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Syntheses, optical and electrochemical properties of 4,4′-bis-[2-(3,4-dibutyl-2-thienylethynyl)]biphenyl and its oligomers

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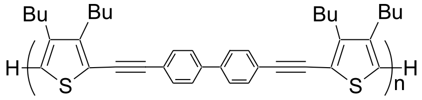
Abstract—New π-conjugated oligomers (**1**–**3**) combined of thiophene rings, C≡C units, and phenylene rings were synthesized. The monomer (**1**) was synthesized by Sonogashira cross-coupling reaction. Lithiation and oxidation of the monomer led to the formation of dimer (**2**) and trimer (**3**). Optical and electrochemical properties of compounds **1**–**3** were studied. The oligomers with thioacetyl moieties were synthesized for self-assembly.

1. Introduction

In 1975, Moore stated that chip densities would double every 2 years.[1] According to the statement, the reduction in size of circuits and increase in speed can only continue for some finite time. This forces us to consider other options. Many researches are focused towards molecular electronics. We seek to use the electronic properties intrinsic in the molecules to fabricate electric devices. π-Conjugated oligomers of defined length and constitution arise from new potential to act as molecular wires in molecular scale electronics. A variety of spectacular molecular architectures are resulted from the efforts aimed at the construction of such wires. In addition, modern synthetic organic and organometallic methodologies are providing powerful tools for the direct acquisition of the molecules and materials capable of fulfilling a huge variety of requirements in terms of mechanical, physical, and chemical properties.[2] Oligoynes,[3] oligothiophenes,[4] and oligophenylenes[5] have been intensively studied. Tour and co-workers have reported the syntheses of oligo(α-thiophene ethynylene)s and oligo(*p*-phenylene ethynylene)s.[6] But linear conjugated oligomers involving combination of three different substructures are seldom discussed. Here, we report the syntheses of π-conjugated molecules **1**–**3** consisting of thiophene rings, C≡C units, and phenylene rings as potential molecular wires. These compounds possess the following features that make them suitable for studies of molecular scale electronics: (1) these compounds are rigid in their frameworks so as to minimize conformational flexibility yet containing butyl groups for maintaining solubility and processability of the final products. The butyl groups have been preferred over long paraffinic chains because they afford better yields during the syntheses of the precursors;[7] (2) alkynyl units separate the aryl units, so ground state contiguous π-overlap will be minimally affected by rotational variations; (3) thiol end groups can be attached to the ends of the compounds; (4) they are stable to light and oxygen, so that they can be manipulated in the air.

Additionally, the syntheses of compounds (**4**, **5**) bearing one or two thioacetyl moieties at terminal positions were presented. On one hand, the thiols resulted from the hydrolyzation of thioacetyl moieties can serve as molecular scale alligator clips for adhesion of the molecular scale wires to the gold probes.[8,9] On the other hand, the molecule with one end-thiol group can be used as a ligand for the functionalizaion of noble metal nanoparticles. And molecules with end-thiol groups at both terminal positions can be used as rigid linkers for the assembly of noble metal nanoparitcles to form 2D structures.



1: n = 1
2: n = 2
3: n = 3

Keywords: Synthesis; π-Conjugated oligomers; Electrochemistry.

