzhou, Henan, China, 450002.

^c*Department of Electrical and Computer Engineering, University of Waterloo, 200
University Ave West, Waterloo, N2L 3G1, Canada.*

Contents

- 1. Materials and Characterization**
- 2. Fabrication and characterization of OTFT devices**
- 3. Fabrication and characterization of all-PSC devices**
- 4. Synthetic procedures**
- 5. Additional data**
- 6. References**

1. Materials and Characterization

All chemicals were purchased from commercial sources and used without further purification unless specified. High-temperature gel-permeation chromatography (HT-GPC) measurements were performed on a Malvern system at 140 °C using 1,2,4-trichlorobenzene as eluent and polystyrene as standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were

Supplementary Information

carried out on a TA Instruments SDT 2960 at a scan rate of $10^{\circ}\text{C min}^{-1}$ 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 .¹ NMR data was recorded with a Bruker Advance 400 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 ($\lambda = 0.15406\text{ nm}$) 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

A bottom-gate bottom-contact (BGBC) 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 $\sim 300\text{ nm}$ -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 ($\sim 40\text{ nm}$), 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 $30\text{ }\mu\text{m}$ and a channel width

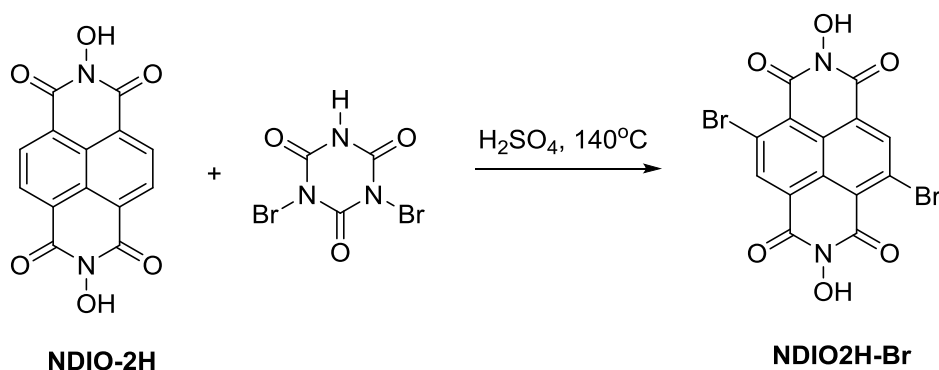
(W) of 1000 μm , and were characterized in the same glove box using an Agilent B2912A Semiconductor Analyser.

3. Fabrication and characterization of all-PSC devices

The all-PSC devices were fabricated in a standard device architecture with the following structure: ITO/PEDOT:PSS/ **P(NDIO2OD-T)**:PTB7-Th/LiF/Al. First, the ITO glass substrates were cleaned by sonication in DI water, acetone and isopropanol successively. Then the substrates were further cleaned in a plasma cleaner. A layer (~ 40 nm) PEDOT:PSS was spin-coated onto the ITO substrates using the Al 4083 PEDOT:PSS dispersion. The substrates were then dried on a hotplate at 145 $^{\circ}\text{C}$ for 20 minutes. An active layer (~ 110 nm) was spin-coated onto of the PEDOT:PSS using a solution of **P(NDIO2OD-T)**:PTB7-Th in chlorobenzene (12 mg mL^{-1} , 1:1 weight ratio). The resultant films were dried in the vacuum for 60 minutes before a layer of LiF (~ 1 nm) and a layer of Al (~ 100 nm) were thermal deposited onto the substrates to give the solar cell devices. The devices were characterized under 100 mW cm^{-2} AM 1.5 G illumination conditions.

4. Synthetic procedures

Synthesis of NDIO-2H-Br

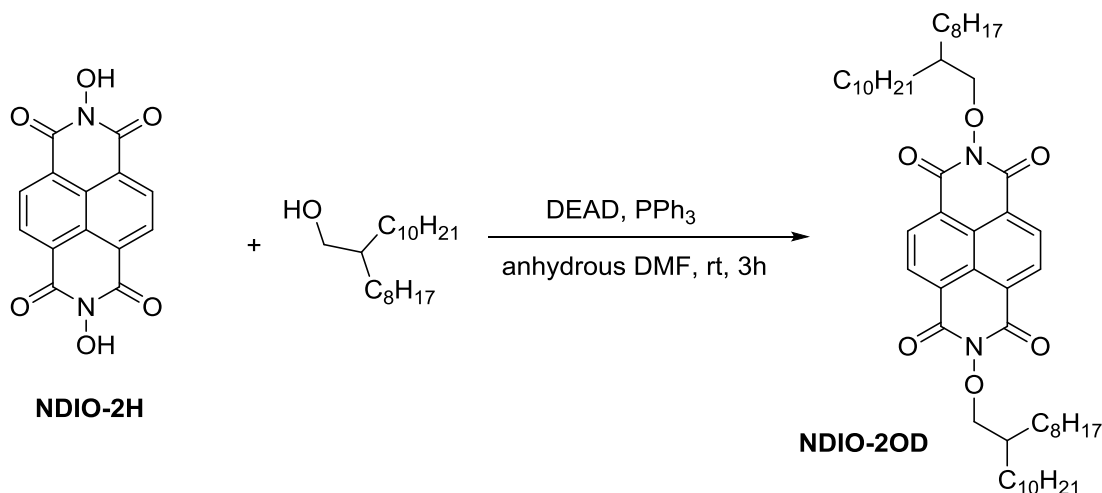


A 50 mL round-bottom flask was loaded on the bench top with 2,7-Dihydroxybenzo[Imn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**NDIO-2H**, 1.491 g, 5

Supplementary Information

mmol) and dibromoisocyanuric acid (DBI, 2.9 g, 10.13 mmol), sulfuric acid (conc., ~40 mL) and a stir-bar. The flask was fitted with a reflux condenser and heated to 140 °C using an oil bath for 48 h. The reaction was allowed to cool to room temperature and was poured into water (~200 mL) containing ice which resulted in the formation of a yellow precipitate. The mixture was stirred in ice water until all the ice had melted and then the yellow precipitate was filtered and washed with distilled water to isolate the product. The compound **NDIO-2H-Br** (1.730 g, 76%) was isolated as a yellow solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.71 (s, 2H), 11.18 (s, 2H, N-OH).

