Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

3,3'-(Ethane-1, 2-diylidene)bis(indolin-2-one) based conjugated polymers for organic thin film transistors

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Contents

Supplementary Information

1. Materials and Characterization

All chemicals were purchased from commercial resources and used without purification. 4-Decyl-1-hexadecyl bromide (C26-Br) was synthesized using the method reported previously.[1] NMR data were recorded on a Bruker DPX 300 MHz spectrometer with chemical shift relative to tetramethylsilane (TMS, 0 ppm). Elemental analysis was performed on an Elementar Vario EL Cube elemental analyzer. UV-Vis spectra were recorded on a Thermo Scientific Genesys 10 UV instrument with polymer solutions in chloroform and polymer films spin-coated onto quartz glass substrates. High-temperature gel-permeation chromatography (HT-GPC) was carried out with 1, 2, 4-trichlorobenzene as an eluent and polystyrene as standards at 140 °C on a Malvern 350 HT-GPC system. Differential scanning calorimetry (DSC) measurements and thermal gravimetric analysis (TGA) were carried out on a TA Instruments DSC Q2000 and a TA Instruments SDT 2960, respectively, at a scan rate of 10 °C min^{-1} under nitrogen. Cyclic voltammetry (CV) measurements were performed on a Digi-Ivy DY2111 Potentiostat using an Ag/AgCl reference electrode, a platinum counter electrode, and a platinum working electrode. CV measurements were collected on polymer films coated on the working electrode in 0.1 M tetrabutylammonium hexafluorophosphate under nitrogen in anhydrous acetonitrile using the ferrocene/ferrocenium (Fc/Fc$^+$) couple as a reference at a scan rate of 50 mV s^{-1}. The HOMO and LUMO energy levels were calculated using the equations: E_{HOMO} (eV) = - ($E_{\mathrm{ox}}^{\mathrm{onset}}$ - $E_{\mathrm{Fc/Fc+}}^{\mathrm{onset}}$) - 4.80 eV, E_{LUMO} (eV) = - ($E_{\mathrm{redox}}^{\mathrm{onset}}$ - $E_{\mathrm{Fc/Fc+}}^{\mathrm{onset}}$) - 4.80 eV. $E_{\mathrm{ox}}^{\mathrm{onset}}$, $E_{\mathrm{redox}}^{\mathrm{onset}}$ and $E_{\mathrm{Fc/Fc+}}^{\mathrm{onset}}$ are the onset oxidation potential, reduction potential for the polymer sample and the onset oxidation potential of ferrocene relative to the Ag/AgCl electrode. The value –4.80 eV is the HOMO energy level of ferrocene.[2] Transmission XRD measurement of polymer samples was performed on a Bruker Smart 6000 CCD 3-circle D8 diffractometer with a Cu RA (Rigaku) X-ray source (λ = 0.15418 nm). The polymer flake samples for the transmission XRD measurement were prepared by forming a polymer film on the wall of a 250 mL round-bottomed flask by evaporating a polymer solution in chloroform on a rotary evaporator, followed by removing the film with methanol. The polymer thin film (~30 μm thick) was then broken into small pieces (~1 mm in diameter) and stacked between two Mylar substrates for the transmission XRD measurement. Reflective XRD diagrams of polymer thin films (~35 nm thick) spin-coated on dodecyltrichlorosilane (DTS)-modified Si/SiO_2 substrates were performed on a Bruker D8 Advance diffractometer with Cu Kα1 radiation (λ = 0.15406 nm). Atomic force microscopic (AFM) images were obtained on polymer thin films on DTS-modified Si/SiO_2 substrates using Dimension 3100 Scanning Probe Microscope.

2. Synthetic Procedures

3,3'-(Ethane-1,2-diylidene)bis(6-bromo-1-propionylindolin-2-one) (1)

This compound was prepared following a similar procedure as that for 3,3'-(ethane-1,2-diylidene)bis(1-propionylindolin-2-one).[3] A reaction mixture of 6-bromoindoline-2,3-dione (3.2 g, 14.2 mmol), propionic anhydride (12 mL) and pyridine (4 mL) in a 25 mL two-necked round bottom flask was heated at reflux under argon for 0.5 h. (A longer reaction time did not improve the yield.) After cooling, the dark red needles were separated, washed with acetone and ether, and dried in air. After washing with chloroform for three times, dark red needles were obtained, which were dried *in vacuo*. Yield: 0.87 g (22.0%). This compound is insoluble in any solvent and was used for the next step without further purification.

3,3'-(Ethane-1,2-diylidene)bis(6-bromoindolin-2-one) (2)

1 (1.30 g) was heated in a solution of potassium hydroxide (0.261 g, 4.66 mmol) in ethanol (35 mL) under reflux for 20 min. The dark blue solid was separated, washed with acetone and ether, and the potassium derivative was neutralized with dilute hydrochloric acid. The red solid (0.77g, 74.7%) was separated, washed with water, and dried *in vacuo*. ^{1}H-NMR (DMSO-d_6, 300 MHz, ppm): 10.76 (d, 2H, J = 9 Hz), 8.65 (d, 1H, J = 12 Hz), 8.10 (q, 2H, J = 12 Hz), 8.01 (d, 1H, J = 9 Hz), 7.20(d, 2H, J = 9 Hz), 6.99 (d, 2H, *J* = 12 Hz). This compound was not characterized by ^{13}C-NMR because of its very poor solubility.

3,3'-(Ethane-1,2-diylidene)bis(6-bromo-1-(2-decyltetradecyl)indolin-2-one) (EBI-24)

To a mixture of **2** (0.4684 g, 1.05 mmol, 1.0 equiv.), K_2CO_3 (0.5688 g, 4.12 mmol, 3.92 equiv.) and DMF (4 mL) in a 25 mL two-necked round bottom flask was added 2-decyltetradecyl bromide (C24-Br) (1.315 g, 3.15 mmol, 3 equiv.). The mixture was stirred at 70 °C under argon for 20 h. Solvent was then evaporated under reduced pressure and 5 mL water was added. The mixture was extracted with DCM three times and the combined organic phase was dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (1 : 1, v : v) as an eluent to obtain EBI-24. Yield: 0.52 g (44.2%). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.95 (s, 2H), 7.46 (d, 2H, *J* = 6 Hz), 7.14(d, 2H, *J* = 9 Hz), 6.91 (s, 2H), 3.56(d, 4H, *J* = 9 Hz), 1.86 (s, 2H), 1.20-1.40 (m, 80H), 0.70-0.87 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75MHz, ppm): 167.30, 144.51, 130.27, 129.02, 125.00, 124.42, 122.37, 122.09, 112.08, 44.41, 31.94, 30.11, 29.79, 29.74, 29.50, 26.58, 22.84, 14.27. Elemental analysis: Found: C, 70.81; H, 9.56; N, 2.45%. Calc. for $C_{66}H_{106}Br_2N_2O_2$: C, 70.82; H, 9.54; N, 2.50%.

