Supporting Information

for

Effect of the π-conjugation length on the properties and photovoltaic performance of A–π–D–π–A type oligothiophenes with a 4,8-bis(thienyl)-benzo[1,2-b:4,5-b’]dithiophene core

Ni Yin¹,², Lilei Wang¹,³, Yi Lin⁴, Jinduo Yi¹, Lingpeng Yan¹, Junyan Dou¹,
Hai-Bo Yang³, Xin Zhao*² and Chang-Qi Ma*¹

Address: ¹Printable Electronics Research Center, Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences, 398 Ruo Shui Road, SEID SIP, Suzhou, Jiangsu, 215123, P. R. China; ²College of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, 1 Ke Rui Road, Suzhou, Jiangsu, 215009, P. R. China; ³Department of Chemistry, Shanghai Key Laboratory of Green Chemistry and Chemical, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China and ⁴Department of Chemistry, Xi’an Jiaotong Liverpool University, 111 Ren Ai Road, Dushu Lake Higher Education Town, Suzhou, Jiangsu, 215123, P. R. China

Email: Xin Zhao* - zhaoxinsz@126.com; Chang-Qi Ma* – cqma2011@sinano.ac.cn

* Corresponding author

Additional experimental data
Experimental

Materials and reagents

Chemicals, including: 2-bromo-3-hexylthiophene (Puyang Huicheng Chemical Co. Ltd.), Pd₂dba₃·CHCl₃ and HPt-Bu₃-BF₄ (Sigma-Aldrich), cctyl cyanoacetate, piperidine, malononitrile, and β-alanine (Energy Chemical Co. Ltd.), 1,1’-[4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl]bis[1,1,1-trimethylstannane] (16, Derthon Optoelectronic Materials Co., Ltd) PC₆₁BM (Solarmer Materials (Beijing) Inc.) and comment organic solvents (Sinopharm Chemical Reagent Co., Ltd and Chinasun Specialty Products Co., Ltd) were purchased from commercial sources. Anhydrous tetrahydrofuran (THF) and chloroform for device fabrication were purified according to a standard method [1]. 2-Bromo-3-hexylthiophene was distilled before use. Other chemicals were used as received. 5-Bromo-4-hexylthiophene-2-carbaldehyde (9) [2], 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trimethylsilane-4-hexylthiophene (6) [3], and 5(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5’-(trimethylsilyl)-3,4’-dihexyl-2,2’-bithiophene (8) [4] were synthesized according to the literature. Synthesis procedures of the aldehyde terminated precursors (CHO-nHT-TBDT) and the final compounds (COOP-nHT-TBDT) are similar to the method reported in our previous paper [5]. Chemical structure characterization, organic solar cell fabrication and testing conditions, as well as the long-term stability testing for organic solar cells have been reported in our previous papers [5,6].
Measurements and characterization

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance III 400 MHz and CDCl₃ as solvent. Chemical shifts are reported as δ values (ppm) with tetramethylsilane (TMS) as the internal standard. GC-MS was measured on Agilent GC-MS 5975C spectrometry. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) spectra were recorded on a Brucker Autoflex Speed using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. UV–vis absorption spectrum was recorded on a PerkinElmer Lambda 750. For UV–vis absorption spectrum measurement in solution, three solutions (around 10⁻³·mol·L⁻¹) were prepared independently, each of which were further diluted to get three diluted solutions (with concentrations around 10⁻⁷ to 10⁻⁶ mol·L⁻¹) for UV–vis absorption measurements. The absorption spectra of the dilute solutions were recorded, and the data points of the absorbance at a certain wavelength vs concentration were then plotted. A good linear relationship was found for all these compounds, suggesting no obvious intermolecular interaction was found in such a concentration range. The molecular molar extinction coefficient (ε) was obtained from the slope of the best-fit line over the above mentioned data points according to the Beer–Lambert equation, \( A = \varepsilon \cdot L \cdot c \). Thin solid films for UV–vis absorption measurements were prepared by spin coating a chloroform solution (8 mg·mL⁻¹) on quartz. Cyclic voltammetry (CV) was obtained in a tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 mol·L⁻¹) supported CH₂Cl₂ solution at room temperature using a RST3000 electrochemical workstation (Suzhou Risetech Instrument Co., Ltd) operated at a scanning rate of 100 mV·s⁻¹. A Pt wire (1.0 mm diameter)
embedded in Teflon column was used as the working electrode, and a Pt sheet and Ag/AgCl electrodes were served as the counter and reference electrodes, respectively. Ferrocene/ferrocenium was used as the internal reference to calibrate the redox potentials.

