

SUPPORTING INFORMATION

Simple oxime functionalized fluorene polymers for organic solar cells

Abdullah Adewale Adeoba,^a Xiangyu Shen,^a Fuzhen Bi,^a Jianan Niu,^a Mingxin Sun,^c
Shuguang Wen,^{*, a, b} Xichang Bao^{*, a, b}

^a CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology

^b Functional Laboratory of Solar Energy, Shandong Energy Institute, Qingdao 266101, China

^c Qingdao New Energy Shandong Laboratory, Qingdao 266101, China

E-mail: wensg@qibebt.ac.cn; baoxc@qibebt.ac.cn

Materials

All reactions were carried out in argon atmosphere. Common solvents were dried and purified by standard procedures. Column chromatography characterizations were performed with the use of silica gel (200-300 mesh). Compound 2 was synthesized according to literature [1] [2]. Other reagents were purchased from commercial sources and used directly unless otherwise noted.

General Characterization

¹H NMR and ¹³C NMR spectra were recorded using a Bruker AVANCE-III 600 spectrometer with tetramethylsilane (TMS) as an internal standard. The absorption spectra were recorded using a Hitachi U-4100 UV-Vis scanning spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation with a three-electrode cell consisting of a platinum working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire counter electrode. CV measurements were carried out in anhydrous acetonitrile containing 0.1 M n-Bu₄NPF₆ as a supporting electrolyte under an argon atmosphere at a scan rate of 100 mVs⁻¹. Ferrocene/ferrocenium (Fc/Fc⁺) couple was used as an internal reference. The HOMO levels of the polymers were determined using the oxidation onset value. Onset potentials are values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of the

CV curves. The contact angles and surface energies were obtained by CSCDIC-200S. Atomic force microscopy (AFM) images were obtained using Agilent 5400 scanning probe microscope in tapping mode with MikroMasch NSC-15 AFM tips. The theoretical simulations and calculations of interactions were conducted by Gaussian 09 package. The optimizations for molecular conformations were conducted based on b3lyp/6-31g(d,p) basis.

Device Fabrications and Evaluations

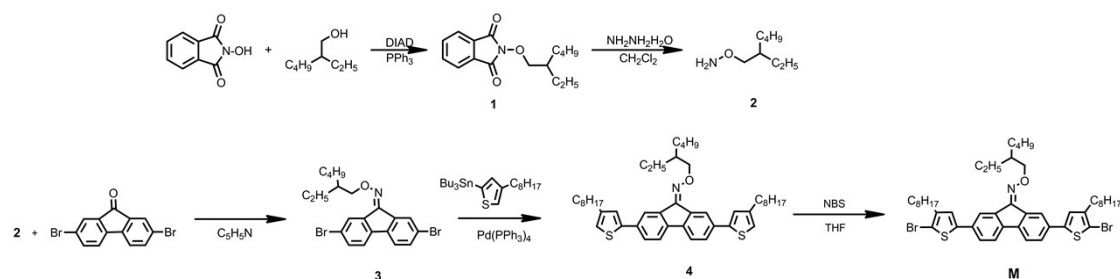
The conventional devices structure of glass/ITO/PDEOT:PSS/active layer /PDINN/Ag were fabricated. The patterned indium tin oxide (ITO, 15 Ω per square) glass substrates were sequentially ultrasonicated with detergent, deionized water, acetone, and isopropanol. The cleaned ITO substrates were dried using the high purity nitrogen and treated with oxygen plasma for 100 seconds. Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS, A1 4083, purchased from H.C. Starck co. Ltd.) solution was filtrated through a 0.22 μm filter, and was spin coated on ITO substrates at 4000 rpm for 25 s to form a thin layer of 30 nm. The polymer and Y6 blend were prepared in chloroform with a concentration of 10 mg/mL for polymer. The solution was stirred several hours at room temperature and spin-coated on the PEDOT:PSS layer at a speed of 3000 rpm for 40 s to form a \sim 100 nm thickness of active layer. The glass was then thermal annealed at 80 $^{\circ}\text{C}$ for 8 min. The cathode interlayer, PDINN (1 mg mL^{-1} in methanol) were stirred on the active layer at a speed of 3000 rpm for 15 s to form a thickness of 5 nm film. Finally, 100 nm Ag were deposited under the 2.0×10^{-5} Pa vacuum condition. The device area was 0.1 cm^2 defined by shadow mask.