3,3'-(Ethane-1,2-diylidene)bis(6-bromo-1-(4-decylhexadecyl)indolin-2-one) (EBI-26)

To a mixture of **2** (0.6245 g, 1.40 mmol, 1.0 equiv.), K_2CO_3 (0.759 g, 5.45 mmol, 3.92 equiv.) and DMF (5.5 mL) in a 25 mL two-necked round bottom flask was added 4-decyl-1-hexadecyl bromide (C26-Br) (1.872 g, 4.20 mmol, 3 equiv.). The reaction mixture was stirred at 70 °C under argon for 20 h. Using the similar work up and purification procedures for EBI-24 afforded EBI-26. Yield: 0.81 g (49.2%). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.95 (s, 2H), 7.45 (d, 2H, *J* = 9 Hz), 7.15(d, 2H, *J* = 9 Hz), 6.94 (s, 2H), 3.65(d, 4H), 1.65 (s, 4H), 1.54 (s, 2H), 1.24 (m, 84H), 0.85 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75MHz, ppm): 166.95, 144.18, 130.50, 129.10 125.18, 124.62, 122.51, 122.24, 111.99, 40.39, 37.25, 33.65, 32.08, 30.25, 29.86, 29.82, 29.81, 29.53, 29.52, 26.82, 22.85, 14.29. Elemental analysis: Found: C, 71.76; H, 9.84; N, 2.17%. Calc. for $C_{70}H_{114}Br_2N_2O_2$: C, 71.52; H, 9.78; N, 2.38%.

Synthesis of PEBIBT-24. To a 25 mL dry flask were added **EBI-24** (0.1504 g, 0.134 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.0659 g, 0.134 mmol) and tri(*o*-totyl)phosphine (3.3 mg, 8 mol %, 0.0011 mmol). After degassing and refilling argon for 3 times, anhydrous chlorobenzene (5.5 ml) and tris(dibenzylideneacetone)-dipalladium (2.5 mg, 0.003 mmol) were added under an argon atmosphere. The flask was sealed and the mixture was stirred for 72 h at 90 °C. After cooling to room temperature, the reaction mixture was poured into methanol (100 ml). The precipitated product was collected by filtration, and then subjected to Soxhlet extraction with acetone and hexane. The residue was dissolved with chloroform, giving product after removal of solvent. Yield: 150 mg (99.3%). HT-GPC (in 1, 2, 4-trichlorobenzene at 140 °C): M_n = 28.7 kDa; M_w = 62.4 kDa; M_w / M_n = 2.17.

Synthesis of PEBIBT-26. To a 25 mL dry flask were added **EBI-26** (0.1600 g, 0.136 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.0670 g, 0.136 mmol) and tri(*o*-totyl)phosphine (3.3 mg, 8 mol %, 0.0011 mmol). After degassing and refilling argon for 3 times, anhydrous chlorobenzene (5.5 ml) and tris(dibenzylideneacetone)-dipalladium (2.5 mg, 0.003 mmol) were added under an argon atmosphere. The flask was sealed and the mixture was stirred for 72 h at 90 °C. After cooling to room temperature, the reaction mixture was poured into methanol (100 mL). The precipitated product was collected by filtration and subjected to Soxhlet extraction with acetone and hexane. The residue was dissolved with chloroform to afford the product after removal of solvent. Yield: 160mg (99.4%). HT-GPC (in 1, 2, 4-trichlorobenzene at 140 °C): M_n = 23.6 kDa; M_w = 52.5 kDa; M_w / M_n = 2.23.

3. Fabrication and Characterization of OTFT Devices

Bottom-gate bottom-contact OTFT configuration was used. Heavily n^{++}-doped conductive silicon wafer functions as the gate electrode and a thermally grown silicon oxide (SiO_2) layer (~300 nm) with a capacitance of ~11.6 nF cm^{-2} on top of the silicon layer was used as the insulating dielectric. The gold source and drain electrodes were deposited by thermal evaporation on the SiO_2 layer using a conventional lithography technique. The substrate was washed with acetone and isopropanol and O_2 plasma. The cleaned substrate was modified with dodecyltrichlorosilane (DTS) in toluene (10 mg mL^{-1}) at 60 °C for 20 min, washed with toluene, and dried. A **PEBIBT-24** or **PEBIBT-26** solution in chloroform (10 mg mL^{-1}) was spin-coated on the substrate at 3000 rpm for 90 s to form a polymer film (~35 nm) , which was annealed at 150 °C or 200 °C on a hotplate for 15 min in a glove box. After annealing, the devices were encapsulated with a ~500 nm-thick poly(methyl methacrylate) (PMMA) layer by spin-coating a PMMA solution in butyl acetate (8 wt%) on the top of polymer semiconductor layer at 3000 rpm for 60 s, followed by drying on a hotplate at 80 °C for 30 min in the glove box. The OTFT devices were characterized in air using an Agilent 4155C Semiconductor Parameter Analyzer. The carrier mobility in the saturated regime, μ_{sat}, is calculated according to equation: $I_{DS} = C_i \mu_{sat} (W/2L) (V_G - V_T)^2$, whereas C_i is the capacitance per unit area of the gate dielectric, W (1000 μm) and L (30 μm) are the semiconductor channel width and length, respectively, I_{DS} is the drain current, V_G is the gate voltage, and V_T is the threshold voltage determined from the V_G axis intercept of the linear extrapolation of the $(I_{DS})^{1/2}$ vs. V_G curve in the saturation regime at $I_{DS} = 0$.