**Fabrication and characterization of organic solar cells**

The devices were fabricated with a traditional structure of glass/ITO/PEDOT:PSS (30 nm)/photoactive layer/LiF (1.5 nm)/Al (100 nm). The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 30 min each, and dried by a nitrogen blow subsequently. After routine solvent cleaning, the ITO substrates were treated with UV ozone for 30 min and 30 nm of PEDOT:PSS (Clevios P VP Al 4083, filtered through 0.45 μm) was spin-coated at 3500 rpm. After transferred into an N₂-filled glovebox, the substrates were baked at 124 °C for 10 min. After that, the active layer was spin-coated from donor-acceptor blend chloroform solutions with different ratios. At last, LiF (1.5 nm) and Al (100 nm) were evaporated onto the active layer under vacuum (pressure below $1 \times 10^{-4}$ Pa) through a shadow mask to form the cathodes. The effective area of the devices was 0.16 cm² or 0.09 cm², and both two types of devices provide similar performance. The active layer thickness was measured using an AlphaStep profilometer (Veeco, Dektak 150). The current density–voltage ($J–V$) characteristics were measured in a N₂-filled glove box using a Keithley 2400 source meter under an AM 1.5G filter (100 mW·cm⁻²) generated by white light of a tungsten halogen lamp, filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter. External quantum efficiencies (EQE)
were measured under simulated one sun operation condition using bias light from a 532 nm solid-state laser (Changchun New Industries, MGL-III-532). Light from a 150 W tungsten halogen lamp (Osram 64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Zolix, Omni-λ300) to select the wavelength. The response was recorded as the voltage by an $I-V$ converter (DNR-IV Convertor, Suzhou D&R Instruments), using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device for EQE measurement was kept behind a quartz window in a nitrogen filled container.

**Long-term stability test of the organic solar cells**

The long-term stability of un-encapsulated devices was tested using a thin film solar cell decay testing system (PVLT-G801M, Suzhou D&R Instruments) under the testing condition that is in accordance with ISOS-L-1. In detail, the un-encapsulated devices were put inside a glove box ($\text{H}_2\text{O} < 10 \text{ ppm, } \text{O}_2 < 10 \text{ ppm}$), and continuously illuminated with LED white light (color temperature, 6000 K). The illumination light intensity was initially set as the output device short circuit current equals to $J_{SC}$ measured under standard conditions. The illumination light intensity was monitored by a photodiode (Hamamatsu S1336-8BQ). Maximum power outputs (mpp) of these devices were checked periodically according to the $J-V$ measurement, and the devices were attached with an external load at the maximum power output point under illumination. The device temperature was monitored to be around 35–40 °C during the testing.
Synthesis of materials

3,4'-dihexyl-5'-(trimethylsilyl)-2,2'-bithiophene-5-carbaldehyde (10):