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2. Results and discussions

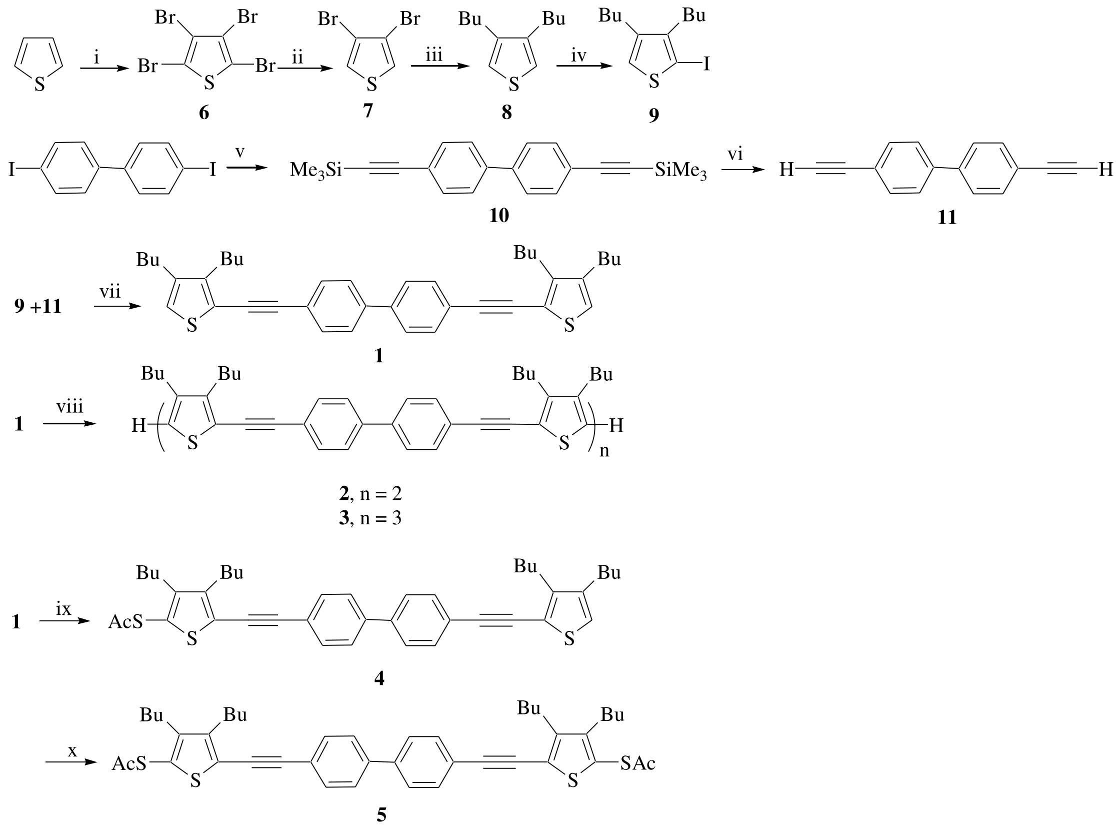
2.1. Molecular design and synthetic strategy

The synthetic strategy employed two reaction types to grow the conjugated chains rapidly. As a monomer unit, compound **1** was synthesized by Pd-mediated Sonogashira cross-coupling reaction. Oligomers **2** and **3** containing two or three monomer units were synthesized by lithiation of **1** and followed with oxidation coupling reactions, using $CuCl_2$ as the oxidant, which were depicted in Scheme 1. The starting material, 3,4-dibutylthiophene (**8**) was prepared according to the procedure described by Tour.[10] Then, it was subjected to react with iodine and mercury oxide, leading to **9** by an adopted procedure reported by Minnis.[11] Diiodide was obtained simultaneously, but it was no need to separate the iodide and diiodide. The iodide **9** intended to decompose in the air and should be used as soon as possible after workup. Commercially available 4,4′-diiodobiphenyl was coupled with (trimethylsilyl) acetylene via a Sonogashira–Hagihara reaction to afford the (trimethylsilyl)ethynyl derivative **10**,[12] which was then desilylated with potassium carbonate to afford the ethynyl derivative **11**. The aryl iodide **9** was coupled with the terminal alkyne **11** to afford compound **1** in a yield of 67% (Scheme 1). Pd/Cu coupling reactions required the strict exclusion of oxygen; degassing and use of a dry box was required to attain reasonable yields. Lithiation of **1** and followed with an oxidative coupling reaction in the presence of $CuCl_2$ led to the formation of dimer (**2**) and trimer (**3**) in yields of 33 and 30%, respectively.[13] Compounds **1**–**3** were stable in the air. They showed good solubilities in dichloromethane, chloroform, THF and benzene, yielding excellent processability for practical application.

Complementary thiol end groups, protected as thioester moieties, were attached to one or both ends of molecule **1** via a one-pot lithiation–sulfide-acetylation protocol.[14] The monothiol-terminated system could be used for self-assembly on gold surfaces. And α, ω-difunctionalized system could serve as a bridge between two gold probes. Thiol-terminated molecules could also be used for the functionalization of noble metal nanoparticles.

