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Synthesis and Characterization of Benzannelated Thienyl Oligomers

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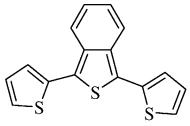
An array of 1,3-diarylbenzo[*c*]thiophenes have been synthesized by the ring-opening of lactones followed by thionation using Lawesson's reagent with concurrent intramolecular cyclization. Photophysical studies of the various benzo[*c*]thiophene analogues are presented. The results of a cyclic voltammetric investigation of the benzo[*c*]thiophenes are also reported.

Introduction

During the past few years, the synthesis and application of thienyl oligomers has been of great interest to chemists and material scientists because of their intrinsic photophysical and redox properties.[1] Thienyl oligomers are also widely used as building blocks in the synthesis of organic materials with potential as organic light-emitting diodes (OLEDs),[2,3] organic solar cells (OSC),[4,5] organic field-effect transistors (OFETs),[6–9] and in photorefractive holography.[10–12] In this regard, thiophene derivatives have played a very significant role. For example, polythiophene is superior to polyphenylene as a semiconductor and poly(thienylenevinylene) has attracted considerable interest as a material with enhanced third-order nonlinear susceptibilities. Arylenevinylenes and heteroarylenevinylenes have also attracted attention in the fabrication of electroluminescent devices.[13] The synthesis and investigation of well-defined model oligomers have recently allowed a greater insight into the structural and electronic peculiarities of the corresponding polymers. The properties of oligomers can exceed those of polymers not only because of their defined chemical structures and conjugation length, but also because of their superior solubility and the convenient processability of these materials. In particular, the extent of conjugation does not have a major effect on thienyl oligomers compared with the corresponding polymers because electronic properties become saturated beyond a particular chain length.[14] An organic transistor containing sexithienylene as the active semiconducting material has been reported.[15]

Since 1992 the synthesis and electrochemical behavior of 1,3-dithienylbenzo[*c*]thiophene have been reported independently by four groups.[16–19] In addition, Cava and coworkers have outlined detailed synthetic studies of 1,3-dithienylbenzo[*c*]thiophene analogues.[20] An $FeCl_3$-mediated oligomerization of 1,3-dithienylbenzo[*c*]thiophene has also been carried out. The synthesis of a novel nucleoside analogue in which a DNA base is replaced by a 1,3-dithienylbenzo[*c*]thiophene has also been reported.[21] Nucleosides of this type are useful as potential probes for understanding the structures and dynamics of nucleic acids and can also be used as fluorescent labels. The enhanced photoluminescence behavior of a 1,3-dithienylbenzo[*c*]thiophene derivative during photobleaching has also been observed.[22]

Substitution at the reactive α-positions of the terminal thiophenes results in chemically stable oligomers.[23] Several workers have reported the electrochemical/chemical synthesis of dialkylsexithiophenes and their use in field-effect transistors (FETs).[24] In recent years, there has been considerable interest in the synthesis of new, low-band-gap oligomers in view of their superior conductivity and nonlinear optical properties. An optoelectronic study of polymers from **1** gave a band gap of ca. 1.7 eV,[16] which is less than that of polythiophenes (ca. 2 eV).[1c]



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The exciting photophysical properties of thienyl oligomers prompted us to explore further the synthesis of benzo[*c*]thiophene derivatives. It has been well established that the annellation of aromatic rings to thiophenes, for example, as in benzo[*c*]thiophene,[25] greatly changes the properties of materials derived from such a substrate, and thus synthetic work has been undertaken to modify 1,3-dithienylbenzo[*c*]thiophenes so as to provide routes to new extended oligomers, for example, vinylenes. This may also provide an opportunity to analyze the spectroscopic and

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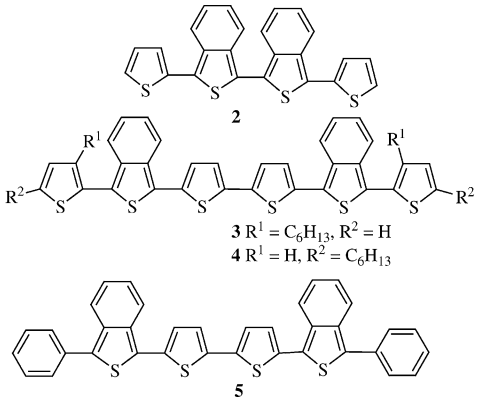
electrochemical behavior of 1,3-diarylbenzo[*c*]thiophene-extended systems.

As a continuation of our work on benzo[*c*]thiophene analogues,[26,27] we report herein a detailed study on the synthesis of the diarylbenzo[*c*]thiophene derivatives **2**–**5**.



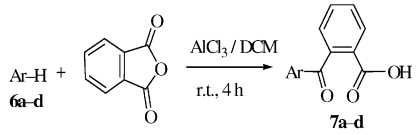
2

3 $R^1 = C_6H_{13}$, $R^2 = H$
4 $R^1 = H$, $R^2 = C_6H_{13}$

5

Results and Discussion

The related lactones are considered as crucial intermediates in the synthesis of various 1,3-diarylbenzo[*c*]-thiophenes and their oligomers. Similarly to the known phthalides **8a** and **8b**,[20] phthalides **8c** and **8d** were synthesized by conventional Friedel–Crafts phthaloylation followed by $NaBH_4$ reduction and intramolecular cyclization (Scheme 1).

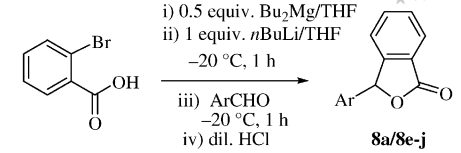


6a–d → (i) $AlCl_3$ / DCM, r.t., 4 h → **7a–d** → (i) $NaBH_4$, (ii) HCl, 40–80% → **8a–d**

Compound	Ar
6a, **7a**, **8a**	2-thienyl
6b, **7b**, **8b**	2,2'-bithienyl-5-yl
6c, **7c**, **8c**	5-hexyl-2-thienyl
6d, **7d**, **8d**	5'-hexyl-2,2'-bithienyl-5-yl

Scheme 1.

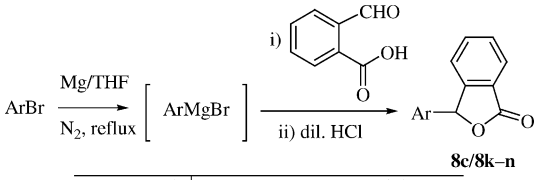
As the conventional Friedel–Crafts phthaloylation was feasible only with thiophene derivatives, it was decided to explore other methods[28–31] that can deliver highly substituted lactones in reasonable yields. We next attempted to prepare the lactones by the magnesio protocol published by Kato et al.[32] Notably, different types of lactones were synthesized by metallation of 2-bromobenzoic acid by using a combination of Bu_2Mg and *n*BuLi under noncryogenic conditions. By adopting this procedure, lactones **8e**–**j** were synthesized in better yields (Scheme 2). Some additional lactones **8k**–**n** were synthesized through the reaction of freshly prepared aryl Grignard reagents with 2-formylbenzoic acid[33] (Scheme 3).



i) 0.5 equiv. Bu_2Mg/THF, ii) 1 equiv. *n*BuLi/THF, –20 °C, 1 h; iii) ArCHO, –20 °C, 1 h; iv) dil. HCl → **8a/8e-j**

Compound	Ar	Yield (%)
8a	2-thienyl	62
8e	*p*-$C_6H_{13}OC_6H_4$	60
8f	*m*,*p*-$(MeO)_2C_6H_3$	52
8g	*p*-$O_2NC_6H_4$	40
8h	3,4-(methylenedioxy)phenyl	66
8i	*o*,*o'*,*p*-$(MeO)_3C_6H_2$	65
8j	9-anthracenyl	55

Scheme 2.

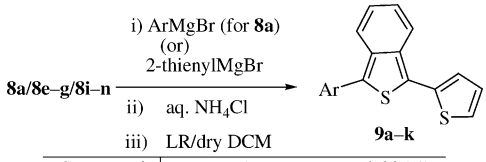


ArBr → (Mg/THF, N_2, reflux) ArMgBr → (i) CHO/OH lactone, ii) dil. HCl) → Ar lactone → **8c/8k–n**

Compound	Ar	Yield (%)
8c	5-hexylthien-2-yl	63
8k	*p*-$MeOC_6H_4$	55
8l	*p*-MeC_6H_4	60
8m	1-naphthyl	58
8n	Ph	61

Scheme 3.

Ring-opening of the various types of lactones **8a**–**n** with aryl/heteroaryl Grignard reagents was then attempted. The 1-aryl-3-thienylbenzo[*c*]thiophene analogues **9a** and **9b** were readily prepared by the interaction of known lactone **8a** with commercially available aryl Grignard reagents followed by thionation using Lawesson's reagent (Scheme 4).



8a/8e–g/8i–n → (i) ArMgBr (for **8a**) (or) 2-thienylMgBr; ii) aq. NH_4Cl; iii) LR/dry DCM → **9a–k**

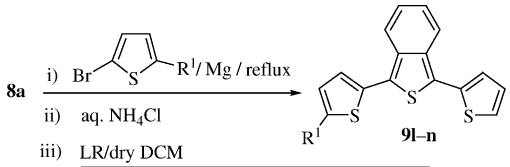
Compound	Ar	Yield (%)
9a	*p*-$Me_2NC_6H_4$	65
9b	*p*-$MeSC_6H_4$	62
9c	*p*-$C_6H_{13}OC_6H_4$	65
9d	3,4-$(MeO)_2C_6H_3$	55
9e	*p*-$O_2NC_6H_4$	42
9f	*p*-$MeOC_6H_4$	40
9g	*p*-MeC_6H_4	60
9h	*o*,*o'*,*p*-$(MeO)_3C_6H_2$	54
9i	1-anthracenyl	45
9j	1-naphthyl	43
9k	*n*-C_6H_5	63

Scheme 4.

Alternatively, the interaction of lactones **8e**–**g**, **8k**, and **8l** with 2-thienylmagnesium bromide followed by thionation afforded unsymmetric 1-aryl-3-thienylbenzo[*c*]thiophenes **9c**–**g**. Under similar conditions, aryl lactones **8i**, **8j**, **8m**, and **8n** were also smoothly transformed into the corresponding benzo[*c*]thiophenes **9h**–**k**.

The interaction of lactone **8a** with 5-alkyl-2-thienylmagnesium bromide followed by thionation led to the isolation

of highly soluble one-end-blocked 1,3-dithienylbenzo[*c*]-thiophene analogues **9l**–**n** (Scheme 5). Similarly, the interaction of lactones **8b** and **8d** with 5-alkyl-2-thienylmagnesium bromide followed by thionation furnished benzo[*c*]-thiophene analogues **9o**–**q** (Scheme 6).

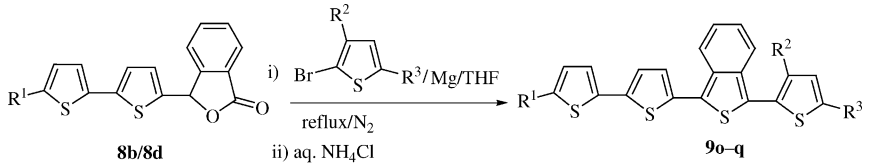


Compound	R^1	Yield (%)
9l	*n*-C_6H_{13}	58
9m	2-ethylhexyl	55
9n	*n*-C_4H_9	49

Scheme 5.