The current density–voltage (J – V) characteristics were recorded with a Keithley 2400 source measurement unit under simulated 100 mW cm^{-2} irradiation from a Newport solar simulator. The external quantum efficiencies (EQEs) were analyzed using a certified Newport measurement system. The hole mobility and electron mobility were measured by space-charge-limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/active layer/ MoO_3 /Ag and ITO/ ZnO /active layer/PDINN/Ag structure, respectively. The SCLC is described by the Mott–Gurney law:

$$J = 9\epsilon\mu V^2/(8L^3)$$

where ϵ represents the dielectric constant of the metal, and μ is the carrier mobility, V is the voltage drop across the device and L is the thickness of the active layer.

Synthetic procedure



2-((2-ethylhexyl)phthalimidoxy) (1)

N-hydroxyphthalimide (21 mmol), 2-ethylhexan-1-ol (21 mmol), and triphenylphosphine (21 mmol) were added to a dry argon filled reaction flask. Anhydrous THF solvent was then added to the mixture and diisopropylazodicarboxylate (DIAD) (1.1 eq) was added dropwise while the solution is being stirred. The mixture was left to stir for 24 h at room temperature after which the solvent was evaporated to give an oily residue which was triturated with Et₂O. The precipitated solid was filtered and the Et₂O solution was vacuum evaporated to give an oil which was purified by column chromatography using petroleum ether and ethyl acetate (9:1) to give a pale yellow oil. Yield : 90%. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.82 (s, 2H), 7.75 (s, 2H), 4.11 (s, 1H), 3.76 (s, 1H), 1.90 – 1.81 (m, 73H), 1.80 – 1.03 (m, 49H).

O-(2-ethylhexyl)hydroxylamine (2)

Hydrazine monohydrate (5 mmol) was added slowly to a solution of (**1**) 120 mL CH₂Cl₂. White solid was observed in minutes. The reaction was left to stir for 24 h at room temperature. The white solid was filtrated away and the crude product purified by flash chromatography (petroleum ether-ethyl acetate 10:1) to afford pale yellow oil with a yield of 63%. ¹H NMR (600 MHz, Chloroform-*d*) δ 3.56 (d, *J* = 6.1 Hz, 1H), 1.59 – 1.51 (m, 0H), 1.41 – 1.17 (m, 4H), 0.89 (m, *J* = 7.4, 7.0 Hz, 3H).

2,7-dibromo-9H-fluoren-9-one O-(2-ethylhexyl) oxime (3)

The intermediate (**2**) above was reacted with a commercially gotten 2,7-dibromo-9H-fluoren-9-one (1 eq) in pyridine under reflux. Na₂SO₄ was added to absorb the water byproduct. The product was concentrated and purified with petroleum ether only on a

flash chromatography and confirmed by ^1H NMR spectroscopic analysis. Yield: 72%. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.39 (d, $J = 1.9$ Hz, 1H), 7.89 (d, $J = 1.8$ Hz, 1H), 7.61 – 7.41 (m, 4H), 4.36 (dd, $J = 6.0, 1.2$ Hz, 2H), 1.84 (m, $J = 6.2, 5.6$ Hz, 1H), 1.56 – 1.24 (m, 11H), 0.96 – 0.73 (m, 3H).

2,7-bis(4-octylthiophen-2-yl)-9H-fluoren-9-one O-(2-ethylhexyl) oxime (4)