2.2. UV–vis and fluorescence spectral studies

The UV–vis absorption and fluorescence spectra of compounds **1**–**3** in dichloromethane were shown in Figures 1 and 2. In the UV–vis absorption spectra, broad bands with little vibronic structure were present. The shapes of the spectra were almost identical. There were two absorption bands for every compound. A weak band appeared around 270–280 nm. A strong band appeared at 352, 366 and 368 nm for **1**, **2** and **3**, respectively. Elongation of the conjugation length from **1** to **2** resulted in a red shift of 14 nm. However, only little red shift was observed from **2** to **3**. Similar chain length dependence was observed for their fluorescence spectra (Fig. 2). The spectroscopic measurements provided definite information on the effective conjugation length, that was, they exhibited a certain



Scheme 1. Preparation of compounds **1**–**5**. Reagents and conditions: (i) Br_2, 84%. (ii) *n*-BuLi, H_2O, 70%. (iii) C_4H_9MgBr, $Ni(dppp)Cl_2$, Et_2O, 61%. (iv) HgO, I_2, 94%. (v) $Me_3SiC\equiv CH$, $Pd(PPh_3)_4$, CuI, Et_3N, rt, 63%. (vi) K_2CO_3, MeOH, Et_2O, rt, 100%. (vii) $Pd(PPh_3)_4$, CuI, Et_3N, rt, 67%. (viii) LDA, $CuCl_2$, 33% for **2** and 30% for **3**. (ix) 1 equiv *n*-BuLi, S_8, AcCl, 23%. (x) 2 equiv *n*-BuLi, S_8, AcCl, 21%.

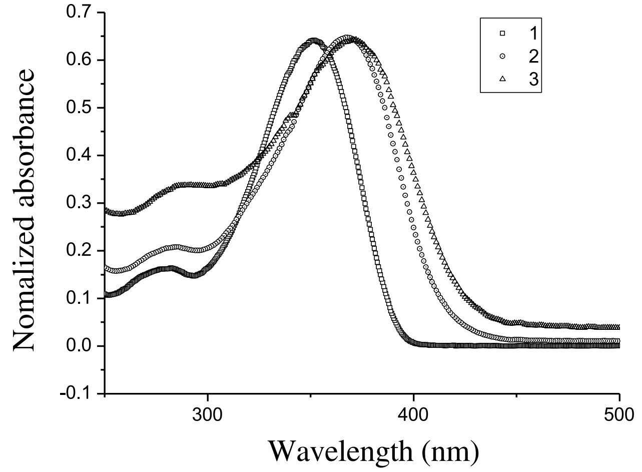


Figure 1. UV–vis absorption spectra of compounds **1**–**3** in CH_2Cl_2.

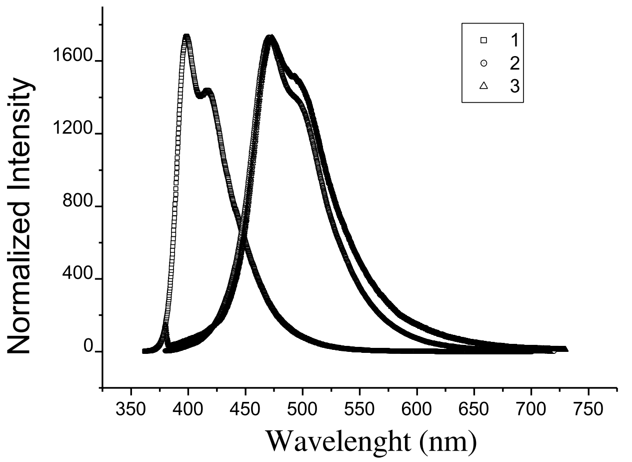


Figure 2. Fluorescence emission spectra of compounds **1**–**3** in CH_2Cl_2. Excited wavelengths are 352, 366 and 368 nm for molecules **1**, **2** and **3**, respectively.

limitation for the extensive conjugation. The saturation in λ_{max} was observed previously and arose because of the limitations to electron delocalization in the longer oligomers. There were several competing factors that must be considered. It has been known that with increasing of π-conjugation chain and more extensive electron delocalization, the absorption maxima should show bathochromic shifts. To enhance the solubility of the systems, the thiophene rings were substituted with *n*-butyl groups. The pendant butyl groups had two contrary effects on the π-systems. The butyl groups could cause distortions of the conjugated systems from planarity if steric interactions were severe enough. On the other hand, if steric interactions were not particularly severe, butyl groups could induce bathochromic shifts, which had been explained by inductive and hyperconjugative effects.[6] These two contradictory factors could take effect concurrently. With increase of chain length, the steric hindrance due to the butyl groups became overwhelmingly dominant, the effective conjugation reached saturation. The fluorescence quantum yields of **1**–**3** in dichloromethane were 62, 13 and 11%, respectively (Table 1). The quantum yields decreased as the conjugation length increased.