3. Additional Data:

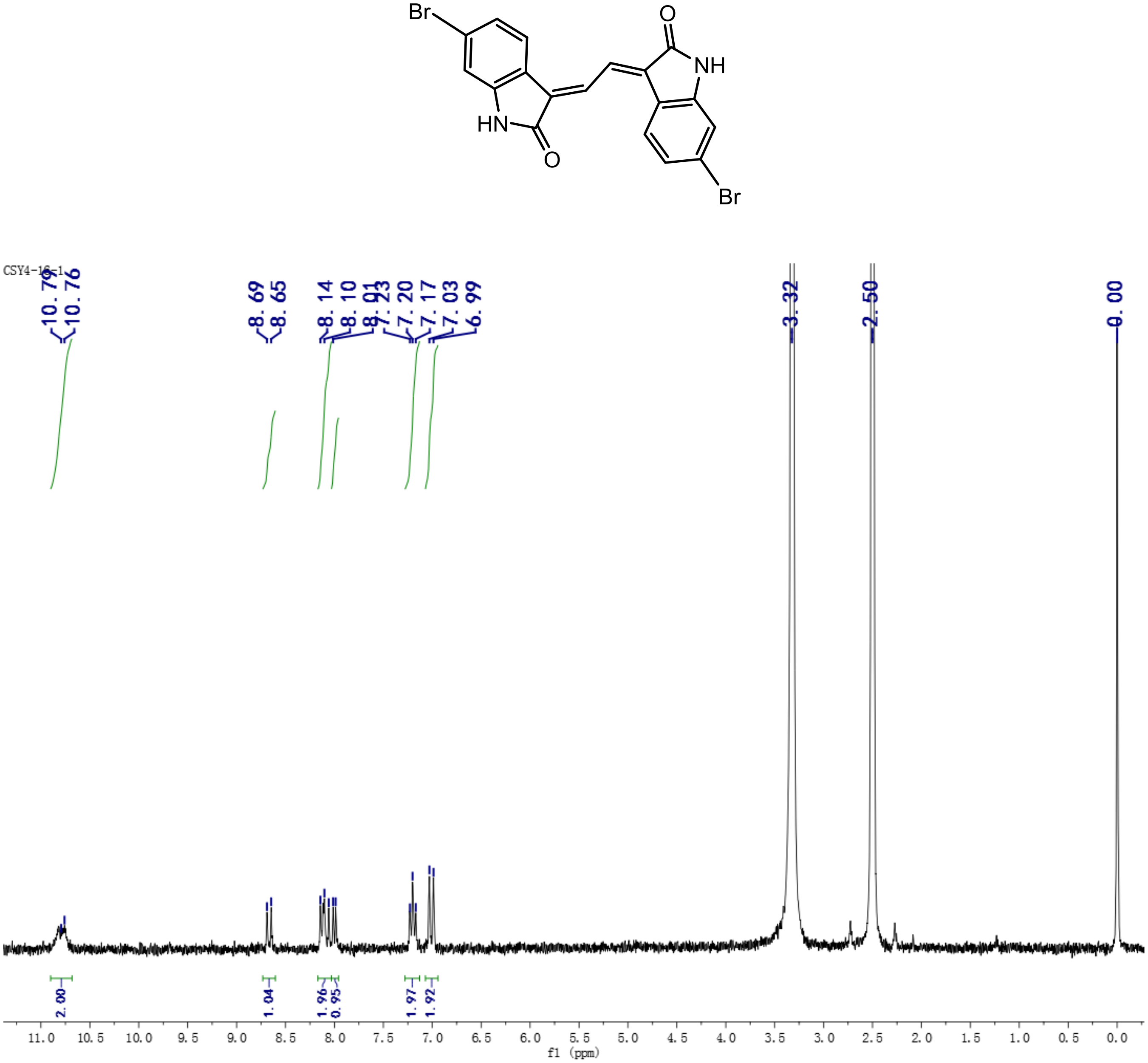


Fig. S1 The 300 MHz ^{1}H NMR spectrum of 3,3'-(ethane-1,2-diylidene)bis(6-bromoindolin-2-one) measured in DMSO-d_6.

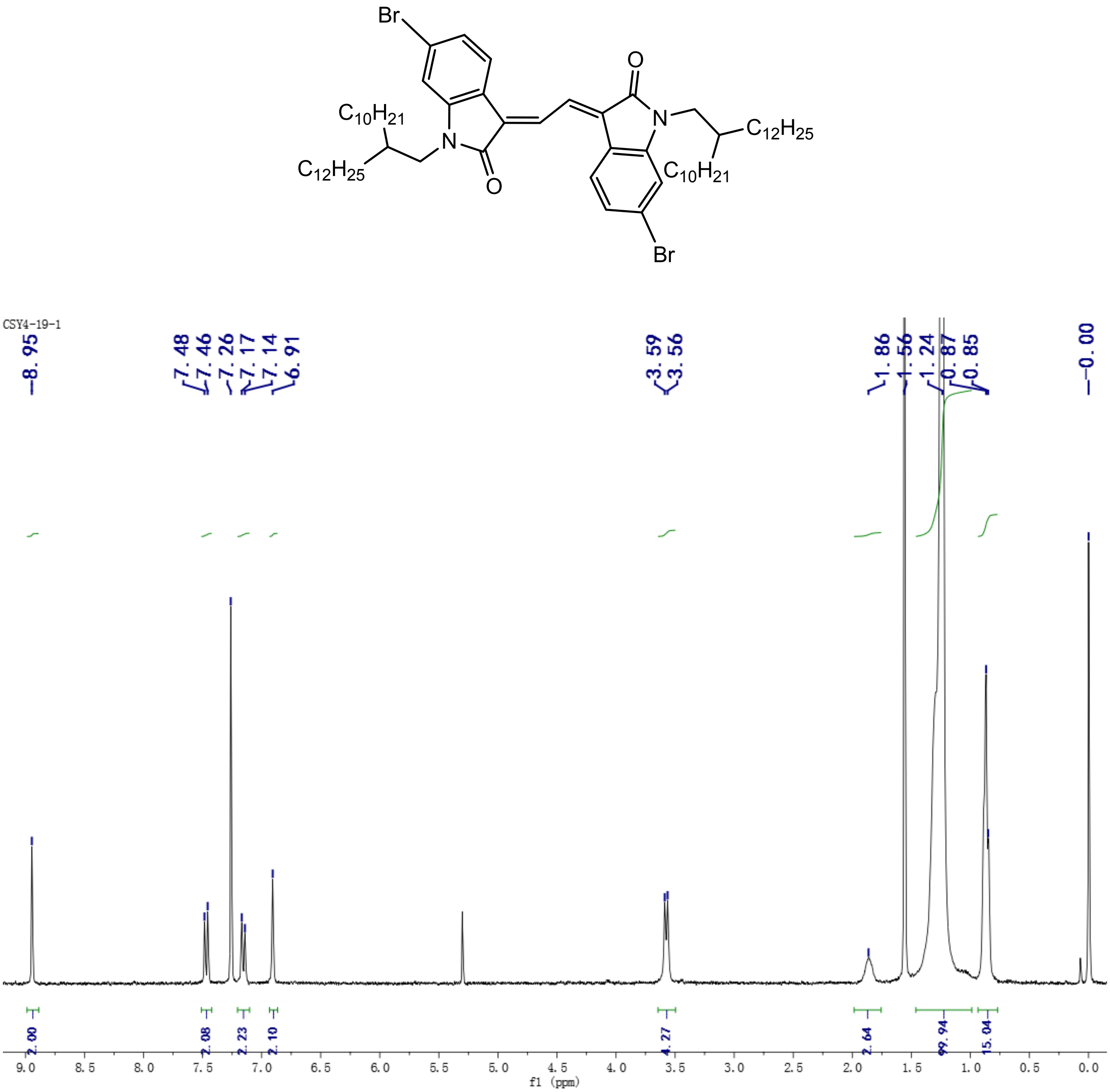


Fig. S2 The300 MHz ^{1}H NMR spectrum of **EBI-24** measured in $CDCl_3$.

