JOC*Article*

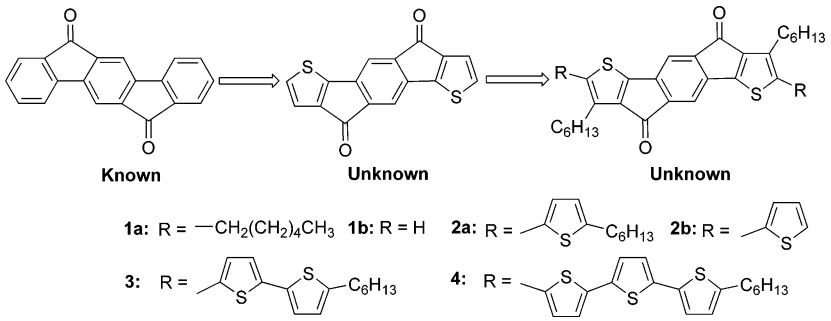
Derivatives of 4,9-Dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione: Synthesis and Properties

Chunchang Zhao,[†] Yong Zhang,[‡] and Man-Kit Ng*,[†]

Departments of Chemistry and Chemical Engineering, University of Rochester, Rochester, New York 14627

ng@chem.rochester.edu

Received March 15, 2007



A new family of organic semiconducting materials (**1**−**4**) integrating the structural components of thiophene and fluorene into a single molecular entity was synthesized and characterized. Optical and electrochemical properties of these previously unknown 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione derivatives were studied in detail. These materials possess unique optical properties with the longest wavelength absorption maxima around 500−800 nm, which gradually reached a saturation limit with the total number of thiophene units approaching eight. They also display dramatic change in the redox properties with increasing conjugation chain lengths. A thin film of oligomer **3** prepared by a solution-casting method showed a well-ordered solid-state structure according to X-ray diffraction analysis.

Introduction

Organic semiconductors based on rigid and linear π-conjugated systems have been well-investigated owing to their potential use as active organic semiconductor layers in a variety of organic electronic devices.[1] Among the various π-conjugated homoaromatic and heteroaromatic systems, oligomers and polymers derived from thiophene and its derivatives have emerged as highly promising candidates for applications in organic field-effect transistors,[2] photovoltaic cells,[3] and high-performance charge-transporting materials[4] owing to their demonstrably high charge-carrier mobility in the solid state. By virtue of their electron-richness, structurally well-defined and solution-processable oligothiophenes normally behave as hole-transporting (p-type) semiconductors in most aforementioned applications. The vastly rich chemistry of thiophene and its derivatives has continued to fuel the development of new types of oligomeric systems, especially those that possess a complementary electronic demand. A recent surge of interest in this

[†] Department of Chemistry.
[‡] Department of Chemical Engineering.

(1) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537−554. (b) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−206. (c) Schwab, P. F. H.; Smith, J. R.; Michl, J. *Chem. Rev.* **2005**, *105*, 1197−1279.

(2) (a) Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. *Science* **1996**, *272*, 1462−1464. (b) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359−369. (c) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99−117. (d) Murphy, A. R.; Liu, J.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D. *Chem. Mater.* **2005**, *17*, 4892−4899. (e) Facchetti, A.; Yoon, M.-H.; Marks, T. J. *Adv. Mater.* **2005**, *17*, 1705−1725. (f) Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411−2425. (g) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrell, T. *J. Am. Chem. Soc.* **2006**, *128*, 3914−3915. (h) Sun, Y.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2005**, *15*, 53−65.

10.1021/jo0704311 CCC: $37.00
Published on Web 07/18/2007

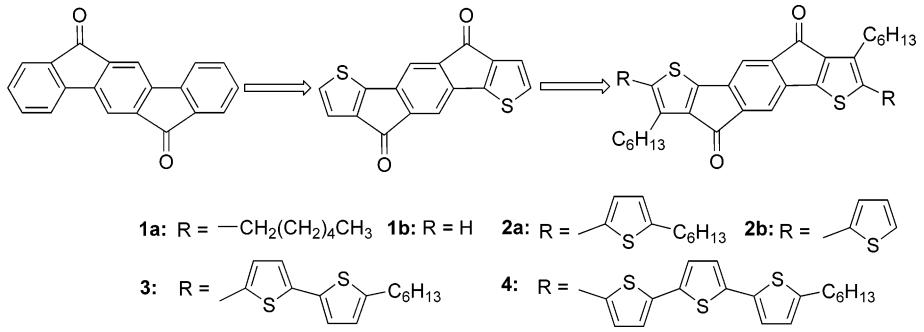


FIGURE 1. Structures of some polycyclic diketone molecules and target molecules.

direction has resulted in the discovery of electronically complementary, n-type oligothiophene-based materials based on conversion to the corresponding (*S*,*S*)-dioxide[5] or functionalization of the oligothiophene backbone with potent electron-withdrawing perfluoroalkyl,[6] pentafluorophenyl,[7] or dicyanomethylene substituents.[8] These results clearly suggest that novel p-type and n-type organic materials could be produced by introducing electron-donating or electron-accepting functionalities into the oligothiophene core, and interesting ambipolar behavior may be achieved within a single multifunctional material.

Fluorene-containing compounds[9] represent another important class of aromatic system that has also received considerable attention due to their unique photophysical properties and feasibility for chemical modification. Fluorene and its derivatives are rigid and planar molecules (when there is no alkyl substitution at the 9-position) that are usually associated with relatively large band gaps and low HOMO energy levels, rendering them highly stable toward photodegradation and thermal oxidation during device operation. Correspondingly, organic devices derived from fluorene-based materials generally exhibit good device properties and desirable longevity when compared to those fabricated from thiophene-based semiconducting materials. The extension of the parent fluorene and of fluorenone to their elongated analogues leads to the corresponding structurally related indenofluorene and indenofluorene-6,12-dione family.[10] These expanded and elongated conjugated systems would be expected to lead to even more interesting electronic and optical properties attributable to a planar and more extensively conjugated structure (Figure 1).

Although significant research effort has been devoted to the design and synthesis of π-conjugated molecular systems based on oligothiophenes and fluorene-containing derivatives as two separate families of semiconducting materials, reports on the integration of these structural components into a single molecular entity are rather limited. The previously unknown 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (Figure 1, center) appears to us as an appealing synthetic target with potentially interesting photophysical properties owing to its unique structural feature that is highly reminiscent of indenofluorene-6,12-dione (Figure 1, left). In this paper, we focus on the design of a new family of soluble organic semiconducting materials based on 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione derivatives, with thiophene rings replacing the two phenyl rings in the parent indenofluorene-6,12-dione molecule (Figure 1). To improve the solubility properties of oligomers **1**−**4**, alkyl groups have been introduced into the central core and/or the terminal α-position in each oligomeric derivative. Herein, the synthesis and characterization of the derivatives of 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione along with their unique optical and electronic properties are reported.