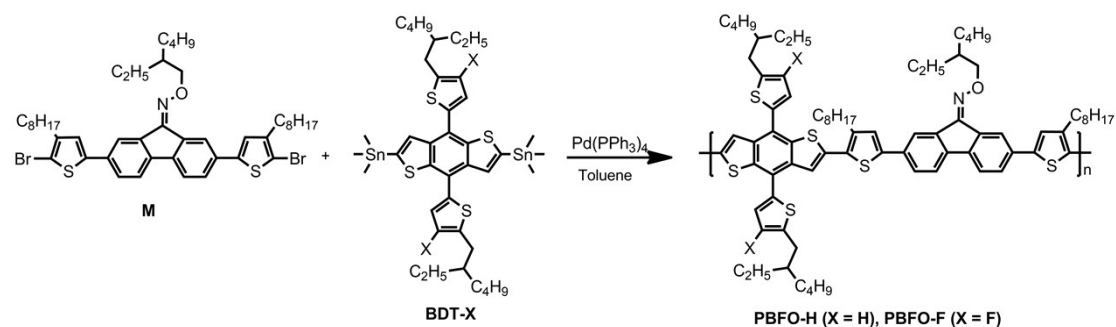
2,7-dibromo-9H-fluoren-9-one O-(2-ethylhexyl) oxime (3.3 mmol) and Tributyl(4-octylthiophen-2-yl)stannane (2.5 eq) were added to an argon-filled vacuum flask. $\text{Pd}_2(\text{dba})_3$ (60 mg) and Tri(*o*-tolyl)phosphine (120.6 mg) were added as catalyst and ligand respectively and the flask was de-oxygenated. Anhydrous toluene (35 mL) was added to the reactants under argon atmosphere and the mixture was reacted under reflux for 24 h. After that, the solvent was evaporated, and the product was separated with column chromatography using petroleum ether-dichloromethane mixture (20:1) to afford a lemon color oil. Yield: 47%. The product was confirmed by ^1H NMR spectroscopic analysis. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.58 (d, $J = 1.7$ Hz, 1H), 7.99 (d, $J = 1.6$ Hz, 1H), 7.71 – 7.55 (m, 4H), 7.26 (s, 1H), 7.19 (d, $J = 1.4$ Hz, 1H), 6.88 (dd, $J = 4.2, 1.2$ Hz, 2H), 4.47 – 4.39 (m, 2H), 2.62 (t, $J = 7.7$ Hz, 4H), 1.86 (p, $J = 6.1$ Hz, 1H), 1.71 – 0.78 (m, 43H).

2,7-bis(5-bromo-4-octylthiophen-2-yl)-9H-fluoren-9-one O-(2-ethylhexyl) oxime

In a dry flask, compound (4) (757 mg, 1.087 mmol) above and N-bromosuccinimide (2.2 eq) was added. Anhydrous THF was used to dissolve the reactants and stirred argon atmosphere. After 24 h, the solvent was evaporated and the product purified petroleum ether-dichloromethane (20:1) on a column chromatograph to give the monomer **M**. Yield: 70 %. The product was confirmed by ^1H and ^{13}C NMR spectroscopic analysis. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, $J = 1.7$ Hz, 1H), 7.90 (d, $J = 1.7$ Hz, 1H), 7.71 – 7.44 (m, 4H), 7.07 (d, $J = 38.1$ Hz, 2H), 4.47 – 4.38 (m, 2H), 2.60 – 2.54 (m, 4H), 1.85 (hept, $J = 6.2$ Hz, 1H), 1.69 – 0.84 (m, 47H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.25 (d, $J = 2.5$ Hz), 139.90, 138.88, 136.63, 133.71 (d, $J = 37.6$ Hz), 131.55, 127.57, 126.86, 125.97, 124.10 (d, $J = 37.9$ Hz), 120.30 (d, $J = 17.8$ Hz), 118.18, 108.38 (d, $J = 9.8$ Hz), 78.86, 39.52, 31.90, 30.78, 30.27 – 27.58 (m), 24.05, 22.92 (d, $J = 72.0$ Hz), 14.15 (d, $J = 7.1$ Hz), 11.29.

Co-polymerization towards PBFO



The monomer **M** (0.05 mmol), BDT-X monomer (0.05 mmol), Pd (PPh₃)₄ (0.05 equivalent) were mixed in a 50 ml double-neck round-bottom flask. The container was purged three times with successive vacuum argon filling cycles. Afterwards, anhydrous toluene (5 mL) was added and argon gas was bubbled through the mixture for 10 mins while providing an outlet for the removal of oxygen. The reaction proceeded for around 4 h before polymer precipitate was being noticed. The reactant was cooled down to room temperature and poured into methanol, filtered and then subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight to give the dried polymer.

PBFO-H: 57 mg (yield: 65%)

PBFO-F: 40 mg (yield: 45%)

Supplementary Figures

(a)

