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Studies in the Dithienylbenzo[*c*]thiophene Series

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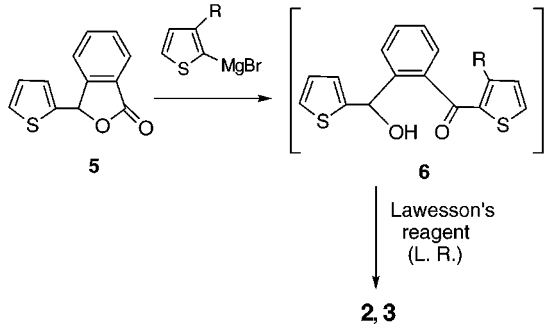
A number of derivatives of 1,3-dithienylbenzo[*c*]thiophene have been synthesized. The mono- and dicarboxaldehydes have been elaborated to give new vinylenes and cyanovinylenes. β-Dodecyl- and hexyl-substituted analogues have been prepared. Results from cyclic voltammetric investigation as well as fluorescence studies are reported.

Introduction

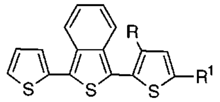
In recent years, there has been tremendous interest in organic molecules that can be further elaborated into materials exhibiting promising electrochemical, optical, and electronic effects that are desirable in the fabrication of electroluminiscent devices, frequency doublers, radio frequency/electromagnetic interference shielding devices, etc.[1−5] In this regard, thiophene derivatives have played a very significant role. For example, polythiophene is superior to polyphenylene as a semiconductor; poly(thienylenevinylene) has attracted considerable interest as a material with enhanced third-order nonlinear susceptibilities. The arylenevinylenes and other heteroarylenevinylenes have also attracted attention in the fabrication of electroluminiscent devices.[6]

Since 1992, the synthesis of 1,3-dithienylbenzo[*c*]thiophene (**1**) and its electrochemical behavior have been reported independently by four groups.[7a−d] Electropolymerization of **1** led to the formation of a material with poor conductivity. The polymer from **1** was also deposited on ITO glass. A detailed optoelectronic study of this polymer provided a value of ~1.7 eV for its band gap—a value intermediate between that of poly(isothianaphthene) (~1.0 eV) and polythiophene (2.0 eV). No further chemical transformations of the ring system of **1** were reported. Since it has been well established that anelation of aromatic rings to thiophene, as, for example, in benzo[*c*]thiophene, greatly changes the properties of materials derived from such a substrate, synthetic work was undertaken to modify 1,3-dithienylbenzo[*c*]thiophene, so as to provide routes to new extended oligomers, vinylenes, etc. This also provided an opportunity to study, albeit qualitatively, the spectroscopic and electrochemical behavior of some of these extended systems.

Scheme 1



We now report recent results from our laboratories on the transformations of 1,3-dithienylbenzo[*c*]thiophene (**1**), as well as the synthesis of the dodecyl derivative **2**, the hexyl derivative **3**, and the bromo derivative **4** and their transformations. Additional oligomers **7** and **8** were prepared.



1 $R = R^1 = H$
2 $R = C_{12}H_{25}$; $R^1 = H$
3 $R = C_6H_{13}$; $R^1 = H$
4 $R = H$; $R^1 = Br$

Results

The first targets were the substituted derivatives **2** and **3**, which were best made by the action of the appropriate thienyl Grignard reagent on the known lactone **5** followed by thionation of the intermediate **6** (Scheme 1).

The bromo derivative **4**, 1,3-dibithienylbenzo[*c*]thiophene (**7**) as well as 1-thienyl-3-bithienylbenzo[*c*]thiophene (**8**) were made by an analogous procedure as shown in Scheme 2.

The substituted benzo[*c*]thiophenes **1**−**3** undergo the Vilsmeier−Haack formylation readily to give the monoaldehydes **9**−**11**, respectively. Dilithiation of **1**−**3** followed by reaction with DMF and standard workup furnished the dialdehydes **12**−**14** (Scheme 3).

Dithienylbenzo[*c*]thiophene (**1**) was converted readily into the bispinacolboronate ester **15**, which coupled with

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[†] 1997 Summer High School Teacher Participant supported by Epscor Grant No. DE-FCO2-91ER75678.

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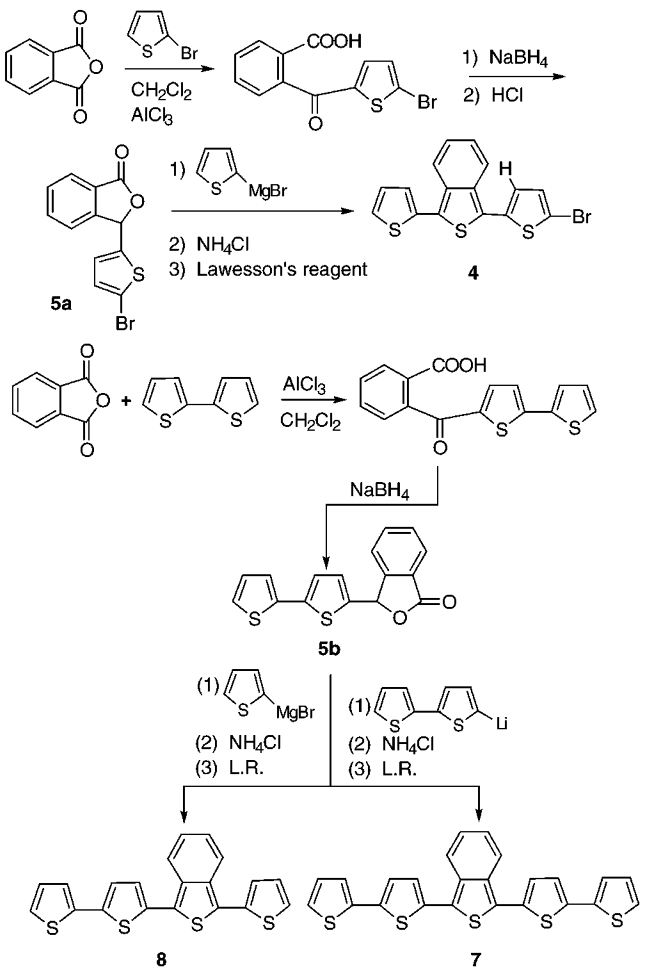
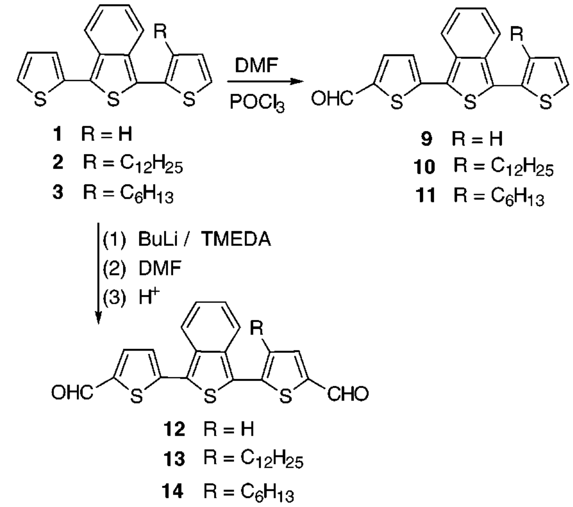
S0022-3263(98)00246-1 CCC: $15.00