Results and Discussion

Synthesis. The reactions used for the preparation of compounds **1a**, **1b**, **2a**, **2b**, **3**, and **4** are outlined in Schemes 1−3. In light of the decreasing solubility of this oligomer series upon

(3) (a) Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater*. **1995**, *7*, 647−648. (b) Liu, S; Kadnikova, E. N.; Liu, Y.; McGehee, M. D.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9486−9487. (c) Roquet, S.; Cravino, A.; Leriche, P.; Aleveque, O.; Frere, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459−3466. (d) Shi, C.; Yao, Y.; Pei, Q. *J. Am. Chem. Soc*. **2006**, *128*, 8980−8986. (e) Hou, J.; Tan, Z.; Yan, Y.; He, Y.; Yang, C.; Li, Y. *J. Am. Chem. Soc*. **2006**, *128*, 4911−4916.

(4) (a) Yoon, M-H.; Dibennedetto, S. A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc*. **2005**, *127*, 1348−1349. (b) Mas-Torrent, M.; Durkut, M.; Hadley, P.; Ribas, X.; Rovira, C. *J. Am. Chem. Soc*. **2004**, *126*, 984−985. (c) Videlot-Ackermann, C.; Ackermann, J.; Brisset, H.; Kawamura, K.; Yoshimoto, N.; Raynal, P.; Kassmi, A. E.; Fages, F. *J. Am. Chem. Soc.* **2005**, *127*, 16346−16347.

(5) Bongini, A.; Barbarella, G.; Zambianchi, M.; Arbizzani, C.; Mastragostino, M. *Chem. Commun.* **2000**, 439−440.

(6) (a) Facchetti, A.; Deng, Y.; Wang, A.; Koide, Y.; Sirringhaus, H.; Marks, T. J.; Friend, R. H. *Angew. Chem., Int. Ed*. **2000**, *39*, 4547−4551. (b) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater*. **2003**, *15*, 33−38. (c) Facchetti, A.; Letizia, J.; Yoon, M.-H.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Chem. Mater*. **2004**, *16*, 4715−4727. (d) Ando, S.; Nishida, J.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *Chem. Mater*. **2005**, *17*, 1261−1264.

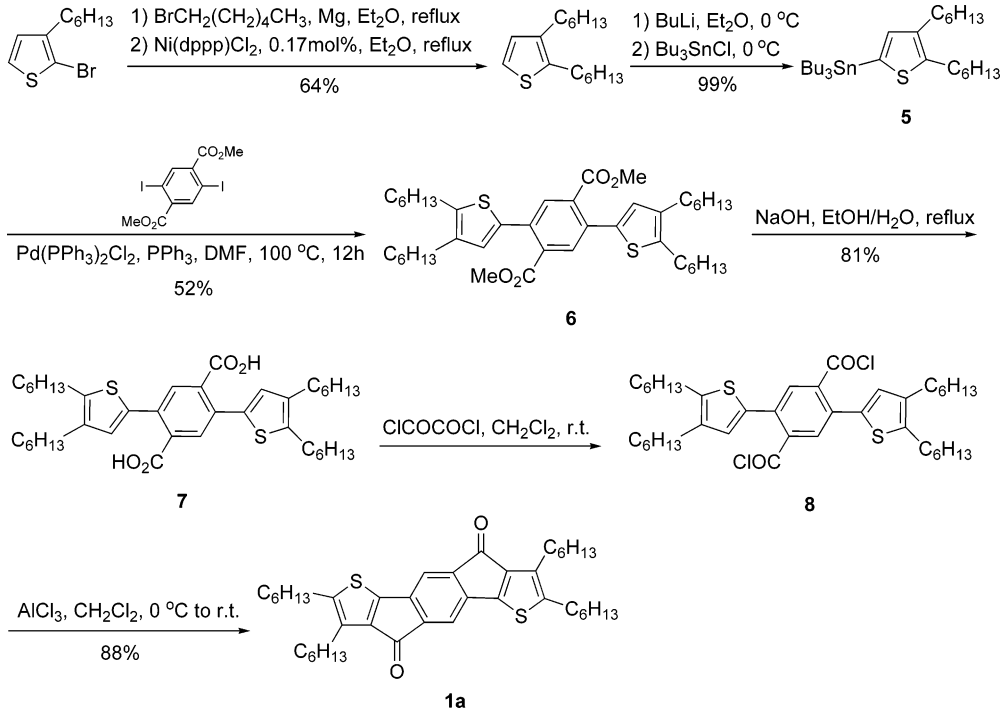
(7) (a) Facchetti, A.; Yoon, M. H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900−3903. (b) Letizia, J. A.; Facchetti, A.; Stern, C. L.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 13476−13477.

(8) (a) Yassar, A.; Demanze, F.; Jaafari, A.; Idrissi, M. E.; Coupry, C. *Adv. Funct. Mater*. **2002**, *12*, 699−708. (b) Pappenfus, T. M.; Burand, M. W.; Janzen, D. A.; Mann, K. R. *Org. Lett.* **2003**, *5*, 1535−1538.

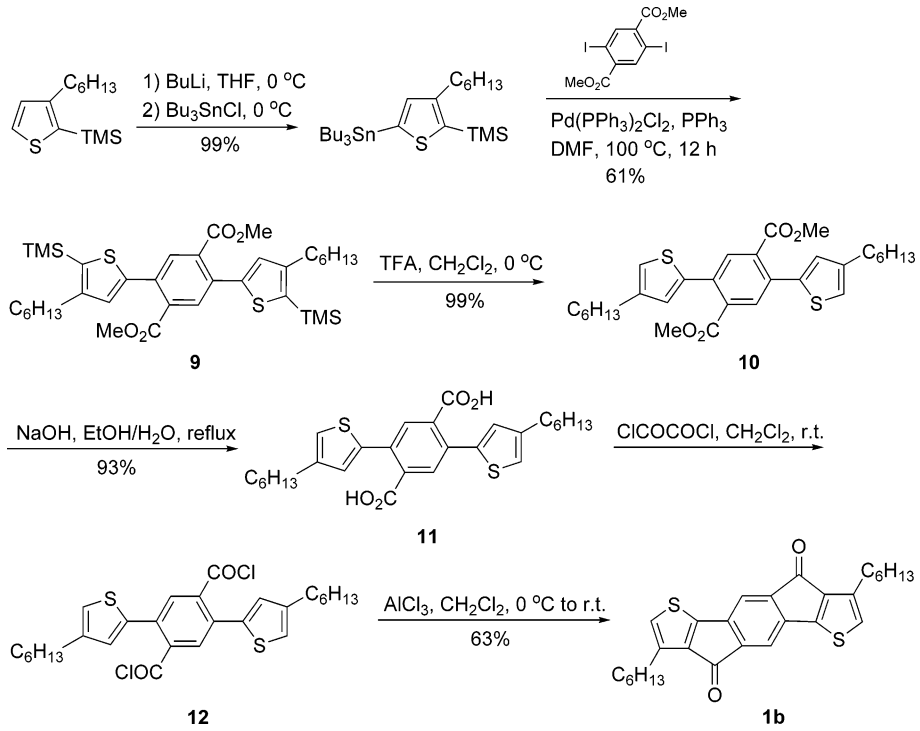
(9) (a) Meng, H.; Bao, Z.; Lovinger, A. J.; Wang, B. C.; Mujsce, A. M. *J. Am. Chem. Soc*. **2001**, *123*, 9214−9215. (b) Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B. C.; Van Pattern, P. G.; Bao, Z. *Chem. Mater*. **2003**, *15*, 1778−1787. (c) Wong, K. T.; Chien, Y. Y.; Chen, R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. H.; Wu, C. C.; Chou, C, H.; Su, Y. O.; Lee, G. H.; Peng, S. M. *J. Am. Chem. Soc*. **2002**, *124*, 11576−11577. (d) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695−13702. (e) Yao, S.; Belfield, K. D. *J. Org. Chem.* **2005**, *70*, 5126−5132.

