Electronic Supplementary Material (ESI) for Energy & Environmental Science
This journal is © The Royal Society of Chemistry 2011

Supporting Information

Linker Effects on Optoelectronic Properties of Alternate Donor-Acceptor Conjugated Polymers

*Jing Li, Ming Yan, Yu Xie, and Qiquan Qiao**

Center for Advanced Photovoltaics, Department of Electrical Engineering & Computer Science,

South Dakota State University, Brookings, South Dakota 57006

To whom correspondence should be addressed. E-mail: qiquan.qiao@sdstate.edu

Materials. All chemicals were purchased from Acros and Aldrich, and used as received. Solvents were dried according to standard procedures. All reactions were carried out under nitrogen.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 NMR spectrometer with $CDCl_3$ as solvent. The molecular weights were determined using gel permeation chromatography (Waters 410) against polystyrene standards with THF as eluent. MALDI mass spectra were recorded on a Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) mass spectrometer using chloroform as solvent and the matrix consisting of 10 mg/mL 2,5-dihydroxybenzoic acid (2, 5-DHB) in chloroform/methanol (10/1).

Synthesis and Characterization of Monomers

The chemical structures and general synthetic strategies for the monomers **1-4** are shown in the Scheme **1**. 3, 4-didodecylthiophene and 2, 1, 3-benzothiadiazole were used as starting materials to prepare other monomers. Monomer 3, 4-didodecylthiophene and 4, 7-dibromobenzo[c][1,2,5]thiadiazole were synthesized according to the literature procedures.[1, 2] By reacting with NBS (N-bromosuccinimide) and NIS (N-iodosuccinimide) in DMF in the absence of light, 3, 4-didodecylthiophene was converted to dibromo and diiodo thiophene derivatives, respectively. Finally, according to similar procedures from literature,[3, 4] the monomer 2, 5 -dibromo-3, 4-didodecylthiophene was converted to monomer **1** and **2**, as shown in Scheme 1. Monomer 4, 7-diethynylbenzo[c][1,2,5]thiadiazole was synthesized by deprotecting 4,7-bis(2-(trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole with aqueous KOH.[5]

Through Pd-catalyzed Suzuki, Heck, and Sonogashira polycondensation, **DA1**, **DA2** and **DA3** were synthesized, respectively and their detail was provided in the main paper. The chemical structures of monomers and polymers were confirmed by ^{1}H, ^{13}C NMR and high resolution mass spectroscopy (HR-MS).

3, 4-didodecylthiophene

3, 4-didodecylthiophene was synthesized according to the literature precedures.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (s, 2H), 2.51-2.47 (t, 4H), 1.63-.161(m, 4H), 1.37-1.20(m, 36H), 0.90-0.86(t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.11, 128.28, 125.01, 119.86, 119.74, 31.96, 30.59, 30.30, 29.73, 29.69, 29.66, 29.57, 29.40, 28.83, 22.72, 14.14.

2, 5 -dibromo-3, 4-didodecylthiophene

To a solution of 3, 4-didodecylthiophene (10 g, 24 mmol) in THF (100 mL) was added a THF solution of NBS (9.3 g, 52 mmol), followed by stirring for 12 h under nitrogen at room temperature in the dark. Then, water was added and the mixture was extracted with ethyl ether (3×50 ml). The combined organic phase was dried over $MgSO_4$ and then evaporated to dryness. The residue was dissolved in hexane and passed through a short pad of silica gel to afford a yellow solid (13 g, yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50-2.40(t, 4H), 1.46(m, 4H), 1.46-1.26(m, 36H), 0.88(m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 141.47, 107.82, 31.98, 29.76, 29.72, 29.62, 29.59, 29.42, 28.99, 22.75, 14.18.