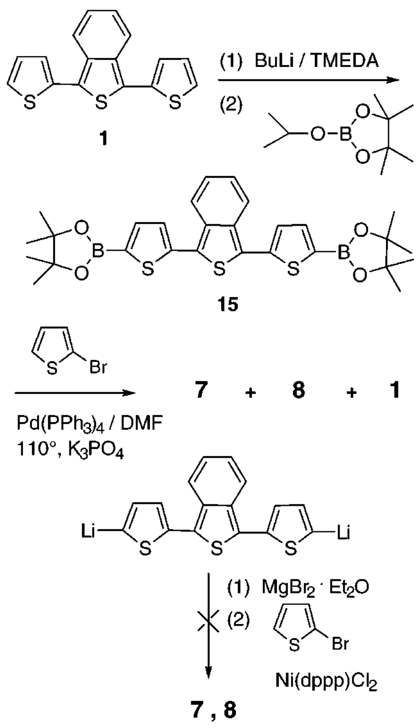
Scheme 2



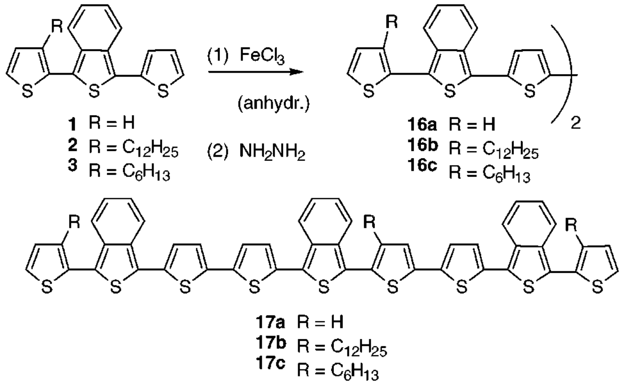
Scheme 3



Scheme 4



Scheme 5



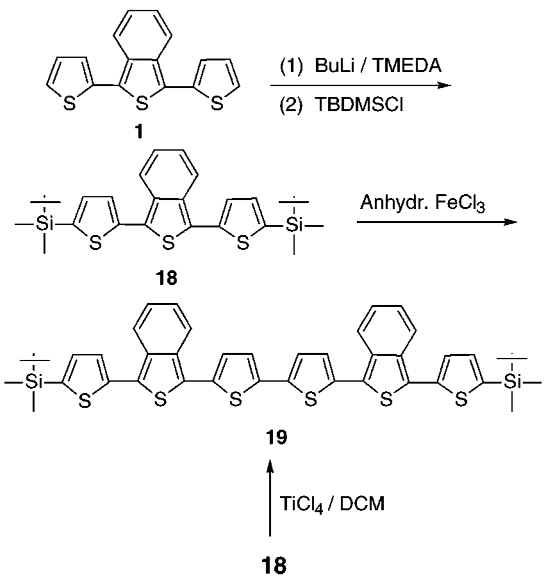
2-bromothiophene in the presence of Pd^0 to give **7** and **8** in 43% and 18% yield, respectively. In contrast, direct coupling of lithiated **1** with 2-bromothiophene in the presence of $Ni(DPPP)Cl_2$ was not successful (Scheme 4).

Several years ago, we, as well as other investigators, reported the electrochemical oxidation of **1** to a blue-black polymer.[7] In contrast, **2** and **3** do not deposit a dark film upon electrochemical oxidation. Oxidation of **1** by anhydrous ferric chloride led to an insoluble dark powder. Analysis by plasma desorption mass spectrometry revealed the presence of a dimer (**16a**) (M^+), trimer (**17a**) (M^+), and tetramer (**17b**) (M^+). However, under controlled conditions, dimer **16a** can be isolated, albeit in an impure state. Under the same conditions of oxidation, **2** gives a separable mixture of dimer **16b** and trimer **17b** (Scheme 5). It is noteworthy that dimer **16** can be viewed as a modified sexithiophene with enhanced solubility. Similar results were obtained by oxidation of **3**, which gave **16c** and **17c**. The NMR spectra of **16b**,**c** and **17b**,**c** are in accord with the assigned structures.

Dithienylbenzo[*c*]thiophene (**1**) was dilithiated and treated with TBDMSCl to give the silyl derivative **18** in 96% yield (Scheme 6). In contrast to **1**, silyl derivative **18** upon treatment with anhydrous ferric chloride furnished only the dimer **19** in 66% yield. Treatment of **18** with titanium tetrachloride in DCM gave a mixture of products from which chromatographic separation led only to the isolation of the dimer **19**.

The monoaldehyde **9** and the dialdehyde **12** undergo ready reaction with carbanions derived from malononitrile and arylmethylene and heteroarylmethylene nitriles to give vinylene cyanides **20**–**24**. They also undergo Wittig reactions to give the vinylenes **25**–**29** (Scheme 7).

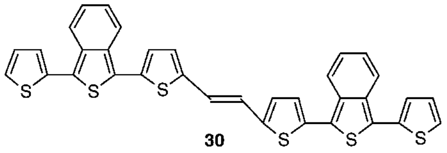
Scheme 6



In contrast to the above carbanion reactions, the carbanion derived from phosphonates leads mainly to an unprecedented decarbonylation of **9**. Subsequently, it was found that aldehydes **9** and **12** undergo decarbonylation readily in the presence of sodium hydride in DMF and potassium *tert*-butoxide in THF or DMF. Sodium hydride in THF leads to recovery of **9**. Apparently, strong bases generate the acylanion, which loses carbon monoxide. In the case of **12**, decarbonylation occurs stepwise as monitored by TLC (Scheme 8).

While the observed decarbonylation is mild and unprecedented in the case of **9** and **12**, under drastic conditions, furfural is transformed into furan by molten alkali.[8]

The aldehydes **9** and **12** were subjected to McMurray-type coupling reaction conditions, but neither the dimer **30** nor the annulene **31** were identifiable in the intractable mixture.



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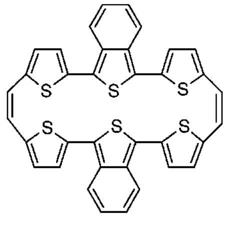

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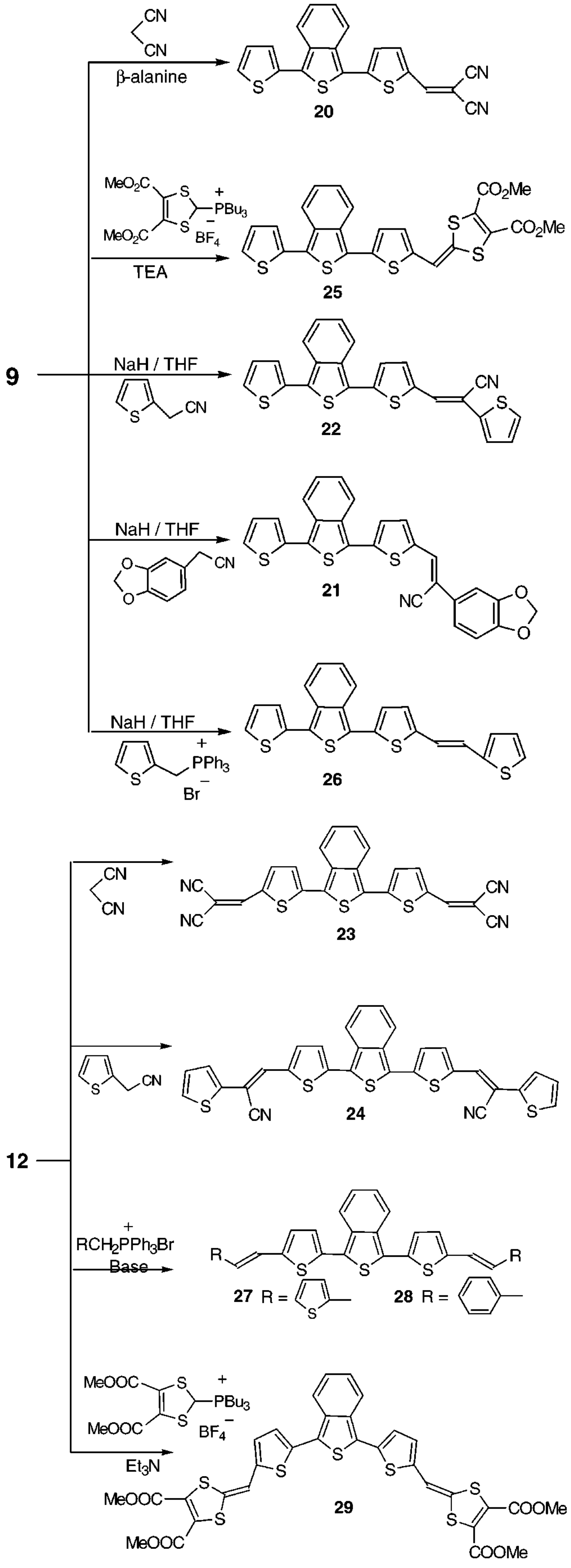
Ultraviolet Spectra

Scheme 7



The UV–vis spectra of the dithienylbenzo[*c*]thiophene derivatives (Table 1) show an interesting pattern analogous to that observed previously in the case of oligothiophene derivatives. In contrast to terthiophene ($\lambda_{\max}^{\mathrm{CHCl_3}}$, 355 nm) dithienylbenzo[*c*]thiophene (**1**) shows a strong longest wavelength absorption at 433 nm ($\Delta = 78$ nm). The introduction of alkyl β-substituents (dodecyl

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[8] Hurd, C. D.; Goldsby, A. R.; Osborne, E. N. *J. Am. Chem. Soc.* **1932**, *54*, 2532.