(10) (a) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157−2159. (b) Hadizad, T.; Zhang, J.; Wang, Z. Y.; Gorjanc, T. C.; Py, C. *Org. Lett.* **2005**, *7*, 795−797. (c) Behrendt, A.; Screttas, C. G.; Bethell, D.; Schiemann, O.; Steele, B. R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2039−2046. (d) Frank, W.; Gompper, R. *Tetrahedron Lett.* **1987**, *28*, 3083−3086. (e) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987−6995. (f) Perepichka, I. F.; Popov, A. F.; Orekhova, T. V.; Bryce, M. R.; Andrievskii, A. M.; Batsanov, A. S.; Howard, J. A. K.; Sokolov, N. I. *J. Org. Chem.* **2000**, *65*, 3053−3063. (g) Wang, C.; Batsanov, A. S.; Bryce, M. R.; Sage, I. *Org. Lett.* **2004**, *6*, 2181−2184. (h) Perepichka, I. F.; Kuzmina, L. G.; Perepichka, D. F.; Bryce, M. R.; Goldenberg, L. M.; Popov, A. F.; Howard, J. A. K. *J. Org. Chem.* **1998**, *63*, 6484−6493.

SCHEME 1. Synthesis of Oligomer 1a



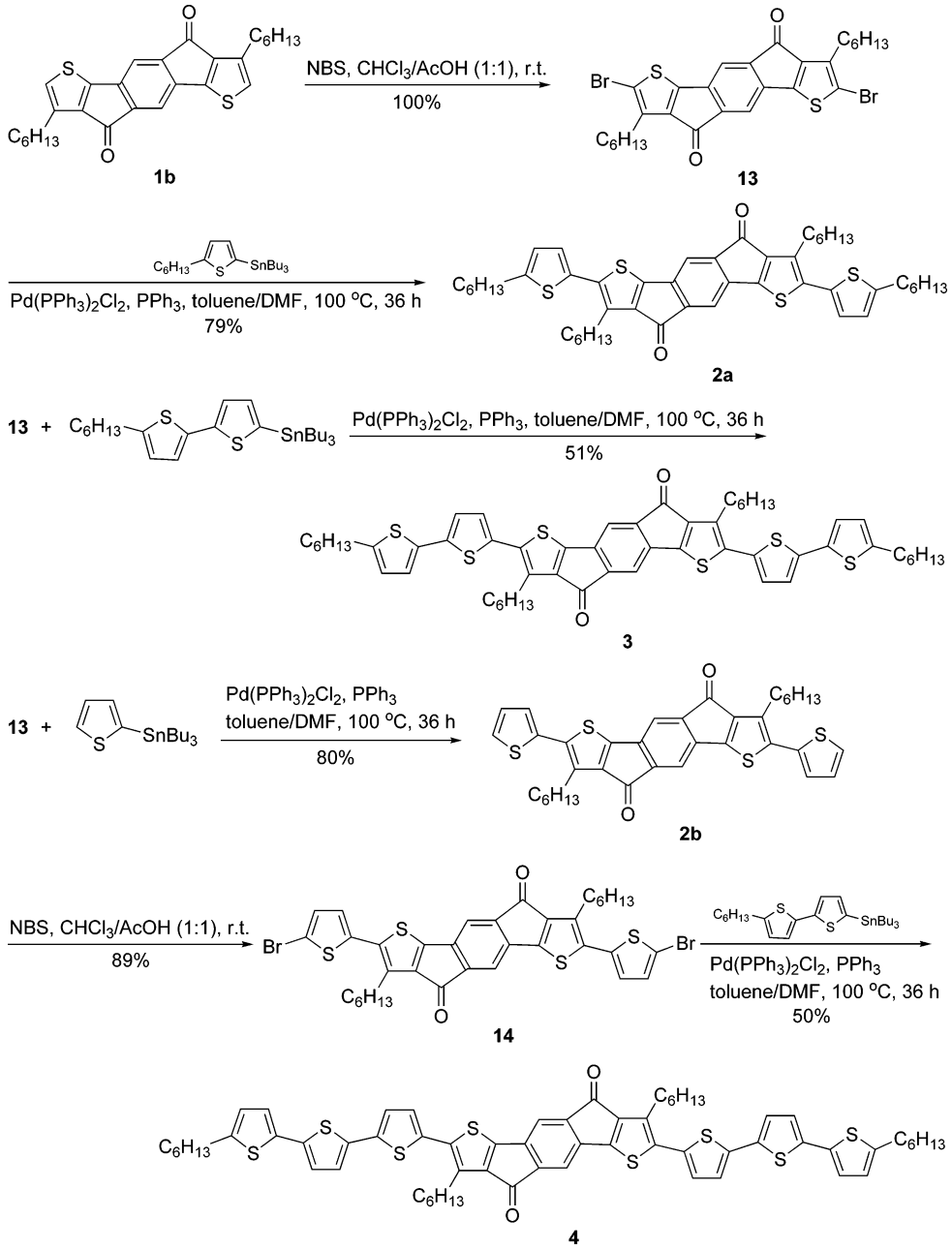
SCHEME 2. Synthesis of Oligomer 1b



chain elongation, a hexyl side group has been introduced on each of the terminal thienyl units in compounds **1a**, **2a**, **3**, and **4**. The key cross-coupling partners for ready access to compounds **1a**, **1b**, **2a**, **2b**, and **3**, namely, 4,5-dihexyl-2-tributylstannylthiophene, 3-hexyl-2-trimethylsilyl-5-tributylstannylthiophene, and 5′-hexyl-5-tributylstannyl-2,2′-bithiophene, were conveniently prepared from a facile lithiation of 2,3-dihexylthiophene, 3-hexyl-2-trimethylsilylthiophene,[11a] and 5-hexyl-2,2′-bithiophene,[11b] respectively, with *n*-butyllithium in ether or tetrahydrofuran, followed by quenching with tributyltin chloride and aqueous workup. A two-folded palladium-catalyzed Stille cross-coupling between methyl 2,5-diiodoterephthalate and 4,5-dihexyl-2-tributylstannylthiophene or 3-hexyl-2-trimethylsilyl-5-tributylstannylthiophene furnished dithienyl-substituted terephthalate diesters **6** and **9** in 52 and 61% yields, respectively. Selective removal of the TMS group on the α-position of the