2-(3,4-didodecyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)

n-Butyllithium (9.2 ml, 2.5 M in hexane, 23 mmol) was added dropwise -78 °C to 2, 5 -dibromo-3, 4-didodecylthiophene (6.0 g, 10 mmol) in 100ml dry THF and the solution was then stirred at -78 °C for 1h, followed by 1h at room temperature. Then after cooled again to -78 °C, pinacolborane (4.2 ml, 26 mmol) was added in one portion and the whole mixture was allowed to warm slowly to room temperature, followed by stirring for overnight. The reaction mixture was diluted with water, extracted with ethyl ether, and dried over $MgSO_4$. After concentrating by rotary evaporation, the residue was purified by column chromatography (hexane: ethyl acetate, 14:1) to give monomer **1** as a colorless liquid (3.5 g, yield 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78(t, 4H), 1.48-1.44(m, 4H), 1.30-1.29(m, 36H), 1.27-1.25(m, 24H), 0.90-0.86(t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 154.12, 83.45, 32.51, 31.97, 29.84, 29.77, 29.72, 29.52, 29.42, 28.53, 24.84, 24.79, 22.74, 14.17. Anal. Calcd. for $C_{40}H_{74}B_2O_4S$: C, 71.42; H, 11.09; Found: C, 71.75; H, 10.98. Calculated for $C_{40}H_{74}B_2O_4S$ ($M+H^+$): 672.55. Found: *m/z* 672.44.

3, 4-didodecyl-2, 5-divinylthiophene (2)

A flask was charged with a mixture of 2, 5-dibromo-3, 4-didodecylthiophene (1.5g, 2.6mmol), tributylvinyltin (1.81g, 5.2mmol), $Pd(PPh_3)_2Cl_2$ (73mg, 0.1mmol), and a few mg of 2,6-di-tert-butylphenol, and toluene (12ml). The mixture was stirred and heated at 100 °C for 24h under N_2. After the reaction was over, it was treated with KF solution (about 10%). The organic layer was dried with Na_2SO_4 and further purified by column chromatography using n-hexane as eluent to get a white solid (0.87g, yield 71%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.85-6.73 (m, 2H), 5.50-5.44(d, 2H), 5.10-5.07(d, 2H), 2.51-2.43(m, 4H), 1.55-1.44(m, 4H), 1.30-1.21(b, 36H), 0.89-0.86(m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ140.84, 134.84, 128.49, 112.61, 31. Anal. Calcd. for $C_{32}H_{56}S$: C, 81.28; H, 11.94; Found: C, 79.49; H, 12.47; Calculated for $C_{32}H_{56}S$ ($M+H^+$): 472.41. Found: *m/z* 473.41.