Scheme 8

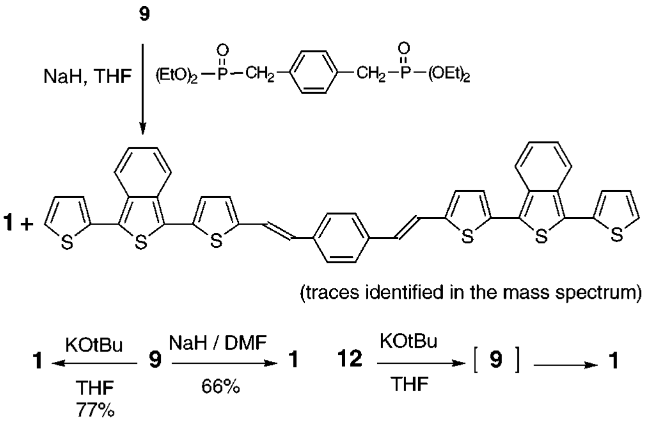

Table 1. UV−vis Spectral Data

entry	compd	$\lambda_{max}^{CH_2Cl_2}$ (nm) (log ϵ)
1	**1**	217 (4.15), 232 (4.40), 286 (4.37), 433 (4.29)
2	**2**	232 (4.59), 412 (4.34)
3	**3**	217 (4.69), 234 (4.42), 281 (4.22), 411 (4.16)
4	**4**	284 (3.89), 433 (3.79)
5	**18**	217 (4.92), 232 (4.52), 296 (4.45), 446 (4.34)
6	**7**	218 (4.30), 231 (4.47), 308 (4.36), 361 (4.30), 482 (4.03)
7	**8**	217 (4.11), 233 (4.30), 254 (4.28), 291 (4.25), 458 (4.11)
8	**19**	232 (4.57), 299 (4.38), 510 (4.62)
9	**16a**	217, 235, 506
10	**16b**	233 (4.57), 483 (5.0)
11	**16c**	233 (4.75), 484 (4.76)
12	**17b**	234 (4.99), 494 (5.0)
13	**17c**	236 (4.64), 502 (4.72)

and hexyl) into **1** lowers the long-wavelength absorption to 412 and 411 nm, respectively, clearly indicative of the twist in the backbone. When the α,α′ positions are blocked by the TBDMS group, a bathochromic shift of ~13 nm (433 nm → 446 nm) is induced, probably by the dπ−pπ interaction due to the silicon. Comparison of the published λ_{max} for α,α′-TMS-substituted terthiophene (368 nm)[9] to that of **18** also shows a bathochromic shift of 78 nm due to the annelation of the benzene ring. The presence of a bromine at the α-position in **1** leads to no change, whereas the presence of a methyl group increases the λ_{max} by 6 nm. Comparison of the longest absorption band (458 nm) of 1-thienyl-3-bithienylbenzo[*c*]thiophene (**8**) with that of quaterthiophene (390 nm)[10] indicates a strong red shift of 68 nm due to the annelation of the benzene ring. The red shift in **7** (λ_{max}, 482 nm) compared to quinquethiophene (416 nm) is also 66 nm. Looking at the dimers **16a** and **16b**, which can be viewed as sexithiophenes, the long-wavelength bands are shifted by 71 and 73 nm from the monomers **2** and **3**. The dimer derived from **1** also showed a red shift of 73 nm.

Table 2. Fluorescence Spectral Data

entry	compd	$\lambda^{nm}_{excitation}$	$\lambda^{nm}_{emission}$
1	**1**	433	532
2	**2**	412	531
3	**3**	412	528
4	**4**	285	533
5	**7**	485	604
6	**8**	460	575
7	**9**	473	592
8	**10**	453	578
9	**11**	452	579
10	**12**	491	571
11	**13**	458	569
12	**14**	458	569
13	**16b**	483	600
14	**16c**	483	582
15	**17b**	498	622
16	**17c**	500	637
17	**18**	451	547
18	**19**	519	593
19	**20**	558	677
20	**21**	503	549
21	**22**	510	655
22	**23**	587	686
23	**24**	560	676
24	**26**	478	606
25	**27**	514	640
26	**28**	511	624
27	**29**	550	

Fluorescence Spectra

Qualitative fluorescence spectra were recorded for a number of compounds (Table 2). Compounds **1**−**4** and **18**, which can be viewed as terthiophenes in which the 3,4-positions of the middle thiophene unit is annelated to a benzene moiety, emit light in the 528−547 nm region irrespective of the excitation wavelength (Table 2, entries 1−4 and 17). The symmetrically benzannelated quinquithiophene **7** (Table 2, entry 5) emits light at 604 nm, ~60−80 nm beyond the values for the terthiophene analogues. The unsymmetrically annelated quaterthiophene analogue **8** (Table 2, entry 6) emits light at 575 nm. Perusal of the $\lambda_{emission}$ of the aldehydes shows a similar pattern. The monoaldehydes **9**−**11** emit light at 592, 578, and 579 nm, respectively (Table 2, entries 7−9). The dialdehydes **12**−**14** emit light ~570 nm with much less variation (Table 2, entries 10−12).

The derivatives **16b**,**c** can be construed as alkyl-substituted sexithiophenes with symmetrical annelation of two benzene rings. Unlike the behavior of the terthiophenes **2** and **3**, **16b**,**c** show an 18 nm difference in their $\lambda_{emission}$ (Table 2, entries 13 and 14). A similar difference of ~15 nm is seen in $\lambda_{emission}$ in the trimeric compounds **17b** and **17c** (Table 2, entries 15 and 16). The aryl and heteroaryl cyanovinylenes **21** and **22** (Table 2, entries 19 and 20) show a considerable shift (106 nm) in the wavelength of emission. The absence of the cyanofunction in **26** produces a shift of almost 50 nm in its emission (Table 2, entry 24) compared to **22** (Table 2, entry 20). The difference in $\lambda_{emission}$ between the dicyanovinylenes **20** and **23** (Table 2, entries 19 and 22) is a modest 9 nm. In contrast to the vinylenes and cyanovinylenes, the dicarbomethoxydithiolidene vinylene **29** shows no fluorescence whatsoever (Table 2, entry 27).

Cyclic Voltammetry

The cyclic voltammograms of the heterocycles (**1**−**3**, **7**, **8**, **16b**,**c**, **18**, and **19**) were determined using a PAR model 263 instrument in dichloroethane containing 0.1 M tetrabutylammonium hexafluorophosphate. The working electrode (WE) was a Pt disk and the counter electrode, Pt wire, the reference electrode being a standard calomel. The data from these determinations are summarized in Table 3. The following observations are pertinent. Triheterocycle **1** is quickly polymerized to give a blue-black deposit on the WE. In contrast, both **2** and **3** show an

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(9) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

(10) Pham, C. V.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark, H. B., Jr.; Zimmer, H. *Phosphorus, Sulfur Silicon* **1989**, *46*, 153.

Table 3. Redox Behavior of 1 and Analogues

entry	compd	pa_1 (V)	pa_2 (V)	pc_1 (V)	pc_2 (V)	polymer/oligomer formation	ΔE_1 (mV)	ΔE_2 (mV)
1	**1**	0.873[a]		0.80[a]		yes	73	
2	**2**	0.94[b]				yes		
3	**3**	0.862[b]				yes		
4	**7**	0.724[a]	1.13[a]	0.914[a]	0.8	yes	100	76
5	**8**	0.813[b]	1.008[b]	1.055		yes		
6	**16b**	0.730[c]		0.602[c]		no	123	
7	**16c**	0.665[c]	0.773[c]	0.734[c]	0.610[c]	no	55	39
8	**18**	0.830[c]		0.750[c]		no	80	
9	**19**	0.626[c]	0.756[c]	0.705[c]	0.565[c]	no	61	51

[a] Quasireversible. [b] Irreversible. [c] Reversible.

irreversible peak at 0.94 and 0.86 V. No deposit was observed on the Pt disk WE. However, the formation of new electroactive species in **2** was discernible by the new peaks at pa 0.650, 0.809 and pc 0.746, 0.612 V.

In the case of **3**, the new electroactive species in solution were detectable by the peaks at pa 0.561, 0.74 and pc 0.605 (broad). The authentic dimer **16b** showed broad reversible peaks at pa 0.730 and pc 0.602 V with no change even after 50 scans. In the case of dimer **16c**, a pair of reversible peaks were seen at pa 0.665, 0.773 and pc at 0.734, 0.610 V.

The tetracycle **8**, which can be viewed as a quaterthiophene ($E_{1/2}$ 0.95 V irr) with one benzene ring annelated to it, exhibits pa 0.813, 1.008 and pc 1.055 (br). There is a quick change, and very soon new peaks appear at pa 0.486, 0.677 and 0.815 V and pc shows a broad signal centered around 0.5 V. There is a deposit on the WE. The WE was washed free of soluble electroactive species, and its CV was determined. It showed pa 0.789 and pc 0.6 V and was reversible.