(11) (a) Spivey, A. C.; Turner, D. J.; Turner, M. L.; Yeates, S. *Org. Lett.* **2002**, *4*, 1899−1902. (b) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 273−276.

SCHEME 3. Synthesis of Oligomers 2a, 2b, 3, and 4



thienyl units in **9** was achieved upon treatment with trifluoroacetic acid (TFA, CH_2Cl_2, 25 °C) to afford compound **10** in 99% yield. Saponification of the resulting diesters **6** and **10** (NaOH, 9:1 v/v EtOH/H_2O, reflux) smoothly provided 2,5-bis-[2′-(4′,5′-dihexylthienyl)]terephthalic acid **7** (81%) and 2,5-bis-[2′-(4′-hexylthienyl)]terephthalic acid **11** (93%), which were readily transformed into the corresponding acid dichlorides **8** and **12** (oxalyl chloride, CH_2Cl_2, 25 °C, 12 h). Upon removal of the volatile materials in vacuo, a Lewis acid-promoted intramolecular Friedel−Crafts cyclization (3 equiv of $AlCl_3$, CH_2Cl_2) of **8** and **12** took place smoothly to give the hitherto unknown conjugated diketones **1a** and **1b** in 88 and 63% yield, respectively.

Bromination of diketone **1b** (2 equiv of NBS, 1/1 v/v $CHCl_3$/AcOH) readily provided dibromo intermediate **13**, which was further subjected to a Stille cross-coupling with 5-hexyl-2-tributylstannylthiophene, 2-tributylstannylthiophene, or 5′-hexyl-5-tributylstannyl-2,2′-bithiophene, respectively, to form the corresponding oligomer **2a** (79%), **2b** (80%), or **3** (51%) in acceptable yields. Dibromo intermediate **14** was obtained in a procedure similar to that employed for **13**, which was then subjected to a cross-coupling reaction with 5′-hexyl-5-tributylstannyl-2,2′-bithiophene to furnish oligomer **4** in 50% yield. Overall, all of the new compounds synthesized exhibit good solubility characteristics in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF, toluene, and chlorobenzene under ambient conditions.

The thermal properties of oligomers **1a**, **1b**, **2a**, **2b**, **3**, and **4** were evaluated by means of thermogravimetric analyses (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min, and the results are summarized in Table 1 and Figure S1 in Supporting Information. It is apparent that these materials exhibited excellent thermal stability with decomposition temperatures (corresponding to 5% weight loss) at 326 °C for **1a**,

TABLE 1. Some Physical Properties of Oligomers 1a, 1b, 2a, 2b, 3, and 4

oligomer	λ_{max}[a] (nm)	$E_1^{1/2}{}_{ox}$[b], $E_2^{1/2}{}_{ox}$ (V vs Fc/Fc^+)	T_d[d] (°C)
1a	338		
	617	0.82	326
1b	330		
	576	0.72[c]	297
2a	332		
	385		
	649	0.63, 0.90	396
2b	327		
	380		
	627	0.38[c]	339
3	352		
	412		
	654	0.45	397
4	423		
	653	0.36	399

[a] Measured in dichloromethane. [b] Performed in Bu_4NPF_6/CH_2Cl_2 solution, $v = 100$ mV/s. [c] Only E_{pc} observed. [d] Temperature of decomposition corresponding to 5% weight loss from TGA analysis under N_2 at a heating rate of 10 °C/min.

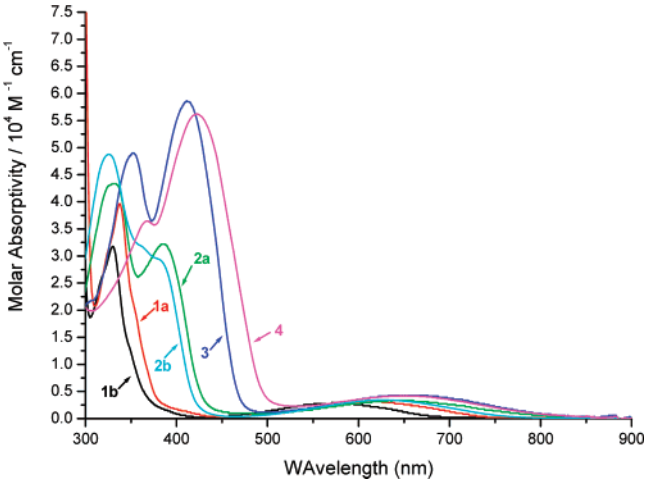


FIGURE 2. UV−vis absorption spectra of compounds **1a**, **1b**, **2a**, **2b**, **3**, and **4** in CH_2Cl_2.

297 °C for **1b**, 396 °C for **2a**, 339 °C for **2b**, 397 °C for **3**, and 399 °C for **4**.