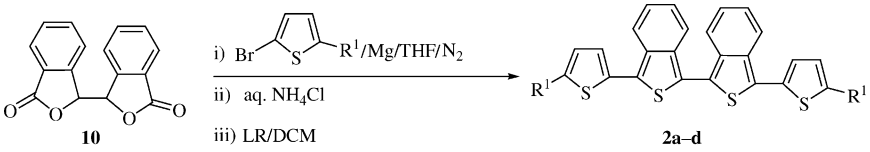
Having synthesized the one-end-blocked benzo[*c*]thiophenes, the next plan was to dimerize them in a controlled manner to afford the corresponding dimerization products in reasonable yields. The controlled dimerization of several thienyl monomers has been reported by oxidation of the corresponding thienyl α-carbanion using $CuCl_2$.[34] Regioselective oligomerization of 3-(alkylsulfanyl)thiophenes using $FeCl_3$ has also been reported.[35] Mustafa and Shephered reported a simple dimerization of β-trimethylsilyl-substituted terthiophenes using ceric ammonium nitrate (CAN).[36] Recently, Kita and co-workers reported a synthesis of 2,2′-bithiophene derivatives that involved oxidative coupling of the corresponding alkylthiophenes using a combination of phenyl iodide bis(trifluoroacetate) and BF_3·OEt_2.[37] A mild $FeCl_3$-mediated oligomerization of β-substituted 1,3-dithienylbenzo[*c*]thiophenes led to the isolation of annelated sexithiophene and nonithiophene analogues.[20] Various conditions using CAN, $FeCl_3$, PIFA/BF_3·OEt_2, and $CuCl_2$ were explored for the dimerization of benzo[*c*]thiophene analogues.

End-blocked and highly soluble benzannelated quaterthienyl derivatives **2a**–**d** were prepared by the treatment of the appropriate freshly prepared 5-alkyl-2-thienylmagnesium bromide with commercially available biphthalide **10** followed by thionation and cyclization (Scheme 7). Ring-opening of the biphthalide **10** with aryl Grignard reagents followed by thionation led to the isolation of the corresponding benzo[*c*]thiophene analogues **11a** and **11b** (Scheme 8).



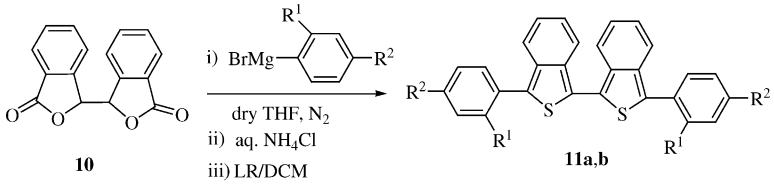
Compound	R^1	R^2	R^3	Yield (%)
9o	H	H	*n*-C_6H_{13}	55
9p	*n*-C_6H_{13}	H	H	60
9q	*n*-C_6H_{13}	*n*-C_6H_{13}	H	62

Scheme 6.



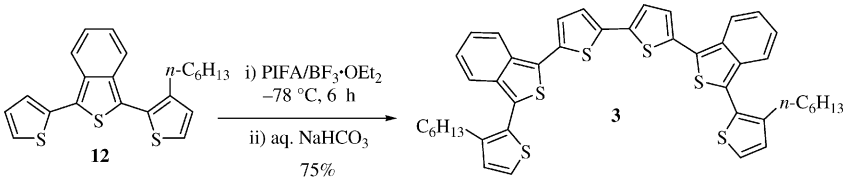
Compound	R^1	Yield (%)
2a	H	58
2b	*n*-C_6H_{13}	51
2c	2-ethylhexyl	55
2d	*n*-C_4H_9	62

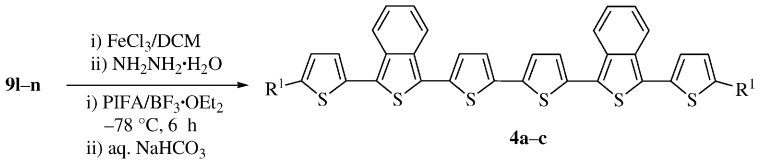
Scheme 7.



Compound	R^1	R^2	Yield (%)
11a	H	Me	53
11b	Me	H	50

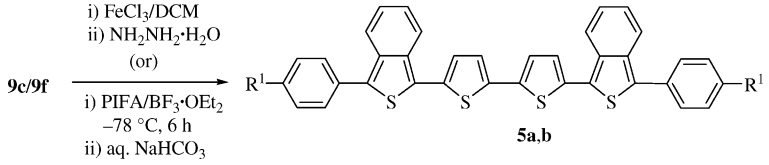
Scheme 8.





Compound	R^1	Yield (%)
4a	*n*-C_4H_9	55,[a] 60[b]
4b	2-ethylhexyl	50,[a] 54[b]
4c	*n*-C_6H_{13}	60,[a] 65[b]

Scheme 9. [a] Yield obtained using $FeCl_3$. [b] Yield obtained using PIFA/BF_3·Et_2O.

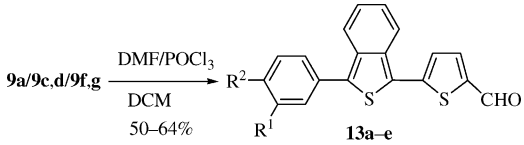


Compound	R^1	Yield (%)
5a	OC_6H_{13}	65,[a] 35[b]
5b	OMe	60,[a] 40[b]

Scheme 10. [a] Yield obtained using $FeCl_3$. [b] Yield obtained using PIFA/BF_3·Et_2O.

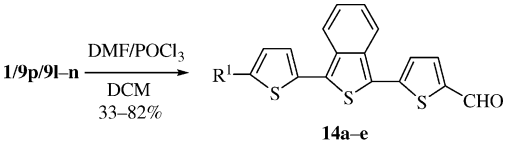
Of these conditions, anhydrous $FeCl_3$ at room temperature and PIFA/BF_3·OEt_2 at a low temperature were found to yield the dimerization products in reasonable yields. Contrary to the $FeCl_3$ conditions,[20] the dimerization of benzo[*c*]thiophene **12** could be selectively performed by using PIFA/BF_3·OEt_2 at a low temperature to afford the known dimeric product **3** in 75% yield (Scheme 9). Similarly, benzo[*c*]thiophenes **9l**–**n**, **9c**, and **9f** could also be smoothly dimerized to the corresponding products **4a**–**c**, **5a**, and **5b** by using $FeCl_3$ as well as PIFA/BF_3·OEt_2 (Schemes 9 and 10).

The push–pull system containing 1,3-diarylbenzo[*c*]thiophene as a conjugated system is regarded as potential nonlinear optical material. In particular, unsymmetrical donor–acceptor-type 2,5-diarylated thiophenes that possess both electron-donating and -withdrawing groups are of much interest in single-layer electroluminescent devices that operate by hole transportation, light emission, or electron transportation.[38–41] Hence, the synthesis of benzo[*c*]thiophene analogues with an electron-acceptor group at one end and a donor group at the other was planned. Accordingly, the one-end-blocked benzo[*c*]thiophenes **9a**, **9c**–**d**, **9f**–**g**, **9l**–**n**, and **9p** were formylated under Vilsmeier–Haack conditions to afford the corresponding monoaldehydes **13a**–**e** and **14a**–**e** (Schemes 11 and 12). The monoaldehydes **13b**–**e** underwent smooth condensation with malononitrile/2-thienylacetonitrile to give the corresponding cyanovinylenes **15a**–**d** and **16a**–**c** (Scheme 13).



Compound	R^1	R^2	Yield (%)
13a	H	NMe_2	60
13b	H	OC_6H_{13}	64
13c	OMe	OMe	50
13d	H	Me	52
13e	H	OMe	62

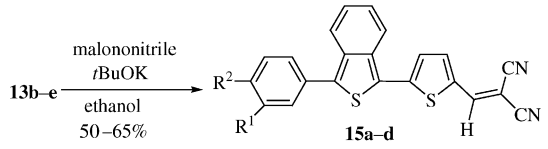
Scheme 11.



Compound	R^1	Yield (%)
14a	H	62
14b	5-hexyl-2-thienyl	60
14c	*n*-C_6H_{13}	66
14d	2-ethylhexyl	54
14e	*n*-C_4H_9	33

Scheme 12.

The optical properties of selected benzo[*c*]thiophenes are listed in Table 1. The UV/Vis absorption spectra of them showed an interesting pattern analogous to that observed previously in the case of oligothiophene derivatives. The



Compound	R^1	R^2	Yield (%)
15a/16a	H	OC_6H_{13}	64/60
15b/16b	OMe	OMe	65/55
15c/16c	H	Me	50/61
15d	H	OMe	52

Scheme 13.

monomeric benzo[*c*]thiophene analogues exhibited a highly intense absorption band around 400 nm due to π–π* electron transfer of the entire conjugated backbone. As expected, benzannelation of the quaterthienyl system (**9o**–**q**) caused a redshift of the λ_{max} value of 75–90 nm. The introduction of α-alkyl substituents (*n*-hexyl, 2-ethylhexyl, and *n*-butyl) into **1** increased the longer-wavelength absorption from 412 to 440 nm. The introduction of an electron-releasing group such as NMe_2, OMe, or Me at one end of the benzo[*c*]thiophene caused a redshift of the absorption maxima of 10–25 nm. However, with the electron-releasing SMe group the λ_{max} value was shifted to a maximum extent (ca. 50 nm). The presence of electron-withdrawing groups at one end of the benzo[*c*]thiophenes (**9e** and **13a**–**e**) resulted in a redshift of the λ_{max} value, which confirms the enhancement of π-electron delocalization. Increasing the number of benzannelations (**9o**–**q** → **2a**–**d**) significantly enhanced the λ_{max} value (ca. 25 nm). Dimerization of one-end-blocked benzo[*c*]thiophenes (**9l**–**n** → **2a**–**d** and **9c/9f** → **2a**–**d**) caused a redshift of the absorption maxima of ca. 70 nm. Compared to the parent α,α′-dihexylsexithiophene (ca. 444 nm),[42] the benzannelated sexithienyl system **4c** exhibited a λ_{max} value at a higher wavelength (520 nm) which confirms the enhancement of conjugation through annelation. A representative UV/Vis absorption spectrum of compound **4c** is presented in Figure 1.

Table 1. Physical data for selected benzo[*c*]thiophenes.

Compound	λ_{max}[a] [nm]	λ_{lum}[b] [nm]	E_g[c] [eV]	$^1E_{pa}$[d] [V]	E_{ox}^{onset} [eV]	HOMO[e] [eV]	LUMO[f] [eV]
1	433	532	2.66	0.87	0.64	5.08	2.42
2a	520	661	2.08	0.43	0.41	4.85	2.77
2b	468	531	2.43	0.57	0.51	4.95	2.52
2d	494	602	2.33	0.64	0.50	4.94	2.61
3	484	582	2.43	0.66	0.59	5.03	2.06
4a	504	600	2.26	0.68	0.52	4.96	2.70
4b	510	587	2.27	0.65	0.63	5.07	2.80
4c	520	630	2.25	0.75	0.71	5.09	2.84
5b	480	588	2.31	0.62	0.56	5.00	2.69
9a	416	566	2.59	0.71	0.54	4.98	2.39
9b	476	518	2.53	0.81	0.73	5.17	2.64
9d	445	526	2.53	0.59	0.50	4.94	2.41
9e	470	611	2.45	1.10	0.98	5.42	2.97
9f	412	525	2.69	0.75	0.70	5.14	2.45
9l	440	561	2.65	0.82	0.69	5.13	2.48
9m	442	600	2.53	0.87	0.74	5.18	2.65
9o	468	592	2.38	0.77	0.67	5.11	2.73

[a] Measured in dilute dichloromethane solution. [b] Excited at the absorption maxima. [c] Estimated from the onset of absorption ($E_g = 1240/\lambda_{onset}$). [d] $^1E_{pa}$ denotes the first anodic peak potential. [e] Calculated using the empirical equation: HOMO = (4.44 + E_{ox}^{onset}). [f] Calculated from LUMO = HOMO – E_g.