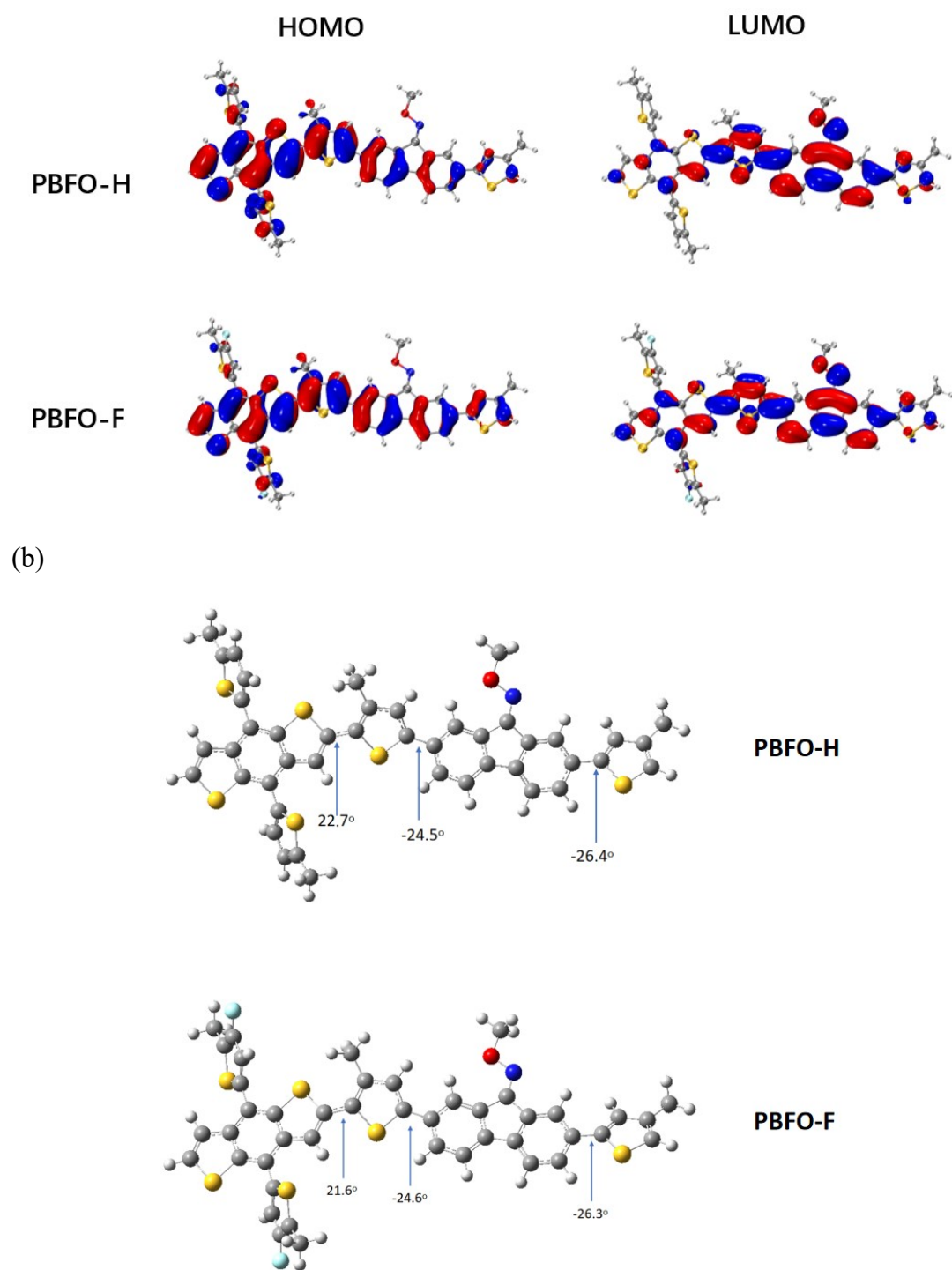


Figure S1. (a) Theory calculated optimized molecular orbitals (a) and geometries (b) of the polymers by DFT calculation at the B3LYP/6-31G(d, p) level;

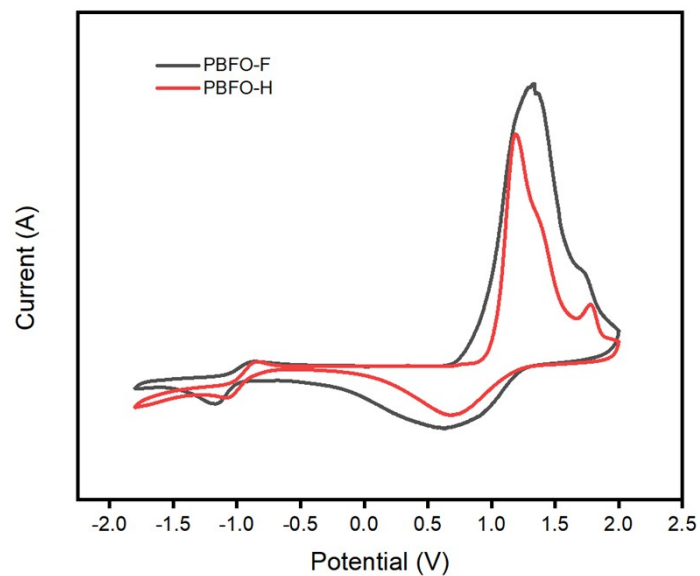


Figure S2. Cyclic voltammograms of PBFO-H and PBFO-F on platinum electrodes in 0.1 M Bu_4NPF_6 in CH_3CN at a scan rate of 100 mV s^{-1} .