Optical Properties. The UV−vis absorption spectra of oligomers **1**−**4** were measured in dichloromethane solutions (Table 1, Figure 2). As shown in Figure 2, each of the thiophene-based diketone compounds exhibits intense absorption bands attributable to the $\pi-\pi^*$ transition of the conjugated backbone. By increasing the number of thiophene units in the series of oligomers **1**−**4**, the absorption maxima (λ_{max}) of the $\pi-\pi^*$ transition in CH_2Cl_2 are bathochromically shifted from 338 nm for **1a** to 385 nm for **2a**, to 412 nm for **3**, and finally to 423 nm for **4**, in good agreement with the formation of a more delocalized and extended π-conjugated system. Particularly noteworthy is the appearance of broad absorption peaks at longer wavelength, which can be assigned to a $\pi-\pi^*$ transition, and the $\pi-\pi^*$ nature of this transition is supported by studying the solvent effects.[12] In cyclohexane, these diketone oligomers displayed weak lowest-energy absorptions around 500−800 nm. On the other hand, in 1-butanol, these absorptions were shifted toward longer wavelengths as expected for the $\pi-\pi^*$ transition of ketones from a nonpolar to a more polar solvent (Figure S2). It is worth mentioning that the absorption maxima of **1a** (338, 617 nm) or **2a** (385, 649 nm) were observed at a slightly longer wavelength compared to those of **1b** (330 nm, 576 nm) or **2b** (380, 627 nm), indicating that the extra alkyl groups in **1a** and **2a** are able to exert a moderate electron-donating effect. With the same central chromophore present in oligomers **2** and **3**, the longer conjugated chains of the oligothiophene in these oligomers progressively resulted in longer absorption maxima ($\lambda_{max} = 617$ nm for **1a**, 649 nm for **2a**, and 654 nm for **3**) along the series. These absorption maxima also rapidly reached a saturation limit, as the change was 32 nm from **1a** to **2a** but only 5 nm was observed from **2a** to **3**. It could be envisaged that elongation with additional oligothiophene units would not extend the longest wavelength absorption maxima to any significant extent. As expected, continual addition of two more thiophene units did not change the longest absorption maximum by comparing the λ_{max} values for **3** and **4** (Table 1), although there was still an observable bathochromic shift for their short wavelength absorptions (412 nm for **3** to 423 nm for **4**). To illustrate the effect of chain elongation and end capping of each thienyl terminus with an electron-donating alkyl substituent, the λ_{max} for $\pi-\pi^*$ transition of the conjugated backbone was continuously red-shifted by about 90 nm from **1b** to **4**. Similarly, the weak longest wavelength absorption maxima were bathochromically shifted by about 80 nm and gradually reached a saturation limit with the total number of thiophene units approaching eight in oligomer **4**.

The absorption spectra of **1**−**4** essentially cover the full ultraviolet−visible region from 280 to 800 nm, but their absorption coefficients between 500 and 800 nm are much smaller when compared to those in the 300−500 nm range. These observations show that our materials are not readily optimized to be used as efficient solar light absorbers in the construction of organic-based solar cell devices. It is known that oligothiophenes with additional dicyanovinyl or tricyanovinyl substituents at a terminal α,ω position can dramatically shift their absorption bands to longer wavelength with larger absorption coefficients.[13] Such an alternative design strategy with dicyanovinyl groups attached to the α,ω position of oligomers **1**−**4** is currently under investigation.

Electrochemical Properties. The redox properties of oligomers **1**−**4** (measured at a concentration of 10^{-3} M) were investigated by cyclic voltammetry in dichloromethane containing 0.01 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte at a scan rate of 100 mV/s at room temperature (Table 1, Figure 3 and Figure S3). A platinum wire was used as the working electrode. Another Pt wire was used as the counter electrode, and $Ag/AgNO_3$ was used as the reference electrode. All reported potentials are calibrated against the ferrocene/ferrocenium (Fc/Fc^+) couple, which was used as the internal standard. All oligomers displayed oxidative processes under the experimental conditions. The data in Table 1 showed the effects of varying numbers of oligothiophene substituents on the redox behaviors of **1**−**4**. A clear trend of

(12) (a) Koster, P. B.; Runsink, J.; Janssen, M. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 393−397. (b) Lambert, T. L.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1991**, 752−754. (c) Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1268−1270.

(13) (a) Bader, M. M.; Custelcean, R.; Ward, M. D. *Chem. Mater*. **2003**, *15*, 616−618. (b) Pappenfus, T. M.; Burand, M. W.; Janzen, D. E.; Mann, K. R. *Org. Lett*. **2003**, *5*, 1535−1538. (c) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Miller, L. L. *J. Am. Chem. Soc*, **2002**, *124*, 4184−4185.

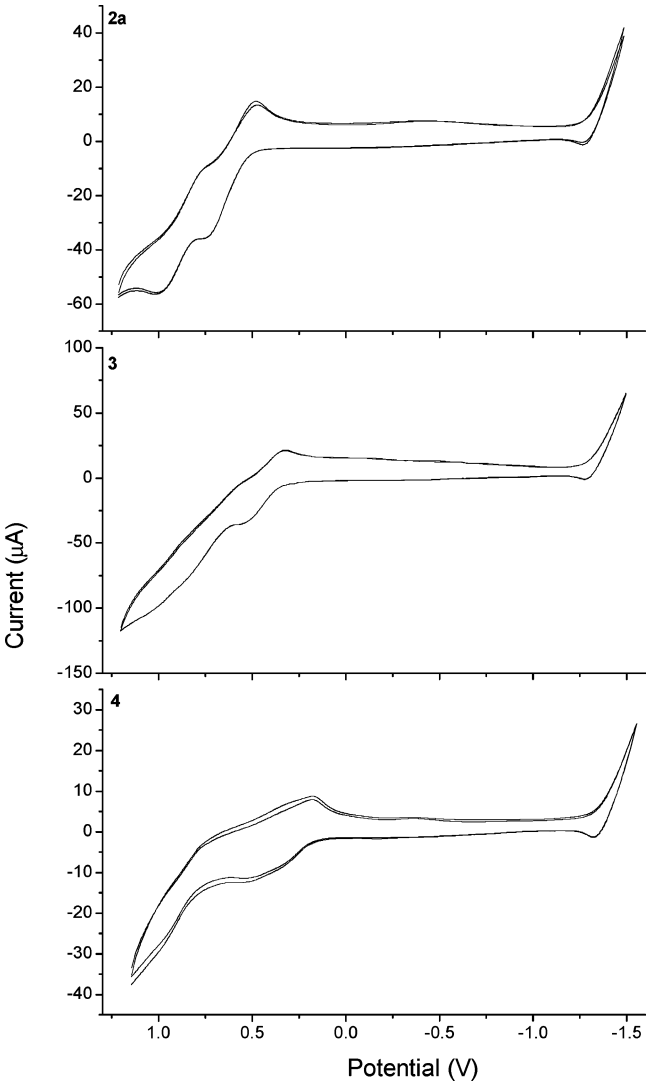


FIGURE 3. Cyclic voltammograms of **2a**, **3**, and **4** ($c = 10^{-3}$ M) in CH_2Cl_2 containing Bu_4NPF_6 (0.01 M) as supporting electrolyte at room temperature, with a scan rate of 100 mV/s. Potentials are versus the ferrocene/ferrocenium (Fc/Fc^+) couple (internal standard).

oxidative peak potentials was observed where the oxidative potential becomes smaller in the order of **1**, **2**, **3**, and **4**. While an irreversible oxidation wave ($E^{1/2} = 0.82$ V vs Fc/Fc^+) was observed for compound **1a**, the elongated oligomer **2a** displays two quasi-reversible oxidation waves with their peak potentials shifted to 0.63 and 0.90 V. Continual addition of two more thiophene units further reduces the $E^{1/2}$ value to 0.45 V for oligomer **3**. For the longest and most electron-rich oligomer **4**, the oxidative potential was finally shifted to 0.36 V. The oxidative peak potentials decrease in the order of **1**, **2**, **3**, and **4**, which can be attributed to the enhanced π-electron delocalization with continuously increasing conjugation length by adding thiophene units.