A solution of 9 (5.60 g, 15.3 mmol), 6 (3.00 g, 10.9 mmol), Pd₂dba₃·CHCl₃ (226 mg, 21.8 µmol) and HPtBu₃·BF₄ (127 mg, 43.6 µmol) in THF (100 mL) was degassed by bubbling N₂ for 30 min. A N₂-degrassed K₂CO₃ solution (1M, 30 mL, 30 mmol) was added and the resulting mixture was vigorously stirred at room temperature overnight under N₂ atmosphere. The solution was extracted with ethyl ether after THF was taken off. The organic layer was dried over Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified by flash chromatography (SiO₂, n-hexane/CH₂Cl₂ = 2:1) to give a yellow oil (4.30 g, 90% yield). ¹H NMR (CDCl₃, 400 MHz) δ ppm: 9.81 (s, 1H), 7.57 (s, 1H), 7.20 (s, 1H), 2.80 (t, J = 8.0 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H), 1.70~1.55 (m, 4H), 1.42~1.31 (m, 12H), 0.92~0.88 (m, 6H), 0.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ ppm: 182.66, 151.15, 141.88, 140.17, 140.11, 139.11, 138.71, 136.20, 130.81, 31.84, 31.78, 31.69, 31.43, 30.36, 29.45, 29.43, 29.21, 14.17, 0.39.

3,4'-dihexyl-5'-iodo-2,2'-bithiophene-5-carbaldehyde (11):

To a solution of 10 (1.20 g, 2.76 mmol) in 12 mL THF was added dropwise a solution of iodine monochloride (6.1 mL, 0.9 M in THF, 5.49 mmol) at −78 °C. Then the reaction mixture was stirred for one hour and stirred at room temperature for another one hour. After that, the reaction was then quenched by Na₂S₂O₅ (1 M, 10 mL, 10 mmol). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic extract was washed with brine, then dried over Na₂SO₄. The solvent
was removed by rotary evaporator and the residue was purified by flash chromatography
(SiO\textsubscript{2}, n-hexane/CH\textsubscript{2}Cl\textsubscript{2} = 2:1) to give a yellow oil (1.01 g, 75% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3},
400 MHz) \(\delta\) ppm: 9.83 (s, 1H), 7.57 (s, 1H), 6.91 (s, 1H), 2.75 (t, \(J = 7.6\) Hz, 2H), 2.65 (t, \(J = 8.0\) Hz, 2H), 1.69-1.56 (m, 4H), 1.43-1.27 (m, 12H), 0.92-0.87 (m, 6H). \textsuperscript{13}C NMR
(100 MHz, CDCl\textsubscript{3}) \(\delta\) ppm: 182.56, 148.14, 140.65, 140.56, 140.49, 139.56, 138.82,
127.97, 76.93, 32.32, 31.67, 31.65, 30.31, 29.96, 29.34, 29.16, 28.93, 22.66, 66.65 14.16,

3,4',4''-trihexyl-5''-(trimethylsilyl)-2,2':5',2''-terthiophene-5-carbaldehyde (12):
A solution of 11 (3.88 g, 7.95 mmol), 6 (4.37 g, 11.9 mmol), Pd\textsubscript{2}(dba)\textsubscript{3}·CHCl\textsubscript{3} (165 mg,
0.159 mmol) and HPt-Bu\textsubscript{3}·BF\textsubscript{4} (92 mg, 0.318 mmol) in THF (80 mL) was degassed by
bubbling N\textsubscript{2} for 30 min. A N\textsubscript{2}-degassed K\textsubscript{2}CO\textsubscript{3} solution (1M, 20 mL, 20 mmol) was added
and the resulting mixture was added and the resulting solution was vigorously stirred at
room temperature overnight under N\textsubscript{2} atmosphere. The solution was extracted with ethyl
ether after THF was taken off. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent
was removed in vacuo. The crude product was purified by flash chromatography (SiO\textsubscript{2},
n-hexane/CH\textsubscript{2}Cl\textsubscript{2} = 2:1) to give 12 (3.90 g, 82% yield) as an orange oil. \textsuperscript{1}H NMR (CDCl\textsubscript{3},
400 MHz) \(\delta\) ppm: 9.81 (s, 1H), 7.58 (s, 1H), 7.11 (s, 1H), 7.09 (s, 1H), 2.82 (t, \(J = 7.6\) Hz,
2H), 2.77 (t, \(J = 8.0\) Hz, 2H), 2.66 (t, \(J = 7.6\) Hz, 2H), 1.72-1.61 (m, 6H), 1.43-1.31 (m,
18H), 0.92-0.88 (m, 9H), 0.37 (s, 9H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) ppm: 182.55, 150.93,
143.86, 141.53, 141.42, 140.13, 139.96, 139.89, 139.83, 139.17, 139.13, 139.02, 134.87,
134.10, 133.51, 133.47, 132.27, 130.41, 130.35, 129.53, 127.69, 120.70, 31.78, 31.70,
31.64, 31.45, 30.53, 30.47, 30.25, 29.42, 29.27, 29.21, 29.18, 29.16, 29.02, 22.64, 22.62, 14.11, 1.96, 1.36, 0.40. MS (MALDI-TOF): calcd. for C$_{34}$H$_{52}$O$_3$Si [M]$^+$, 600.29; found, 600.32.