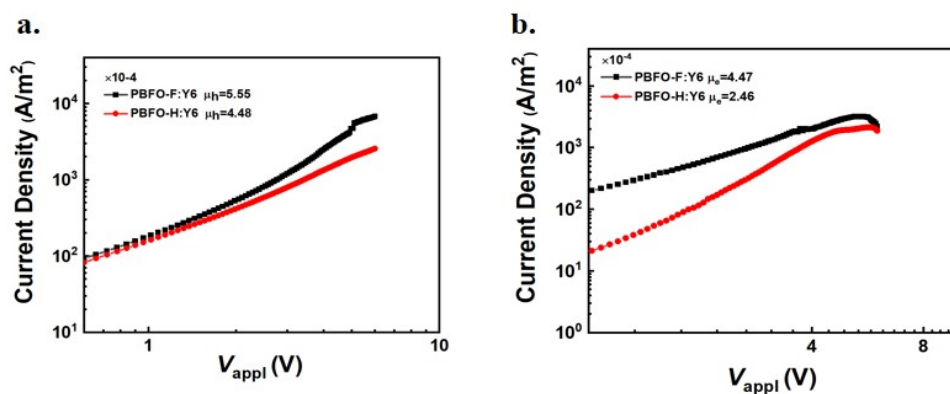


Figure S3. J - V curves of (a) hole-only diodes and (b) electron-only diodes of blend films.

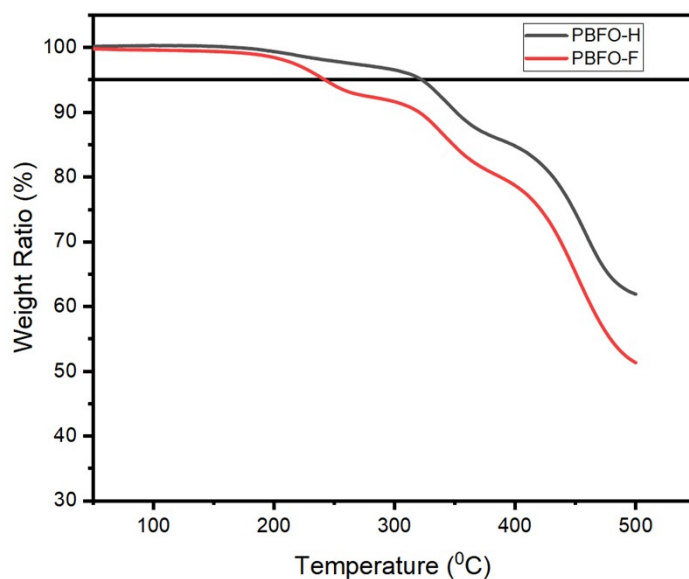


Figure S4. TGA curves of the polymers measured at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen.

Table S1. Photovoltaic performance of the devices based on PBFO-H:Y6 with different processing conditions under the illumination of AM1.5G, 100 mW/cm^2 .

PBFO-H :Y6	D:A Ratio	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
additive-free	1:1.2	0.79	18.32	44.76	6.46 (6.40 ± 0.07)
0.4%CN	1:1.2	0.79	17.55	42.35	5.86 (5.53 ± 0.40)
0.3%DIO	1:1.2	0.76	20.62	46.39	7.31 (7.00 ± 0.35)
0.2%DIO	1:1	0.77	19.94	47.38	7.26 (6.93 ± 0.34)
	1:1.2	0.77	20.83	45.91	7.32 (6.85 ± 0.40)
	1:1.4	0.75	18.75	43.74	6.16 (5.95 ± 0.27)

Table S2. Photovoltaic performance of the devices based on PBFO-F:Y6 with different processing conditions under the illumination of AM1.5G, 100 mW/cm^2 .