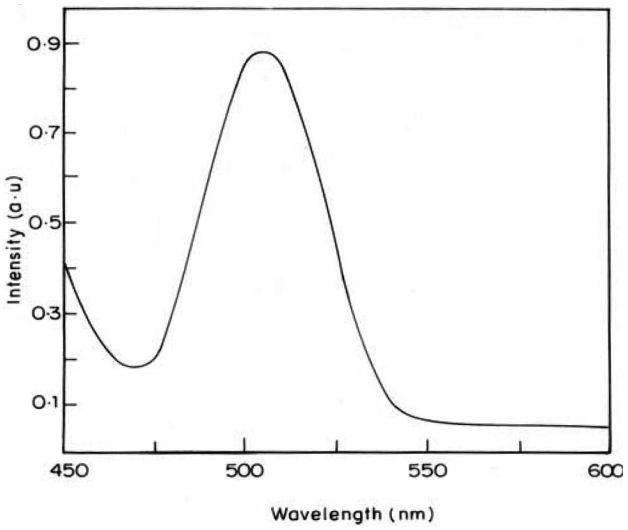


Figure 1. UV/Vis absorption spectrum of **4c**.

The photoluminescence spectra of the benzo[*c*]thiophene analogues exhibited emission in the orange region, which was gradually redshifted with increasing conjugation. Of the benzo[*c*]thiophene analogues **9a**–**g**, only **9b** and **9g** emitted light in the relatively high energy region of 510–518 nm. As in the case of the absorption spectra, the luminescence of the benzo[*c*]thiophenes was also redshifted with increasing π-conjugation. The emission spectrum of compound **2d** is presented in Figure 2.

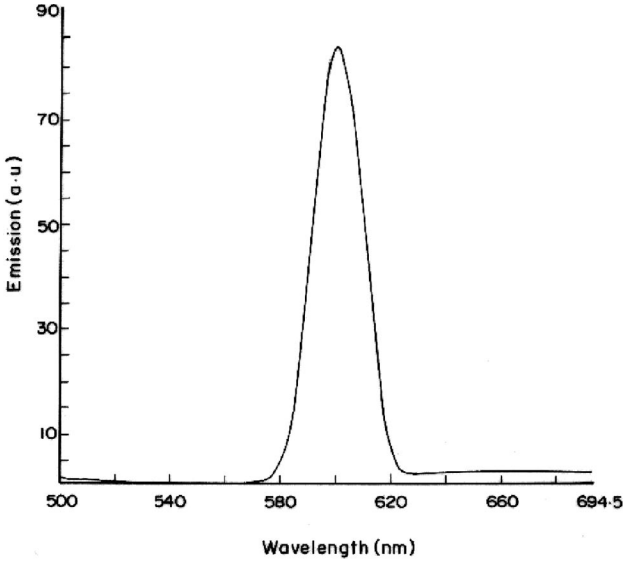


Figure 2. Emission spectrum of **2d**.

The oxidation potentials and the onset oxidation values of the benzo[*c*]thiophenes are presented in Table 1. Increasing the ratio of nonclassical thiophene to thiophene (**9o–q** → **2a–d**) significantly reduced its oxidation potential. Of the thienyl oligomers, the quaterthienyl system **2a**, which contains two benzo[*c*]thiophene units, exhibited the lowest oxidation potential (0.43 eV). Dimerization of the thienyl oligomers significantly enhances its electro-oxidative behavior. The cyclic voltammogram of benzo[*c*]thiophene **2d** is presented in Figure 3.

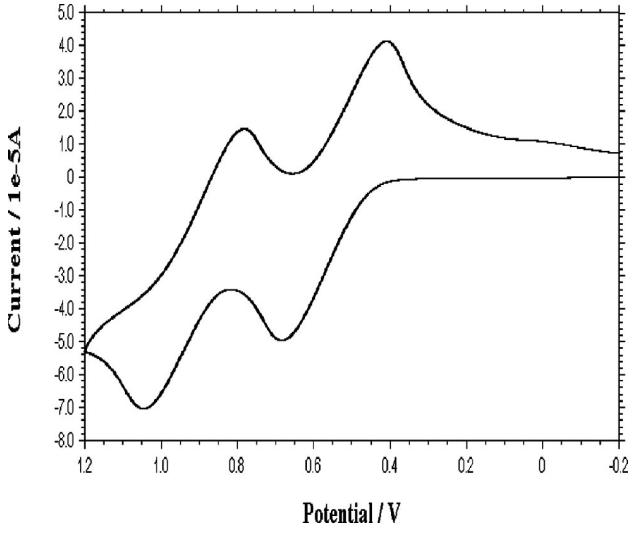


Figure 3. Cyclic voltammogram of **2d**.

The HOMO and LUMO energy levels of selected benzo[*c*]thiophenes were calculated from the corresponding absorption onset and the onset oxidation potential and the values are presented in Table 1. In general, annelation of the benzene ring to terthiophene reduced the E_g value from 3 to 2.6 eV (terthiophene → **1**). Of the benzo[*c*]thiophene analogues, compound **2a**, which has a 1:1 ratio of classical/nonclassical thiophene, has the lowest E_g value (2.1 eV). Dimerization of benzo[*c*]thiophene **9f** led to a decrease and increase in the HOMO and LUMO energy levels, respectively. Consequently, the E_g value of the resulting product **5b** is reduced. Dimerization of the α-alkyl-substituted benzo[*c*]thiophenes (**9l**,**m** → **4a**,**b**) also resulted in a lowering of the E_g value. Compared with α,ω-dihexylsexithiophene (E_g = 2.7 eV),[44] the benzannelated sexithiophene **4c** exhibited a low band-gap value (E_g = 2.2 eV). The corresponding β,β′-dihexylbenzannelated thiophene **3** has a slightly enhanced band-gap value (E_g = 2.4 eV).

Conclusions

A range of 1,3-diarylbenzo[*c*]thiophenes have been synthesized by using Lawesson's sulfur transfer reagent. The diarylbenzothiophenes were functionalized to give aldehydes, vinylenes, and cyanovinylenes. For the first time the one-end-blocked benzannelated quaterthienyl systems have been prepared in reasonable yields. Dimerization of the one-end-blocked terthienyl system (**9l–n**) led to the formation of highly soluble and stable sexithiophenes (**4a–c**) in moderate yields. The ter-, quater-, and quinque-heterocycles were studied by fluorescence spectroscopy and cyclic voltammetry. The highly soluble nature of the benzannelated α,ω-dialkylsexithiophenes could find use in transistor applications.

Experimental Section

General Methods: All melting points (Toshnival) are uncorrected. NMR spectra (JEOL 400 MHz, Bruker 300 and 500 MHz) were determined in $CDCl_3$ solution containing TMS as internal standard unless otherwise stated. Organic extracts were dried with anhydrous Na_2SO_4. All UV/Vis spectra were recorded with an Elico SL-159 spectrophotometer using 10^{-3} M solutions of the diarylbenzothiophenes in CH_2Cl_2. The emission spectra were recorded with a Perkin-Elmer LS-45 Model spectrophotometer using 10^{-3} M solutions of the diarylbenzothiophenes in CH_2Cl_2. Cyclic voltammetry of 10^{-3} M solutions of the diarylbenzothiophenes was carried out with a CHI 600C electrochemical analyzer. All the measurements were carried out under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode was employed as a working electrode, a saturated Ag/AgCl electrode as the reference electrode, and platinum wire as the auxiliary electrode. Tetrabutylammonium hexafluorophosphonate ($TBAPF_6$) was used as the supporting electrolyte at a concentration of 10^{-1} M. All the potentials were calibrated with ferrocene as the internal standard.

3-(2-Thienyl)phthalide (8a): A hot solution of 2-(2-thenoyl)benzoic acid (30.0 g, 0.129 mmol) in aqueous sodium hydrogen carbonate (16.0 g in 2 L of H_2O) was treated with $NaBH_4$ (49. 0 g, 1.29 mmol) in portions. After standing overnight, it was heated in a steam bath for 1 h, cooled to room temperature, and then cautiously acidified with 12% aqueous hydrochloric acid to pH = 2. The mixture was stirred at room temperature for 2 h, and the white solid obtained was filtered to give **8a**[20] (22.0 g, 80%).

3-(2,2′-Bithienyl-5-yl)phthalide (8b): The bithenoylbenzoic acid (12.0 g) was prepared 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. M.p. 161 °C. The above intermediate acid was reduced to phthalide **8b** in 77% yield by a procedure similar to that of 2-thienylphthalide **8a**. M.p. 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.7 Hz, 1 H), 7.74 (t, J = 7.3 Hz, 1 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.50 (d, J = 7.1 Hz, 1 H), 7.22 (d, J = 4.1 Hz, 1 H), 7.12 (d, J = 4.1 Hz, 1 H), 7.08–7.10 (m, 2 H), 6.99–7.01 (m, 1 H), 6.62 (s, 1 H) ppm. MS (EI): m/z (%) = 298 (100) $[M]^+$. $C_{16}H_{10}O_2S_2$ (298.01): calcd. C 64.40, H 3.38, S 21.49; found C 64.29, H 3.33, S 21.53.

3-(5-Hexyl-2-thienyl)phthalide (8c): The phthalide **8c** was obtained in 40% yield by a procedure similar to that of 2-thienylphthalide **8a**. M.p. 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.0 Hz, 1 H), 7.67 (t, J = 7.4 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.46 (d, J = 8.0 Hz, 1 H), 6.94 (d, J = 3.2 Hz, 1 H), 6.67 (d, J = 3.0 Hz, 1 H), 6.58 (s, 1 H), 2.72 (t, J = 7.6 Hz, 2 H), 1.59 (m, 2 H), 1.28 (m, 6 H), 0.85 (t, J = 5.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.72, 148.73, 148.58, 135.74, 134.13, 129.58, 127.94, 125.95, 125.45, 123.79, 123.12, 78.26, 31.37, 30.14, 29.59, 28.60, 22.41, 13.96 ppm. MS (EI): m/z (%) = 300 (100) $[M]^+$. $C_{18}H_{20}O_2S$ (300.12): calcd. C 71.96, H 6.71, S 10.67; found C 71.82, H 6.80, S 10.75.

3-(5′-Hexyl-2,2′-bithienyl-5-yl)phthalide (8d): The phthalide **8d** was obtained in 50% yield by a procedure similar to that of 2-thienylphthalide **8a**. M.p. 102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95

(d, J = 7.8 Hz, 1 H), 7.70 (t, J = 7.0 Hz, 1 H), 7.59 (t, J = 7.5 Hz, 1 H), 7.48 (d, J = 7.5 Hz, 1 H), 7.02 (d, J = 3.6 Hz, 1 H), 7.0 (d, J = 3.9 Hz, 1 H), 6.91 (d, J = 3.9 Hz, 1 H), 6.64 (d, J = 3.6 Hz, 1 H), 6.60 (s, 1 H), 2.76 (t, J = 7.5 Hz, 2 H), 1.59–1.62 (m, 2 H), 1.28–1.32 (m, 6 H), 0.88 (t, J = 6.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.67, 148.44, 146.31, 140.39, 136.67, 134.36, 133.89, 129.86, 128.79, 125.97, 125.70, 124.87, 124.04, 123.19, 122.50, 78.08, 31.54, 30.14, 28.71, 22.55, 14.06 ppm. $C_{22}H_{22}O_2S_2$ (382.11): calcd. C 69.07, H 5.80, S 16.76; found C 69.17, H 5.66, S 16.89.