The pentacycle **7** is a monobenzannelated quinquethiophene ($E_{1/2}$ 0.89 V irr) and shows peaks pa at 0.724, 1.13 V and pc at 0.914 and 0.8 V. In contrast to the examples above, the silyl-capped terheterocycle **18** exhibits Coulombic reversibility, the peaks occurring at pa 0.839 and pc at 0.765 V. The silylcapped dimeric compound also shows Coulombic reversibility with peaks at pa 0.626, 0.756 and pc at 0.705 and 0.565 V.

Conclusion

The known 1,3,2-dithienylbenzo[*c*]thiophene (**1**) has been functionalized to give a bis-TBDMS-capped triheterocycle, vinylenes, cyanovinylenes, and dicyanovinylenes. Several new β-alkyl-substituted analogues of **1** have been synthesized and characterized. Ferric chloride oxidation of the triheterocycles has been carried out, and the major products have been shown to be dimeric molecules. The fluorescence spectra of the tri-, tetra-, and pentaheterocycles have been recorded. The results show that several heterocycles described above may be suitable for the fabrication of LED devices. A number of sexithiophene analogues incorporating specific benzenoid annelation have been described. These could find use in transistor[11] applications by virtue of their enhanced solubility compared to sexithiophene itself.

Experimental Section

All melting points are uncorrected. NMR spectra were determined in $CDCl_3$ solution containing TMS as internal standard unless otherwise stated. Organic extracts were dried over anhydrous Na_2SO_4. All UV−vis spectra were recorded in CH_2Cl_2 solution.

2-Thienyl phthalide (5).[7a,b] An improved preparation of **5** is described below. A hot solution of 2-(2-thenoylbenzoic acid) (30.0 g, 0.129 mol) in aqueous sodium bicarbonate (15.9 g in 2 L of H_2O) was treated with $NaBH_4$ (49.0 g, 1.29 mol) in portions. After standing overnight, it was heated for 1 h on the steam bath, cooled to room temperature, and then *cautiously* acidified with 12% aqueous hydrochloric acid to pH 2. The mixture was stirred for 2 h at room temperature, and the white solid was filtered to give **5** (22.31 g, 80%).

1-(3-Dodecylthienyl)-3-thienylbenzo[*c*]thiophene (2). 2-Bromo-3-dodecylthiophene (8 g, 0.024 mol) was added slowly to a refluxing mixture of magnesium turnings (0.705 g, 0.029 mol) and iodine (20 mg) in dry THF. After the formation of the Grignard reagent (6 h reflux), the cooled reagent was added slowly via an addition funnel to a solution of lactone **5** in THF (50 mL) at −10 °C. The reaction mixture was stirred for 6 h at room temperature and was poured onto ice containing NH_4Cl. The intermediate was extracted into CH_2Cl_2 and dried (Na_2SO_4), and the extract was treated with Lawesson's reagent (5 g, 0.012 mol) and was stirred at room temperature for 6 h. Standard workup and filtration through a column of basic alumina furnished **2** as a thick liquid (8.7 g, 77%): ^1H NMR δ 7.95 (d, 1H, $J = 8.5$ Hz), 7.55 (d, 1H, $J = 8.6$ Hz), 7.38 (d, 2H, $J = 5.2$ Hz), 7.35 (d, 1H, $J = 3.3$ Hz), 7.17−7.06 (m, 4H), 2.65 (t, 2H, $J = 7.8$ Hz), 1.72−1.66 (m, 2H), 1.29−1.19 (m, 18H), 0.91 (t, 3H, $J = 5$ Hz); MS 466 (M^+, 100), 311 (36), 277 (24), 227 (47); UV−vis 412 (4.34), 232 (4.59). Anal. Calcd for $C_{28}H_{34}S_3$: C, 72.03; H, 7.36; S, 20.61. Found: C, 71.97; H, 7.31; S, 20.49.

1-(3-Hexyl-2-thienyl)-3-(2′-thienyl)benzo[*c*]thiophene (3). The Grignard reagent from 2-bromo-3-hexylthiophene was reacted with lactone **5** as described above. Workup provided **3** (8 g, 64.5%) as an oil: ^1H NMR δ 7.96 (d, 1H, $J = 8.8$ Hz), 7.55 (d, 1H, $J = 8.7$ Hz), 7.38 (d, 2H, $J = 5.1$ Hz), 7.38 (d, 1H, $J = 3.6$ Hz), 7.16 (t, 1H, $J = 4.6$ Hz), 7.11 (t, 1H, $J = 5.4$ Hz), 7.07 (d, 2H, $J = 5.4$ Hz), 2.65 (t, 2H, $J = 7.9$ Hz), 1.59 (q, 2H, $J = 7.4$ Hz), 1.24 (m, 6H), 0.82 (t, 3H, $J = 7.1$ Hz); MS 382 (M^+, 100), 311 (55), 277 (41), 264 (36), 227 (92); UV−vis 411 (4.16), 281 (4.22) 234 (4.42). Anal. Calcd for $C_{22}H_{22}S_3$: C, 69.05; H, 5.81; S, 25.14. Found: C, 68.96; H, 5.81; S, 25.06.

3-[2-(5-Bromothienyl)phthalide] (5a). A suspension of pthalic anhydride (11.84 g, 0.08 mol) in CH_2Cl_2 (200 mL) was treated with anhydrous $AlCl_3$ (20 g, 0.15 mol). The mixture was stirred for 0.5 h at room temperature and was treated dropwise with a solution of 2-bromothiophene (15.6 g, 0.096 mol) in CH_2Cl_2 (100 mL). Standard workup yielded the 2-(5-bromo-2-thenoyl)benzoic acid as a yellow solid (21 g; 84%): mp 158 °C; ^1H NMR δ 8.07 (d, 1H, $J = 7.2$ Hz), 7.65 (t, 1H, $J = 7.6$ Hz), 7.58 (t, 1H, $J = 7.4$ Hz), 7.42 (d, 1H, $J = 7.2$ Hz), 7.02 (d, 1H, $J = 3.96$ Hz), 6.97 (d, 1H, $J = 4$ Hz); MS 312 (M^{+2}, 57), 310 (M^+, 51), 230 (57), 223 (46), 110 (100). This intermediate acid (9.96 g, 0.032 mol) was reduced as described for the synthesis of **5** in hot sodium bicarbonate solution (4.77 g in 750 mL H_2O) using $NaBH_4$ (14.79 g, 0.388 mol). Yield of **5a** was 8.3 g (88.3%): mp 123 °C (crystallizes from MeOH or hexane); ^1H NMR δ 7.92 (d, 1H, $J = 7.1$ Hz), 7.72 (t, 1H, $J = 7.3$ Hz), 7.61 (t, 1H, $J = 7.3$ Hz), 7.45 (d, 1H, $J = 7.2$ Hz), 6.95

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[11] Horowitz, G.; Deloffre, F.; Garnier, F.; Hajlaoui, R.; Hmyene, M.; Yassar, A. *Synth. Met.* **1993**, *54*, 435.

(d, 1H, *J* = 4.1 Hz), 6.85 (d, 1H, *J* = 4.2 Hz), 6.55 (s, 1H). Anal. Calcd for $C_{12}H_7BrO_2S$: C, 48.84; H, 2.40; S, 10.87. Found: C, 48.82; H, 2.36; S, 10.79.

1-(5-Bromothienyl)-2-thienylbenzo[*c*]thiophene (4). Thienylmagnesium bromide (from 2-bromothiophene **9**) was added to a solution of phthalide **5a** (3 g, 0.01 mol) in THF at −10 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 2 h, poured over ice-cooled NH_4Cl solution, and extracted with methylene chloride (3 × 40 mL). The solution was treated with Lawesson's reagent (2.1 g, 0.01 mol) and stirred at room temperature for 4 h. Methylene chloride was removed, and the residue was gently heated (fume hood) on a steam bath with ethanol (40 mL). The crude product was adsorbed on alumina (neutral) and placed in a Soxhlet apparatus, and the product was extracted using hexane as eluent: yield 1.6 g (42.1%); mp 90 °C (methanol); ^{1}H NMR δ 7.96 (d, 1H, *J* = 3.5 Hz), 7.95 (d, 1H, *J* = 3.6 Hz), 7.39−7.35 (m, 3H), 7.16−7.13 (m, 4H); MS 378 (M^{+1}, 30), 377 (M^+, 31), 298 (100), 264 (30), 253 (30), 221 (42); UV−vis 433 (3.79), 284 (3.89); HRMS calcd for $C_{16}H_9BrS_3$ 377.9029, found 377.9038.