The synthesis of 2,7-bis((2-octyldodecyl)oxy)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDIO2OD)

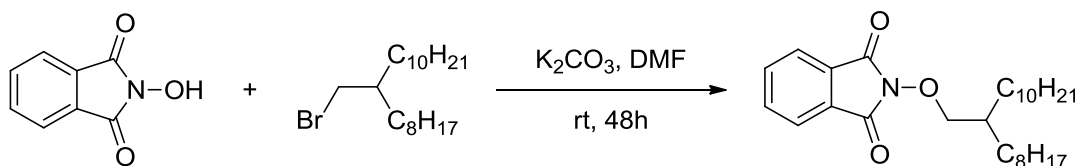


Under N₂, NDIO-2H (0.596 g, 2.0 mmol) and PPh₃ (1.31 g, 5.0 mmol) were suspended in anhydrous DMF (10 mL). 2-Octyl-1-dodecanol (1.49 g, 5.0 mmol) and DEAD (0.87 g mL, 5.0 mmol) was added drop-wise over 10 min. The mixture was stirred for 3 h. The residue was extracted with CH₂Cl₂. The organic layer was washed with water and brine, Combined organic layers were dried with Na₂SO₄, solvent was removed in vacuo and the residue was purified with column chromatography on silica gel in Petroleum ether/dichloromethane (2:1 by vol.) afforded a light yellow solid (0.58 g, 34%). ¹H NMR (400 MHz, CDCl₃) δ: 0.90-0.86 (m, 6H, -CH₃), 1.59-1.27 (m, 32H, -CH₂CH₃), 1.92-1.90 (t, 1H, -CH), 4.16-4.15 (d, *J*= 7.2 Hz, 2H, -CHCH₂-), 8.80 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.15, 22.72, 26.78, 29.37,

Supplementary Information

29.39, 29.64, 29.67, 29.71, 30.01, 31.11, 31.94, 37.68, 80.09, 126.17, 127.34, 131.37, 159.53.

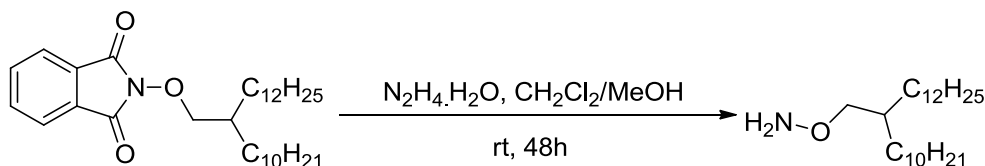
Synthesis of 2-((2-octyldodecyl)oxy)isoindoline-1,3-dione (1)



To a solution of 9-(bromomethyl)nonadecane (5.0 g, 13.83 mmol, 1.0 equiv) and N-hydroxyphthalimide (3.39 g, 20.75 mmol, 1.5 equiv) in DMF (200 mL) was added K₂CO₃ (3.82 g, 27.66 mmol, 2.0 equiv). The reaction was stirred for 48 h at room temperature and quenched with saturated aq. NaHCO₃ (150 mL). The reaction mixture was extracted with CH₂Cl₂ and the combined organic layer was washed with H₂O and saturated aq. NaHCO₃ until the aqueous layer became colorless. The organic layer was then washed with brine and dried over Na₂SO₄. After removal of the solvent in vacuo, the target compound was afforded as light yellow oil (5.68 g, yield: 92.5%).

¹H NMR (400 MHz, CDCl₃) δ: 0.90-0.86 (t, 6H, -CH₃), 1.52-1.27 (s, 32H, -CH₂CH₃), 1.83-1.79 (m, 1H, -CH), 4.10-4.08 (d, *J* = 6.0 Hz, 2H, -CHCH₂-), 7.75-7.73 (q, 2H), 7.84-7.82 (q, 2H).
¹³C NMR (100 MHz, CDCl₃) δ: 14.13, 22.70, 26.63, 29.34, 29.37, 29.59, 29.64, 29.68, 30.00, 31.91, 31.93, 37.39, 81.61. HR MS Calcd for C₂₈H₄₅NO₃ [M + H]⁺: *m/z* 444.3472, Found: 444.3477.

Synthesis of O-(2-octyldodecyl)hydroxylamine (2)

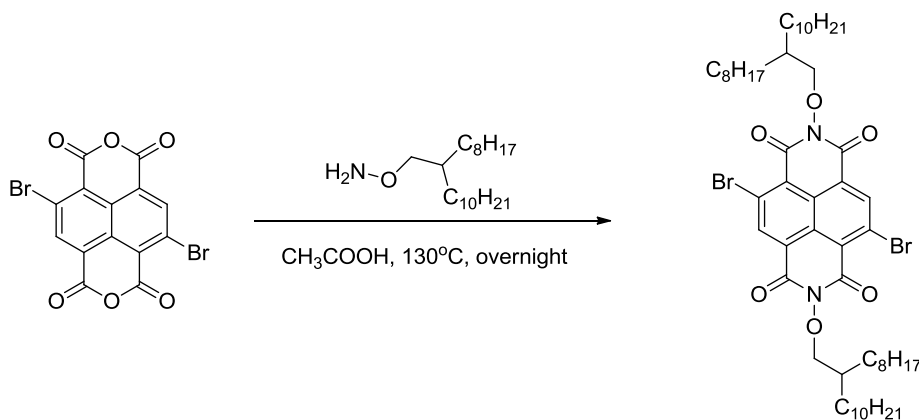


Supplementary Information

To a solution of 2-((2-octyldodecyl)oxy)isoindoline-1,3-dione (5.68 g, 12.80 mmol, 1.0 equiv) in 50:50 (by volume) EtOH/CH₂Cl₂ (140 mL) was added H₂NNH₂•H₂O (2.11 mL, 43.53 mmol, 3.4 equiv). The reaction mixture was stirred vigorously for 48 h at room temperature and concentrated in vacuo. CH₂Cl₂ and 1 M NaOH (aq) were added to the residue and the mixture was stirred for 1 h. Upon separation of the layers, the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with 1 M NaOH (aq), H₂O, brine, and dried over Na₂SO₄. After removal of solvent in vacuo, the target compound was afforded as light yellow oil (3.68 g, yield: 91.7%).