Synthesis of Phthalides by the Metalation Method (Low-Temperature Conditions): A solution of 2-bromobenzoic acid (1 g, 4.97 mmol) in THF (20 mL) was cooled below –15 °C under nitrogen, and 1.0 M of Bu_2Mg in hexane (2.6 mL, 2.6 mmol) was slowly added to the solution below –5 °C. Then 1.6 M *n*-BuLi in hexane (3.4 mL, 5.30 mmol) was slowly added to the solution below –15 °C over 20 min whilst stirring. The solution became a viscous slurry during the addition of Bu_2Mg and then gradually changed to a less viscous yellowish slurry during the addition of *n*BuLi. After stirring below –15 °C for 1 h, a solution of thiophene-2-carbaldehyde (1.11 g, 9.95 mmol) in THF was added to the mixture below –15 °C. After stirring below –15 °C for 1 h, the reaction mixture was quenched with 2 M HCl (10 mL). The resulting mixture was stirred at room temperature overnight. EtOAc (30 mL) was added to the resulting mixture and the mixture was stirred for a few minutes. The organic layer was separated and washed with H_2O (5 mL), 5% aqueous $NaHCO_3$ (10 mL), and saturated brine solution (5 mL) successively. After drying with anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the crude solid thus obtained was purified by silica gel chromatography [hexane/ethyl acetate (EA), 9:1] to afford phthalide **8a**[20] as white solid (1.32 g, 62%).

3-[4-(Hexyloxy)phenyl]isobenzofuran-1(3*H*)-one (8e): The phthalide **8e** was obtained in 60% yield by a procedure similar to that used for the preparation of 2-thienylphthalide **8a** (metalation method). M.p. 61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 7.2 Hz, 1 H), 7.60 (t, J = 7.0 Hz, 1 H), 7.50 (t, J = 7.6 Hz, 1 H), 7.27 (d, J = 6.8 Hz, 1 H), 7.11 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.33 (s, 1 H), 3.89 (t, J = 6.6 Hz, 2 H), 1.70–1.77 (quint, J = 6.9 Hz, 2 H), 1.40–1.43 (m, 2 H), 1.28–1.32 (m, 4 H), 0.85 (t, J = 5.8 Hz, 3 H) ppm. MS (EI): m/z (%) = 310 (100) $[M]^+$. $C_{20}H_{22}O_3$ (310.16): calcd. C 77.39, H 7.14; found C 77.30, H 7.18.

3-(3,4-Dimethoxyphenyl)isobenzofuran-1(3*H*)-one (8f): The phthalide **8f** was obtained in 52% yield by a procedure similar to that used for the preparation of 2-thienylphthalide (metalation method). M.p. 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.3 Hz, 1 H), 7.66 (t, J = 7.3 Hz, 1 H), 7.56 (t, J = 7.5 Hz, 1 H), 7.33 (d, J = 7.3 Hz, 1 H), 6.86 (br. s, 2 H), 6.68 (s, 1 H), 6.36 (s, 1 H), 3.88 (s, 3 H), 3.80 (s, 3 H) ppm. $C_{16}H_{14}O_4$ (270.09): calcd. C 71.10, H 5.22; found C 70.92, H 5.31.

3-(4-Nitrophenyl)isobenzofuran-1(3*H*)-one (8g): The phthalide **8g** was obtained in 40% yield by a procedure similar to that used for the preparation of 2-thienylphthalide **8a** (metalation method). M.p. 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.8 Hz, 2 H), 7.99 (d, J = 7.3 Hz, 1 H), 7.68 (t, J = 6.8 Hz, 1 H), 7.61 (t, J = 7.5 Hz, 1 H), 7.53 (d, J = 8.7 Hz, 2 H), 7.35 (d, J = 6.8 Hz, 1 H), 6.50 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.85, 148.46, 143.53, 134.77, 129.99, 127.51, 126.13, 125.10, 124.27, 122.60, 80.95 ppm. MS (EI): m/z (%) = 255 (100) $[M]^+$. $C_{14}H_9NO_4$ (255.05): calcd. C 65.88, H 3.55, N 5.49; found C 65.96, H 3.61, N 5.42.

1′,3′-Dihydro-1,5′-bibenzo[*c*]furan-3(1*H*)-one (8h): The phthalide **8h** was obtained in 66% yield by a procedure similar to that used for the preparation of 2-thienylphthalide **8a** (metalation method). M.p. 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 7.2 Hz, 1 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.53 (t, J = 7.4 Hz, 1 H), 7.28 (d, J = 7.6 Hz, 1 H), 6.78–6.80 (m, 2 H), 6.56 (s, 1 H), 6.29 (s, 1 H), 5.93 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.30, 149.51, 148.52, 148.22, 134.27, 129.99, 129.36, 125.75, 125.55, 122.87, 121.47, 108.39, 107.23, 101.40, 82.69 ppm. $C_{15}H_{10}O_4$ (254.06): calcd. C 70.86, H 3.96; found C 70.70, H 4.05.

3-(2,4,6-Trimethoxyphenyl)benzo[*c*]furan-1(3*H*)-one (8i): The phthalide **8i** was obtained in 65% yield by a procedure similar to that used for the preparation of 2-thienylphthalide **8a** (metalation method). M.p. 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 7.84 Hz, 1 H), 7.71 (t, J = 6.8 Hz, 1 H), 7.59 (t, J = 7.3 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 1 H), 6.48 (s, 2 H), 6.35 (s, 1 H), 3.83 (s, 3 H), 3.81 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.44, 153.67, 149.46, 138.69, 134.39, 131.39, 131.86, 129.49, 125.65, 125.47, 122.85, 103.99, 82.83, 60.80, 56.20 ppm. $C_{17}H_{16}O_5$ (300.1): calcd. C 67.99, H 5.37; found C 68.11, H 5.32.

3-(Anthracen-9-yl)benzo[*c*]furan-1(3*H*)-one (8j): The phthalide **8j** was obtained in 55% yield by a procedure similar to that used for the preparation of 2-thienylphthalide **8a** (metalation method). M.p. 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 8.47–8.50 (m, 1 H), 8.16 (d, J = 7.4 Hz, 1 H), 8.01–8.11 (m, 2 H), 7.93 (s, 1 H), 7.55–7.63 (m, 5 H), 7.34–7.38 (m, 1 H), 7.28–7.32 (m, 1 H), 7.10 (d, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.89, 151.36, 134.58, 131.69, 130.69, 129.55, 129.30, 127.51, 126.56, 126.35, 126.05, 124.98, 124.27, 123.98, 122.38, 79.06 ppm. MS (EI): m/z (%) = 310 (20) $[M]^+$. $C_{22}H_{14}O_2$ (310.1): calcd. C 85.14, H 4.55; found C 85.01, H 4.50.

Synthesis of Phthalide by the Grignard Method

3-(5-Hexyl-2-thienyl)phthalide (8c): A solution of 2-bromo-5-hexylthiophene (1 g, 4.06 mmol) in dry diethyl ether (25 mL) was added dropwise to a refluxing mixture of magnesium turnings (0.10 g, 4.47 mmol) containing a catalytic amount of iodine (20 mg) in dry THF (20 mL) under nitrogen. After addition of the bromo compound, the reaction mixture was heated at reflux for 2 h to ensure complete formation of the Grignard reagent. The above Grignard reagent was slowly added to a solution of 2-formylbenzoic acid (0.60 g, 4.06 mmol) in THF at room temperature. The reaction mixture was stirred at room temperature for 6 h. Then 2 N HCl was added to the above reaction mixture and stirred for 0.5 h. The solvent was completely removed and the solid filtered and dried with Na_2SO_4. The crude product was purified by column chromatography (hexane/EA, 9:1) to afford phthalide **8c** as white solid (0.76 g, 63%).

3-(4-Methoxyphenyl)benzo[*c*]furan-1(3*H*)-one (8k): The phthalide **8k** was obtained in 55% yield by a procedure similar to that used for the preparation of 3-(5-hexyl-2-thienyl)phthalide (Grignard method). M.p. 117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.3 Hz, 1 H), 7.65 (t, J = 7.5 Hz, 1 H), 7.55 (t, J = 7.5 Hz, 1 H), 7.30 (d, J = 6.8 Hz, 1 H), 7.16 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 8.2 Hz, 2 H), 6.41 (s, 1 H), 3.80 (s, 3 H) ppm. MS (EI): m/z (%) = 240 (100) $[M]^+$. $C_{15}H_{12}O_3$ (240.08): calcd. C 74.99, H 5.03; found C 74.83, H 5.11.

3-(*p*-Tolyl)benzo[*c*]furan-1(3*H*)-one (8l): The phthalide **8l** was obtained in 60% yield by a procedure similar to that used for the preparation of 3-(5-hexyl-2-thienyl)phthalide (Grignard method). M.p. 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 7.32 Hz, 1 H), 7.62 (t, J = 6.8 Hz, 1 H), 7.52 (t, J = 7.3 Hz, 1 H),

7.31 (d, J = 6.8 Hz, 1 H), 7.13–7.19 (m, 4 H), 6.37 (s, 1 H), 2.35 (s, 3 H) ppm. MS (EI): m/z (%) = 224 (100) $[M]^+$. $C_{15}H_{12}O_2$ (224.08): calcd. C 80.34, H 5.39; found C 80.41, H 5.43.

3-(1-Naphthyl)benzo[*c*]furan-1(3*H*)-one (8m): The phthalide **8m** was obtained in 58% yield by a procedure similar to that used for the preparation of 3-(5-hexyl-2-thienyl)phthalide (Grignard method). M.p. 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.2 Hz, 1 H), 7.99 (d, J = 7.3 Hz, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.86 (s, 1 H), 7.81 (dd, J = 3.4, 2.44 Hz, 2 H), 7.53–7.62 (m, 2 H), 7.44 (dd, J = 3.4, 2.9 Hz, 2 H), 7.35–7.38 (m, 1 H), 7.21–7.23 (m, 1 H) ppm. MS (EI): m/z (%) = 260 (100) $[M]^+$. $C_{18}H_{12}O_2$ (260.08): calcd. C 83.06, H 4.65; found C 82.96, H 4.62.

***N*,*N*-Dimethyl-4-[3-(thiophen-2-yl)benzo[*c*]thiophen-1-yl]benzenamine (9a):** Reaction of 4-(dimethylamino)phenylmagnesium bromide (9.25 mL, 0.5 M) with phthalide **8a**[20] (1.0 g, 4.62 mmol) followed by workup and thionation using Lawesson's reagent (0.93 g, 2.31 mmol) led to **9a** (1.0 g, 65%). M.p. 84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, J = 9.1 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.57 (d, J = 9.1 Hz, 2 H), 7.34–7.36 (m, 2 H), 7.05–7.16 (m, 3 H), 6.84 (d, J = 8.4 Hz, 2 H), 3.04 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.10, 135.41, 130.22, 127.89, 124.97, 124.87, 124.63, 123.68, 121.80, 121.43, 112.81, 40.59 ppm. MS (EI): m/z (%) = 335 (22) $[M + 1]^+$. $C_{20}H_{17}NS_2$ (335.08): calcd. C 71.60, H 5.10, N 4.18, S 19.12; found C 71.50, H 5.07, N 4.20, S 19.23.

1-[4-(Methylthio)phenyl]-3-(thiophen-2-yl)benzo[*c*]thiophene (9b): Reaction of 4-(methylthio)phenylmagnesium bromide (9.28 mL, 0.5 M) with phthalide **8a**[20] (1.0 g, 4.62 mmol) followed by workup and thionation using Lawesson's reagent (0.93 g, 2.31 mmol) led to **9b** (62%). M.p. 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.4 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.66–7.68 (m, 1 H), 7.55 (d, J = 7.6 Hz, 2 H), 7.12–7.35 (m, 6 H), 2.42 (s, 3 H) ppm. $C_{19}H_{14}S_3$ (338.03): calcd. C 67.41, H 4.17, S 28.42; found C 67.47, H 4.20, S 28.33.