Table 1. The absorption λ_{max} (in CH_2Cl_2), emission λ_{max} (in CH_2Cl_2), and fluorescent quantum yields of oligomers **1**–**3**

Oligomer	UV λ_{max} (nm)	Em λ_{max} (nm)	Φ_F[a]
1	352	398	0.62
2	366	471	0.13
3	368	474	0.11

Excited wavelengths are 352, 366 and 368 nm for molecules **1**, **2** and **3**, respectively.

[a] Use 9,10-diphenylanthracene ($\Phi_F = 1.0$) to compare with in cyclohexane.

2.3. Electrochemical studies

The electrochemical behaviors of compounds **1**–**3** were studied by cyclic voltammetry. The oxidation wave was observed around 1.22 V for compound **1**, which showed no tendency for reduction under CV conditions but rather underwent irreversible oxidations in CH_2Cl_2, due to the fact that the corresponding radical cations were not stable. Electrochemical polymerization and film deposition for compound **1** was carried out using multiple scan cyclic voltammetry. Upon multiple cycling of **1** in CH_2Cl_2 solution, a new redox process developed at a lower potential (∼0.4 V) due to the reversible redox process of the as-deposited polymer (Fig. 3). The current response of this new redox process continued to increase in intensity upon additional cycling consistent with the deposition of an electroactive polymer onto the surface of the working electrode. As for products **2** and **3**, quasi-reversible redox behaviors were observed with oxidation peaks at 1.18 and 1.16 V, respectively. And no evidence for dimerization or polymer growth could be observed with continued cyclic sweeping through oxidizing potentials (Fig. 4). The electrochemical behavior of compound **1** was similar with that of 3,4-dibutyl thiophene, which displayed a typical electrochemical polymerization on the surface of anode. The difference between compound **1** and its dimer and trimer was due to stabilizing of radical cations with the increasing of conjugating length. Oligo(thiophene)s also displayed different electrochemical behavior with the different conjugating length. Only oxidation waves could

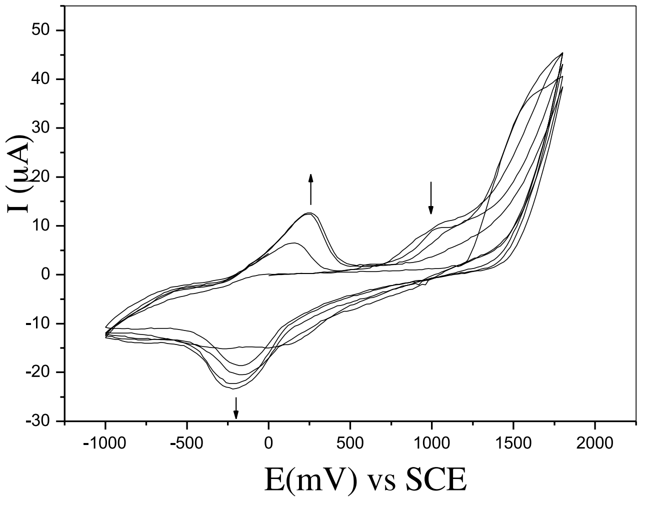


Figure 3. Cyclic voltammetric scanning electropolymerization of **1** (10^{-4} M in 0.1 M $Bu_4N^+PF_6^-/CH_2Cl_2$, 5 cycles. Pt working and counter electrodes, scan rate 100 mV s^{-1}).