3,4',4''-trihexyl-5''-iodo-2,2':5',2''-terthiophene-5-carbaldehyde (13):

To a solution of 12 (0.65 g, 1.08 mmol) in 5 ml THF was added dropwise a solution of iodine monochloride (2.4 mL, 0.9 M in THF, 2.16 mmol) at $-78^\circ$C. Then the reaction mixture was stirred for one hour and stirred at room temperature for another one hour. After that, the reaction was then quenched by Na$_2$S$_2$O$_5$ (1 M, 5 mL, 5 mmol). The organic layer was separated and the aqueous layer was extracted with CHCl$_3$. The combined organic extract was washed with brine, then dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporator and the residue was purified by flash chromatography (SiO$_2$, n-hexane/CH$_2$Cl$_2$ = 2:1) to give 13 (0.49 g, 70% yield) as an orange oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm: 9.81 (s, 1H), 7.56 (s, 1H), 7.08 (s, 1H), 6.79 (s, 1H), 2.79 (t, $J = 8.0$ Hz, 2H), 2.71 (t, $J = 7.6$ Hz, 2H), 2.54 (t, $J = 8.0$ Hz, 2H), 1.71-1.56 (m, 6H), 1.41-1.25 (m, 18H), 0.91-0.87 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ ppm: 182.42, 147.25, 140.96, 140.23, 140.11, 139.77, 138.96, 132.82, 132.37, 130.18, 126.78, 74.76, 32.28, 31.57, 30.43, 30.18, 29.91, 29.36, 29.17, 29.10, 29.09, 28.86, 22.56, 14.04. MS (MALDI-TOF): calcd. for C$_{31}$H$_{43}$OS$_3$ [M]$^+$, 654.15; found, 654.13.

3,4',4''-tetrahexyl-5''-(trimethylsilyl)-2,2':5',2''-6-quinathiophene-5-carbaldehyde (14):

A solution of 11 (1.70 g, 3.48 mmol), 8 (2.41 g, 4.53 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (72.0 mg,
69.6 µmol) and HPBu_3·BF_4 (41.0 mg, 0.14 mmol) in THF (30 mL) was degassed by bubbling N_2 for 30 min. A N_2-degrassed K_2CO_3 solution (1M, 10 mL, 10 mmol) was added and the resulting mixture was vigorously stirred at room temperature for 48 h under N_2 atmosphere. The solution was extracted with CHCl_3 after THF was taken off. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. The crude product was purified by flash chromatography (SiO_2, n-hexane/CHCl_3 = 2:1) to give an orange oil (2.30 g, 86% yield). ^1H NMR (CDCl_3, 400 MHz) δ ppm: 9.82 (s, 1H), 7.58 (s, 1H), 7.12 (s, 1H), 7.08 (s, 1H), 6.99 (s, 1H), 2.84-2.75 (m, 6H), 2.65 (t, J = 7.2 Hz, 2H), 1.72-1.59 (m, 8H), 1.43-1.32 (m, 24H), 0.92-0.88 (m, 12H), 0.37 (s, 9H). ^13C NMR (100 MHz, CDCl_3) δ ppm: 182.53, 150.87, 143.75, 141.38, 140.21, 140.07, 140.02, 139.96, 139.74, 139.63, 139.46, 139.15, 135.28, 133.48, 133.07, 132.74, 132.40, 132.32, 131.80, 130.51, 129.19, 129.05, 129.02, 127.34, 120.27, 31.80, 31.72, 31.49, 30.60, 30.54, 30.47, 30.26, 29.23, 14.13, 1.97, 1.37, 0.43. MS (MALDI-TOF): calcd. for [M]^+, 766.38; found, 766.40.