3-(2-Bithienyl)phthalide (5b). The bithenoyl benzoic acid (12 g) was made from 2,2′-bithiophene (8.4 g, 0.051 mol) and phthalic anhydride (7.5 g, 0.051 mol) in CH_2Cl_2 in 76% yield: mp 161 °C; ^{1}H NMR δ 8.08 (d, 1H, *J* = 7.8 Hz), 7.65 (t, 1H, *J* = 7.5 Hz), 7.56 (t, 1H, *J* = 7.5 Hz), 7.57 (d, 1H, *J* = 7.4 Hz) 7.35 (s, 1H), 7.32 (d, 1H, *J* = 4.3 Hz), 7.14 (d, 1H, *J* = 3.9 Hz), 7.09 (d, 1H, *J* = 4 Hz), 7.05 (t, 1H, *J* = 4.4 Hz).

The above acid was reduced to phthalide **5b** in 77% yield by a procedure similar to that of 3-thienylphthalide: mp 164 °C; ^{1}H NMR δ 7.97 (d, 1H, *J* = 7.7 Hz), 7.74 (t, 1H, *J* = 7.3 Hz), 7.61 (t, 1H, *J* = 7.6 Hz), 7.50 (d, 1H, *J* = 7.1 Hz), 7.22 (d, 1H, *J* = 4.1 Hz), 7.12 (d, 1H, *J* = 4.1 Hz), 7.08 (m, 2H), 6.99 (m, 1H), 6.62 (s, 1H); MS 298 (M^+, 100), 254 (41), 253 (52), 221 (30); UV−vis 217 (4.15), 232 (4.40), 286 (4.37), 433 (4.29). Anal. Calcd for $C_{16}H_{10}O_2S_2$: C, 64.40; H, 3.38; S, 21.49. Found: C, 64.29; H, 3.33; S, 21.53.

1,3-(Dibithienyl)benzo[*c*]thiophene (7). A solution of bithiophene (1.67 g, 0.01 mol) in dry THF (100 mL) was treated with *n*-BuLi (4 mL, 2.5 M) and TMEDA (1.5 mL, 0.01 mol) at −78 °C under N_2. The temperature was slowly raised to 0 °C and stirred for 30 min. Then it was slowly added to a solution of lactone **5b** (1.5 g, 0.005 mol) in dry THF (50 mL) at −10 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h, poured over ice-cooled NH_4Cl solution, and extracted with methylene chloride (3 × 50 mL). The solution was treated with Lawesson's reagent (1 g) followed by conventional workup, and column chromatography separation on basic alumina (hexane) gave **7**: 0.8 g (35%); mp 175 °C; ^{1}H NMR δ 8 (d, 1H, *J* = 2.8 Hz), 7.98 (d, 1H, *J* = 2.8 Hz), 7.35−7.15 (m, 10H), 7.05 (t, 2H, *J* = 4.4 Hz); MS 462 (M^+, 95), 335 (11), 231 (19); UV−vis 482 (4.03), 361 (4.30), 308 (3.46), 231 (4.47), 218 (4.30). Anal. Calcd for $C_{24}H_{14}S_5$: C, 62.29; H, 3.06; S, 34.65. Found: C, 6237; H, 3.06 S, 34.52.

1-Bithienyl-3-thienylbenzo[*c*]thiophene (8). Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (0.82 g, 5.0 mmol) with phthalide **5b** (1.0 g, 3.3 mmol) followed by workup and thionation with Lawesson's reagent (0.7 g) led to **8**: 0.5 g (39%); mp 94 °C; ^{1}H NMR δ 7.94 (m, 2H), 7.39 (d, 1H, *J* = 51. Hz), 7.35 (d, 1H, *J* = 3.6 Hz), 7.26 (d, 1H, *J* = 3.6 Hz), 7.23 (d, 1H, *J* = 3.6 Hz), 7.2 (d, 1H, *J* = 3.7 Hz), 7.16 (m, 4H), 7.05 (m, 1H); MS 380 (M^+, 100), 335 (15), 253 (12), 190 (32); UV−vis 458 (4.11), 291 (4.25), 254 (4.28), 233 (4.30), 217 (4.11). Anal. Calcd for $C_{24}H_{14}S_5$: C, 63.11; H, 3.18; S, 33.70. Found: C, 63.01; H, 3.19; S, 33.62.

Aldehyde 9. $POCl_3$ (2.96 mL, 0.032 mol) was slowly added to a mixture of CH_2Cl_2 (40 mL) and DMF (2.45 mL, 0.032 mol) at 0 °C. After the addition was over, the mixture was stirred at room temperature until a pale yellow color formed. It was then added to **1** (9 g, 0.03 mol) dissolved in CH_2Cl_2 (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 10 h, and the solvent was completely removed. Aqueous NaOH was added, the mixture was heated on a steam bath for 1 h and cooled, and the product was filtered and air-dried. Then it was passed through a column (Al_2O_3, 50% chloroform/hexane) with a yield of 8 g (82.5%). A small amount of the solid was recrystallized from methanol to give orange-red needles: mp 112 °C (MeOH); ^{1}H NMR 9.96 (s, 1H), 8.05 (t, 2H, *J* = 7.4 Hz), 7.75 (d, 1H, *J* = 7.2 Hz), 7.50−7.36 (m, 2H), 7.34−7.1 (m, 4H); MS 326 (M^+, 100), 297 (26), 264 (26), 253 (27), 221 (10); UV−vis 474 nm (4.46), 293 (4.16), 239 (4.22). Anal. Calcd for $C_{17}H_{10}OS_3$: C, 62.54; H, 3.09; S, 29.47. Found: C, 62.45; H, 3.06; S, 29.37.

Aldehyde 10. Substrate **2** (5.5 g, 0.0118 mol) was reacted with the Vilsmeier reagent prepared from DMF (1.2 mL, 0.0155 mol) and $POCl_3$ (1.4 mL, 0.015 mol) as described for **9** to yield after workup product **10** (5.3 g; 91%) as a thin liquid: ^{1}H NMR δ 9.91 (s, 1H), 8.06 (d, 1H, *J* = 8.9 Hz), 7.77 (d, 1H, *J* = 4 Hz), 7.62 (d, 1H, *J* = 8.8 Hz), 7.44 (d, 1H, *J* = 4.1 Hz), 7.43 (d, 1H, *J* = 5.6 Hz), 7.27 (t, 1H, *J* = 6.8 Hz), 7.18 (t, 1H, *J* = 8.9 Hz), 7.08 (d, 1H, *J* = 5.2 Hz), 2.65 (t, 2H, *J* = 7.6 Hz), 7.59 (m, 2H), 1.20 (m, 18), 0.87 (t, 3H, *J* = 6.9 Hz); MS 494 (M^+, 100), 466, 339 (55), 277 (26), 244 (20), 227 (70); UV−vis 453 (4.44), 237 (4.48). Anal. Calcd for $C_{29}H_{34}OS_3$: C, 70.38; H, 6.94; S, 19.44. Found: C, 70.42; H, 6.96; S, 19.31.

Aldehyde 11. This was prepared in a similar manner using $POCl_3$ (0.32 mL, 3.4 mmol), DMF (0.26 mL, 3.4 mmol), and **3** (1.0 g, 2.62 mmol). After workup, it was obtained as a thin liquid (0.85 g; 79%): ^{1}H NMR δ 9.84 (s, 1H), 7.98 (d, 1H, *J* = 8.8 Hz), 7.69 (d, 1H, *J* = 4 Hz), 7.53 (d, 1H, *J* = 8.4 Hz), 7.36 (d, 1H, *J* = 4.3 Hz), 7.35 (d, 1H, *J* = 5.5 Hz), 7.19 (t, 1H, *J* = 6.6 Hz), 7.07 (t, 1H, *J* = 6.7 Hz), 7.01 (d, 1H, *J* = 53 Hz), 2.57 (t, 2H, *J* = 7.9 Hz), 1.51 (q??, 2H, *J* = 7.2 Hz), 1.17 (m, 6H), 0.74 (t, 3H, *J* = 6.9 Hz); MS 410 (M^+, 86), 339 (69), 298 (26), 277 (58), 227 (100); UV−vis 4.53 (4.31), 236 (4.36), 217 (4.19). Anal. Calcd for $C_{23}H_{22}OS_3$: C, 67.26; H, 5.41; S, 23.42. Found: C, 66.99; H, 5.37; S, 23.18.