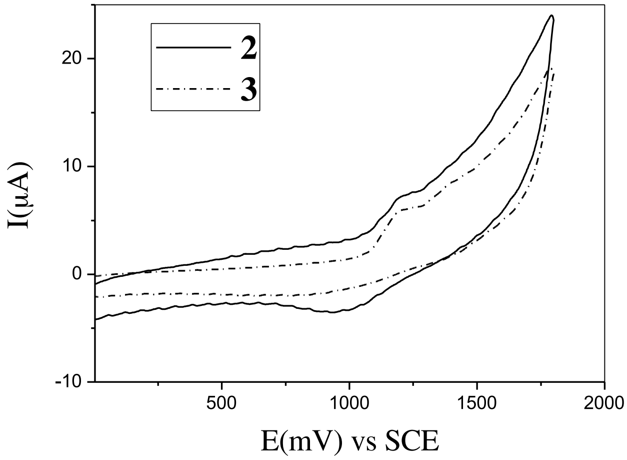


Figure 4. Cyclic voltammetric scanning electropolymerization of compounds **2** and **3**, 10^{-4} M in 0.1 M $Bu_4N^+PF_6^-/CH_2Cl_2$. Pt working and counter electrodes, scan rate 100 mV s^{-1}.

be observed for shorter oligomers, and reversible redox wave could be observed for longer oligomers.[15]

CVs of compounds **4** and **5** were also conducted for comparison. With masked thiol end-groups at the terminal positions, **4** and **5** presented peak oxidation potentials at 1.30 V, which were slightly higher than that of the parent molecule **1**. This should be due to the electron withdrawing effect of the thioacetyl groups.

3. Conclusions

We reported the synthesis of π-conjugated molecule **1** from the easy accessible materials with high efficiency. This molecule had a linear π-conjugated system with a length scale about 2 nm, and this π-conjugated system could be easily elongated by one-pot lithiation and oxidation coupling reaction. Dimer (**2**) and trimer (**3**) of compound **1** were obtained in moderate yields. These compounds could serve as building blocks for other functional molecular wires with precise conjugation lengths.

4. Experimental

4.1. General

Melting points were measured with a Buchi Melting Point B-540 instrument and uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker 300 MHz or Varian 200 MHz spectrometers. All chemical shifts were quoted in ppm relative to TMS. Infrared spectra were obtained on a Perkin–Elmer System 2000 FT-IR spectrometer. Mass spectra were determined with AEI-MS50-MS or MALDI-TOF-MS. Elemental analysis was performed on Carlo-Erba-1106 instrument. HRMS was performed on UK GCT-Micromass. Absorption spectra were measured with Hitachi (model U-3010) UV–vis spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) Spectrophotometer in a 1-cm quartz cell. Cyclic voltammetric experiments were performed on an EGDG PAR 370 system at a scan rate of 100 mV in CH_2Cl_2 using Bu_4NPF_6 as electrolyte, platinum electrodes as counter and work electrodes and SCE as reference electrode. *n*-Butyllithium (2.5 M solution in hexanes) and LDA (1.5 M in cyclohexane) were purchased from Acros or Aldrich Chemical Co., Inc. 4,4′-Diiodobiphenyl and (trimethylsilyl) acetylene were from Alfa Aesar. $Ni(dppp)Cl_2$, $Pd(PPh_3)_4$ from Aldrich Chemical Co., Inc. were used as received. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium/benzophenone immediately prior to use. All other reagents and solvents (standard grade) were used as received unless otherwise noted. All reactions involving *n*-BuLi or LDA were carried out under an atmosphere of dry N_2. Sonogashira cross-coupling reactions required the strict exclusion of oxygen and water.

4.1.1. 4,4′-Bis(trimethylsilyl)biphenyl 10. To a solution of 4,4′-diiodobiphenyl (2.00 g, 4.9 mmol), $Pd(PPh_3)_4$ (0.113 g, 0.098 mmol), CuI (0.037 g, 0.196 mmol) in THF (10 mL) was added 0.744 g (1 mL, 7.35 mmol) of triethylamine. A solution of 1.01 g (1.045 mL, 10.29 mmol) of (trimethylsilyl)acetylene in 5 mL of THF was then added slowly. The solution was stirred overnight at room temperature and white precipitate appeared, which was removed by filtration. The filtrate was evaporated, and the residue was purified by silica gel column chromatography (hexane) to give **10** (1.07 g, 63%) as a white solid. Mp 169 °C. IR (KBr, cm^{-1}): 2959, 2156, 1488, 1249, 861, 847, 824, 759. MS (EI): 346 (M^+). ^1H NMR: 7.53 (s, 8H), 0.27 (s, 18H).