¹H NMR (400 MHz, CDCl₃) δ: 0.90-0.86 (t, 6H, -CH₃), 1.26 (s, 32H, -CH₂CH₃), 1.60 (s, 1H, -CH), 3.56-3.54 (d, *J* = 6.0 Hz, 2H, -CHCH₂-), 5.24 (s, NH₂). ¹³C NMR (100 MHz, CDCl₃) δ: 14.11, 22.69, 26.84, 29.35, 29.36, 29.62, 29.66, 29.69, 30.08, 31.40, 31.93, 37.17, 79.79. HR MS Calcd for C₂₀H₄₃NO [M + H]⁺: *m/z* 314.3417, Found:314.3429.

Synthesis of 4,9-dibromo-2,7-bis((2-octyldodecyl)oxy)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDIO2OD-Br)



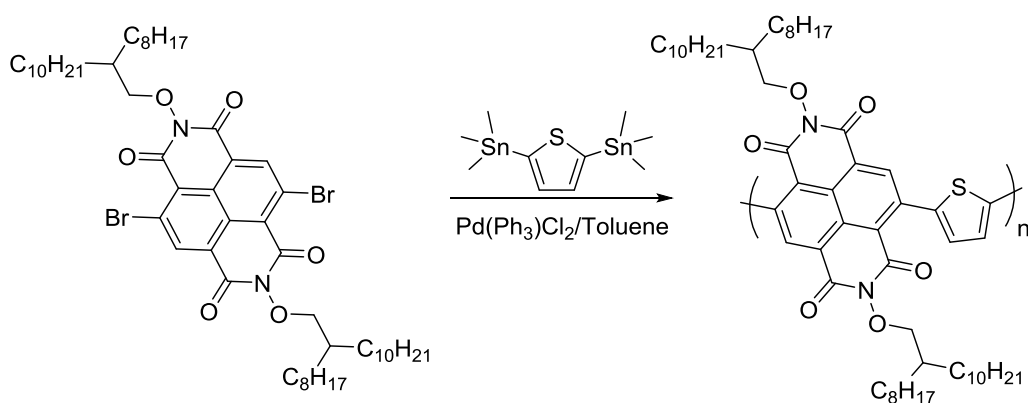
4,9-Dibromoisochromeno[6,5,4-*def*]isochromene-1,3,6,8-tetraone (2.00 g, 4.70 mmol) was dissolved in acetic acid (80 mL) and *O*-(2-octyldodecyl)hydroxylamine (3.24 g, 10.33 mmol, 2.2 equiv) was added to the mixture. The reaction mixture was stirred at 130 °C overnight. The mixture was cooled to room temperature, poured into ice water and then filtered after all ice melted. The resulting solid was chromatographed on a silica gel

Supplementary Information

column using CH₂Cl₂/petroleum ether (v:v = 1:2) to afford a yellow solid. The solid was washed with hot isopropanol to obtain the pure target compound (0.904 g, yield: 18.9%).

¹H NMR (400 MHz, CDCl₃) δ: 0.89-0.84 (m, 6H, -CH₃), 1.56-1.23 (m, 32H, -CH₂CH₃), 1.99 (s, 1H, -CH), 4.15-4.14 (d, *J* = 7.2 Hz, 2H, -CHCH₂-), 8.99 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.13, 22.68, 22.69, 26.33, 29.30, 29.35, 29.55, 29.60, 29.63, 29.64, 30.03, 31.54, 31.89, 31.92, 36.46, 45.44, 124.06, 125.27, 127.72, 128.37, 139.15, 161.00, 161.16.

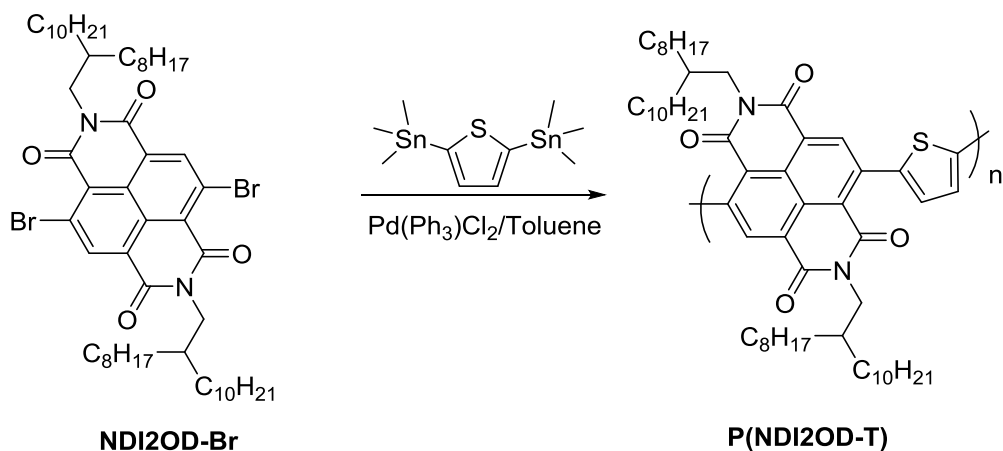
Synthesis of P(NDIO2OD-T)



To a 25 mL Schlenk flask, **NDIO2OD-Br** (70.0 mg, 68.8 μmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (33.8 mg, 68.8 μmol) and Pd(PPh₃)₂Cl₂ (1.9 mg, 2.75 μmol) were added. After degassing and refilling argon three times, toluene (5 mL) was added. The reaction mixture was stirred at 90 °C for 48 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 to give **P(NDIO2OD-T)** (60.4 mg, 94%). HT-GPC (140 °C) data: *M_n* = 68.5 kDa, PDI = 2.30.