1-[4-(Hexyloxy)phenyl]-3-(thiophen-2-yl)benzo[*c*]thiophene (9c): A solution of 2-bromothiophene (2.89 g, 17.72 mmol) in dry THF (20 mL) was added (15 min) to a refluxing mixture of magnesium turnings (0.51 g, 21.27 mmol) containing a catalytic amount of iodine (20 mg) in dry THF (100 mL) under N_2. After addition of the bromo compound, the reaction mixture was heated at reflux for 2 h to ensure the completion of the Grignard reaction. Then the above Grignard reagent was slowly added through an additional funnel to a solution of phthalide **8f** (5.0 g, 16.12 mmol) in dry THF (30 mL) at room temperature. The reaction mixture was stirred at room temperature for 6 h and poured into ice-cold water containing ammonium chloride solution. The crude product was extracted with DCM (75 mL) and dried (Na_2SO_4). Then it was treated with Lawesson's reagent (3.26 g, 8.05 mmol) at room temperature for 6 h. The solvent (DCM) was removed, and the residue was gently heated (fume hood) in a steam bath with ethanol (20 mL). The crude product was purified by column chromatography on neutral alumina using hexane as eluent to afford compound **9c** as a yellow solid (4.1 g, 65%). M.p. 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.4 Hz, 1 H), 7.72 (d, J = 8.4 Hz, 1 H), 7.52 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 4.0 Hz, 2 H), 6.94–7.09 (m, 5 H), 3.95 (t, J = 6.2 Hz, 2 H), 1.77 (quint, J = 7.1 Hz, 2 H), 1.32–1.51 (m, 6 H), 0.90 (t, J = 6.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.87, 136.24, 135.81, 135.15, 134.20, 130.30, 127.71, 127.01, 126.61, 125.01, 124.94, 123.93, 121.27, 114.98, 68.05, 31.55, 29.18, 25.69, 22.58, 14.04 ppm. MS (EI): m/z (%) = 392 (49) $[M]^+$. $C_{24}H_{24}OS_2$ (392.13): calcd. C 73.43, H 6.16, S 16.34; found C 73.35, H 6.14, S 16.29.

1-(3,4-Dimethoxyphenyl)-3-(thiophen-2yl)benzo[*c*]thiophene (9d): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (1.0 g, 6.13 mmol) and magnesium turnings (0.161 g, 6.74 mmol) with phthalide **8f** (1.66 g, 6.13 mmol) followed by workup and thionation using Lawesson's reagent (1.24 g, 3.06 mmol) led to **9d** (1.19 g, 55%). M.p. 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.3 Hz, 1 H), 7.76 (d, J = 8.8 Hz, 1 H), 7.34–7.36 (m, 2 H), 7.21–7.25 (m, 2 H), 7.11–7.17 (m, 3 H), 6.98 (d, J = 8.3 Hz, 1 H), 3.95 (s, 6 H) ppm. MS (EI): m/z (%) = 352 (10) $[M]^+$. $C_{20}H_{16}O_2S_2$ (352.06): calcd. C 68.15, H 4.58, S 18.19; found C 68.10, H 4.53, S 18.24.

1-(4-Nitrophenyl)-3-(thiophen-2-yl)benzo[*c*]thiophene (9e): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (0.99 g, 6.11 mmol) and magnesium turnings (0.161 g, 6.74 mmol) with phthalide **8g** (1.56 g, 6.11 mmol) followed by workup and thionation using Lawesson's reagent (1.23 g, 3.05 mmol) led to **9e** (0.86 g, 42%). M.p. 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 8.8 Hz, 2 H), 8.02 (d, J = 2.4 Hz, 1 H), 7.83 (d, J = 9.2 Hz, 2 H), 7.44 (d, J = 4.8 Hz, 1 H), 7.40 (dd, J = 2.4, 1.2 Hz, 1 H), 7.17–7.24 (m, 4 H) ppm. MS (EI): m/z (%) = 338 (100) $[M + 1]^+$. $C_{18}H_{11}NO_2S_2$ (337.02): calcd. C 64.07, H 3.29, N 4.15, S 19.01; found C 64.03, H 3.33, N 4.12, S 18.95.

1-(4-Methoxyphenyl)-3-(thiophen-2-yl)benzo[*c*]thiophene (9f): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (2.0 g, 12.26 mmol) and magnesium turnings (0.35 g, 14.58 mmol) with phthalide **8k** (2.94 g, 12.26 mmol) followed by workup and thionation using Lawesson's reagent (2.47 g, 6.10 mmol) led to **9f** (1.57 g, 40%). M.p. 107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.7 Hz, 1 H), 7.77 (d, J = 8.4 Hz, 1 H), 7.61 (d, J = 8.4 Hz, 2 H), 7.37–7.40 (m, 2 H), 7.10–7.19 (m, 3 H), 7.05 (d, J = 8.7 Hz, 2 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.43, 136.17, 135.32, 134.95, 134.04, 130.49, 127.80, 126.45, 125.42, 125.80, 125.21, 125.13, 124.58, 124.09, 121.41, 121.33, 114.59, 55.43 ppm. MS (EI): m/z (%) = 322 (100) $[M + 1]^+$. $C_{19}H_{14}OS_2$ (332.05): calcd. C 70.77, H 4.38, S 19.89; found C 70.70, H 4.36, S 19.80.

1-(Thiophen-2-yl)-3-(*p*-tolyl)benzo[*c*]thiophene (9g): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (2.0 g, 12.26 mmol) and magnesium turnings (0.32 g, 13.49 mmol) with phthalide **8l** (2.74 g, 12.23 mmol) followed by workup and thionation using Lawesson's reagent (2.47 g, 6.11 mmol) led to **9g** (2.24 g, 60%). M.p. 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.8 Hz, 2 H), 7.53–7.62 (m, 4 H), 7.33 (d, J = 3.4 Hz, 1 H), 7.11 (d, J = 7.3 Hz, 2 H), 6.97 (t, J = 4.4 Hz, 1 H), 6.83 (t, J = 4.1 Hz, 1 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.51, 139.72, 136.74, 133.72, 129.55, 128.68, 127.71, 125.07, 124.98, 124.58, 123.64, 121.88, 121.47, 121.33, 120.09, 119.82, 21.27 ppm. MS (EI): m/z (%) = 306 (100) $[M]^+$. $C_{19}H_{14}S_2$ (306.05): calcd. C 74.47, H 4.60, S 20.93; found C 74.55, H 4.53, S 20.92.

3-(Thiophen-2-yl)-1-(2,4,6-trimethoxyphenyl)benzo[*c*]thiophene (9h): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (1.0 g, 6.13 mmol) and magnesium turnings (0.161 g, 6.74 mmol) with phthalide **8i** (1.84 g, 6.13 mmol) followed by workup and thionation using Lawesson's reagent (1.24 g, 3.06 mmol) led to **9h** (1.26 g, 54%) as a viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.4 Hz, 1 H), 7.78 (d, J = 7.6 Hz, 1 H), 7.34–7.35 (m, 2 H), 7.08–7.14 (m, 3 H), 6.85 (s, 2 H), 3.92 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.59, 137.88, 135.78, 135.25, 135.09, 134.89, 133.73, 129.35, 127.80, 126.45, 125.33, 124.57, 124.40, 121.45, 121.14, 106.43, 60.95, 56.22 ppm. MS (EI): m/z (%) = 382 (70) $[M]^+$. $C_{21}H_{18}O_3S_2$ (382.07): calcd. C 65.94, H 4.74, S 16.77; found C 65.99, H 4.72, S 16.70.

1-(Anthracen-9-yl)-3-(thiophen-2-yl)benzo[*c*]thiophene (9i): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (1.0 g, 6.13 mmol) and magnesium turnings (0.161 g, 6.74 mmol) with phthalide **8j** (1.90 g, 6.13 mmol) followed by workup and thionation using Lawesson's reagent (1.24 g, 3.06 mmol) led to **9i** (1.08 g, 45%). M.p. 170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1 H), 8.05 (d, J = 8.3 Hz, 2 H), 7.88 (d, J = 8.8 Hz, 2 H), 7.84 (d, J = 9.2 Hz, 1 H), 7.42–7.56 (m, 6 H), 6.89–7.32 (m, 4 H) ppm. MS (EI): m/z (%) = 392 (10) $[M]^+$. $C_{26}H_{16}S_2$ (392.07): calcd. C 79.55, H 4.11, S 16.34; found C 79.46, H 4.18, S 16.36.

1-(Naphthalen-1-yl)-3-(thiophen-2-yl)benzo[*c*]thiophene (9j): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (1.0 g, 6.13 mmol) and magnesium turnings (0.161 g, 6.74 mmol) with phthalide **8m** (1.54 g, 6.13 mmol) followed by workup and thionation using Lawesson's reagent (1.24 g, 3.06 mmol) led to **9j** (0.87 g, 43%) as a viscous yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.8 Hz, 1 H), 7.77 (d, J = 8.2 Hz, 1 H), 7.73 (d, J = 8.2 Hz, 1 H), 7.47 (d, J = 7.3 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 1 H), 7.22 (d, J = 4.4 Hz, 2 H), 7.25–7.29 (m, 1 H), 7.34–7.37 (m, 1 H), 7.03–7.15 (m, 4 H), 6.82–6.91 (m, 1 H) ppm. MS (EI): m/z (%) = 342 (66) $[M]^+$. $C_{22}H_{14}S_2$ (342.05): calcd. C 77.15, H 4.12, S 18.73; found C 77.10, H 4.10, S 18.80.

1-Phenyl-3-(thiophen-2-yl)benzo[*c*]thiophene (9k): Reaction of 2-thienylmagnesium bromide from 2-bromothiophene (1.70 g, 10.47 mmol) and magnesium turnings (0.30 g, 12.51 mmol) with phthalide **8n** (2.0 g, 9.52 mmol) followed by workup and thionation using Lawesson's reagent (1.92 g, 4.74 mmol) led to **9k** (1.75 g, 63%) as a viscous yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.3 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 1 H), 7.66 (d, J = 7.3 Hz, 2 H), 7.49 (t, J = 6.6 Hz, 2 H), 7.32–7.40 (m, 2 H), 7.11–7.19 (m, 4 H) ppm. MS (EI): m/z (%) = 292 (22) $[M]^+$. $C_{18}H_{12}S_2$ (292.04): calcd. C 73.93, H 4.14, S 21.93; found C 73.73, H 4.20, S 22.07.

1-(5-Hexylthiophen-2-yl)-3-(thiophen-2yl)benzo[*c*]thiophene (9l): Reaction of 5-hexyl-2-thienylmagnesium bromide from 2-bromo-5-hexylthiophene (1.25 g, 5.09 mmol) and magnesium turnings (0.13 g, 5.41 mmol) with phthalide **8a** (1 g, 4.62 mmol) followed by workup and thionation using Lawesson's reagent (0.93 g, 2.31 mmol) led to **9l** (1.02 g, 58%) as a viscous orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, J = 2.5, 3.5 Hz, 1 H), 7.11–7.13 (m, 2 H), 7.08–7.12 (m, 2 H), 6.80–6.83 (m, 3 H), 6.78 (m, 1 H), 2.83 (t, J = 7.6 Hz, 2 H), 1.25–1.71 (m, 8 H), 0.89 (t, J = 7.1 Hz, 3 H) ppm. MS (EI): m/z (%) = 382 (100) $[M]^+$. $C_{32}H_{36}S_4$ (382.09): calcd. C 69.06, H 5.80, S 25.14; found C 69.16, H 5.85, S 24.99.