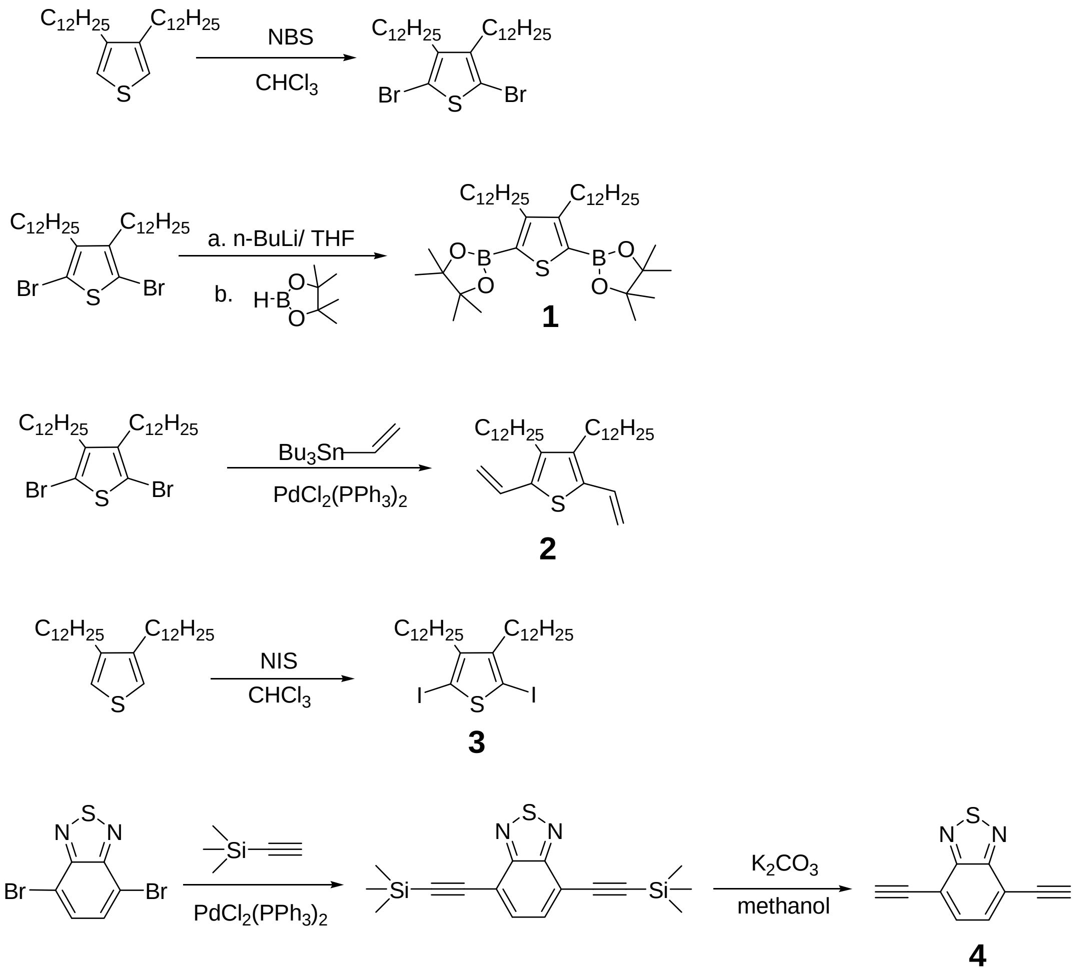
2, 5-diiodo-3, 4-didodecylthiophene (3)

To a solution of 3, 4-didodecylthiophene (2 g, 4.8 mmol) in THF (25 mL) was added a solution of NIS (2.35 g, 10 mmol) in THF (20ml), and the reaction mixture was stirred for 12 h under nitrogen at room temperature in the dark. Then, water was added and the mixture was extracted with ethyl ether (3×50 ml). The combined organic phase was dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in hexane and passed through a short pad of silica gel to afford **3** as a solid with little pink (2.9 g, yield 91%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.52-2.48 (t, 4H), 1.50-1.40(m, 4H), 1.35-1.20(m, 36H), 0.95-0.81(t, 6H) ^{13}C NMR (400 MHz, $CDCl_3$): δ 146.37, 112.38, 31.96, 31.65, 31.56, 29.90, 29.83, 29.73, 29.69, 29.59, 29.39, 29.14, 29.02, 22.73, 14.16. Anal. Calcd for $C_{28}H_{50}I_2S$: C, 50.00; H, 7.49; Found: C, 49.43; H, 6.17; Calculated for $C_{28}H_{50}I_2S$ ($M+H^+$): 672.17. Found: *m/z* 672.08.

4, 7-diethynylbenzo[c][1,2,5]thiadiazole (4)

After compound 4, 7- bis(2-(trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole was synthesized and deprotected from the reported method, compound **4** was obtained.[5] For 4, 7- bis(2-(trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole, ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 2H), 0.33(s, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 154.30, 133.25, 117.35, 103.72, 100.10, 0.02. For compound **4**, ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 2H), 3.69(s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 154.35, 133.25, 116.75, 85.37, 78.92.

Scheme 1. Chemical structures and synthesis route of monomers.