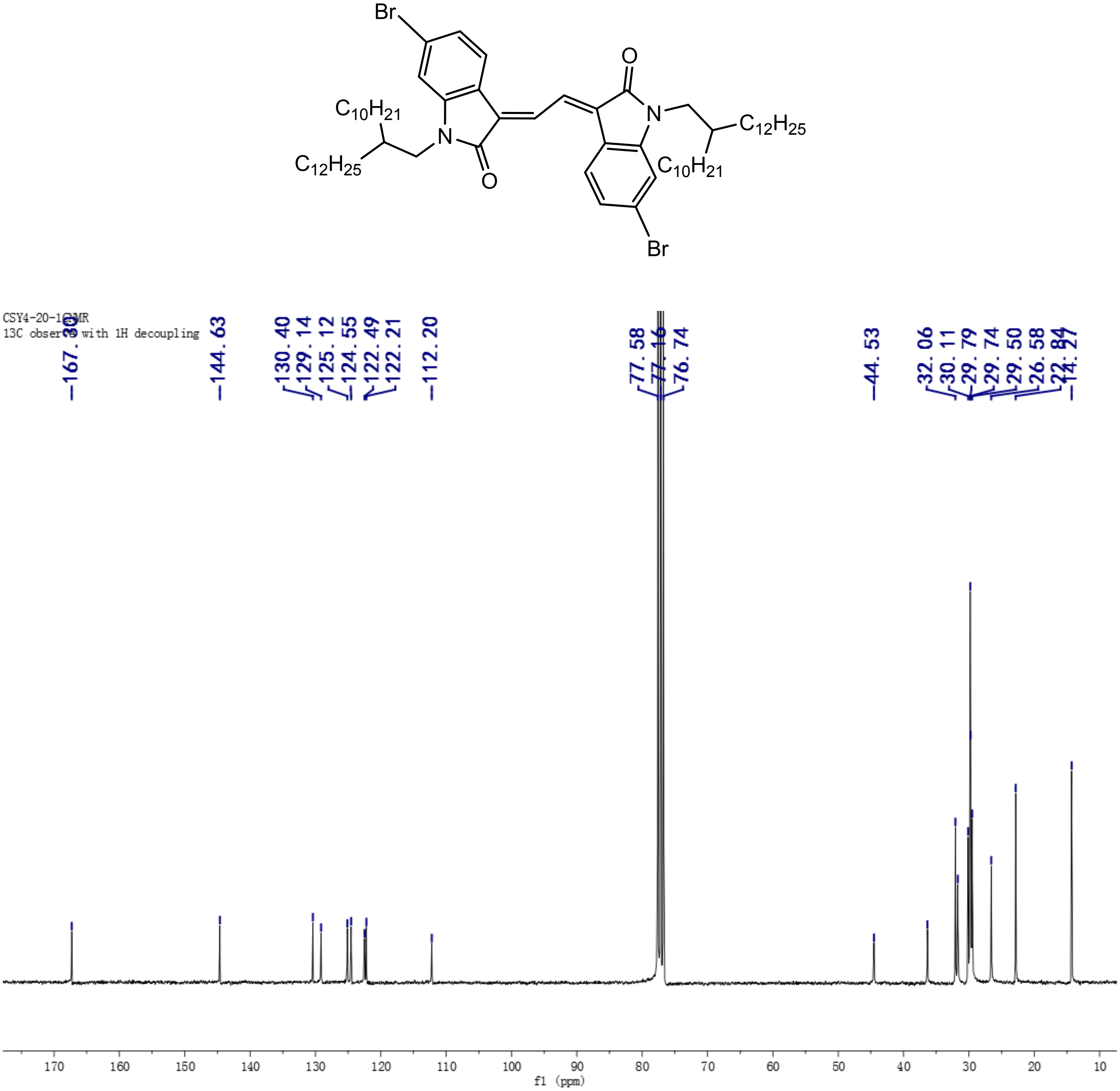


Fig. S3 The 75 MHz ^{13}C NMR spectrum of **EBI-24** measured in $CDCl_3$.

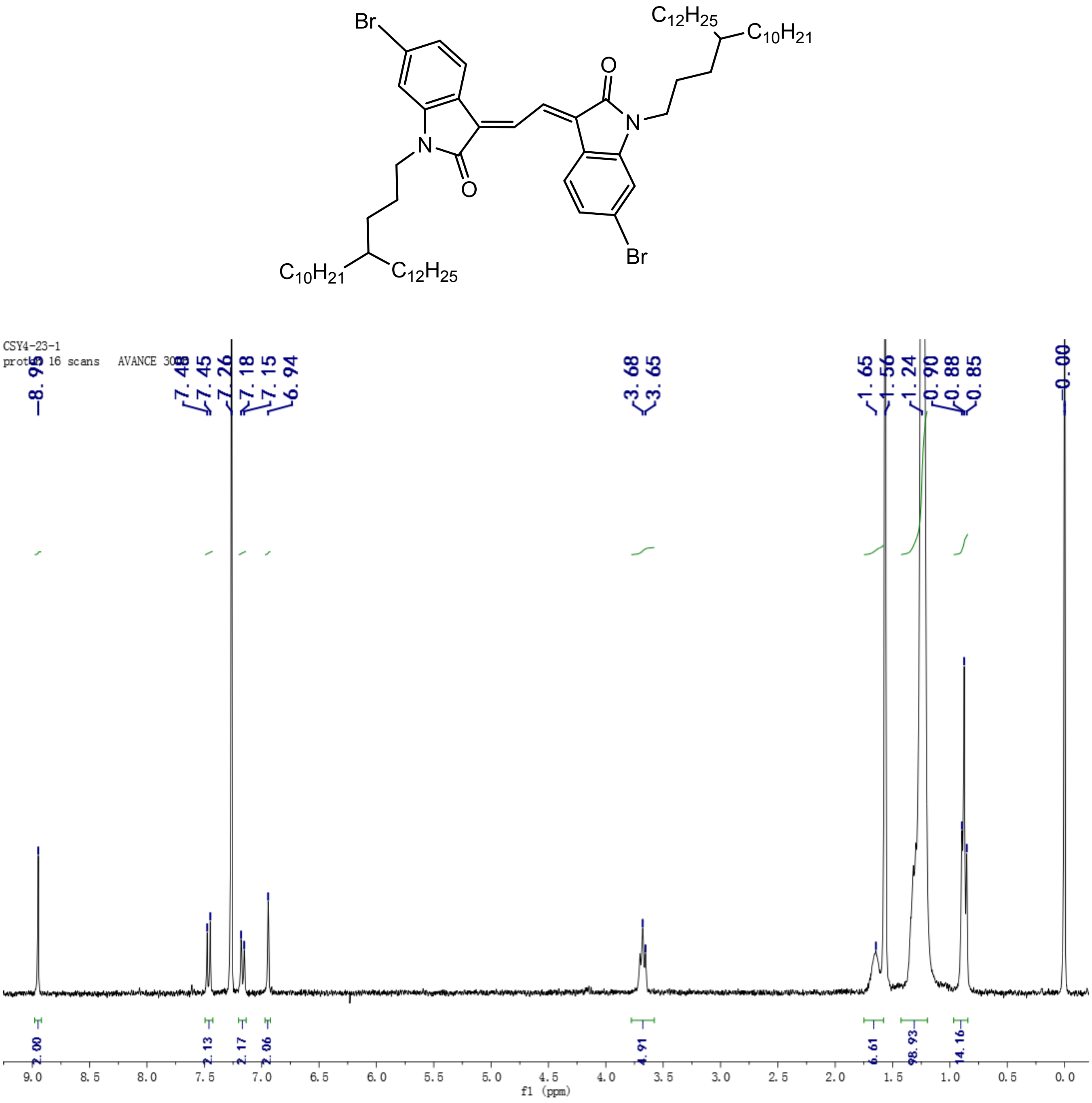


Fig. S4 The 300 MHz ^{1}H NMR spectrum of **EBI-26** measured in $CDCl_3$.