3,4',4'',4'''-tetrahexyl-5''-iodo-2,2':5',2''':5'',2''''-quathiophene-5-carbaldehyde (15):

To a solution of 14 (1.40 g, 1.83 mmol) in 10 mL THF was added dropwise a solution of iodine monochloride (4.1 mL, 0.9 M in THF, 3.65 mmol) at −78 °C. Then the reaction mixture was stirred for one hour and stirred at room temperature for another one hour. After that, the reaction was then quenched by Na_2S_2O_5 (1 M, 5 mL, 5 mmol). The organic layer was separated and the aqueous layer was extracted with ethyl ether. The combined organic extract was washed with brine, then dried over Na_2SO_4. The solvent was removed by rotary evaporator and the residue was purified by flash chromatography (SiO_2,
4,8-bis[5-(2-ethylhexyl)-2-thienyl]-2,6-bis[3,3’-dihexyl-5’-aldehyde-5,2’-bithiophen-2-yl]benzo[1,2-b:4,5-b’]dithiophene (18)

A mixture of 11 (470 mg, 0.962 mmol), 16 (396 mg, 0.437 mmol), and Pd(PPh₃)₄ (50 mg, 43.7 µmol) was stirred at 80 °C in DMF (4 mL) for 16 h. After cooled to room temperature, the reaction mixture was added dropwise to anhydrous methanol (15 mL) and stirred for 0.5 hour at room temperature. A dark red solid was obtained by filtering through a Büchner funnel. The residue was purified by flash chromatography (SiO₂, n-hexane/CH₂Cl₂ = 1:1) to give 17 (465 mg, 82 %) as dark red solid. ¹H NMR (CDCl₃, 400 MHz) δ ppm: 9.83 (s, 2H), 7.70 (s, 2H), 7.59 (s, 2H), 7.35 (d, J = 3.6 Hz, 2H), 7.14 (s, 2H), 6.91 (d, J = 3.6 Hz, 2H), 2.89~2.80 (m, 12H), 1.73~1.65 (m, 10H), 1.40~1.25 (m, 40H), 0.97~0.87 (m, 24H).

¹³C NMR (100 MHz, CDCl₃) δ ppm: 182.56, 146.11, 142.48, 141.71, 140.97, 140.57, 140.30, 139.17, 139.00, 136.96, 136.79, 136.46, 134.03, 133.02, 131.76, 130.64, 127.85, 125.52, 123.55, 122.12, 41.50, 34.31, 32.55, 31.89, 31.64, 31.61, 30.55, 30.22, 29.52, 29.41, 29.24, 29.10, 28.94, 25.73, 23.05, 22.64, 22.59, 14.17, 14.11, 14.08, 10.92. MS
(MALDI-TOF): calcd. for C_{76}H_{98}O_2S_8 [M]^+, 1298.53; found 1298.46.

4,8-bis[5-(2-ethylhexyl)-2-thienyl]-2,6-bis[3,3',3''-trihexyl-5''-aldehyde-5,2':5',2''-terthiophen-2-y1]benzo[1,2-b:4,5-b']dithiophene (19):