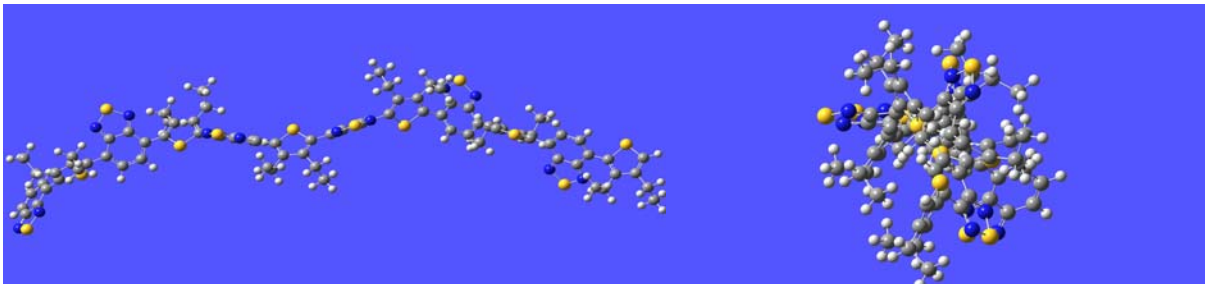
2. Quantum-chemical Calculation

All calculations were performed with Gaussian09 via the density functional theory (DFT) at the B2LYP/6-31G (d, p) level. The calculated detail including HOMOs, LUMOs, E_g and their comparison with experimental results of the synthesized polymers are listed in Table S1. Figure S1 shows the side-view and front-view configuration of a single chain oligomer calculated from geometrical optimization using Gaussian09. The single chain structure showed that **DA1** had a poorer planarity than **DA2** and **DA3**. It is important to mention that the Gaussian09 geometrical optimization results showed that **DA3** exhibited a higher planarity than **DA2**. However this was not consistent with steady-state absorption/emission spectroscopy and time-resolved fluorescence dynamics measured by femtosecond fluorescence up-conversion system. To double-check this, we used Materials Studio package from Accelrys to re-calculate the dihedral angles of the optimized configuration. As discussed in the main paper, the dihedral angle (~ 59^o for **DA1,** ~ 1^o for **DA2**, and ~ 8^o for **DA3**) between the thiophene and thiadiazole units was consistent with steady-state absorption/emission spectroscopy and time-resolved fluorescence dynamics measured by femtosecond fluorescence up-conversion system. We thought the geometrical optimization from Materials Studio package from Accelrys might be more trustable than

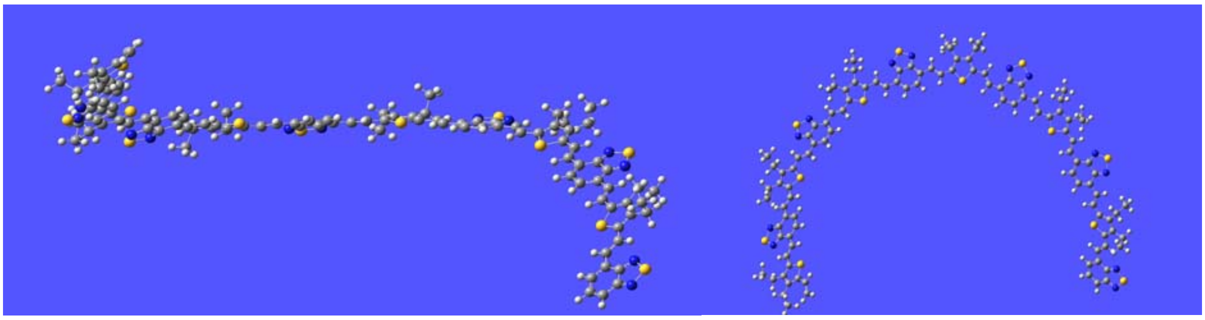
Gaussian09 package. In a previous report by Zhang et al., they also used Materials Studio package from Accelrys to calculate the dihedral angles between adjacent dithienothiophenes in a homopolymer and found that the vinylene linker led the smallest dihedral angle than those with the direct link and ethynylene linker.[6]

Table S1. HOMOs, LUMOs and bandgaps calculated by B3LYP/6-31G (d, p) of oligomer from **DA1**, **DA2** and **DA3** (with different repeating units). The experimental results from the polymer of **DA1**, **DA2** and **DA3** are also listed for comparison.