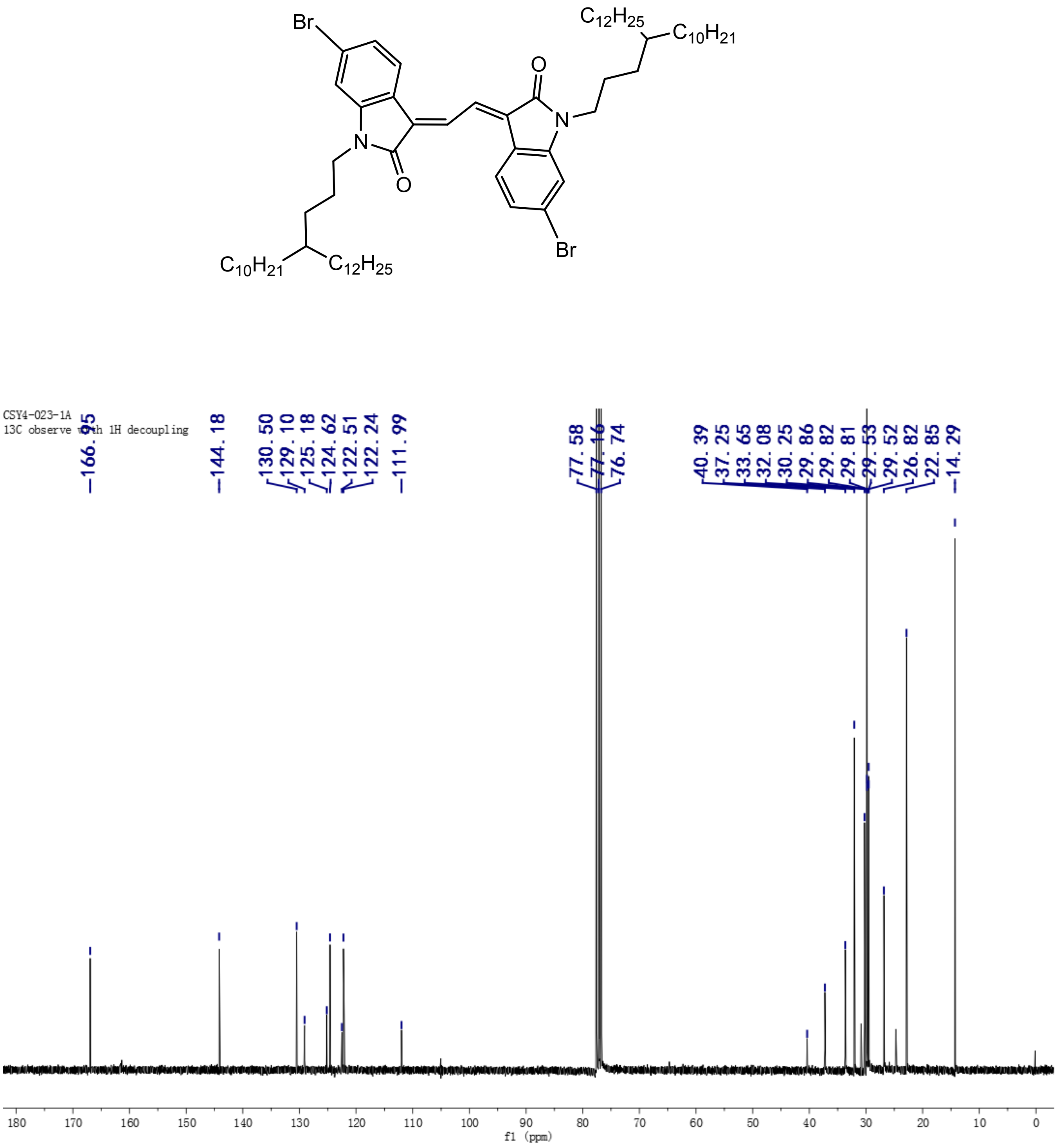


Fig. S5 The 75 MHz ^{13}C NMR spectrum of **EBI-26** measured in $CDCl_3$.

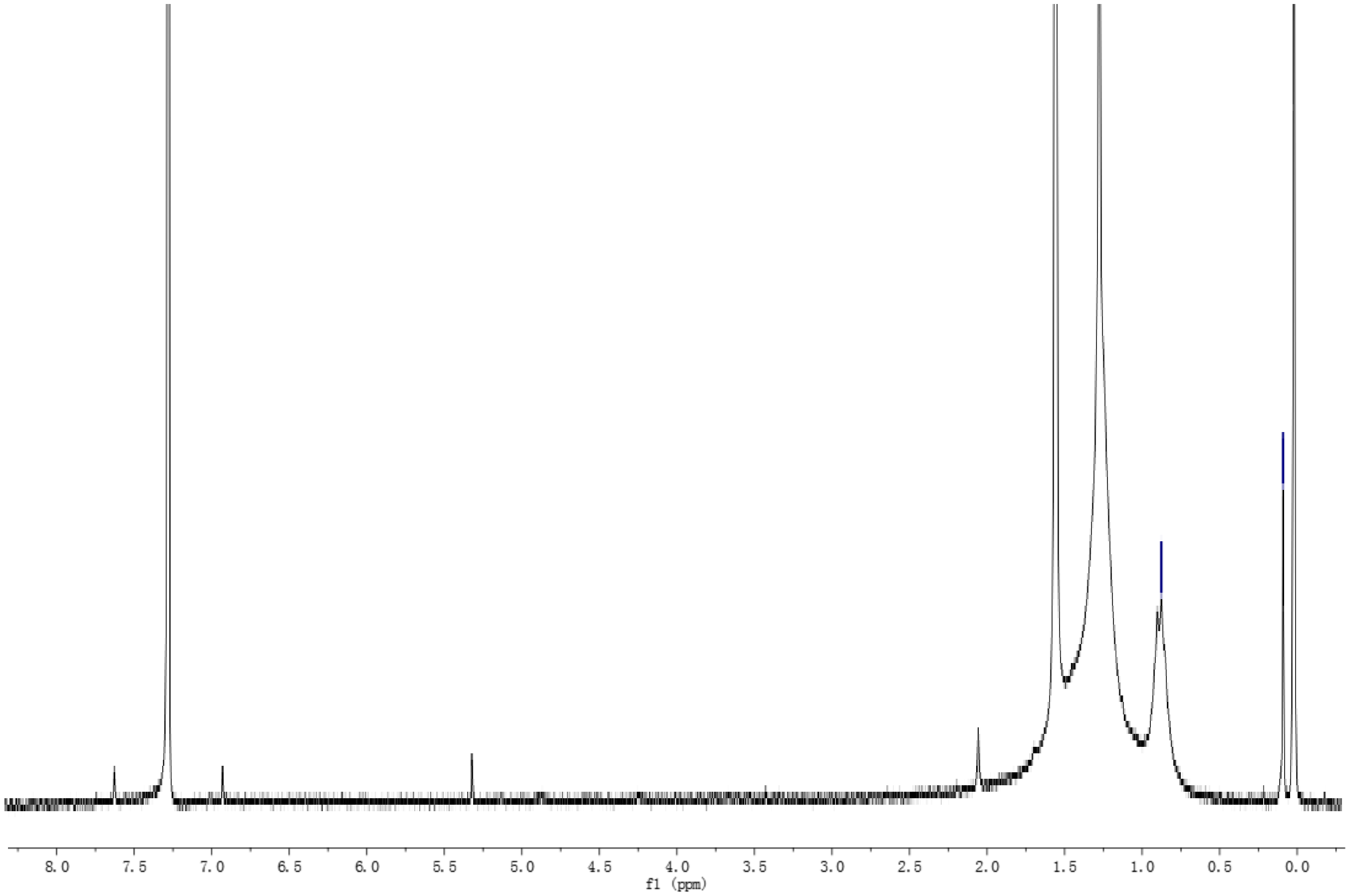


Fig. S6 The 300 MHz ^{1}H NMR spectrum of **PEBIBT-24** measured in $CDCl_3$.