A mixture of 13 (321 mg, 0.491 mmol), 16 (202 mg, 0.223 mmol), and Pd(PPh$_3$)$_4$ (26 mg, 22.3 µmol) was stirred at 80 °C in DMF (3 mL) for 16 h. After cooled to room temperature, the reaction mixture was added dropwise to anhydrous methanol (10 mL) and stirred for 0.5 h at room temperature. A dark red solid was obtained by filtering through a Büchner funnel. The residue was purified by flash chromatography (SiO$_2$, n-hexane/CH$_2$Cl$_2$ = 1:1) to give 19 (220 mg, 60 %) as a dark red solid. $^1$H NMR (CDCl$_3$, 400 MHz) δ ppm: 9.83 (s, 2H), 7.68 (s, 2H), 7.59 (s, 2H), 7.35 (d, $J$ = 3.6 Hz, 2H), 7.13 (s, 2H), 7.03 (s, 2H), 6.91 (d, $J$ = 3.6 Hz, 2H), 2.89~2.78 (m, 16H), 1.74~1.65 (m, 14H), 1.49~1.31 (m, 52H), 0.98~0.88 (m, 30H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm: 182.51, 145.93, 141.49, 141.17, 140.40, 140.31, 140.07, 139.05, 136.92, 136.72, 134.50, 132.72, 131.39, 130.47, 129.31, 127.26, 125.44, 123.46, 121.61, 41.47, 34.28, 32.53, 31.64, 30.57, 30.39, 30.21, 29.57, 29.41, 29.26, 29.12, 28.92, 25.71, 23.02, 22.63, 22.58, 14.15, 14.07, 10.89. MS (MALDI-TOF): calcd. for C$_{96}$H$_{126}$O$_2$S$_{10}$ [M]$^+$, 1630.69; found 1631.65.

4,8-bis[5-(2-ethylhexyl)-2-thienyl]-2,6-bis[3,3',3''-tetrahexyl-5''-aldehyde-5,2':5',2''-quathiophen-2-y1]benzo[1,2-b:4,5-b']dithiophene (20):

A mixture of 15 (500 mg, 0.609 mmol), 16 (250 mg, 0.277 mmol), and Pd(PPh$_3$)$_4$ (32 mg, 27.7 µmol) was stirred at 80 °C in DMF (3 mL) for 16 h. After cooled to room temperature,
the reaction mixture was added dropwise to anhydrous methanol (15 mL) and stirred for
0.5 h at room temperature. A dark red solid was obtained by filtering through a Büchner
funnel. The residue was purified by flash chromatography (SiO\(_2\), \(n\)-hexane/CHCl\(_3\) = 2:1) to
give 20 (398 mg, 81 %) as a dark red solid. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) ppm: 9.83 (s, 2H),
7.68 (s, 2H), 7.59 (s, 2H), 7.36 (d, \(J = 3.6\) Hz, 2H), 7.13 (s, 2H), 7.01 (d, \(J = 1.6\) Hz, 4H),
6.92 (d, \(J = 3.6\) Hz, 2H), 2.89–2.79 (m, 20H), 1.74–1.66 (m, 18H), 1.46–1.28 (m, 64H),
1.00–0.92 (m, 36H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) ppm: 182.53, 145.91, 141.44, 141.27,
140.30, 140.26, 140.24, 140.05, 139.11, 139.02, 137.01, 136.94, 136.85, 134.97, 133.25,
132.91, 132.56, 131.08, 130.95, 130.52, 129.16, 128.98, 127.78, 125.46, 123.31, 121.49,
41.50, 34.32, 32.56, 31.68, 31.64, 31.60, 30.46, 30.25, 29.62, 29.22, 29.16, 28.96, 25.74,
23.06, 22.67, 22.64, 22.62, 14.19, 14.12, 10.92. MS (MALDI-TOF): calcd. for
C\(_{116}\)H\(_{154}\)O\(_2\)S\(_{12}\)[M]\(^+\), 1962.86; found 1962.73.