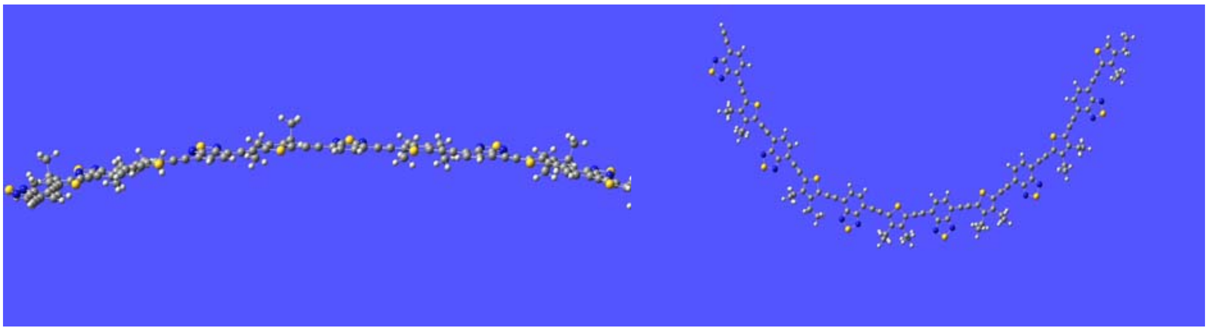
	DA1			**DA2**			**DA3**		
Number of repeat units	HOMO (eV)	LUMO (eV)	Eg (eV)	HOMO (eV)	LUMO (eV)	Eg (eV)	HOMO (eV)	LUMO (eV)	Eg (eV)
1	-5.821	-2.391	3.43	-5.473	-2.768	2.706	-5.458	-2.66	2.797
2	-5.575	-2.5	3.074	-4.818	-2.746	2.072	-5.108	-2.894	2.214
3	-5.498	-2.556	2.942	-4.687	-2.845	1.842	-4.9964	-3.005	1.991
4	-5.441	-2.582	2.859	-4.629	-2.892	1.737	-4.95	-3.062	1.888
5	-5.43	-2.6	2.84	-4.569	-2.922	1.647	-4.93	-3.086	1.843
6	-5.41	-2.61	2.81	-4.551	-2.941	1.61	-4.915	-3.092	1.822
7	-5.40	-2.60	2.79	-4.54	-2.952	1.59	-4.922	-3.116	1.806
8	-5.368	-2.628	2.74	-4.544	-2.954	1.59	-4.902	-3.117	1.785
Experimental results	-5.69	-3.40	2.29	-5.15	-3.50	1.65	-5.43	-3.45	1.98



DA1



DA2



DA3

Figure S1. The side-view and front-view configuration of a single chain oligomer of **DA1**, **DA2** and **DA3**, respectively, calculated from geometry optimization with Gaussian 09.

References and Notes

(1) Ashraf, R. S.; Klemm, E., *J. Polym. Sci., Part A: Polym. Chem.* **2005,** 43, 6445.
(2) Pilgram, K.; Zupan, M.; Skiles, R., *J. Heterocycl. Chem.* **1970,** 7, 629.
(3) Lu, G.; Usta, H.; Risko, C.; Wang, L.; Facchetti, A.; Ratner, M. A.; Marks, T. J., *J. Am. Chem. Soc.* **2008,** 130, 7670.
(4) Mikroyannidis, J. A.; Barberis, V. P., *J. Polym. Sci., Part A: Polym. Chem.* **2007,** 45, 1481.
(5) Huang, X.; Meng, J.; Dong, Y.; Cheng, Y.; Zhu, C., *J. Polym. Sci., Part A: Polym. Chem.* **2010,** 48, 997.
(6) Zhang, S.; Fan, H.; Liu, Y.; Zhao, G.; Li, Q.; Li, Y.; Zhan, X., *J. Polym. Sci., Part A: Polym. Chem.* **2009,** 47, 2843.