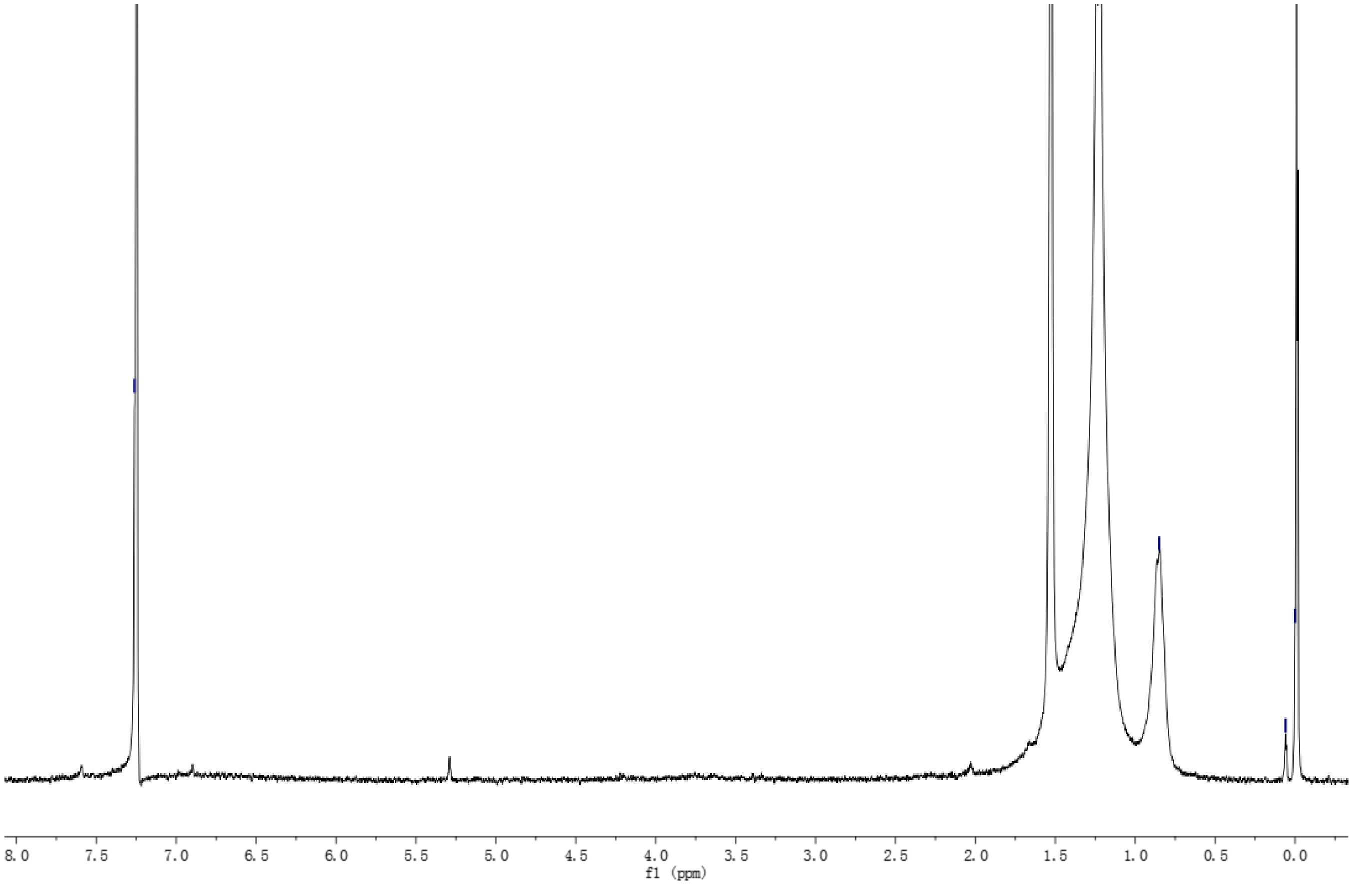


Fig. S7 The 300 MHz ^{1}H NMR spectrum of **PEBIBT-26** measured in $CDCl_3$.

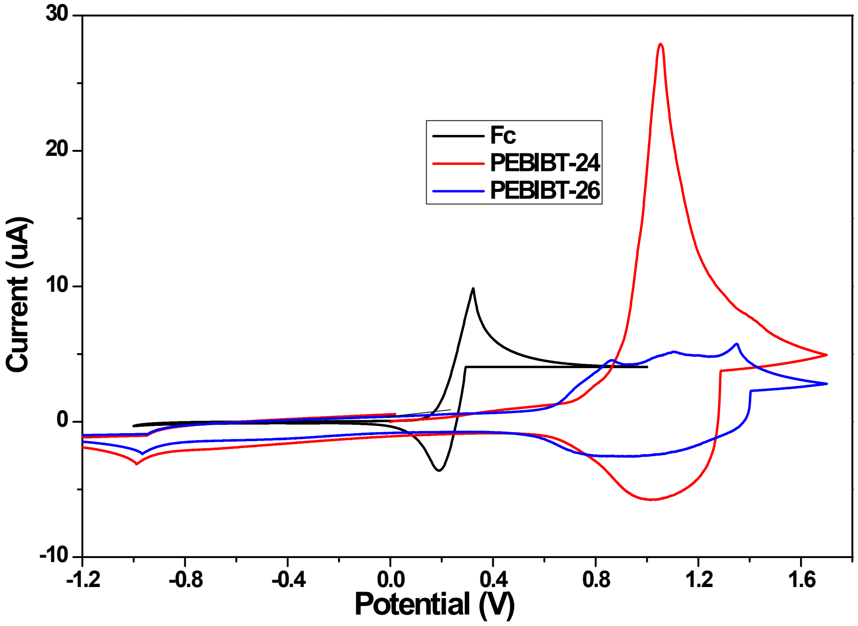
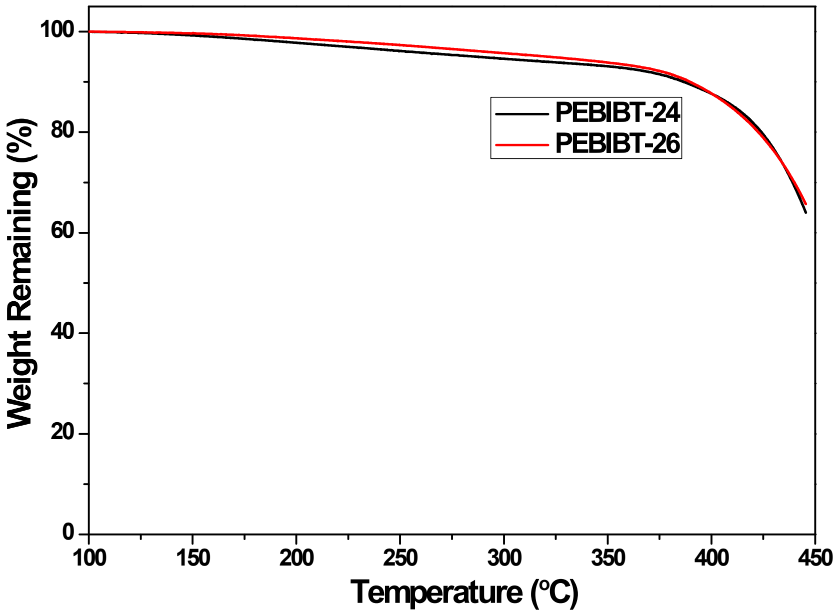