1-[5-(2-Ethylhexyl)thiophen-2-yl]-3-(thiophen-2-yl)benzo[*c*]thiophene (9m): According to a procedure similar to that used for the preparation of **9l**, benzothiophene **9m** was prepared (2.08 g, 55%) as a viscous orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (t, J = 7.2 Hz, 1 H), 7.45–7.47 (m, 1 H), 7.22–7.29 (m, 2 H), 7.04 (t, J = 3.8 Hz, 1 H), 6.97 (d, J = 3.6 Hz, 1 H), 6.91 (d, J = 7.8 Hz, 1 H), 6.89 (d, J = 7.6 Hz, 1 H), 6.63 (d, J = 3.2 Hz, 1 H), 2.81 (d, J = 6.8 Hz, 2 H), 1.40–1.57 (m, 9 H), 0.99–1.08 (m, 6 H) ppm. MS (EI): m/z (%) = 410 (22) $[M]^+$. $C_{24}H_{26}S_3$ (410.12): calcd. C 70.19, H 6.38, S 23.43; found C 70.10, H 6.36, S 23.54.

1-(5-Butylthiophen-2-yl)-3-(thiophen-2-yl)benzo[*c*]thiophene (9n): According to a procedure similar to that used for the preparation of **9l**, benzothiophene **9n** was prepared (1.60 g, 49%) as a viscous orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, J = 2.8, 3.6 Hz, 1 H), 7.29 (t, J = 5.2 Hz, 1 H), 7.07–7.12 (m, 3 H), 6.88 (t, J = 4.4 Hz, 1 H), 6.80 (d, J = 3.2 Hz, 1 H), 6.75 (m, 1 H), 6.49 (d, J = 4.2 Hz, 1 H), 2.70 (t, J = 7.8 Hz, 2 H), 1.34–1.64 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. MS (EI): m/z (%) = 354 (46) $[M]^+$. $C_{20}H_{18}S_3$ (354.06): calcd. C 67.75, H 5.12, S 27.13; found C 67.70, H 5.10, S 27.20.

1-(5-Hexylthiophen-2-yl)-3-[5-(thiophen-2-yl)thiophen-2-yl]benzo-[*c*]thiophene (9o): Reaction of 5-hexyl-2-thienylmagnesium bromide from 2-bromo-5-hexylthiophene (0.45 g, 1.84 mmol) and magnesium turnings (0.052 g, 2.19 mmol) with phthalide **8b** (0.5 g, 1.67 mmol) followed by workup and thionation using Lawesson's reagent (0.33 g, 0.83 mmol) led to **9o** (0.42 g, 55%). M.p. 42 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.97 (m, 2 H), 7.22–7.25 (m, 3 H), 7.18–7.21 (m, 1 H), 7.11–7.16 (m, 3 H), 7.03–7.05 (m, 1 H), 6.81 (d, J = 3.8 Hz, 1 H), 2.85 (t, J = 7.6 Hz, 2 H), 1.71–1.77 (quint, J = 7.05 Hz, 2 H), 1.41–1.44 (m, 2 H), 1.27–1.36 (m, 4 H), 0.92 (t, J = 6.87 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.86, 128.05, 125.82, 125.47, 125.01, 124.65, 124.60, 123.76, 31.70, 30.37, 28.96, 22.72, 14.23 ppm. MS (EI): m/z (%) = 464 (100) $[M]^+$. $C_{26}H_{24}S_4$ (464.08): calcd. C 67.20, H 5.20, S 27.60; found C 67.08, H 5.30, S 27.62.

1-[5-(5-Hexylthiophen-2-yl)thiophen-2-yl]-3-(thiophen-2-yl)benzo[*c*]-thiophene (9p): Prepared according to a procedure similar to that for **9o**. Yield: 60%, viscous red liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.95 (m, 2 H), 7.29–7.34 (m, 2 H), 7.18 (d, J = 3.9 Hz, 1 H), 7.05–7.12 (m, 4 H), 7.00 (d, J = 3.3 Hz, 1 H), 6.67 (d, J = 3.6 Hz, 1 H), 2.77 (t, J = 7.7 Hz, 2 H), 1.64–1.71 (m, 2 H), 1.30–1.41 (m, 6 H), 0.89 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.78, 137.87, 135.68, 135.37, 135.13, 134.43, 133.87, 127.90, 126.61, 126.37, 125.95, 125.56, 125.51, 124.94, 124.88, 124.84, 123.60, 123.47, 121.67, 121.62, 31.63, 31.60, 30.27, 28.83, 22.64, 14.15 ppm. $C_{26}H_{24}S_4$ (464.08): calcd. C 67.20, H 5.20, S 27.60; found C 67.10, H 5.40, S 27.50.

1-(3-Hexylthiophen-2-yl)-3-[5-(5-hexylthiophen-2-yl)thiophen-2-yl]-benzo[*c*]thiophene (9q): Prepared according to a procedure similar to that for **9o**. Yield: 62%, viscous red liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.4 Hz, 1 H), 7.60 (d, J = 8.4 Hz, 1 H), 7.38 (d, J = 5.1 Hz, 1 H), 7.24 (d, J = 3.3 Hz, 1 H), 7.10–7.15 (m, 2 H), 7.06–7.08 (m, 1 H), 7.04 (t, J = 3.0 Hz, 2 H), 6.70 (d, J = 3.6 Hz, 1 H), 2.80 (t, J = 8.0 Hz, 2 H), 2.64 (t, J = 7.8 Hz, 2 H), 1.66–1.72 (m, 2 H), 1.53–1.60 (m, 2 H), 1.20–1.41 (m, 12 H), 0.90 (t, J = 6.8 Hz, 3 H), 0.82 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.76, 142.57, 137.91, 137.86, 134.45, 134.37, 134.01, 129.31, 127.98, 127.72, 126.03, 125.87, 124.91, 124.64, 124.30, 123.59, 123.44, 121.83, 121.27, 31.57, 30.82, 30.23, 29.08, 29.01, 28.76, 22.58, 22.54, 14.07, 14.03 ppm. $C_{32}H_{36}S_4$ (548.17): calcd. C 70.02, H 6.61, S 23.37; found C 70.22, H 6.51, S 23.27.

3,3′-Bis(thiophen-2-yl)-1,1′-bibenzo[*c*]thiophene (2a): A solution of thienylmagnesium bromide in dry THF was prepared using 2-bromothiophene (0.91 g, 5.58 mmol) and magnesium turnings (0.16 g, 6.66 mmol). Then the Grignard reagent was slowly added through an addition funnel to a solution of diphthalide **10** (0.5 g, 1.87 mmol) in dry THF (30 mL) at room temperature. The reaction mixture was then quenched with aq. ammonium chloride. It was then extracted with DCM (75 mL) and treated with Lawesson's reagent (0.76 g, 1.87 mmol) at room temperature for 6 h. The solvent (DCM) was removed, and the residue was gently heated (fume hood) in a steam bath with ethanol (20 mL). The crude product was purified by column chromatography on neutral alumina (hexane as eluent) to afford product **2a** as a brown solid 0.48 g, 58%). M.p. 175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.4 Hz, 2 H), 7.89 (d, J = 8.1 Hz, 2 H), 7.36–7.42 (m, 4 H), 7.11–7.23 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.98, 135.57, 135.18, 128.50, 127.94, 125.70, 125.04, 124.81, 124.27, 121.89, 121.46 ppm.

$C_{24}H_{14}S_4$ (430.0): calcd. C 66.94, H 3.28, S 29.78; found C 66.89, H 3.26, S 29.85.

3,3′-Bis(5-hexylylthiophen-2-yl)-1,1′-bibenzo[*c*]thiophene (2b): Prepared according to a procedure similar to that for **2a**. Yield: 51%, viscous orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.8 Hz, 2 H), 7.82 (d, J = 8.2 Hz, 2 H), 7.08–7.19 (m, 6 H), 6.82 (d, J = 3.9 Hz, 2 H), 2.86 (t, J = 7.56 Hz, 4 H), 1.70–1.77 (quint, J = 6.8 Hz, 4 H), 1.33–1.53 (m, 12 H), 0.90 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.76, 136.83, 134.74, 129.11, 125.33, 124.92, 124.66, 123.69, 121.88, 121.62, 31.58, 30.27, 28.83, 22.58, 14.08 ppm. $C_{36}H_{38}S_4$ (598.19): calcd. C 72.19, H 6.39, S 21.42; found C 72.11, H 6.42, S 21.47.

3,3′-Bis[5-(2-ethylhexyl)thiophen-2-yl]-1,1′-bibenzo[*c*]thiophene (2c): Prepared according to a procedure similar to that for **2a**. Yield: 55%, viscous orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.7 Hz, 2 H), 7.9 (d, J = 8.8 Hz, 2 H), 7.1–7.3 (m, 6 H), 6.9 (d, J = 3.4 Hz, 2 H), 2.8 (d, J = 6.3 Hz, 4 H), 1.3–1.7 (m, 16 H), 0.89–1.0 (m, 14 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.29, 136.83, 134.68, 133.26, 129.14, 125.98, 125.34, 124.92, 123.66, 121.64, 121.51, 34.2, 32.36, 28.8, 25.5, 23.0, 14.14, 10.8 ppm. $C_{40}H_{46}S_4$ (654.25): calcd. C 73.34, H 7.08, S 19.58; found C 73.30, H 7.00, S 19.70.

3,3′-Bis(5-butylthiophen-2-yl)-1,1′-bibenzo[*c*]thiophene (2d): Prepared according to a procedure similar to that for **2a**. Yield: 62%. M.p. 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 9.2 Hz, 2 H), 7.84 (d, J = 9.2 Hz, 2 H), 7.10–7.20 (m, 6 H), 6.82 (d, J = 3.0 Hz, 2 H), 2.88 (t, J = 7.2 Hz, 4 H), 1.71–1.77 (quint, J = 7.1 Hz, 4 H), 1.44–1.50 (m, 4 H), 1.00 (t, J = 3.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.78, 136.92, 134.84, 133.11, 125.43, 125.06, 124.79, 123.82, 122.00, 121.74, 33.86, 30.07, 22.38, 13.99 ppm. $C_{32}H_{30}S_4$ (542.12): calcd. C 70.80, H 5.57, S 23.63; found C 70.71, H 5.60, S 23.69.

1-(*p*-Tolyl)-3-[1-(*p*-tolyl)benzo[*c*]thiophen-3-yl]benzo[*c*]thiophene (11a): Reaction of *p*-tolylmagnesium bromide from 4-bromotoluene (1.58 g, 9.34 mmol) and magnesium turnings (0.26 g, 10.83 mmol) with diphthalide **10** (1.0 g, 3.75 mmol) followed by workup and thionation with Lawesson's reagent (1.52 g, 3.75 mmol) led to **11a** (0.88 g, 53%). M.p. 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.86 (m, 4 H), 7.60 (d, J = 8.0 Hz, 4 H), 7.30 (d, J = 7. 0 Hz, 4 H), 7.09–7.11 (m, 4 H), 2.43 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.62, 136.89, 135.75, 134.87, 131.14, 129.79, 129.11, 124.35, 121.85, 121.21, 21.26 ppm. $C_{30}H_{22}S_2$ (446.12): calcd. C 80.68, H 4.96, S 14.36; found C 80.60, H 4.92, S 14.48.