Synthesis of P(NDI2OD-T)

Supplementary Information



To a 25 mL Schlenk flask, NDI2OD-Br (70 mg, 71 μmol), 2,5-bis(trimethylstannyl)-thiophene (29 mg, 71 μmol) and Pd(PPh₃)₂Cl₂ (2.0mg, 2.8 μmol) were added. After degassing and refilling argon three times, toluene (4 mL) was added. The reaction mixture was stirred at 90 °C for 48 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 to give P(NDI2OD-T) with yield 94%. HT-GPC (140 °C) data: $M_n = 93.8$, PDI = 3.42.

5. Additional data

Supplementary Information

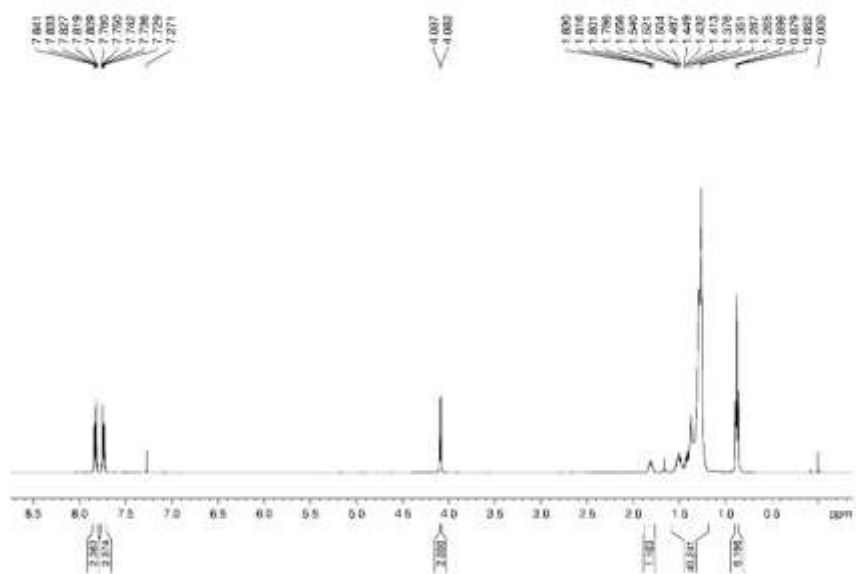


Fig. S1 400 MHz ¹H NMR spectrum for 2-((2-decyltetradecyl)oxy)isoindoline-1,3-dione (**1**) in chloroform-d.

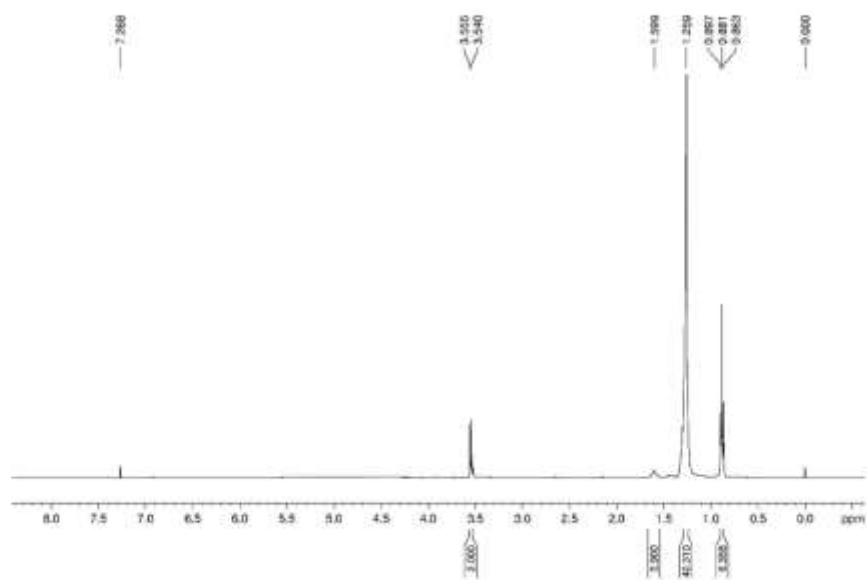


Fig. S2 400 MHz ¹H NMR spectrum for *O*-(2-decyltetradecyl)hydroxylamine (**2**) in chloroform-d.

Supplementary Information

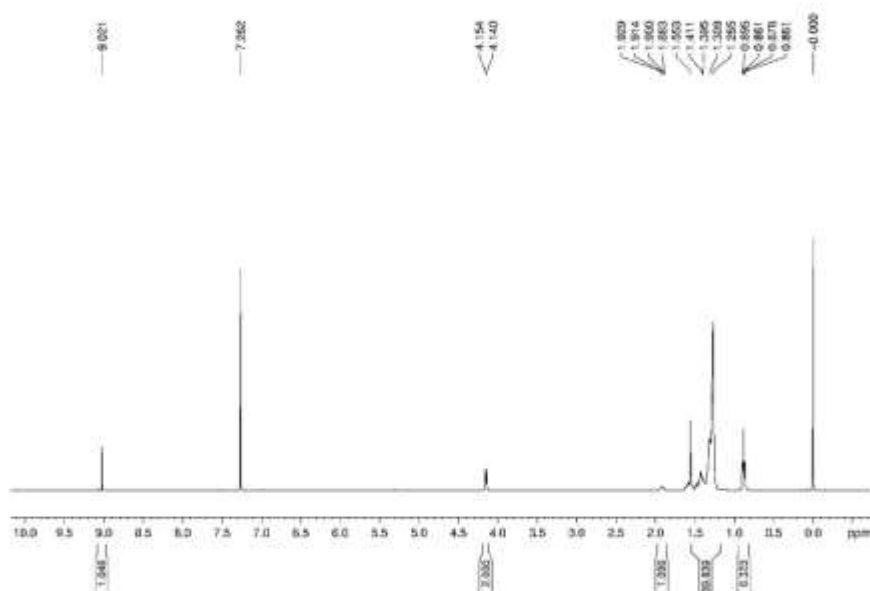


Fig. S3 400 MHz ^1H NMR spectrum for 4,9-dibromo-2,7-bis((2-octyldodecyl)oxy)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**NDIO2OD-Br**) in chloroform-d.