4.1.2. 4,4′-Diethynylbiphenyl 11. To a solution of **10** (4.66 g, 13.47 mmol) in methanol (30 mL) and diethyl ether (30 mL) was added potassium carbonate (18.61 g, 134.68 mmol). The solution was allowed to stir for 6 h before being poured into water. The aqueous layer was extracted with dichloromethane, and the organic extracts were washed with brine. The combined organic layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation. No further purification was necessary to afford 2.72 g (100%) of **11** as a white solid. Mp 167 °C. (lit.[16] Mp 165.5–166.5 °C). IR (KBr, cm^{-1}): 3277, 2104, 1488, 857, 825. MS (EI): 202 (M^+). ^1H NMR: 3.16 (s, 2H), 7.54–7.60 (m, 8H).

4.1.3. 4,4′-Bis-[2-(3,4-dibutyl-2-thienylethynyl)]biphenyl 1. Following the method used for the synthesis of **10**. Used were **9** (6.80 g, 21.6 mmol), $Pd(PPh_3)_4$ (0.499 g, 0.432 mmol), CuI (0.165 g, 0.864 mmol), THF (30 mL), triethylamine (4.5 mL), **11** (2.182 g, 10.8 mmol),THF (50 mL). The solvent was evaporated and the residue was purified by silica gel column chromatography (silica gel, petroleum/dichloromethane 4:1) to give compound **1**(4.27 g, 67%) as a pale-yellow solid. Mp 67 °C. IR (KBr, cm^{-1}): 2956, 2928, 2858, 2199, 1635, 1493, 1406, 868, 819, 743. ^1H NMR (300 MHz, $CDCl_3$): δ 0.94–2.76 (m, 36H), 6.87 (s, 2H), 7.55–7.60 (m, 8H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.0, 22.6, 22.7, 28.0, 28.8, 31.9, 32.2, 84.3, 94.6, 118.5, 121.5, 122.8, 126.9, 131.7, 139.8, 142.1, 147.1. MS (EI): 590 (M^+). Anal. Calcd for $C_{40}H_{46}S_2$: C, 81.30; H, 7.85; S, 10.85. Found: C, 81.51; H, 8.00; S, 11.06.

4.1.4. 5,5′-Bis[4′-(3,4-dibutyl-thien-2-ylethynyl)-biphenyl-4-ylethynyl]-3,4,3′,4′-tetrabutyl-[2,2′]-bithiophenyl 2. A solution of **1** (0.130 g, 0.22 mmol) in anhydrous

THF (10 mL) was added to lithium diisopropylamine (0.18 mL, 0.26 mmol, 1.5 M in cyclohexane) in 10 mL of anhydrous THF at −78 °C under nitrogen. The reaction mixture were stirred at −78 °C for 30 min, then anhydrous powered $CuCl_2$ (0.0296 g, 0.22 mmol) was added in one portion, upon which the color of the solution changed to black. The solution was stirred until it returned to rt then for an additional 30 min at 30 °C. The mixture was poured into 20 mL of water, containing 10 mL of 1 M hydrochloric acid. Then it was extracted twice with 100 mL of diethyl ether. The combined organic layers were washed with water, dried over sodium sulfate and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum/dichloromethane 2:1) to give 0.043 g (33%) of **2** as a yellow solid. Mp 97 °C. IR (KBr, cm^{-1}): 2956, 2929, 2862, 2197, 1687, 1602, 1491, 1460, 821, 740. MS (MALDI-TOF): 1177 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–2.76 (m, 72H), 6.88 (s, 2H), 7.56–7.62 (m, 16H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 83.78, 84.34, 94.58, 95.88, 118.43, 118.92, 121.48, 122.60, 122.78, 126.84, 126.87, 130.12, 131.66, 139.73, 139.91, 141.86, 142.09, 147.05, 147.57. HRMS calcd for $C_{80}H_{90}S_4$: 1178.5925. Found: 1178.5919.