Fig. S8 Cyclic voltammograms (CV) of **PEBIBT-24** and **PEBIBT-26** thin films in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 50 mV s^{-1} under nitrogen, using ferrocene (Fc) as a standard.



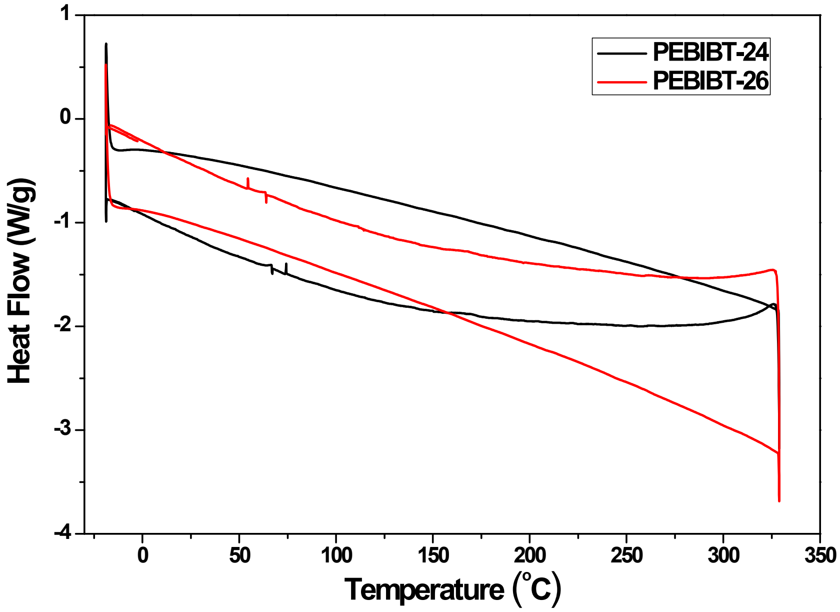


Fig. S9 Thermal analysis data of **PEBIBT-24** and **PEBIBT-26**. Top: TGA curves with a heating rate of 10 °C·min^{-1} under nitrogen. Bottom: DSC curves with a heating / cooling rate of 10 °C·min^{-1} under nitrogen.

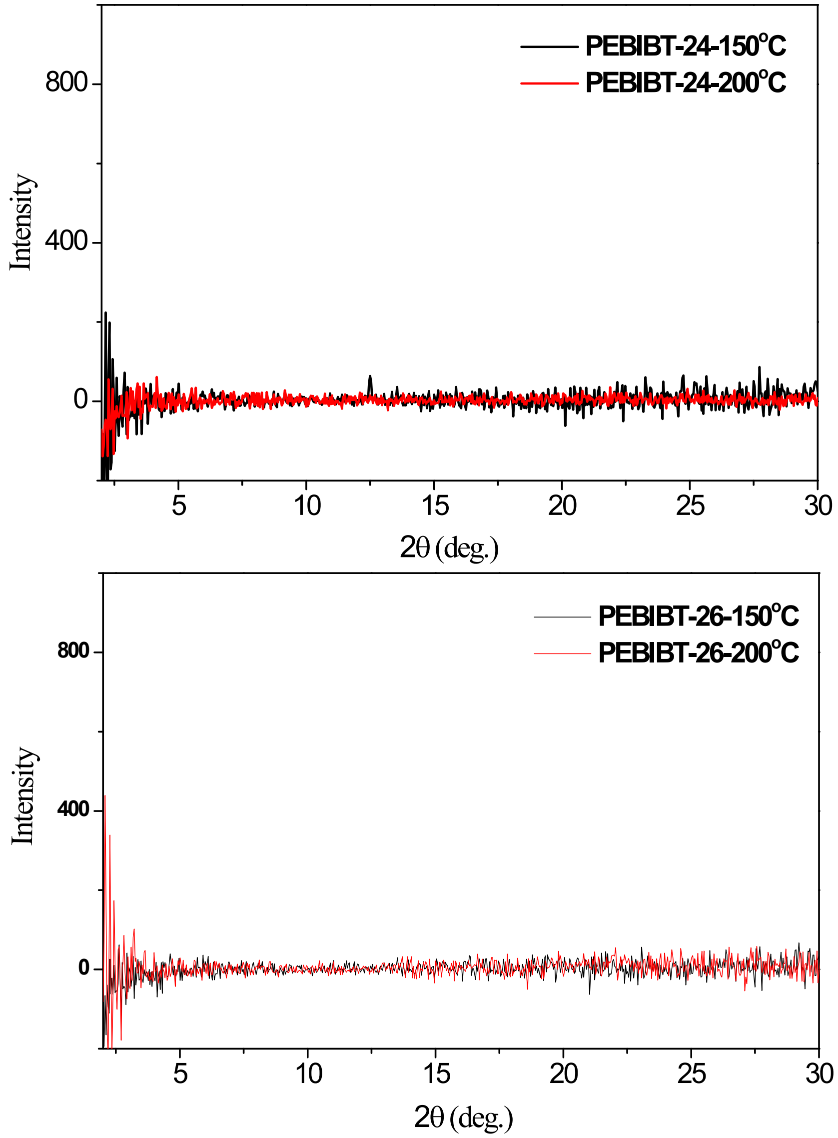


Fig. S10 XRD diagrams of **PEBIBT-24** and **PEBIBT-26** thin films (~35 nm) on DTS-modified Si/SiO_2 substrates annealed at different temperatures for 15 min in nitrogen.