The feasibility of solution-processable fabrication of ordered organic thin films on substrates is an important parameter when evaluating organic semiconducting materials for use in low-cost electronic devices.[14] As the ultimate goal of this work is to prepare new materials that are solution-processable while maintaining good film-forming properties, we have investigated the solid-state structure of the thin film of oligomer **3** (cast from chloroform solution onto Si wafer) by using a wide-angle X-ray diffraction method (Figure 4). Sharp reflection peaks are readily observed in the X-ray diffractogram of the annealed (120 °C, 4 h) thin film of **3**. The appearance of clearly resolved and intense diffraction peaks indicates that **3** forms a well-ordered layered structure on the silicon wafer substrate as observed for α,ω-dihexyloligothiophenes.[15] The *d*-spacing obtained from the first reflection peak at 3.85° corresponds to a value of 2.29 nm.

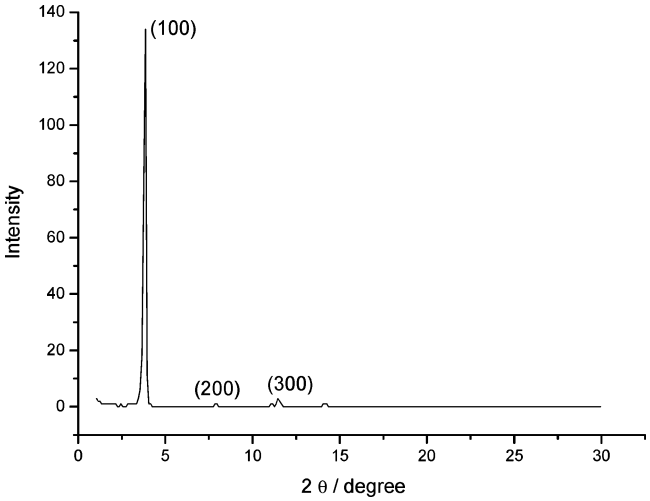


FIGURE 4. X-ray diffraction spectrum of the thin film of oligomer **3** deposited at room temperature and annealed at 120 °C for 4 h.

Conclusion

In summary, new and soluble 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione derivatives **1**−**4** have been synthesized and characterized. The thermal, optical, and electrochemical properties of these oligomers have been studied in detail. Oligomers **1**−**4** exhibited excellent thermal stability with decomposition temperatures (corresponding to 5% weight loss) at 326 °C for **1a**, 297 °C for **1b**, 396 °C for **2a**, 339 °C for **2b**, 397 °C for **3**, and 399 °C for **4**. These materials possess unique optical properties with the longest energy absorption maxima at around 500−800 nm, which reached a saturation limit with increasing number of thiophene units. They also displayed dramatic change in the redox properties with increasing chain lengths, as shown by the gradual decrease of oxidative peak potentials. In addition, this class of materials can be readily fabricated into well-ordered thin films by solution-based methods according to X-ray diffraction analysis.

Experimental Section

2,3-Dihexylthiophene. To a suspension of magnesium turnings (0.98 g, 41 mmol) in 10 mL of anhydrous ether and several drops of 1,2-dibromoethane was added a solution of 1-bromohexane

(14) (a) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812−8813. (b) Murphy, A. R.; Frechet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc*. **2004**, *126*, 1596−1597. (c) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrell, T. *J. Am. Chem. Soc.* **2006**, *128*, 3914−3915.

(15) (a) Garnier, F.; Yassar, A.; Hajlaoui, R.; Hotowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc*. **1993**, *115*, 8716−8721. (b) Moret, M.; Campione, M.; Borghesi, A.; Miozzo, L.; Sassella, A.; Trabattoni, S.; Lotz, B.; Thierry, A. *J. Mater. Chem*. **2005**, *15*, 2444−2449.

(6.1 g, 37 mmol) in 40 mL of ether. The reaction mixture was then refluxed for 15 h. The Grignard solution was transferred via cannula to an addition funnel and added dropwise to a mixture of Ni(dppp)-Cl_2 (28 mg, 0.05 mmol) and 2-bromo-3-hexylthiophene (7.16 g, 29 mmol) in ether (20 mL) at 0 °C. The resulting mixture was refluxed for 16 h, cooled to room temperature, hydrolyzed with 1 N HCl (30 mL) and 70 mL of ice water followed by extraction with ether. The combined organic extracts were dried (Na_2SO_4), and the solvent was removed in vacuo to afford a yellow oil, which was purified by distillation under high vacuum to give 4.71 g (64%) of analytically pure compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, 1H), 6.81 (d, 1H), 2.71 (t, 2H), 2.50 (t, 2H), 1.66−1.50 (m, 4H), 1.41−1.26 (m, 12H), 0.91−0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.6, 128.6, 120.8, 31.9, 31.7, 31.6, 30.8, 29.2, 28.9, 28.2, 27.7, 22.6, 22.5, 14.0; HRMS (ESI) calcd for $C_{16}H_{28}S$: 252.1906. Found: 252.1915.

4,5-Dihexyl-2-tributylstannylthiophene (5). To a stirred solution of 2,3-dihexylthiophene (2.52 g, 10 mmol) in 35 mL of anhydrous ether at 0 °C was added dropwise a solution of *n*-BuLi (2.5 M, 5.2 mL). The resulting solution was stirred for 20 min at 0 °C and warmed to room temperature over 30 min. The mixture was cooled to 0 °C, and tributyltin chloride (4.89 g, 15 mmol) was added dropwise. The resulting mixture was stirred at 0 °C for 10 min, warmed to room temperature over 30 min, poured into water, and extracted with ether. The combined organic extracts were washed with saturated NaCl, dried, and filtered, and the filtrate was concentrated under reduced pressure to afford organostannane **5**. This crude product was used for next step without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 2.72 (t, 2H), 2.50 (t, 2H), 1.64−1.51 (m, 10H), 1.39−1.27 (m, 18H), 1.13−1.06 (m, 6H), 0.92−0.82 (m, 15H).

3-Hexyl-2-trimethylsilyl-5-tributylstannylthiophene. This compound was prepared form 3-hexyl-2-trimethylsilylthiophene according to the procedure for **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 2.70 (t, 2H), 1.58−1.36 (m, 8H), 1.35−1.29 (m, 12H), 1.10−1.08 (m, 6H), 0.91−0.87 (m, 12H), 0.33 (s, 9H).