PBFO-F : Y6	D:A Ratio	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
additive-free	1:1.2	0.88	16.9	42.09	6.29 (5.78 ± 0.45)
0.3%DIO	1:1.2	0.82	22.54	48.78	9.04 (9.00 ± 0.10)
0.4%CN	1:1.2	0.87	14.77	37.45	4.82 (4.53 ± 0.37)

0.2%DIO	1:1	0.84	23.17	55.2	10.71 (10.50 ± 0.26)
	1:1.2	0.83	23.58	50.62	9.92 (9.78 ± 0.22)
	1:1.4	0.82	21.24	42.06	7.32 (7.3 ± 0.08)

Table S3. Hole and electron mobilities of PBFO-F:Y6 and PBFO-H:Y6 devices.

Device	μ_h ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_e ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	μ_h/μ_e
PBFO-F:Y6	5.55	4.47	1.24
PBFO-H:Y6	4.48	2.46	1.82

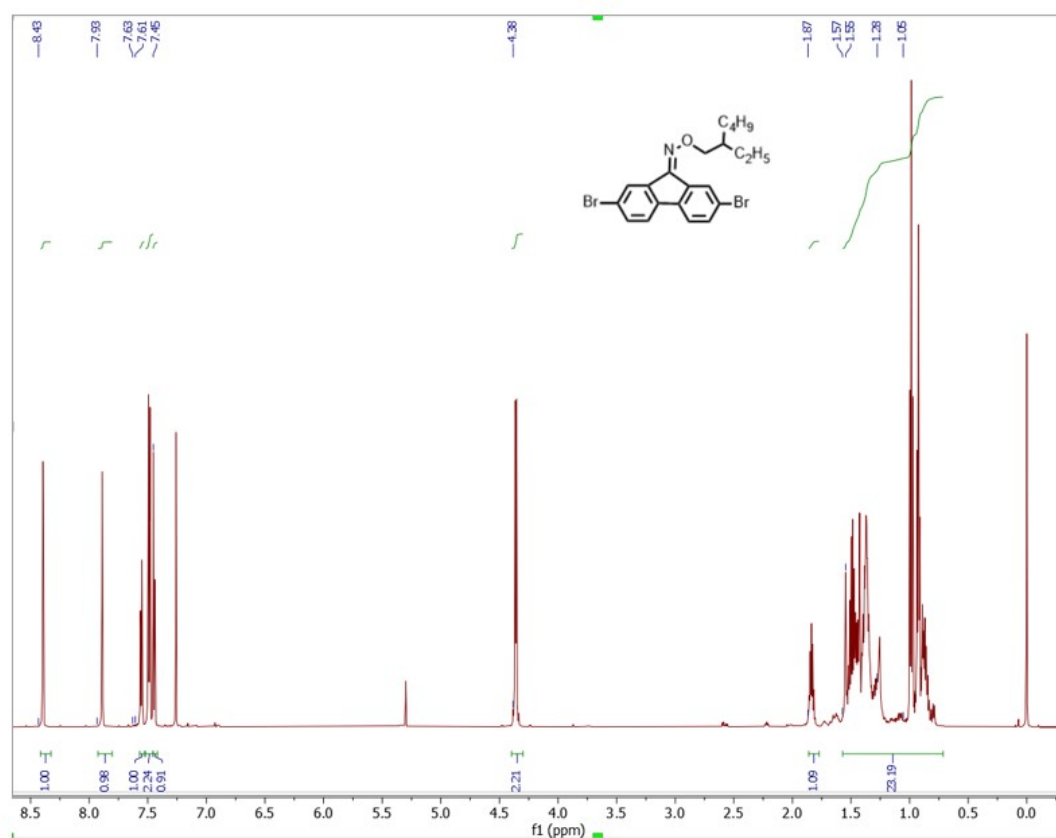


Figure S5. ¹H NMR spectra of 2,7-dibromo-9H-fluoren-9-one O-(2-ethylhexyl) oxime.