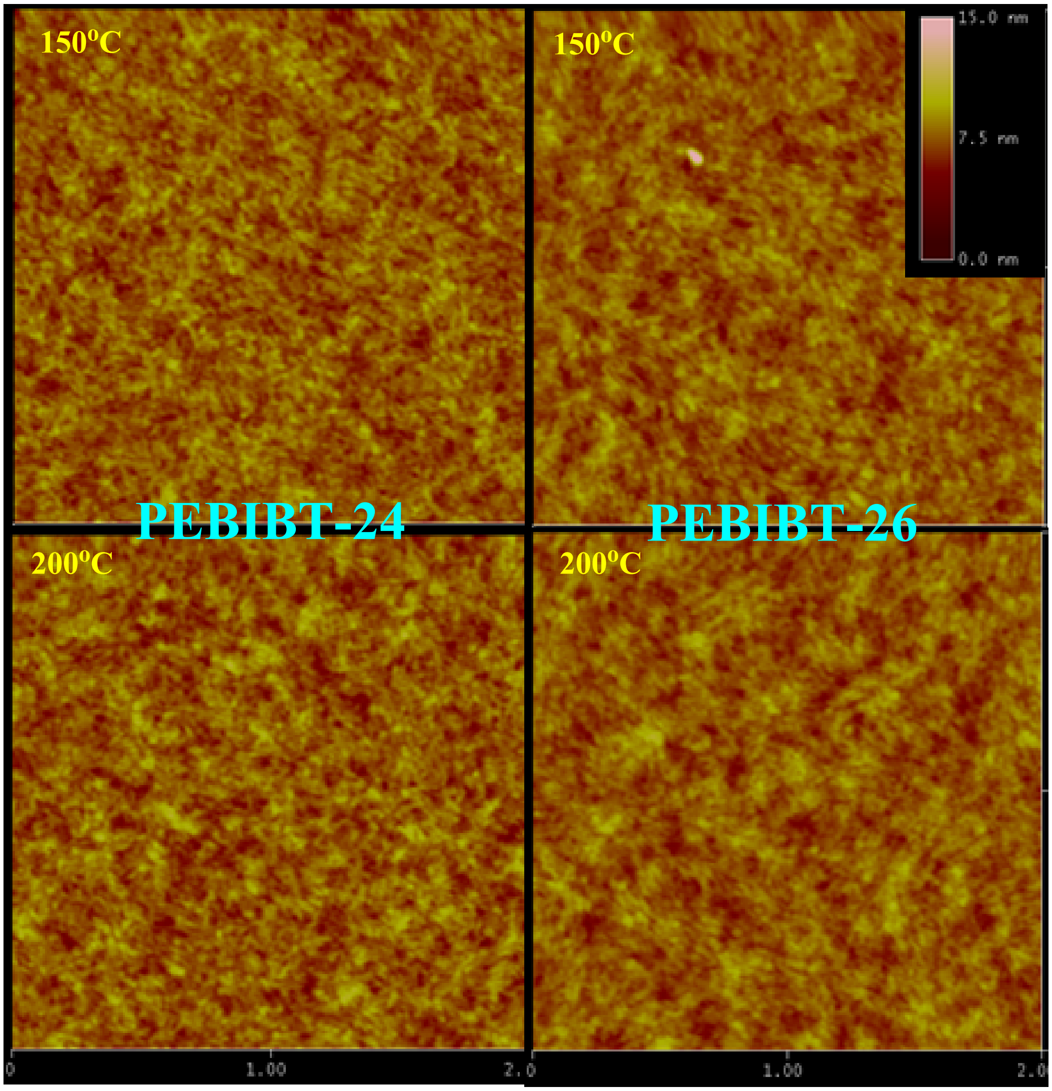
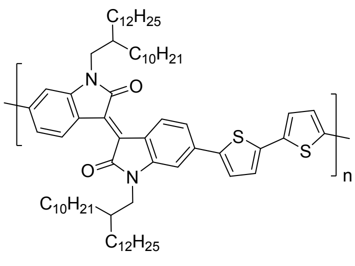


Fig. S11 AFM images (height) of spin-coated **PEBIBT-24** and **PEBIBT-26** thin films (~35 nm) on the DTS-modified SiO_2 / Si substrate annealed at different temperatures for 15 min in nitrogen. The root mean square (RMS) roughness is 0.8 nm for the 150 °C-annealed **PEBIBT-24** thin film, 0.9 nm for the 200 °C-annealed **PEBIBT-24** thin film, 0.8 nm for the 150 °C-annealed **PEBIBT-26** thin film, and 0.8 nm for the 200 °C-annealed **PEBIBT-26** thin film.

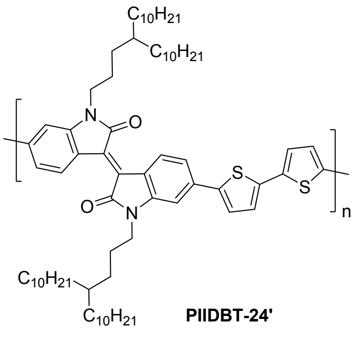
Table S1. Summary of UV-Vis and CV data of **PEBIBT-24** and **PEBIBT-26** in comparison with those of **PIIDBT-24**, **PIIDBT-24'**, and **PIBDFBT-40** reported in the literature.

Polymer	λ_{max} (solution),[b] nm	λ_{max} (film),[d] nm	E_g (opt),[f] eV	E_{HOMO} (CV),[g] eV	E_{LUMO} (CV),[g] eV
PEBIBT-24	654	As-spun: 641, 689(sh) Anneal:[e] 634, 666(sh), 689(sh)	1.6 1.6	-5.42	-3.77
PEBIBT-26	651	As-spun: 638, 686(sh) Anneal:[e] 640, 666(sh), 691(sh)	1.6 1.6	-5.31	-3.88
PIIDBT-24[a] **(ref. 4)**	647(sh),[c] 706	637(sh), 701	1.60	-5.70	-3.70
PIIDBT-24'[a] **(ref. 4)**	673(sh), 718	653(sh), 719	1.58	-5.52	-3.74
PIBDFBT-40[a] **(ref. 5)**	794	792 (sh), 834	1.31	-5.72	-4.15

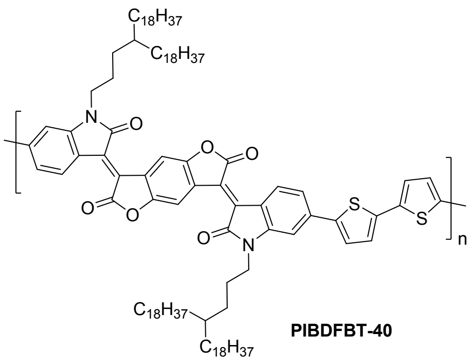
a) Data for **PIIDBT-24**, **PIIDBT-24'**, and **PIBDFBT-40** taken from the literature; b) Measured in chloroform; c) sh: absorption shoulder; d) Measured on thin films spin-coated on quartz substrates; e) Annealed at 100, 150, or 200 °C for 15 min; f) Estimated from the onset absorption wavelength of thin films; g) Determined by cyclic voltammetry using ferrocene as a reference.



PIIDBT-24



PIIDBT-24'



PIBDFBT-40

Table S2. Summary of performance of OTFT devices based on **PEBIBT-24** and **PEBIBT-26**.

Polymer	Annealing temperature (°C)	μ (cm^{2}V^{-1}s^{-1}) average (max)[a]	V_T(V)[b]	I_{on}/I_{off}[c]
PEBIBT-24	150	0.026(0.030)	-39	~10^4
	200	0.021(0.028)	-29	~10^4
PEBIBT-26	150	0.039(0.044)	-22	~10^8-10^9
	200	0.028(0.033)	-21	~10^7-10^8

[a] Average (maximum) mobility calculated from the saturation region at a drain-source voltage (V_{DS}) of -100 V.

[b] Threshold voltage.

[c] Current on-to-off ratio.

4. References

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