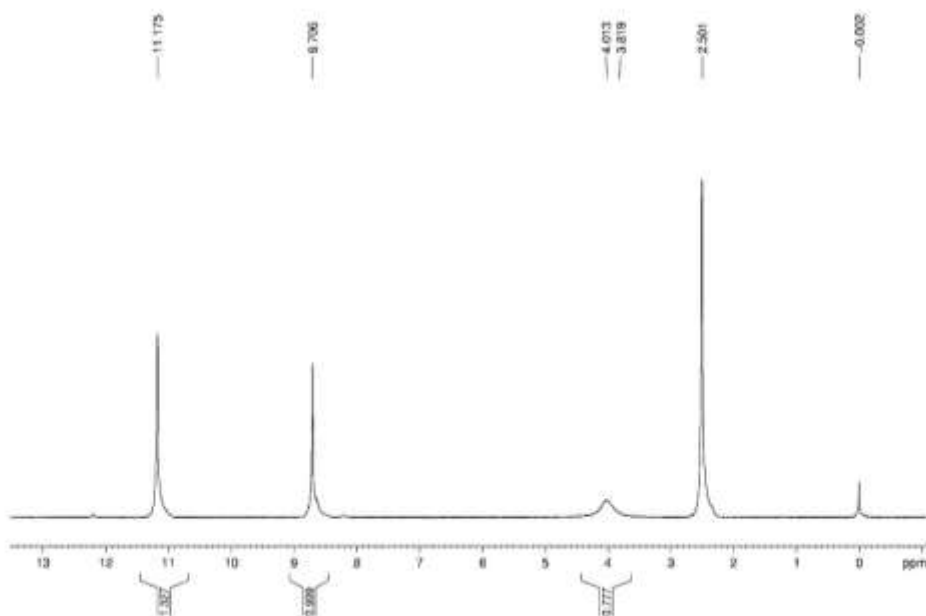


Fig. S4 400 MHz ^1H NMR spectrum of compound **NDIO2H-Br**.

Supplementary Information

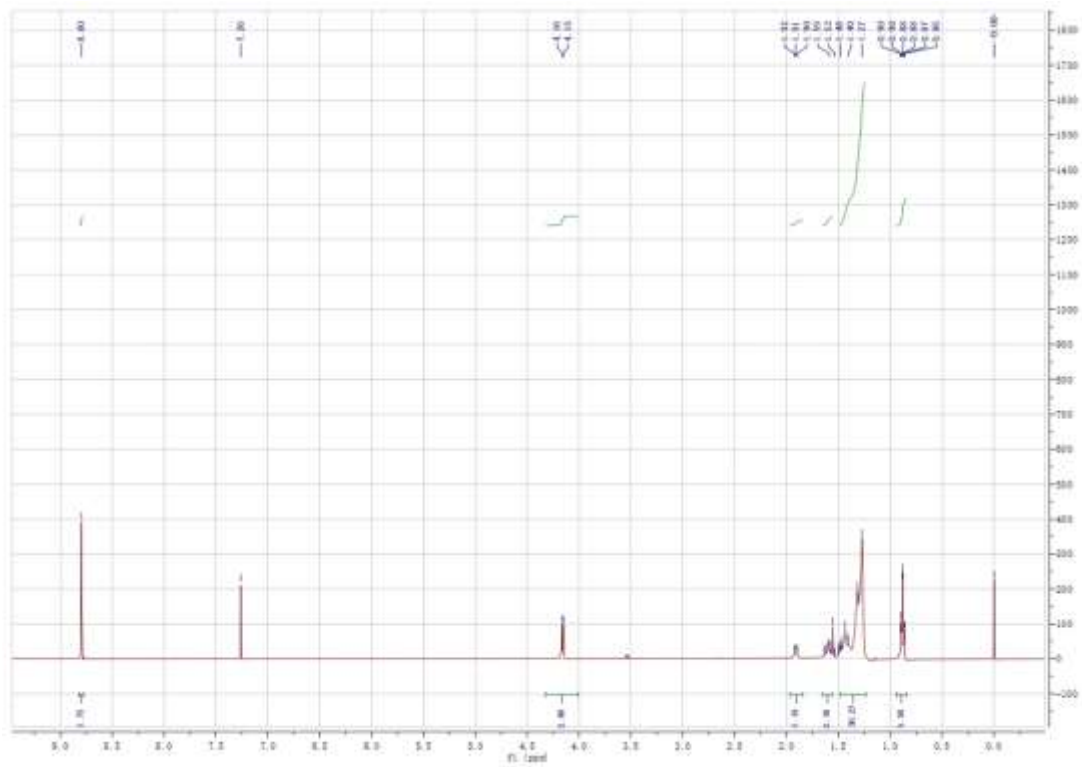


Fig. S5 400 MHz ^1H NMR spectrum of compound 4,9-dibromo-2,7-bis((2-octyldodecyl)oxy)benzo[1,3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (**NDIO2OD**) in chloroform-*d*.

Supplementary Information

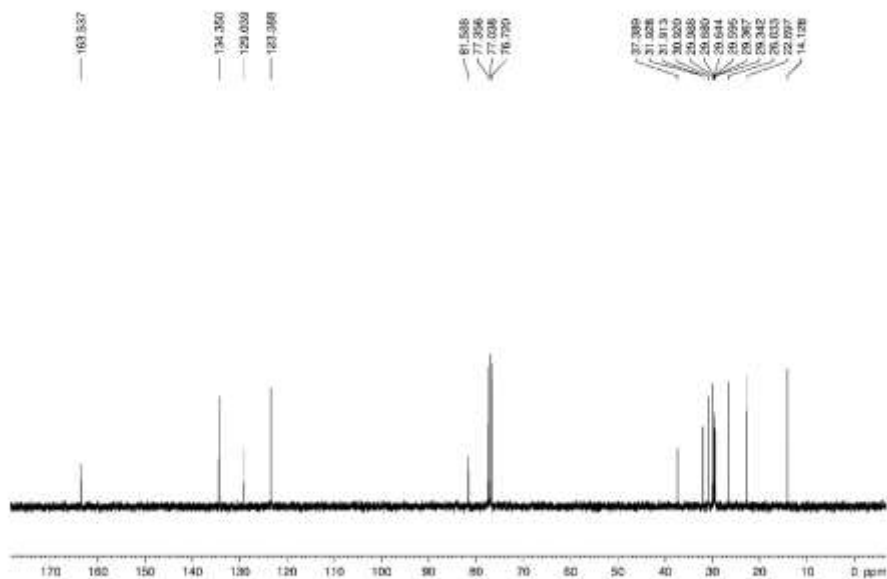


Fig. S6 100 MHz ¹³C NMR spectrum for 2-((2-decyltetradecyl)oxy)isoindoline-1,3-dione (**1**) in chloroform-d.