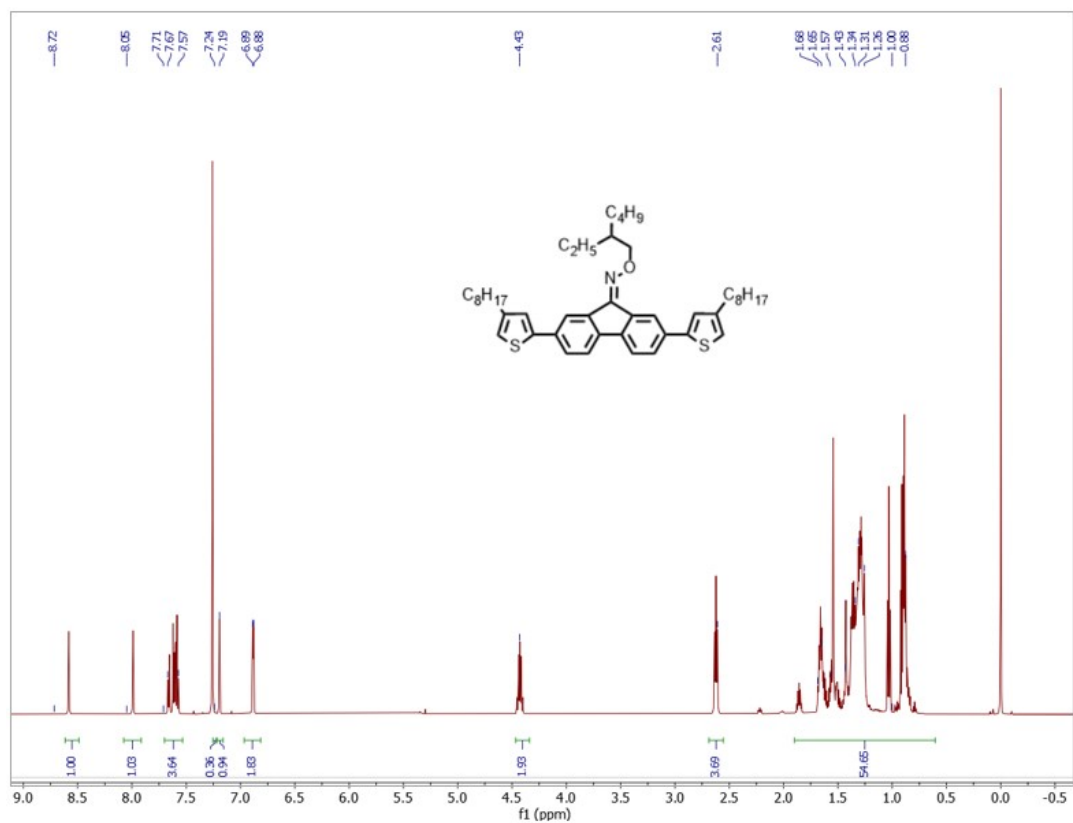


Figure S6. ¹H NMR spectra of 2,7-bis(4-octylthiophen-2-yl)-9H-fluoren-9-one O-(2-ethylhexyl) oxime.