1,3-Di(2-thienyl)benzo[*c*]thiophene-5,5′-dicarboxaldehyde (12). A solution of **1** (5 g, 0.0168 mol) and TMEDA (10.1 mL, 0.067 mol) in dry THF (150 mL) was cooled to −78 °C under N_2 and was treated with a solution of *n*-BuLi (50 mL, 2 M). The temperature was slowly raised to 0 °C, and the mixture was stirred at that temperature for 1 h. The mixture was recooled to −78 °C and was treated with dry DMF (45 mL, 0.58 mol). The mixture was then stirred at room temperature for 12 h and poured into crushed ice containing HCl. The precipitate of **12** was filtered after stirring for 2 h, washed with water, and dried in vacuo to give 5.2 g (87.5% yield): mp 241 °C (crystallized from toluene); ^{1}H NMR δ 9.93 (s, 2H), 8.09 (d, 1H, *J* = 3.6 Hz), 8.07 (d, 1H, *J* = 3.6 Hz), 7.80 (d, 2H, *J* = 3.6 Hz), 7.49 (d, 2H, *J* = 3.6 Hz), 7.33 (d, 1H, *J* = 3.5 Hz), 7.31 (d, 1H, *J* = 3.1 Hz); MS 354 (M^+, 100), 326 (3.3), 281 (10.9), 239 (34.7); UV−vis 491 (4.63), 304 (4.32), 232 (4.52), 217 (4.37). Anal. Calcd for $C_{18}H_{10}O_2S_3$: C, 60.98; H, 2.85; S, 27.14. Found: C, 61.45; H, 2.93; S, 27.24.

1-(3-Dodecyl-2-thienyl)-3-(2′-thienyl)benzo[*c*]thiophene-5,5′-dicarboxaldehyde (13). A solution of substrate **2** (1 g, 2.1 mmol) and TMEDA (0.81 mL, 5.35 mmol) in 30 mL of dry THF was cooled to −78 °C under N_2 and was treated with 2.3 mL of 2.4 M *n*-BuLi. The mixture was stirred at the same temperature for 2 h, and DMF (1 mL) was added to the orange-red solution. The temperature was slowly raised to room temperature, and the mixture was stirred for 30 min. It was then poured over crushed ice and HCl, stirred for 2 h, extracted with ether, and dried (Na_2SO_4). It was then passed through a column of alumina to get **13** as a dark red liquid with a yield of 0.85 g (75.8%): ^{1}H NMR δ 9.94 (s, 1H), 9.92 (s, 1H), 8.08 (d, 1H, *J* = 8.9 Hz), 7.79 (d, 1H, *J* = 4 Hz), 7.75 (s, 1H), 7.69 (d, 1H, *J* = 8.8 Hz), 7.48 (d, 1H, *J* = 4 Hz), 7.31 (t, 1H, *J* = 8.7 Hz), 7.23 (t, 1H, *J* = 8.7 Hz), 2.73 (t, 2H, *J* = 7.5 Hz), 1.64 (t, 2H, *J* = 7.4 Hz), 1.23 (m, 18H), 0.87 (t, 3H, *J* = 7 Hz); MS 522 (M^+, 100), 494 (53), 367 (43), 337 (24), 309 (23), 277 (25), 255 (38), 227 (39); UV−vis 460 (4.47), 303 (4.26), 236 (4.44). Anal. Calcd for $C_{30}H_{34}O_2S_3$: C, 68.91; H, 6.57; S, 18.40. Found: C, 68.97; H, 6.64; S, 18.31.

1-(3-Hexyl-2-thienyl)-3-(2′-thienyl)benzo[*c*]thiophene-5,5′-dicarboxaldehyde (14). Dialdehyde **14** was prepared exactly as described above from substrate **3** (1.0 g, 2.6 mmol), *n*-BuLi (2.84 mL, 6.8 mmol), TMEDA (1.1 mL, 6.8 mmol), and

DMF (1 mL) as a red liquid (0.84 g, 73%): ^{1}H NMR δ 9.94 (s, 1H), 9.92 (s, 1H), 8.07 (d, 1H, $J = 8.8$ Hz), 7.8 (d, 1H, $J = 3.9$ Hz), 7.75 (s, 1H), 7.7 (d, 1H, $J = 8.8$ Hz), 7.48 (d, 1H, $J = 4.1$ Hz), 7.31 (t, 1H, $J = 6.7$ Hz), 7.23 (t, 1H, $J = 6.9$ Hz), 2.73 (t, 2H, $J = 7.6$ Hz), 1.64 (d, 2H, $J = 6.7$ Hz), 1.2 (m, 6H), 0.83 (t, 3H, $J = 6.8$ Hz); MS 438 (M^+, 93), 410 (100), 367 (33), 339 (46), 227 (90); UV−vis 459 (4.65), 268 (4.57), 235 (4.60), 217 (4.50). Anal. Calcd for $C_{24}H_{22}O_2S_3$: C, 65.71; H, 5.06; S, 21.93. Found: C, 65.60; H, 5.12; S, 22.01.

Bis-borolane (15). The dilithiation of **1** (1 g, 3.36 mol) was carried out as described previously, pinacol boronate (3.4 mL, 0.022 mol) was added, and the mixture was stirred for 10 h. Workup led to the isolation of a sticky residue that was triturated with methanol to give a solid (0.9 g; 52.8%): mp 162 °C; ^{1}H NMR δ 8.06 (d, 1H, $J = 3.1$ Hz), 8.04 (d, 1H, $J = 3$ Hz), 7.65 (d, 1H, $J = 3.7$ Hz), 7.43 (d, 1H, $J = 3.6$ Hz), 7.17 (d, 1H, $J = 2.2$ Hz), 7.15 (d, 1H, $J = 3.1$ Hz), 1.37 (s, 24 H); MS 550 (M^+, 23), 424 (56), 298 (99), 274 (100); HRMS calcd for $B_2C_{28}H_{32}O_4S_3$ 548.1721, found 548.1712.

Suzuki Coupling of Borolane (15) with 2-Bromothiophene. A solution of borolane **15** (0.16 g, 0.3 mmol) and 2-bromothiophene (0.12 mL, 1.2 mmol) in dry DMF (10 mL) was treated with tetrakis(triphenylphosphine)palladium (0.05 g, 0.4 mmol) and K_3PO_4 (0.39 g, 1.83 mmol) at 110 °C. The mixture was maintained at the same temperature for 24 h under N_2 and poured over 200 mL of H_2O. Extraction with methylene chloride followed by chromatography on basic alumina (40:1 hexane−CH_2Cl_2 → 20:1 hexane−CH_2Cl_2) yielded compound **7** (0.06 g, 43%) and compound **8** (0.02 g, 18%).

Ferric Chloride Oxidation of (1). A solution of **1** (0.5 g, 1.68 mmol) in CH_2Cl_2 (40 mL) was treated with anhydrous $FeCl_3$ (0.31 g, 1.8 mmol) under nitrogen. The mixture was stirred at room temperature for 6 h and diluted with more CH_2Cl_2 (50 mL). The dark mixture was treated with a dilute solution of $NH_2NH_2{\cdot}H_2O$. Evaporation afforded a dark powder containing **16a**.

Ferric Chloride Oxidation of 2 To Give 16b and 17b. The oxidation of **2** (0.6 g, 1.1 mmol) was carried out in CH_2Cl_2 as described above using anhydrous $FeCl_3$ (0.191 g, 1.2 mmol). After workup, the residue from CH_2Cl_2 was resolved by chromatography (SiO_2; hexane−CH_2Cl_2 10:1) to give unreacted **2** (0.2 g), dimer **16b** (0.25 g; 62.5% based on recovered starting material) as a thin red oil and trimer **17b**, also an oil (0.05 g, 12.5): ^{1}H NMR spectrum of **16b** δ 7.95 (d, 2H, $J = 8.9$ Hz), 7.5 (d, 2H, $J = 8.8$ Hz), 7.31 (d, 2H, $J = 5.2$ Hz), 7.22 (d, 2H, $J = 3.8$ Hz), 7.18 (d, 2H, $J = 3.8$ Hz), 7.10 (t, 2H, $J = 8.5$ Hz), 7.02 (t, 2H, $J = 8.5$ Hz), 6.99 (d, 2H, $J = 5.4$ Hz), 2.58 (t, 4H, $J = 7.5$ Hz), 1.52 (m, 4H), 1.15 (m, 36 H), 0.79 (t, 6H, $J = 6.93$ Hz); PDMS spectrum 931.5 (M^+); UV−vis 483 (4.59), 233 (4.57); ^{1}H NMR spectrum of **17b** δ 8.06−7.57 (m, 6H), 7.41−4.39 (d, 2H, $J = 5.2$ Hz), 7.32−7.11 (m, 13H), 7.08−7.07 (d, 2H, $J = 5.2$ Hz), 2.69−2.66 (m, 6H), 1.68−1.58 (m, 6H), 1.56−1.49 (m, 54H), 10.80−0.77 (m, 9H); MS 1396.6 (M^+); UV−vis 494 (5.0), 234 (4.99). Anal. Calcd for $C_{56}H_{66}S_6$: C, 72.19; H, 7.15; S, 20.65. Found: C, 71.98; H, 7.17; S, 20.41.