4,8-bis[5-(2-ethylhexyl)-2-thienyl]2,6-bis[3,3’-dihexyl-5’(2-cyano-3octyloxy-3oxo-
1-propenyl)- 5,2’-bithiophen-2-yl]benzo[1,2-b:4,5-b’]dithiophene (2):

Octyl cyanoacetate (154 mg, 0.780 mmol) was added to a solution of 18 (390 mg,
0.300 mmol) and piperidine (0.1 mL) in dry CHCl\(_3\) (80 mL) and then the solution was
stirred for 24 h under N\(_2\) at 60 °C. Water was added and the reaction mixture was
extracted with CHCl\(_3\), the combined extracts were washed three times with water and then
dried (MgSO\(_4\)). The solvent was evaporated under reduced pressure and the crude
product further purified through column chromatography (SiO\(_2\), \(n\)-hexane/CHCl\(_3\) = 3:2) to
afford a dark powder (0.434 g, 87%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) ppm: 8.20 (s, 2H), 7.71
(s, 2H), 7.58 (s, 2H), 7.36 (d, J = 3.6 Hz, 2H), 7.21 (s, 2H), 6.92 (d, J = 3.6 Hz, 2H), 4.29 (t, J = 6.8 Hz, 4H), 2.89~2.81 (m, 12H), 1.79~1.63 (m, 14H), 1.47~1.26 (m, 60H), 0.97~0.87 (m, 30H). 13C NMR (100 MHz, CDCl3) δ ppm: 163.15, 146.11, 146.03, 141.89, 141.66, 140.90, 140.67, 139.18, 137.00, 136.74, 136.45, 133.68, 133.52, 132.98, 131.04, 127.88, 125.55, 123.58, 122.14, 116.03, 97.77, 66.59, 41.49, 34.31, 32.55, 31.79, 31.63, 31.59, 30.58, 30.09, 29.57, 29.19, 29.11, 28.94, 28.58, 30.09, 29.57, 29.19, 29.11, 28.94, 28.58, 25.82, 25.73, 23.04, 22.65, 22.59, 14.17, 14.10, 14.08, 10.91.

MS (MALDI-TOF): calcd. for C98H132N2O4S8 [M]+, 1656.79; found 1656.76.

4,8-bis[5-(2-ethylhexyl)-2-thienyl]-2,6-bis[3,3',3''-trihexyl-5''-(2-cyano-3-octyloxy-3-oxo-1-propenyl)-5,2':5',2''-terthiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene (3):

Octyl cyanoacetate (51 mg, 0.257 mmol) was added to a solution of 19 (140 mg, 0.0858 mmol) and piperidine (0.1 mL) in dry CHCl3 (40 mL) and then the solution was stirred for 24 h under N2 at 60 °C. Water was added and the reaction mixture was extracted with CHCl3, the combined extracts were washed three times with water and then dried (Na2SO4). The solvent was evaporated under reduced pressure and the crude product further purified through column chromatography (SiO2, n-hexane/CHCl3 = 1:1) to afford a dark powder (0.136 g, 80%). 1H NMR (CDCl3, 400 MHz) δ ppm: 8.20 (s, 2H), 7.68 (s, 2H), 7.57 (s, 2H), 7.36 (d, J = 3.2 Hz, 2H), 7.19 (s, 2H), 7.04 (s, 2H), 6.92 (d, J = 3.6 Hz, 2H), 4.29 (t, J = 6.8 Hz, 4H), 2.89~2.78 (m, 16H), 1.79~1.63 (m, 18H), 1.47~1.26 (m, 72H), 0.98~0.88 (m, 36H). 13C NMR (100 MHz, CDCl3) δ ppm: 163.18, 146.01, 145.94, 141.90, 141.53, 140.97, 140.58, 140.42, 139.04, 136.92, 136.71, 134.45, 133.45, 133.25,
4,8-bis[5-(2-ethylhexyl)-2-thienyl]-2,6-bis[3,3',3'',3'''-tetrahexyl-5''-(2-cyano-3-octyloxy-3-oxo-1-propenyl)-5,2':5',2'';5'',2'''-quathiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene (4):

Octyl cyanoacetate (94 mg, 0.489 mmol) was added to a solution of compound 20 (385 mg, 0.196 mmol) and piperidine (0.1 mL) in dry CHCl₃ (80 mL) and then the solution was stirred for 24 h under N₂ at 60 °C. Water was added and the reaction mixture was extracted with CHCl₃, the combined extracts were washed three times with water and then dried (Na₂SO₄). The solvent was evaporated under reduced pressure and the crude product further purified through column chromatography (SiO₂, n-hexane/CHCl₃ = 1:1) to afford a dark brown solid (0.366 g, 80%). 