5′-Hexyl-5-tributylstannyl-2,2′-bithiophene. This compound was prepared form 5-hexyl-2,2′-bithiophene according to the procedure for **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, 1H), 7.03 (d, 1H), 6.97 (d, 1H), 6.66 (d, 1H), 2.77 (t, 2H), 1.67−1.53 (m, 8H), 1.39−1.26(m, 12H), 1.12−1.08(m, 6H), 0.97−0.86 (m, 12H).

Dimethyl 2,5-bis[2′-(4′,5′-dihexylthienyl)]-1,4-benzenedicarboxylate (6). Dimethyl 2,5-diido-1,4-benzenedicarboxylate (1.115 g, 2.5 mmol) was added to a solution of **5** (5.41 g, 10 mmol) in anhydrous DMF (30 mL), and the resulting mixture was purged with N_2 for 30 min. A mixture of $Pd(PPh_3)_2Cl_2$ (53 mg, 0.075 mmol) and PPh_3 (40 mg, 0.15 mmol) was then added, and the reaction mixture was heated to 100 °C overnight. Excess DMF was removed under high vacuum, and the residue was dissolved in ethyl acetate and treated with 10% aqueous KF. The mixture was filtered through a pad of Celite. The filtrate was dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The crude product was purified by flash chromatography (silica gel, eluent: hexane/CH_2Cl_2 = 7:1) to afford 0.9 g (52%) of **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 6.79 (s, 2H), 3.77 (s, 6H), 2.72 (t, 4H), 2.48 (t, 4H), 1.67−1.58 (m, 8H), 1.41−1.26 (m, 24H), 0.97−0.95 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 140.8, 138.5, 135.6, 133.0, 132.7, 130.9, 128.4, 52.4, 31.7, 31.7, 31.6, 30.8, 29.1, 28.9, 28.2, 27.9, 22.6, 22.5, 14.0; HRMS (ESI) calcd for $C_{42}H_{62}O_4S_2$: 694.4084. Found: 694.4089.

Dimethyl 2,5-bis[2′-(4′-hexyl-5′-trimethylsilylthienyl)]-1,4-benzenedicarboxylate (9). Compound **9** was prepared by the coupling of dimethyl 2,5-diido-1,4-benzenedicarboxylate with 3-hexyl-2-trimethylsilyl-5-tributylstannylthiophene in 61% yield according to the procedure for **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.01 (s, 2H), 3.77 (s, 6H), 2.65 (t, 4H), 1.66−1.54 (m, 4H), 1.40−1.31 (m, 12H), 0.90 (t, 6H), 0.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 150.8, 144.0, 134.8, 133.1, 132.9, 131.2, 130.2, 52.5, 31.8, 31.8, 31.5, 29.4, 22.6, 14.1, 0.4; HRMS (ESI) calcd for $C_{36}H_{54}O_4S_2Si_2$: 670.3002. Found: 693.2910 $[M + Na]^+$.

Dimethyl 2,5-bis[2′-(4′-hexylthienyl)]-1,4-benzenedicarboxylate (10). To a stirred solution of **9** (6.71 g, 10 mmol) in CH_2Cl_2 at 0 °C was added slowly a solution of trifluoroacetic acid (2 mL) in 20 mL of CH_2Cl_2. The resulting mixture was further stirred for 1 h at 0 °C, washed with water, dried over Na_2SO_4, and filtered, and the filtrate was concentrated to give 5.25 g (99%) of **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 2H), 6.96 (d, 2H), 6.92 (d, 2H), 3.77 (s, 6H), 2.61 (t, 4H), 1.64−1.54 (m, 4H), 1.35−1.29 (m, 12H), 0.88 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 143.7, 139.9, 133.4, 133.2, 131.4, 128.2, 121.3, 52.5, 31.6, 30.44, 30.41, 28.9, 22.6, 14.0; HRMS (ESI) calcd for $C_{30}H_{38}O_4S_2$: 526.2212. Found: 527.2301 $[M + H]^+$.

2,5-Bis[2′-(4′,5′-dihexylthienyl)]-1,4-benzenedicarboxylic acid (7). A mixture of **6** (940 mg, 1.35 mmol) and sodium hydroxide (216 mg, 5.4 mmol) in 27 mL of ethanol and 3 mL of water was refluxed overnight. The solvent was evaporated under vacuum to about half of its original volume. Water was added, and the resulting aqueous layer was treated with HCl to obtain a solid, which was filtered and dried to afford 730 mg (81%) of **7**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.39 (b, 2H), 7.55 (s, 2H), 6.97 (s, 2H), 2.70 (t, 4H), 2.45 (t, 4H), 1.60−1.48 (m, 8H), 1.36−1.27 (m, 24H), 0.92−0.80 (m, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.6, 140.5, 138.9, 135.5, 134.3, 131.3, 129.7, 128.9, 31.7, 31.5, 31.4, 30.6, 28.9, 28.7, 28.0, 27.5, 22.5, 22.4, 14.4, 14.3; LRMS (APCI) calcd for $C_{40}H_{58}O_4S_2$: 666.4. Found: 667.6 $[M + H]^+$.

2,5-Bis[2′-(4′-hexylthienyl)]-1,4-benzenedicarboxylic acid (11). Compound **11** was prepared by saponification of **10** in 93% yield according to the procedure for **7**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.39 (b, 2H), 7.62 (s, 2H), 7.23 (s, 2H), 7.09 (s, 2H), 2.54 (t, 4H), 1.58−1.50 (m, 4H), 1.27 (m, 12H), 1.07 (t, 6H); LRMS (APCI) calcd for $C_{28}H_{34}O_4S_2$: 498.2. Found: 497.2 $[M - H]^-$.

2,5-Bis[2′-(4′,5′-dihexylthienyl)]-1,4-benzenedicarboxylic acid dichloride (8). A solution of **7** (360 mg, 0.54 mmol) and oxalyl chloride (0.5 mL, 5.7 mmol) in 30 mL of dry CH_2Cl_2 and several drops DMF was stirred for 12 h at room temperature. The solvent was removed under vacuum to obtain the crude acid dichloride, which was used for next step without further purification.

2,5-Bis[2′-(4′-hexylthienyl)]-1,4-benzenedicarboxylic acid dichloride (12). Compound **12** was prepared from **11** according to the procedure for **8**.

2,3,7,8-Tetrahexyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]-dithiophene-4,9-dione (1a). A solution of acid dichloride (380 mg, 0.54 mmol) in 30 mL of CH_2Cl_2 was added to a suspension of anhydrous $AlCl_3$ (216 mg, 1.62 mmol) in 10 mL of CH_2Cl_2 at 0 °C. The resulting mixture was further stirred for 20 min, then at room temperature for 3 h. The reaction mixture was poured into ice water and 1 M hydrochloric acid and extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, eluent: hexane/CH_2Cl_2 = 5:1) to afford 300 mg (88%) **1a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 2H), 2.70 (t, 4H), 2.62 (t, 4H), 1.65−1.56 (m, 8H), 1.40−1.26 (m, 24H), 0.97−0.90 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 154.7, 1444.9, 140.2, 139.9, 139.4, 135.2, 113.5, 31.6, 31.58, 31.5, 30.0, 29.1, 28.8, 28.1, 26.3, 22.6, 22.5, 14.03, 14.0; HRMS (ESI) calcd for $C_{40}H_{54}O_2S_2$: 630.3560. Found: 630.3558.