Ferric Chloride Oxidation of 3 To Give 16c and 17c. Oxidation of **3** (0.5 g, 1.3 mmol) with anhydrous $FeCl_3$ (0.22 g, 1.3 mmol) followed by reductive workup as described above led to the isolation of **16c** as an oil (0.15 g; 43%)-based recovered starting material as well as **17c** (0.08 g; 23%), also an oil: ^{1}H NMR spectrum **16c** δ 8.01 (d, 2H, $J = 8.8$ Hz), 7.57 (d, 2H, $J = 8.8$ Hz), 7.39 (d, 2H, $J = 5.2$ Hz), 7.29 (d, 2H, $J = 3.7$ Hz), 7.27 (d, 2H, $J = 3.8$ Hz), 7.18 (t, 2H, $J = 8.8$ Hz), 7.1 (t, 2H, $J = 8.8$ Hz), 7.07 (d, 2H, $J = 5.3$ Hz), 2.66 (t, 4H, $J = 7.3$ Hz), 1.59 (q, 4H, $J = 6.8$ Hz), 1.22 (m, 12H), 0.82 (t, 6H, $J = 6.4$ Hz); MS 762 (M^+), 728, 548 (11), 382 (100), 314 (45); UV−vis 484 (4.76), 233 (4.75), 217 (4.51). Anal. Calcd for $C_{44}H_{42}S_6$: C, 69.23; H, 5.56; S, 25.21. Found: C, 69.31: H, 5.58; S, 25.07; ^{1}H NMR spectrum **17c** δ 8.04−7.57 (m, 6H), 7.41−7.39 (d, 2H, $J = 4.9$ Hz), 7.29−7.11 (m, 13H), 7.09−7.07 (d, 2H, $J = 5.2$ Hz), 2.68−2.64 (t, 6H, $J = 7.2$ Hz), 1.67−1.58 (m, 6H), 1.25−1.22 (m, 18H), 0.85−0.81 (t, 9H, $J = 6.5$ Hz); UV−vis 502 (4.72), 236 (4.64). Anal. Calcd for $C_{66}H_{62}S_9{\cdot}H_2O$: C, 68.22; H, 5.56; S, 24.84. Found: C, 68.32; H, 5.53; S, 24.84.

1,3-[5,5′-Bis-(*tert*-butyldimethylsilyl)-2,2′-thienyl]benzo[*c*]thiophene (18). Dilithiation of **1** (1.0 g, 3.36 mmol) in dry THF (50 mL) was carried out as described earlier using *n*-BuLi (3.9 mL, 2.4 M) and TMEDA (1.52 mL, 9.4 mmol). A solution of *tert*-butyldimethylsilyl chloride (1.6 g, 10.6 mmol) in dry THF (15 mL) was added to the cooled (−78 °C) dilithiation mixture. The cooling bath was removed, and the mixture was stirred and was slowly warmed to room temperature (1/2 h). Workup and chromatography of the crude product on basic alumina (hexane eluant) led to the isolation of **18** (1.7 g, 96%): mp 107 °C; ^{1}H NMR 8.01 (d, 1H, $J = 3.2$ Hz), 7.99 (d, 1H, $J = 2.9$ Hz), 7.43 (d, 2H, $J = 3.5$ Hz), 7.26 (d, 2H, $J = 3.5$ Hz), 7.16 (d, 1H, $J = 3$ Hz), 7.14 (d, 1H, $J = 2.9$ Hz), 0.99 (s, 18 H), 0.36 (s, 12H); UV−vis 446 (4.34), 296 (4.45), 232 (4.52), 217 (4.42). Anal. Calcd for $C_{28}H_{38}S_3Si_2$: C, 63.80; H, 7.28; S, 18.25. Found: C, 63.90; H, 7.27; S, 18.15.

Dimerization of 18 To Give 19. Oxidative dimerization of **18** (0.1 g, 0.19 mmol) in CH_2Cl_2 (20 mL) with anhydrous $FeCl_3$ (0.035, 0.21 mmol) was carried out as described before. Dimer **19** (0.031 g; 66%) based on recovered starting material) was isolated: mp 186 °C; ^{1}H NMR 8.01 (m, 4H), 7.44 (d, 2H, $J = 3.5$ Hz), 7.3 (d, 2H, $J = 3.8$ Hz) 7.28−7.25 (m, 6H), 7.18 (t, 4H, $J = 4.4$ Hz); UV−vis 510 (4.62), 299 (4.38), 232 (4.57). Anal. Calcd for $C_{44}H_{46}S_6Si_2$: C, 64.17; H, 5.74; S, 23.37. Found: C, 64.27; H, 5.67; S, 23.27.

Cyanovinylene 20. A mixture of monoaldehyde **9** (0.1 g, 0.31 mmol), malononitrile (0.05 g, 0.76 mmol), and β-alanine (0.03 g, 0.33 mmol) in dry THF (50 mL) was refluxed for 24 h. The solvent was removed, water was added, and the solid (**20**) was filtered, washed with more water and methanol, and dried (0.08 g; 70.2%): mp 178 °C; ^{1}H NMR δ 8.05 (d, 1H, $J = 3.9$ Hz), 8.03 (d, 1H, $J = 3.9$ Hz), 7.76 (s, 1H), 7.71 (d, 1H, $J = 4.1$ Hz), 7.69−7.45 (m, 3H), 7.36 (t, 1H, $J = 8.9$ Hz), 7.26 (m, 1H), 7.19 (t, 1H, $J = 4.7$ Hz); MS 374 (M^+, 100), 329 (11), 253 (8%), 208 (8), 187 (17); UV−vis 555 (4.25), 297 (3.98), 231 (4.04). Anal. Calcd for $C_{20}H_{10}N_2S_3{\cdot}0.25CH_3OH$: C, 63.58; H, 2.90; N, 7.32; S, 25.15. Found: C, 63.49; H, 2.74; N, 7.18; S, 25.23.

Cyanovinylene 21. A mixture of aldehyde **9** (0.2 g, 0.61 mmol) and 4-piperonylmethyl cyanide (0.197 g, 1.2 mmol) was added to a stirred suspension of NaH (0.059 g) in dry THF (50 mL). The mixture was quenched with NH_4Cl solution after being stirred for 10 h at room temperature. The solvent was removed, and the solid **21** was filtered and washed with methanol: mp 184−185 °C; ^{1}H NMR δ 8.04 (d, 1H, $J = 8.8$ Hz), 7.98 (d, 1H, $J = 8.7$ Hz), 7.50 (d, 1H, $J = 41$ Hz), 7.49 (s, 1H), 7.42−7.37 (m, 3H), 7.23−7.15 (m, 4H), 7.11 (d, 1H, $J = 1.8$ Hz), 6.87 (d, 1H, $J = 8.1$ Hz), 6.03 (s, 2H); MS 469 (M^+, 30.6), 206 (61), 195 (48), 189 (49), 121 (100); UV−vis 499 (4.44), 383 (4.05), 290 (4.27), 231 (4.35). Anal. Calcd for $C_{26}H_{15}N_2O_2S_3$: C, 66.49; H, 3.23; N, 2.98; S, 20.49. Found: C, 66.27; H, 3.25; N, 2.89; S, 20.33.

Cyanovinylene 22. Aldehyde **9** (0.25 g, 0.77 mmol) was condensed with thiopheneacetonitrile (0.19 g, 1.5 mmol) in the presence of NaH (0.15 g) in dry THF (40 mL) as described above. Workup led to the isolation of **22** (0.3 g, 91% yield): mp 161 °C; ^{1}H NMR δ 0.03 (d, 1H, $J = 8.6$ Hz), 797 (d, 1H, $J = 8.6$ Hz), 7.57 (d, 1H, $J = 3.4$ Hz), 7.44 (s, 1H), 7.41 (d, 1H, $J = 5$ Hz), 7.37 (m, 2H), 7.39 (d, 1H, $J = 2.5$ Hz), 7.28 (d, 1H, $J = 4.7$ Hz), 7.25 (d, 1H, $J = 5.4$ Hz), 7.21 (d, 1H, $J = 4.3$ Hz), 7.17 (d, 1H, $J = 5$ Hz), 7.07 (t, 1H, $J = 3.9$ Hz); MS 431 (M^+, 62), 386 (36), 365 (50), 253 (49), 215 (100), 149 (81); UV−vis 506 (4.48), 291 (4.26), 231 (4.35). Anal. Calcd for $C_{23}H_{13}NS_4$: C, 63.99; H, 3.09; N, 3.25; S, 29.72. Found: C, 63.73; H, 3.21; N, 3.41; S, 29.47.