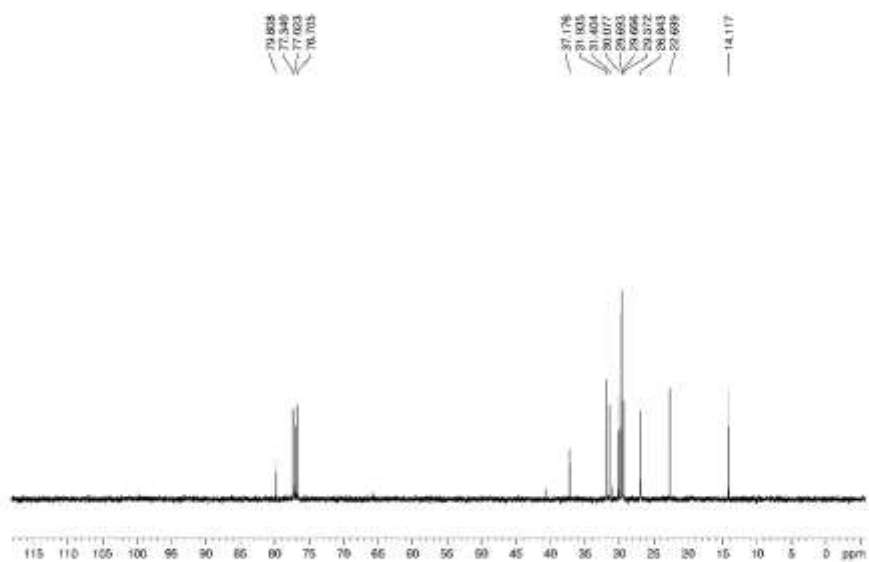


Fig. S7 100 MHz ¹³C NMR spectrum for *O*-(2-decyltetradecyl)hydroxylamine (**2**) in chloroform-d.

Supplementary Information

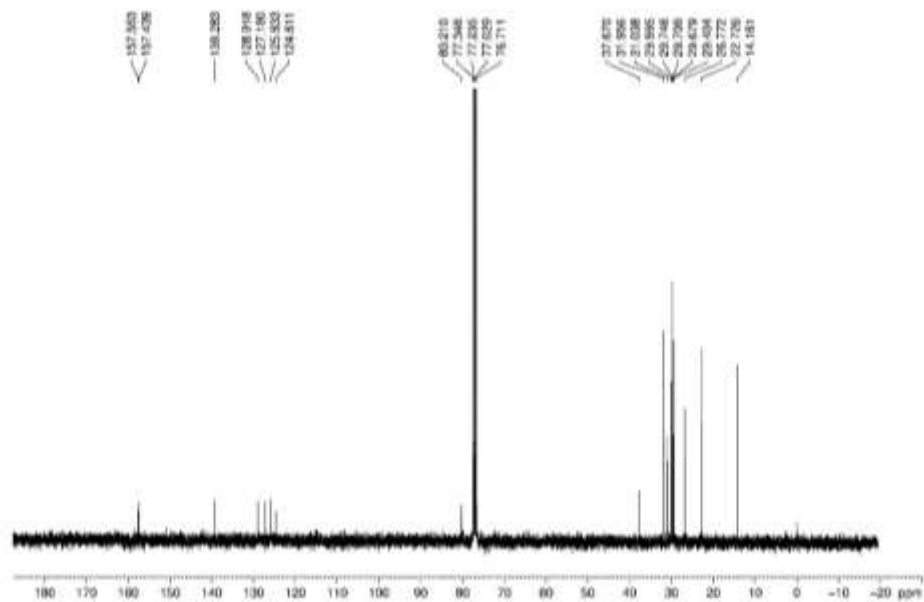


Fig. S8 100 MHz ^{13}C NMR spectrum for 4,9-dibromo-2,7-bis((2-decyltetradecyl)oxy)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**NDIO2OD-Br**) in chloroform-d.

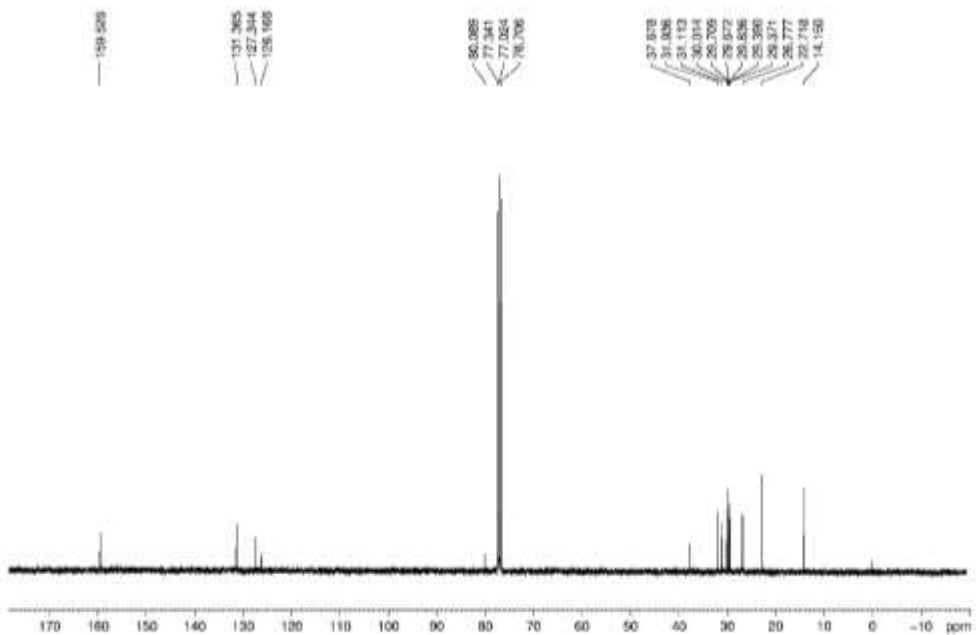


Fig. S9 100 MHz ^{13}C NMR spectrum for 2,7-bis((2-decyltetradecyl)oxy)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (**NDIO2OD**) in chloroform-d.