4.1.5. 4,4′-Bis-{5-[4′-(3,4-dibutyl-thien-2-ylethynyl)-biphenyl-4-yl-ethynyl]-[2,2′]-bithiophenyl-5′-ylethynyl}-biphenyl 3. 0.039 g (30%) of **3** was also isolated as a yellow solid. Mp 153 °C. IR (KBr, cm^{-1}): 2956, 2927, 2858, 2197, 1688, 1603, 1492, 1460, 821, 743. MS (MALDI-TOF): 1767 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90–2.82 (m, 108H), 6.93 (s, 2H), 7.64–7.65 (m, 24H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.80, 13.97, 14.01, 22.56, 22.67, 22.74, 22.79, 27.54, 27.96, 28.56, 28.71, 29.68, 31.87, 32.19, 32.46, 32.85, 83.76, 83.80, 84.32, 94.56, 95.86, 118.41, 118.90, 121.47, 122.59, 122.63, 122.77, 126.83, 126.86, 130.11, 131.66, 139.72, 139.86, 139.90, 141.85, 142.08, 147.04, 147.56. Anal. Calcd for $C_{120}H_{134}S_6$: C, 81.49; H, 7.64; S, 10.88. Found: C, 81.24; H, 7.50; S, 10.64.

4.1.6. [4-[2-(3,4-Dibutyl-2-thienylethynyl)-4′-[thioacetic acid-S-[2-(3,4-dibutyl-2-thienylethynyl)]ester]biphenyl 4. To a solution of **1** (0.198 g, 0.336 mmol) in THF (10 mL) at −78 °C was added dropwise *n*-butyllithium (0.201 mL, 0.503 mmol). The solution was stirred at −78 °C for 30 min then warmed to 0 °C and sulfur powder (0.011 g, 0.336 mmol) was added. The reaction remained at 0 °C for 30 min. The solution was recooled to −78 °C, and acetyl chloride (0.029 mL, 0.403 mmol) was added in one portion. The solution was allowed to warm to room temperature overnight. The mixture was extracted with dichloromethane and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by silica gel chromatography using 4:1 petroleum/dichloromethane as eluent to provide 0.051 g (23%) of **4** as a yellow solid. Mp 82.3–83.0 °C. MS (EI): 664 (M^+), 622 ($M-COCH_3+1$). IR (KBr, cm^{-1}): 2956, 2861, 2198, 1910, 1725, 1492, 1460, 1112, 821, 741, 605. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 0.89–2.79 (m, 36H), 6.89 (s, 1H), 7.57–7.63 (m, 8H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.92, 14.04, 14.08, 22.63, 22.75, 22.78, 22.82, 22.94, 27.88, 28.03, 28.79, 29.63, 29.76, 31.94, 32.27, 32.43, 32.53, 32.79, 53.47, 83.26, 84.45, 91.65, 96.83, 118.50, 120.53, 121.56, 122.32, 122.90, 123.82, 126.90, 126.93, 127.38, 131.50, 131.71, 131.81, 139.71, 140.22, 142.13, 147.10, 147.37, 148.23, 194.23. HRMS calcd for $C_{42}H_{48}OS_3$: 664.2867. Found: 664.2870.

4.1.7. {4,4′-Bis-[2-thioacetic acid-S-(3,4-dibutyl-2- thienyl-ethynyl)]ester}biphenyl 5. It was prepared similarly as compound **4**. Used were **1** (0.296 g, 0.502 mmol), THF (10 mL), *n*-butyllithium (0.8 mL, 2.007 mmol), sulfur powder (0.048 g, 1.505 mmol), acetyl chloride (0.107 mL, 1.505 mmol). The residue was purified by silica gel chromatography by first using 4:1 petroleum/dichloromethane and then increasing to 2:1 petroleum/dichloromethane to provide 0.078 g (21%) of **5** as a yellow solid. Mp 93.7–95.0 °C. MS (EI): 738 (M^+), 696 ($M-COCH_3+1$), 654 ($M-COCH_3$–$COCH_3+2$), 622 ($M-$ $COCH_3$ –$COCH_3$ –S $+2$). IR (KBr, cm^{-1}): 2956, 2862, 2197, 1911, 1726, 1492, 1461, 1113, 945, 821, 738. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 6H), 0.09–2.78 (m, 36H), 7.57–7.63 (m, 8H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 13.84, 13.96, 22.72, 22.77, 27.83, 28.76, 29.56, 32.38, 32.47, 83.28, 96.74, 120.56, 122.42, 123.76, 126.92, 131.78, 140.11, 147.34, 148.17, 194.19. HRMS calcd for $C_{44}H_{50}O_2S_4$: 738.2694. Found: 738.2688.

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