Bis(cyanovinylene) 23. A mixture of dialdehyde **12** (0.4 g, 1.13 mmol), malononitrile (0.3 g, 4.5 mmol), and β-alanine (0.1 g) in dry THF (100 mL) was refluxed for 2 h. Workup led to the isolation of **23** (0.45 g, 88.6%): mp >350 °C; ^{1}H NMR δ 8.15 (d, 1H, $J = 3$ Hz), 8.09 (d, 1H, $J = 3.9$ Hz), 7.82 (s, 2H), 7.78 (d, 2H, $J = 4.3$ Hz), 7.57 (d, 2H, $J = 4.1$ Hz), 7.44 (d, 1H, $J = 3.9$ Hz), 7.42 (d, 1H, $J = 2.8$ Hz); MS 450 (M^+, 100), 431 (27), 149 (75); UV−vis 590 (4.61), 354 (4.06), 251 (4.14). Anal. Calcd for $C_{24}H_{10}N_4S_3$: C, 63.97; H, 2.24; N, 12.44; S, 21.35. Found: C, 63.96; H, 2.23; N, 12.34; S, 21.27.

Bis(cyanovinylene) 24. Dialdehyde **12** (0.1 g, 0.28 mmol) was condensed with 2-thiopheneacetonitrile (0.14 g, 1.13 mmol) in THF solution in the presence of NaH (0.05 g, 2.1 mmol). The crude product isolated after workup was extracted from a Soxhlet cup using $CHCl_3$ to give pure **24** (0.14 g, 87.5%): mp 222 °C; ^1H NMR δ 8.08 (d, 1H, $J = 3.5$ Hz), 8.07 (d, 1H, $J = 3.42$), 7.6 (d, 2H, $J = 3.96$ Hz), 7.67 (s, 2H), 7.42 (d, 2H, $J = 4$ Hz), 7.36 (d, 2H, $J = 3.53$ Hz), 7.28 (m, 4H), 7.08 (t, 2H, $J = 4.3$ Hz); MS 564 (M^+, 100), 563 (84), 502 (16), 282 (11), 211 (14), 169 (11); UV−vis 555 (4.58), 422 (3.97), 267 (4.06), 296 (3.98), 244 (4.03). Anal. Calcd for $C_{30}H_{16}N_2S_5{\cdot}0.75CHCl_3$: C, 56.44; H, 2.58; N, 4.28; S, 24.50. Found: C, 56.57; H, 2.58; N, 4.27; S, 24.47.

1,3-Dithiolidene Derivative 25. Monoaldehyde **9** (0.2 g, 0.61 mmol) was condensed with 1,3-dithiolyl-4,5-dicarbomethoxyphosphonium tetrafluoroborate (0.62 g, 1.2 mmol) in the presence of Et_3N (2 mL) in CH_2Cl_2 solution (40 mL) to give **25** as a red solid (0.21 g, 64.8%): mp 122 °C; ^1H NMR δ 7.98−7.94 (m, 2H), 7.39−7.36 (m, 2H), 7.30 (d, 1H, $J = 3.6$ Hz), 7.17−7.14 (m, 3H), 6.91 (d, 1H, $J = 3.7$ Hz), 6.67 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H); MS 528 (M^+, 100), 494 (11), 470 (9), 382 (25), 354 (36), 309 (41), 277 (40), 227 (56); UV−vis 485 (4.46), 368 (4.11), 232 (4.38). Anal. Calcd for $C_{24}H_{16}O_4S$: C, 54.51; H, 3.06; S, 30.33. Found: C, 54.66; H, 3.08; S, 30.20.

Thienylenevinylene 26. Monoaldehyde **9** (0.33 g, 1 mmol) was condensed with (2-thienylmethyl)triphenylphosphonium bromide (0.88 g, 2 mmol) in the presence of NaH (0.06 g, 2.5 mmol) in dry THF (40 mL) to give after standard workup vinylene **26** (0.1 g, 25%): mp 94 °C; ^1H NMR δ 8.02−8 (dd, 1H), 7.97−7.94 (dd, 1H), 7.38 (d, 1H, $J = 5$ Hz), 7.36 (d, 1H, $J = 3.4$ Hz), 7.24 (d, 1H, 5.1 Hz), 7.2 (d, 1H, $J = 5.1$ Hz), 7.17−7.14 (m, 3H), 7.06 (d, 2H, $J = 6.3$ Hz), 7.04 (d, 1H, $J = 3.9$ Hz), 7.02−7 (m, 2H); MS 406 (M^+, 100), 372, 340, 277, 253, 203; UV−vis 478 (4.23), 358 (4.26), 291 (4.30), 232 (4.30), 217 (4.17). Anal. Calcd for $C_{22}H_{14}S_4$: C, 64.98; H, 3.48; S, 31.55. Found: C, 64.92; H, 3.46; S, 31.45.

Bis(thienylenevinylene) 27. A mixture of dialdehyde **12** (0.2 g, 0.56 mmol) and (2-thienylmethyl)triphenylphosphonium bromide (0.745 g, 1.7 mmol) was added to a suspension of NaH (0.061 g) in dry THF (100 mL) and was stirred for 2 days at room temperature. Standard workup afforded **27** as black powder (0.25 g, 86%): mp 92 °C; ^1H NMR δ 8.02−8 (m, 2H), 7.9−7.3 (m, 4H), 7.25−7 (m, 12H); MS 514 (M^+), 277 (100); UV−vis 514 (4.46), 357 (4.48); HRMS calcd for $C_{28}H_{18}S_5$ 514.0012, found 514.000.

Bis(phenylenevinylene) 28. A suspension of anhydrous K_2CO_3 (1 g), benzyltriphenylphosphonium chloride (0.3 g, 0.77 mmol), and dialdehyde **12** (0.1 g, 0.282 mmol) in dry MeCN was stirred at room temperature for 10 h. The solvent was removed, and water was added. The precipitate of **28** was washed with water and methanol. It was purified via filtration through a column of Al_2O_3 (2:3 chloroform−hexane eluant) to give pure **28** (0.13 g, 86%): mp 172 °C; ^1H NMR δ 8.05 (d, 1H, $J = 2.1$ Hz), 8.03 (d, 1H, $J = 3.9$ Hz), 7.51 (d, 4H, $J = 10.1$ Hz), 7.37 (t, 4H, $J = 7.92$ Hz), 7.27 (m, 5H), 7.19 (m, 3H), 7.09 (d, 2H, $J = 3.96$ Hz), 6.99−6.95 (d, 2H, $J = 16.2$ Hz); MS 502 (M^+, 100), 341 (38), 211 (31), 207 (32), 156 (63); UV−vis 510 (4.61), 348 (4.57), 275 (4.51), 241 (4.47). Anal. Calcd for $C_{32}H_{22}S_3$: C, 76.44; H, 4.42; S, 19.14. Found: C, 76.19; H, 4.35; S, 18.99.

Bis(4,5-dicarbomethoxy-1,3-dithiolidene) Derivative 29. A mixture of (4,5-dicarbomethoxy-1,3-dithiolyl)triphenylphosphonium tetrafluoroborate (2.8 g, 0.0056 mol) and dialdehyde **12** (0.5 g, 0.0014 mol) in CH_2Cl_2 (250 mL) was treated with Et_3N (5 mL). The orange solution turned purple. After 4 h at room temperature, the volatile material was removed in vacuo and the residue was triturated with MeOH to give **29** (1 g, 93.4%): mp 238 °C; ^1H NMR δ 7.98 (d, 1H, 2.9 Hz), 7.96 (d, 1H, $J = 3.24$ Hz), 7.30 (d, 2H, $J = 3.9$ Hz), 7.19 (d, 1H, $J = 2.95$ Hz), 7.13 (d, 1H, $J = 3.04$ Hz), 6.92 (d, 2H, $J = 3.96$ Hz), 6.67 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H); UV−vis 528 (4.52), 397 (4.30), 234 (4.48). Anal. Calcd for $C_{32}H_{22}O_8S_7$: C, 50.63; H, 2.93; S, 29.58. Found: C, 50.81; H, 2.90; S, 29.48.

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