Supplementary Information

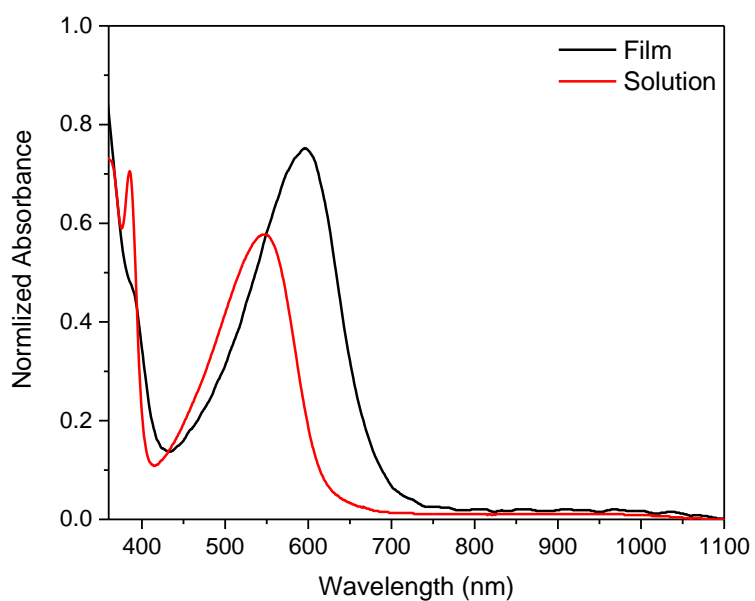


Fig. S10 The absorption spectra of P(NDIOD-T) in solution (chloroform) and thin film, showing λ_{max} at 548 nm and 596 nm, respectively. The optical band gap of the film is 1.83 eV.

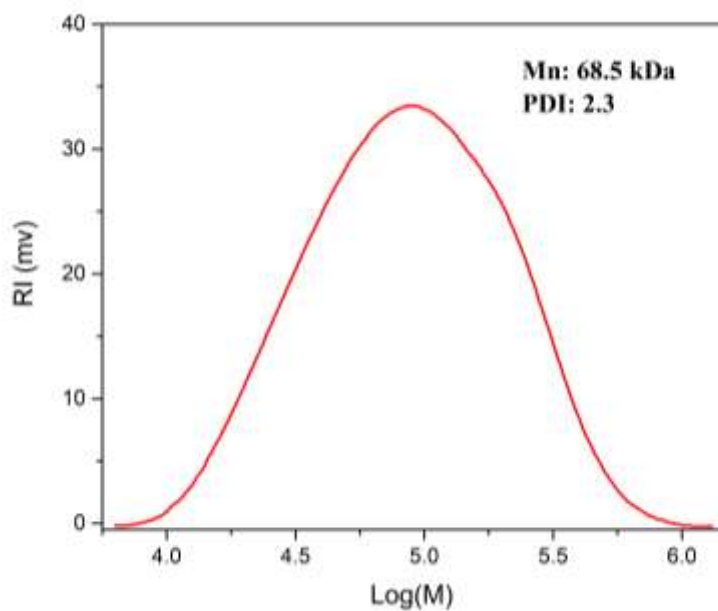


Fig. S11 The molecular weight distribution of P(NDIO2OD-T) obtained from HT-GPC at 140 °C.

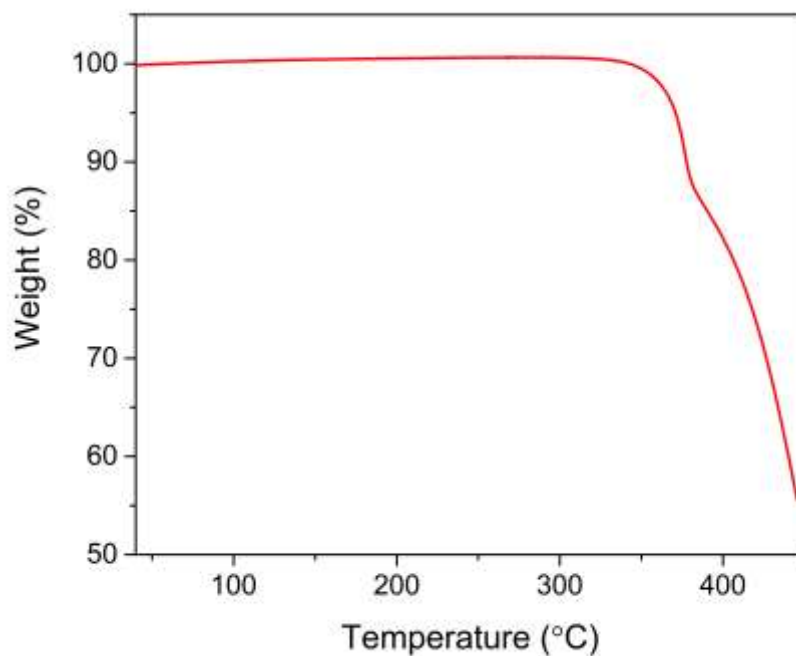


Fig. S12 The TGA diagram of **P(NDIO2OD-T)** under nitrogen at a scan rate of 10 °C min⁻¹.