¹H NMR (CDCl₃, 400 MHz) δ ppm: 8.20 (s, 2H), 7.68 (s, 2H), 7.57 (s, 2H), 7.32 (d, J = 3.2 Hz, 2H), 7.18 (s, 2H), 7.01 (s, 4H), 6.90 (d, J = 3.6 Hz, 2H), 4.29 (t, J = 6.8 Hz, 4H), 2.89–2.78 (m, 20H), 1.79–1.65 (m, 22H), 1.49–1.26 (m, 84H), 0.98–0.88 (m, 42H). 

¹³C NMR (100 MHz, CDCl₃) δ ppm: 163.22, 146.04, 145.91, 142.00, 141.02, 140.41, 140.30, 139.02, 137.01, 136.94, 136.85, 134.95, 133.44, 133.19, 132.75, 132.19, 131.20, 130.99, 130.93, 129.21, 129.00, 127.78, 125.46, 123.31, 121.50, 116.08, 97.51, 66.56, 41.50, 34.31, 32.56, 31.79, 31.66, 31.62, 30.60, 30.49, 30.46, 30.12, 29.62, 29.43, 29.33, 29.30, 29.27, 29.20, 29.17, 28.95, 28.59, 25.82, 25.74, 23.05, 22.66, 14.18, 14.10, 10.92. 

References


UV-Vis absorption and excitation coefficient measurement

Figure S1: (a) UV–vis absorption spectra of 2 at different concentrations; (b) The fitting line of the data points of the absorbance at a certain wavelength vs. concentration.

Figure S2: (a) UV–vis absorption spectra of 3 at different concentrations; (b) The fitting line of the data points of the absorbance at a certain wavelength vs. concentration.

Figure S3: (a) UV–vis absorption spectra of 4 at different concentrations; (b) The fitting line of the data points of the absorbance at a certain wavelength vs. concentration.
**Figure S4:** Current density (J)–voltage (V) curves of (a) 2:PC<sub>61</sub>BM; (b) 3:PC<sub>61</sub>BM; (c) 4:PC<sub>61</sub>BM BHJ solar cells at different D/A ratios.
EQE spectra of organic solar cells at different blended ratio

Figure S5: EQE curves of BHJ solar cells incorporating (a) 2:PC₆₁BM, (b) 3:PC₆₁BM and (c) 4:PC₆₁BM blends of various weight ratios.

J–V curves comparison of 4:PC₆₁BM and 4:PC₇₁BM-based devices

Figure S6: Current density (J)—voltage (V) curves of devices based on 4 and PC₆₁BM or PC₇₁BM at 1:0.4 (w/w).
UV–vis absorption spectra of COOP-nHT-TBDT:PC\textsubscript{61}BM blended films

Figure S7: (a) Absorption spectra of 2 and 2:PC\textsubscript{61}BM (1:0.6, w/w), (b) 3 and 3:PC\textsubscript{61}BM (1:0.4, w/w) and (c) 4 and 4:PC\textsubscript{61}BM (1:0.4, w/w) spin-coated from CHCl\textsubscript{3} onto glass substrates.
Figure S8: (a) $^1$H and (b) $^{13}$C NMR spectra of COOP-2T-TBDT (CDCl$_3$, 400MHz)
Figure S9: (a) $^1$H and (b) $^{13}$C NMR spectra of COOP-3T-TBDT (CDCl$_3$, 400MHz)
Figure S10: (a) $^1$H and (b) $^{13}$C NMR spectra of COOP-4T-TBDT (CDCl$_3$, 400MHz)
MALDI-TOF MS results

Figure S11: MS (MALDI-TOF) spectrum of 2.

Figure S12: MS (MALDI-TOF) spectrum of 3.

Figure S13: MS (MALDI-TOF) spectrum of 4.