1-(*o*-Tolyl)-3-[1-(*o*-tolyl)benzo[*c*]thiophen-3-yl]benzo[*c*]thiophene (11b): Reaction of *o*-tolylmagnesium bromide from 2-bromotoluene (1.58 g, 9.34 mmol) and magnesium turnings (0.26 g, 10.83 mmol) with diphthalide **10** (1.0 g, 3.75 mmol) followed by workup and thionation using Lawesson's reagent (1.52 g, 3.75 mmol) led to **11b** (0.83 g, 50%). M.p. 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.8 Hz, 2 H), 7.65 (d, J = 7.2 Hz, 2 H), 7.47–7.51 (m, 8 H), 7.42–7.27 (m, 4 H), 2.52 (s, 6 H) ppm. MS (EI): m/z (%) = 446 (26) $[M]^+$. $C_{30}H_{22}S_2$ (446.12): calcd. C 80.68, H 4.96, S 14.36; found C 80.74, H 4.91, S 14.35.

1-(3-Hexylthiophen-2-yl)-3-(5-{5-[3-(3-hexylthiophen-2-yl)-2-benzothiophen-1-yl]thiophen-2-yl}thiophen-2-yl)benzo[*c*]thiophene (3): $BF_3{\cdot}Et_2O$ (0.06 g, 0.47 mmol) and PIFA (0.20 g, 0.47 mmol) were added sequentially to a stirred solution of **12** (0.2 g, 0.52 mmol) in CH_2Cl_2 (10 mL) at –78 °C under nitrogen. The reaction mixture was stirred at the same temperature for 6 h. Aqueous workup with saturated aq. $NaHCO_3$ (10 mL) at 0 °C followed by column chromatographic purification (silica gel; EA/hexane, 1:1) gave the known dimer **3**[20] as a red very viscous liquid (0.14 g, 75%).

1-[4-(Hexyloxy)phenyl]-3-[5-(5-{3-[4-(hexyloxy)phenyl]benzo[*c*]-thiophen-1-yl}thiophen-2-yl)thiophen-2-yl]benzo[*c*]thiophene (5a). Using $FeCl_3$: A solution of benzo[*c*]thiophene **9c** (0.2 g, 0.51 mmol) in dry DCM (10 mL) was treated with anhydrous $FeCl_3$ (0.09 g, 0.61 mmol) under nitrogen. The mixture was stirred at room temperature for 10 h and diluted with more DCM (10 mL). The dark mixture was treated with a dilute solution of $NH_2NH_2{\cdot}H_2O$ (10 mL). The crude product was extracted with DCM (30 mL), dried (Na_2SO_4), and the solvent was removed. The crude product was purified by column chromatography on neutral alumina (ethyl acetate as eluent) to give dimer **5a** (0.13 g, 65%) as a dark solid. M.p. 220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.8 Hz, 2 H), 7.75 (d, J = 8.8 Hz, 2 H), 7.57 (d, J = 8.76 Hz, 4 H), 7.24–7.28 (m, 4 H), 7.14–7.18 (m, 2 H), 7.07–7.11 (m, 2 H), 7.01 (d, J = 8.8 Hz, 4 H), 4.03 (t, J = 6.6 Hz, 4 H), 1.81 (q, J = 6.8 Hz, 4 H), 1.31–1.57 (m, 12 H), 0.92 (t, J = 6.8 Hz, 6 H) ppm. MS (MALDI-TOF): m/z = 782 $[M]^+$. $C_{48}H_{46}O_2S_4$ (782.24): calcd. C 73.62, H 5.92, S 16.38; found C 73.51, H 5.85, S 16.39. **Using PIFA/$BF_3{\cdot}OEt_2$:** $BF_3{\cdot}Et_2O$ (0.06 g, 0.45 mmol) and PIFA (0.19 g, 0.45 mmol) were added sequentially to a stirred solution of **9c** (0.2 g, 0.51 mmol) in CH_2Cl_2 (10 mL) at –78 °C under nitrogen. The reaction mixture was stirred at the same temperature for 6 h. Aqueous workup with saturated aq. $NaHCO_3$ (10 mL) at 0 °C followed by column chromatographic purification (silica gel; EA/hexane, 1:1) gave the dimer **5a** (0.07 g, 35%).

1-(4-Methoxyphenyl)-3-(5-{5-[3-(4-methoxyphenyl)benzo[*c*]-thiophen-1-yl]thiophen-2-yl}thiophen-2-yl)benzo[*c*]thiophene (5b). Using $FeCl_3$: Prepared according to a procedure similar to that for **5a**. Yield: 60%. M.p. 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.8 Hz, 2 H), 7.75 (d, J = 8.8 Hz, 2 H), 7.59 (d, J = 8.8 Hz, 4 H), 7.22–7.29 (m, 4 H), 7.15–7.19 (m, 2 H), 7.08–7.11 (m, 2 H), 7.03 (d, J = 8.8 Hz, 4 H), 3.89 (s, 6 H) ppm. MS (MALDI-TOF): m/z = 642 $[M]^+$. $C_{38}H_{26}O_2S_4$ (642.08): calcd. C 70.99, H 4.08, S 19.95; found C 70.95, H 4.04, S 19.99. **Using PIFA/$BF_3{\cdot}OEt_2$:** Prepared according to a procedure similar to that for **5a** (from PIFA/$BF_3{\cdot}OEt_2$). Yield: 0.08 g (40%).

1-(5-Butylthiophen-2-yl)-3-(5-{5-[3-(5-butylthiophen-2-yl)-2-benzothiophen-1-yl]thiophen-2-yl}thiophen-2-yl)benzo[*c*]thiophene (4a). Using $FeCl_3$: Prepared according to a procedure similar to that for **5a**. Yield: 55%, viscous red liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.8 Hz, 2 H), 7.89 (d, J = 8.7 Hz, 2 H), 7.60 (d, J = 3.9 Hz, 2 H), 7.29 (d, J = 3.9 Hz, 2 H), 7.07–7.18 (m, 6 H), 6.71 (d, J = 3.4 Hz, 2 H), 2.78 (t, J = 7.5 Hz, 4 H), 1.60–1.65 (quint, J = 6.8 Hz, 4 H), 1.34–1.40 (m, 4 H), 0.89 (t, J = 7.3 Hz, 6 H) ppm. MS (GC): m/z = 706 $[M]^+$. $C_{40}H_{34}S_6$ (706.1): calcd. C 67.94, H 4.85, S 27.21; found C 67.91, H 4.90, S 27.28. **Using PIFA/$BF_3{\cdot}OEt_2$:** Prepared according to a procedure similar to that for **5a** (from PIFA/$BF_3{\cdot}OEt_2$). Yield: 0.06 g (60%).

1-[5-(2-Ethylhexyl)thiophen-2-yl]-3-[5-(5-{3-[5-(2-ethylhexyl)-thiophen-2-yl]benzo[*c*]thiophen-1-yl}thiophen-2-yl)thiophen-2-yl]-2-benzothiophene (4b). Using $FeCl_3$: Prepared according to a procedure similar to that for **5a**. Yield: 50%, viscous red liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–8.06 (m, 4 H), 7.36–7.40 (m, 6 H), 7.16–7.21 (m, 4 H), 6.83–6.91 (m, 2 H), 2.85 (d, J = 5.8 Hz, 4 H), 0.9–1.71 (m, 30 H) ppm. MS (GC): m/z = 818 $[M]^+$. $C_{48}H_{50}S_6$ (818.22): calcd. C 70.37, H 6.15, S 23.48; found C 70.46, H 6.10, S 23.44. **Using PIFA/$BF_3{\cdot}OEt_2$:** Prepared according to a procedure similar to that for **5a** (from PIFA/$BF_3{\cdot}OEt_2$). Yield: 0.05 g (54%).

1-(5-Hexylthiophen-2-yl)-3-(5-{5-[3-(5-hexylthiophen-2-yl)-2-benzothiophen-1-yl]thiophen-2-yl}thiophen-2-yl)benzo[*c*]thiophene

(4c). Using $FeCl_3$: Prepared according to a procedure similar to that for **5a**. Yield: 60%, viscous red liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99–8.03 (m, 4 H), 7.73 (d, J = 3.6 Hz, 2 H), 7.39 (d, J = 4.0 Hz, 2 H), 7.15–7.25 (m, 6 H), 6.82 (d, J = 3.2 Hz, 2 H), 2.84 (t, J = 7.8 Hz, 4 H), 1.71 (quint, J = 6.9 Hz, 4 H), 1.25–1.42 (m, 12 H), 0.90 (t, J = 6.0 Hz, 6 H) ppm. MS (GC): m/z = 762 $[M]^+$. $C_{44}H_{42}S_6$ (762.16): calcd. C 69.24, H 5.55, S 25.21; found C 69.31, H 5.58, S 25.11. **Using PIFA/BF_3·OEt_2:** Prepared according to a procedure similar to that for **5a** (from PIFA/BF_3·OEt_2). Yield: 0.06 g (65%).

5-{3-[4-(Dimethyamino)phenyl]benzo[*c*]thiophen-1-yl}thiophene-2-carbaldehyde (13a): $POCl_3$ (0.06 mL, 0.65 mmol) was slowly added to a mixture of dry DCM (10 mL) and DMF (0.05 mL, 0.65 mmol) at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature until it turned pale yellow (Vilsmeier reagent). Then it was added to a solution benzo[*c*]thiophene **9a** (0.2 g, 0.59 mmol) in dry DCM (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for an additional 10 h. Then the solvent was completely removed and the residue treated with aqueous NaOH (5 g in 100 mL of water) at room temperature for 15 min. The crude product was then extracted with DCM (50 mL), dried (Na_2SO_4), and the solvent removed. Column chromatography of the crude product on neutral alumina (eluent: 10% EA in hexane) afforded product **13a** as an orange solid (0.13 g, 60%). M.p. 70 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1 H), 8.02 (d, J = 8.4 Hz, 1 H), 7.79 (d, J = 8.8 Hz, 1 H), 7.68 (d, J = 3.4 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.34 (br. s, 1 H), 7.07–7.24 (m, 3 H), 6.82 (br. s, 1 H), 3.01 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 182.50, 150.12, 140.69, 137.18, 134.89, 130.15, 126.21, 124.22, 123.97, 122.18, 121.11, 114.21, 112.70, 40.44 ppm. $C_{21}H_{17}NOS_2$ (363.08): calcd. C 69.39, H 4.71, N 3.85, S 17.64; found C 69.45, H 4.75, N 3.81, S 17.68.

5-{3-[4-(Hexyloxy)phenyl]benzo[*c*]thiophen-1-yl}thiophene-2-carbaldehyde (13b): The aldehyde **13b** was obtained in 64% yield according to a procedure similar to that used for **13a**. M.p. 86 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 8.02 (d, J = 8.8 Hz, 1 H), 7.76 (d, J = 8.8 Hz, 1 H), 7.72 (d, J = 4.0 Hz, 1 H), 7.55 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 4.0 Hz, 1 H), 7.21–7.23 (m, 1 H), 7.09–7.11 (m, 1 H), 7.00 (d, J = 8.8 Hz, 2 H), 3.99 (t, J = 6.6 Hz, 2 H), 1.77 (quint, J = 7.2 Hz, 2 H), 1.45–1.49 (m, 2 H), 1.32–1.38 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.26, 159.60, 141.28, 137.14, 136.36, 135.32, 130.56, 126.24, 125.23, 124.68, 124.42, 121.90, 121.17, 115.23, 68.23, 31.57, 29.19, 25.71, 22.59, 14.01 ppm. MS (EI): m/z (%) = 420 (100) $[M]^+$. $C_{25}H_{24}O_2S_2$ (420.12): calcd. C 71.39, H 5.75, S 15.25; found C 71.50, H 5.70, S 15.30.