3,8-Dihexyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (1b). Compound **1b** was prepared from acid chloride **12** in 63% yield according to the procedure for **1a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 6.80 (s, 2H), 2.72 (t, 4H), 1.67−1.62 (m, 4H), 1.37−1.28 (m, 12H), 0.88 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 158.3, 140.8, 140.5, 139.5, 139.4, 124.4, 114.2, 31.5, 29.3, 28.9, 28.3, 22.5, 14.0; HRMS (ESI) calcd for $C_{28}H_{30}O_2S_2$: 462.1682. Found: 462.1688.

2,7-Dibromo-3,8-dihexyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]-dithiophene-4,9-dione (13). To a solution of **1b** (925 mg, 2 mmol)

in 60 mL of $CHCl_3$/AcOH (1:1) was added *N*-bromosuccinimide (NBS) (818 mg, 4.6 mmol) in small portions at room temperature and stirred for 12 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The combined organic layers were washed with saturated $NaHCO_3$, $Na_2S_2O_3$, water, and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford 1.24 g (100%) of **13**, which was pure enough for the next step: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 2.71 (t, 4H), 1.62−1.58 (m, 4H), 1.37−1.30 (m, 12H), 0.88 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 156.3, 139.6, 139.46, 139.45, 137.9, 114.5, 113.3, 31.5, 28.9, 28.8, 27.2, 22.6, 14.1; HRMS (ESI) calcd for $C_{28}H_{28}O_2S_2Br_2$: 617.9892. Found: 617.9895.

3,8-Dihexyl-2,7-bis[2′-(5′-hexylthienyl)]-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (2a). To a solution of **13** (410 mg, 0.66 mmol) in 50 mL of toluene/DMF (4:1) was added 5-hexyl-2-(tributylstannyl)thiophene (905 mg, 1.98 mmol), and the resulting mixture was purged with N_2 for 30 min. A mixture of $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and PPh_3 (21 mg, 0.08 mmol) was then added, and the reaction mixture was heated to 100 °C for 36 h. Excess solvent was removed under high vacuum The crude product was purified by flash chromatography (silica gel, eluent: hexane/CH_2Cl_2 = 5:1) to get 330 mg (79%) of **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 6.96 (d, 2H), 6.75 (d, 2H), 2.87−2.80 (t, 8H), 1.72−1.54 (m, 8H), 1.40−1.26 (m, 24H), 0.92−0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 155.2, 147.4, 140.5, 140.3, 139.5, 136.5. 136.1, 132.0, 126.3, 124.5, 114.0, 31.5, 30.1, 29.9, 29.2, 28.7, 26.9, 22.5, 14.0; HRMS (ESI) calcd for $C_{48}H_{58}O_2S_4$: 794.3314. Found: 794.3326.

3,8-Dihexyl-2,7-bis(2′-thienyl)-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (2b). Compound **2b** was prepared by coupling of **13** with 2-(tributylstannyl)thiophene in 80% yield according to the procedure for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, 2H), 7.18 (s, 2H), 7.16 (dd, 2H), 7.09 (dd, 2H), 2.87 (t, 4H), 1.66−1.61 (m, 4H), 1.40−1.37 (m, 4H), 1.31−1.27 (m, 8H), 0.92−0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 155.6, 140.5, 140.4, 139.5, 136.8, 135.8, 134.7, 127.5, 126.7, 126.3, 114.2, 31.5, 29.9, 29.2, 27.0, 22.5, 14.0; HRMS (ESI) calcd for $C_{36}H_{34}O_2S_4$: 626.1436. Found: 626.1436.

2,7-Bis[2′-(5′′-hexyl-5′,2′′-bithienyl)]-3,8-dihexyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (3). Compound **3** was prepared by coupling of **13** with 5′-hexyl-5-tributylstannyl-2,2′-bithiophene in 51% yield according to the procedure for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 7.04 (m, 4H), 7.01 (d, 2H), 6.70 (d, 2H), 2.90 (t, 4H), 2.80 (t, 4H), 1.70−1.65 (m, 8H), 1.40−1.37 (m, 8H), 1.33−1.29 (m, 16H), 0.91−0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 155.3, 146.1, 140.7, 140.4, 139.4, 138.7, 136.5, 135.9, 133.9, 132.8, 127.0, 124.9, 123.7, 123.2, 114.1, 31.5, 30.2, 29.9, 29.2, 28.8, 27.1, 22.6, 22.6, 14.09, 14.07; HRMS (ESI) calcd for $C_{56}H_{62}O_2S_6$: 958.3069. Found: 958.3080.

3,8-Dihexyl-2,7-bis[2′-(5′-bromothienyl)]-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (14). Compound **14** was prepared from **2b** in 89% according to the procedure for **13**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.05 (d, 2H), 6.91 (d, 2H), 2.83 (t, 4H), 1.64−1.52 (m, 4H), 1.40−1.35 (m, 4H), 1.31−1.29 (m, 8H), 0.91−0.87 (m, 6H).

2,7-Bis[2′-(5′′′-hexyl-5′,2′′;5′′,2′′′-terthienyl)]-3,8-dihexyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene-4,9-dione (4). Compound **4** was prepared by coupling of **14** with 5′-hexyl-5-tributylstannyl-2,2′-bithiophene in 50% yield according to the procedure for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 2H), 7.04 (d, 2H), 7.03 (d, 2H), 7.01 (d, 2H), 6.97−6.95 (m, 4H), 6.66 (d, 2H), 2.88 (t, 4H), 2.77 (t, 4H), 1.69−1.54 (m, 8H), 1.43−1.29 (m, 24H), 0.92−0.91 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 155.4, 145.9, 140.7, 140.4, 137.8, 134.6, 134.3, 133.4, 127.0, 124.9, 124.5, 123.6, 123.5, 114.1, 31.5, 30.2, 29.9, 29.2, 28.8, 27.2, 22.61, 22.58, 14.12, 14.08, 13.98; HRMS (ESI) calcd for $C_{64}H_{66}O_2S_8$: 1122.2823. Found: 1122.2784.

Acknowledgment. We wish to thank the University of Rochester, ACS PRF, and NYSTAR James D. Watson Investigator Program for financial support.

Supporting Information Available: List of materials and general experimental methods; NMR spectra of the new compounds, cyclic voltammograms, and TGA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0704311