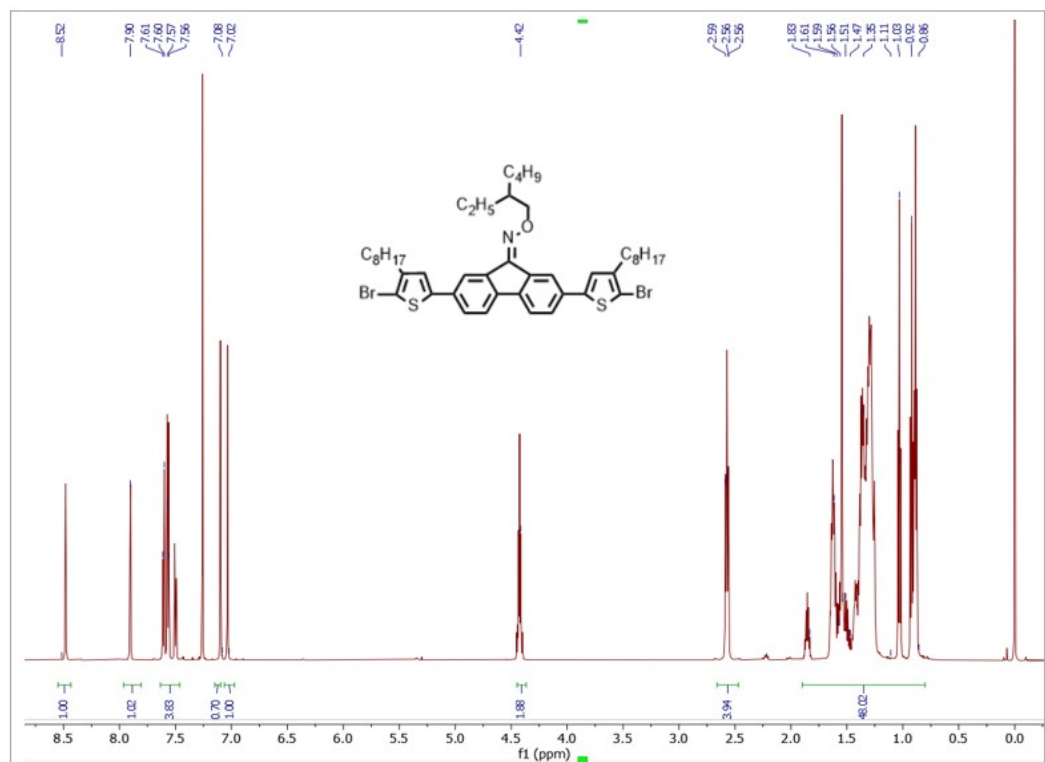


Figure S7. ¹H NMR spectra of 2,7-bis(5-bromo-4-octylthiophen-2-yl)-9H-fluoren-9-one O-(2-ethylhexyl) oxime.

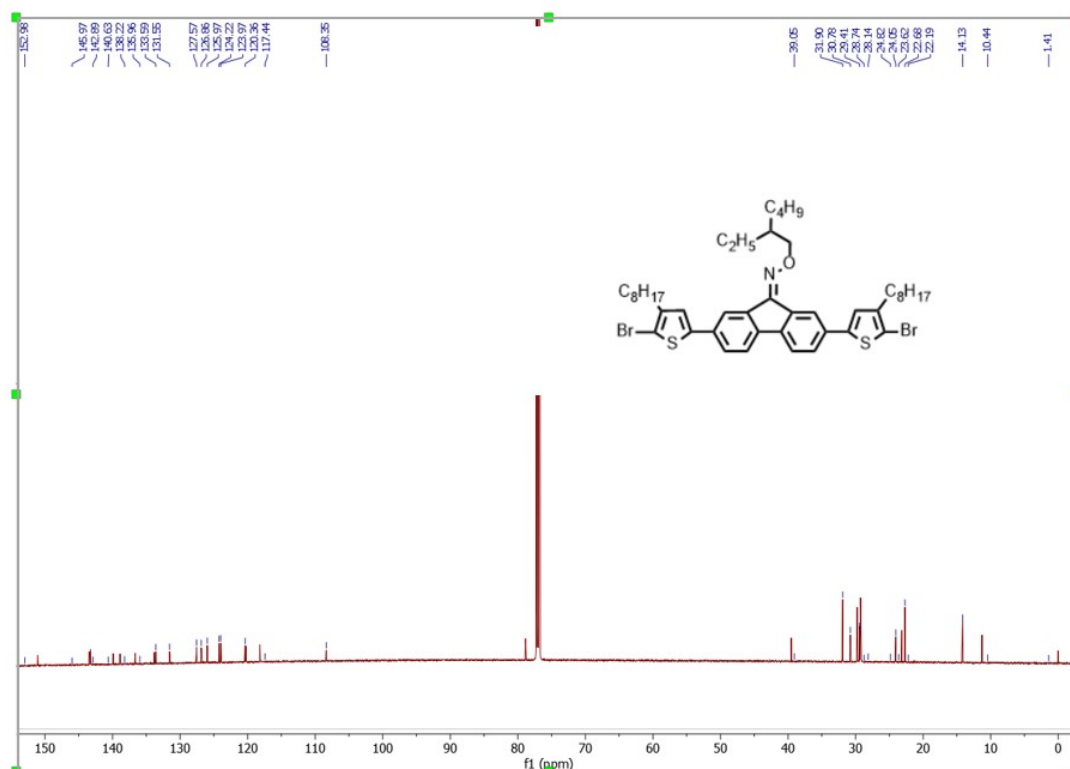


Figure S8. ¹³C NMR spectra of 2,7-bis(5-bromo-4-octylthiophen-2-yl)-9H-fluoren-9-one O-(2-ethylhexyl) oxime.

References

- [1] D. Zhu, Q. Zhu, C. Gu, D. Ouyang, M. Qiu, X. Bao, R. Yang, Alkoxy Side Chain Substituted Thieno[3,4-c]pyrrole-4,6-dione To Enhance Photovoltaic Performance with Low Steric Hindrance and High Dipole Moment, *Macromolecules* 49 (2016) 5788-5795.
- [2] Aldo Balsamo, Simone Bertini, Giambattista Gervasio, Annalina Lapuccia, E.O. Susanna Nencetti, Simona Rapposella, Armando Rossello, G. Soldani, Enantiopure 3-(arylmethylidene)aminoxy-2-methylpropionic acids: synthesis and antiinflammatory properties *European Journal of Medicinal Chemistry* (2001) 799-807.