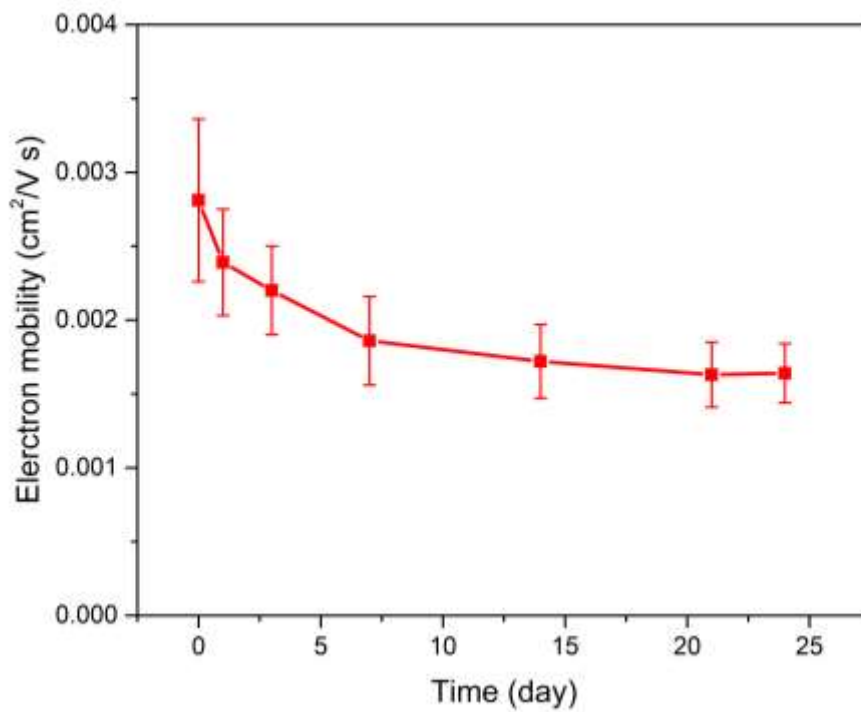


Figure S13 The long-term stability of **P(NDIO2OD-T)**-based OTFT device in ambient conditions.

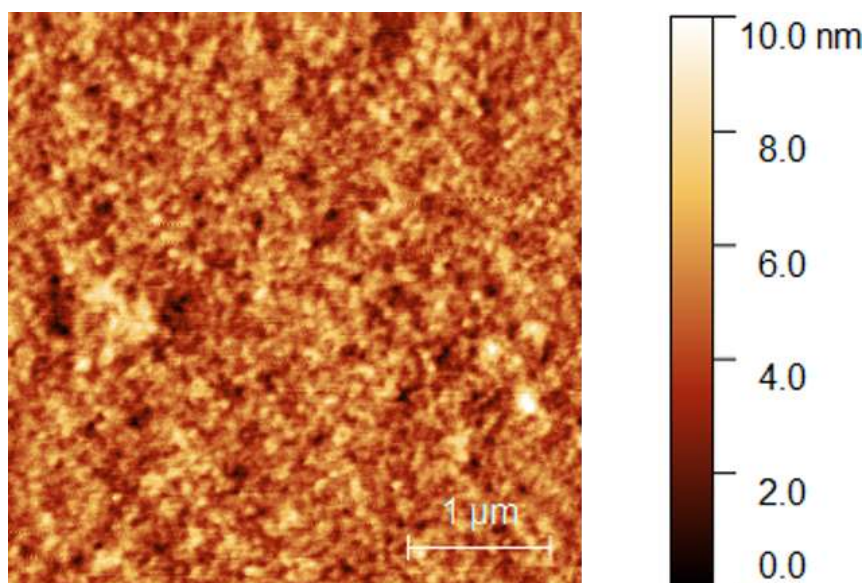


Fig. S14 The AFM image (4×4 μm) of the PTB7-Th: P(NDIO2OD-T) blend on the PEDOT:PSS/ITO substrate.

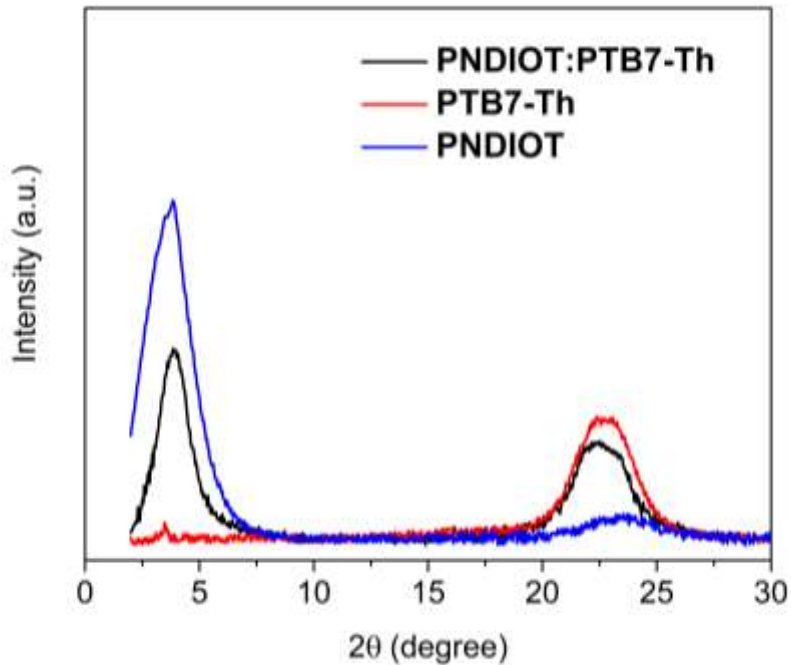


Fig. S15 the reflective XRD patterns of the P(NDIO2OD-T), PTB7-Th and P(NDIO2OD-T):PTB7-Th on the PEDOT:PSS/ITO substrate.

Table S1 A summary of the OTFT performance of **P(NDIO2OD-T)** in both nitrogen and air.

Environment	T _{Ann} (°C)	$\mu_{e,avg}$ (std) (cm ² V ⁻¹ s ⁻¹)	$\mu_{e,max}$ (cm ² V ⁻¹ s ⁻¹)	V _{th} (V)	I _{on} /I _{off}
Nitrogen	100	0.0020 (0.0005)	0.0029	15	~10 ³
	150	0.0041 (0.0009)	0.0054	13	~10 ⁴
	200	0.0016 (0.0002)	0.0021	21	~10 ³
Air	150	0.0028 (0.0008)	0.0039	33	~10 ⁴

6. References

- 1 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bassler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551–554.