5-[3-(3,4-Dimethoxyphenyl)benzo[*c*]thiophen-1-yl]thiophene-2-carbaldehyde (13c): The aldehyde **13c** was obtained in 50% yield according to a procedure similar to that used for **13a**. M.p. 138 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1 H), 8.05 (d, J = 8.8 Hz, 1 H), 7.80 (d, J = 8.8 Hz, 1 H), 7.75 (d, J = 3.9 Hz, 2 H), 7.42 (d, J = 3.8 Hz, 2 H), 7.13–7.25 (m, 2 H), 7.00 (d, J = 8.3 Hz, 1 H), 3.96 (s, 6 H) ppm. MS (EI): m/z (%) = 380 (47) $[M]^+$. $C_{21}H_{16}O_3S_2$ (380.05): calcd. C 66.29, H 4.24, S 16.86; found C 66.20, H 4.21, S 16.90.

5-[3-(*p*-Tolyl)benzo[*c*]thiophen-1-yl]thiophene-2-carbaldehyde (13d): The aldehyde **13d** was obtained in 52% yield according to a procedure similar to that used for **13a**. M.p. 126 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1 H), 8.05 (d, J = 9.2 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 1 H), 7.76 (d, J = 3.9 Hz, 1 H), 7.56 (d, J = 7.8 Hz, 2 H), 7.43 (d, J = 3.8 Hz, 1 H), 7.31 (d, J = 8.3 Hz, 2 H), 7.24–7.28 (m, 1 H), 7.13–7.17 (m, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.24, 146.44, 141.37, 138.46, 138.08, 137.11, 136.35, 135.51, 130.34, 129.88, 129.18, 126.21, 124.80, 124.57, 121.84, 121.15, 21.29 ppm. MS (EI): m/z (%) = 334 (57) $[M]^+$. $C_{20}H_{14}OS_2$ (334.05): calcd. C 71.82, H 4.22, S 19.17; found C 71.93, H 4.20, S 19.13.

5-[3-(4-Methoxyphenyl)benzo[*c*]thiophen-1-yl]thiophene-2-carbaldehyde (13e): The aldehyde **13e** was obtained in 62% yield according to a procedure similar to that used for **13a**. M.p. 130 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 8.02 (d, J = 8.8 Hz, 1 H), 7.75 (d, J = 8.8 Hz, 1 H), 7.72 (dd, J = 1.2, 2.8 Hz, 1 H), 7.56 (d, J = 8.8 Hz, 2 H), 7.39 (dd, J = 2.4, 1.6 Hz, 1 H), 7.21–7.25 (m, 1 H), 7.10–7.13 (m, 1 H), 7.01 (d, J = 8.4 Hz, 2 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.26, 159.88, 146.55, 141.50, 141.25, 137.13, 136.29, 130.54, 126.19, 125.61, 124.67, 121.44, 121.80, 121.28, 114.65, 55.39 ppm. MS (EI): m/z (%) = 350 (100) $[M]^+$. $C_{20}H_{14}O_2S_2$ (350.04): calcd. C 68.54, H 4.03, S 18.30; found C 68.42, H 4.09, S 18.40.

5-{3-[5-(5-Hexylthiophen-2-yl)thiophen-2-yl]benzo[*c*]thiophen-1-yl}thiophene-2-carbaldehyde (14b): The aldehyde **14b** was obtained in 60% yield as a viscous orange liquid according to a procedure similar to that used for **13a**. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.85 (s, 1 H), 7.95 (t, J = 7.0 Hz, 2 H), 7.67 (d, J = 4.2 Hz, 1 H), 7.14–7.24 (m, 3 H), 7.06 (d, J = 3.9 Hz, 1 H), 7.01 (d, J = 3.3 Hz, 1 H), 6.69 (d, J = 3.3 Hz, 1 H), 2.79 (t, J = 7.5 Hz, 2 H), 1.63–1.70 (m, 2 H), 1.31–1.40 (m, 6 H), 0.90 (t, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.18, 146.26, 145.80, 141.54, 139.00, 137.00, 136.40, 135.28, 134.06, 132.93, 130.41, 126.85, 126.48, 125.15, 125.02, 124.31, 123.81, 123.65, 122.09, 121.36, 31.59, 31.56, 30.25, 28.79, 22.60, 14.11 ppm. $C_{27}H_{24}OS_4$ (492.07): calcd. C 65.81, H 4.91, S 26.03; found C 65.71, H 4.81, S 26.16.

5-[3-(5-Hexylthiophen-2-yl)benzo[*c*]thiophen-1-yl]thiophene-2-carbaldehyde (14c): The aldehyde **14c** was obtained in 66% yield as a viscous orange liquid according to a procedure similar to that used for **13a**. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 7.99 (d, J = 8.4 Hz, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.71 (d, J = 3.8 Hz, 1 H), 7.36 (d, J = 4.5 Hz, 1 H), 7.15–7.25 (m, 3 H), 6.81 (d, J = 3.0 Hz, 1 H), 2.84 (t, J = 7.6 Hz, 2 H), 1.69–1.75 (quint, J = 6.8 Hz, 2 H), 1.33–1.43 (m, 6 H), 0.90 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.38, 148.01, 146.21, 141.45, 137.24, 136.45, 135.24, 132.32, 131.41, 126.53, 126.37, 125.27, 124.98, 124.95, 123.86, 122.31, 121.35, 31.67, 30.37, 28.92, 22.69, 14.21 ppm. $C_{23}H_{22}OS_3$ (410.08): calcd. C 67.28, H 5.40, S 23.43; found C 67.35, H 5.45, S 23.40.

5-{3-[5-(2-Ethylhexyl)thiophen-2-yl]benzo[*c*]thiophen-1-yl}thiophene-2-carbaldehyde (14d): The aldehyde **14d** was obtained in 54% yield as a viscous orange liquid according to a procedure similar to that used for **13a**. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.87 (s, 1 H), 7.91–8.00 (m, 2 H), 7.77 (d, J = 3.8 Hz, 1 H), 7.37 (d, J = 3.8 Hz 1 H), 7.21–7.25 (m, 2 H), 7.16–7.20 (m, 1 H), 6.80 (d, J = 3.8 Hz, 1 H), 2.7 (d, J = 6.9 Hz, 2 H), 1.62–1.64 (m, 1 H), 1.40–1.42 (m, 2 H), 1.31–1.38 (m, 6 H), 0.8–0.9 (m, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.38, 146.62, 146.24, 141.43, 137.25, 136.47, 135.20, 132.58, 131.45, 126.53, 126.33, 126.26, 124.95, 123.80, 122.34, 121.35, 41.55, 34.32, 32.48, 28.96, 25.64, 23.11, 14.26, 10.95 ppm. MS (EI): m/z (%) = 438 (97) $[M]^+$. $C_{25}H_{26}OS_3$ (438.11): calcd. C 68.45, H 5.97, S 21.93; found C 68.40, H 6.00, S 22.02.

5-[3-(5-Butylthiophen-2-yl)benzo[*c*]thiophen-1-yl]thiophene-2-carbaldehyde (14e): The aldehyde **14e** was obtained in 33% yield as a viscous orange liquid according to a procedure similar to that used for **13a**. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1 H), 7.89–7.94 (m, 2 H), 7.64 (d, J = 3.9 Hz, 1 H), 7.30–7.31 (d, J = 3.9 Hz, 1 H), 7.07–7.18 (m, 3 H), 6.74 (d, J = 3.4 Hz, 1 H), 2.80 (t, J =

7.5 Hz, 2 H), 1.61–1.66 (quint, *J* = 6.9 Hz, 2 H), 1.34–1.40 (sept, *J* = 6.7 Hz, 2 H), 0.89 (t, *J* = 7.32 Hz, 3 H) ppm. MS (EI): *m*/*z* (%) = 382 (37) $[M]^+$. $C_{21}H_{18}OS_3$ (382.05): calcd. C 65.93, H 4.74, S 25.14; found C 65.82, H 4.72, S 25.19.

2-[(5-{3-[4-(Hexyloxy)phenyl]benzo[*c*]thiophen-1-yl}thiophen-2-yl)-methylene]malononitrile (15a): Monoaldehyde **13b** (0.2 g, 0.47 mmol) and malononitrile (0.034 g, 0.52 mmol) were condensed in the presence of *t*BuOK (0.064 g, 0.57 mmol) as base in dry ethanol. The above reaction mixture was stirred at room temperature for 12 h, and the solid was filtered. The crude solid was purified by column chromatography (hexane/EA, 90:10). Yield: 0.14 g (64%). M.p. 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.76 Hz, 1 H), 7.99 (d, *J* = 9.28 Hz, 1 H), 7.70–7.81 (m, 2 H), 7.57–7.59 (m, 1 H), 7.46 (d, *J* = 3.9 Hz, 1 H), 7.39 (d, *J* = 3.9 Hz, 1 H), 7.02–7.19 (m, 3 H), 6.89 (s, 1 H), 4.01 (t, *J* = 6.6 Hz, 2 H), 1.83 (quint, J = 7.2 Hz, 2 H), 1.36–1.56 (m, 6 H), 0.90 (t, *J* = 7.0 Hz, 3 H) ppm. MS (EI): *m*/*z* (%) = 468 (17) $[M]^+$. $C_{28}H_{24}N_2OS_2$ (468.13): calcd. C 71.76, H 5.16, N 5.98, S 13.68; found C 71.70, H 5.10, N 6.06, S 13.77.

2-({5-[3-(3,4-Dimethoxyphenyl)benzo[*c*]thiophen-1-yl]thiophen-2-yl}methylene)malononitrile (15b): The cyano derivative **15b** was obtained in 65% yield according to a procedure similar to that used for **15a**. M.p. 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.8 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.74 (s, 1 H), 7.68 (d, *J* = 3.9 Hz, 1 H), 7.46 (d, *J* = 4.3 Hz, 1 H), 7.32–7.36 (m, 1 H), 7.18–7.24 (m, 2 H), 7.16 (d, *J* = 1.4 Hz, 1 H), 7.01 (d, *J* = 8.3 Hz, 1 H), 3.90 (s, 6 H) ppm. MS (EI): *m*/*z* (%) = 428 (77) $[M]^+$. $C_{24}H_{16}N_2O_2S_2$ (428.07): calcd. C 67.27, H 3.76, N 6.54, S 14.97; found C 67.20, H 3.70, N 6.60, S 15.00.

2-({5-[3-(*p*-Tolyl)benzo[*c*]thiophen-1-yl]thiophen-2-yl}methylene)-malononitrile (15c): The cyano derivative **15c** was obtained in 50% yield according to a procedure similar to that used for **15a**. M.p. 257 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.8 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.76 (s, 1 H), 7.71 (d, *J* = 4.4 Hz, 1 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.47 (d, *J* = 4.4 Hz, 2 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.18–7.22 (m, 1 H), 2.45 (s, 3 H) ppm. $C_{23}H_{14}N_2S_2$ (382.06): calcd. C 72.22, H 3.69, N 7.32, S 16.77; found C 72.12, H 3.72, N 7.35, S 16.81.

2-({5-[3-(4-Methoxyphenyl)benzo[*c*]thiophen-1-yl]thiophen-2-yl}-methylene)malonitrile (15d): The cyano derivative **15d** was obtained in 52% yield according to a procedure similar to that used for **15a**. M.p. 206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.7 Hz, 1 H), 7.82 (d, *J* = 9.0 Hz, 1 H), 7.76 (s, 1 H), 7.71 (d, *J* = 4.2 Hz, 1 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 3.9 Hz, 1 H), 7.36 (t, *J* = 8.1 Hz, 1 H), 7.17–7.24 (m, 1 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 3.92 (s, 3 H) ppm. MS (EI): *m*/*z* (%) = 398 (15) $[M]^+$. $C_{23}H_{14}N_2OS_2$ (398.08): calcd. C 69.32, H 3.54, N 7.03, S 16.09; found C 69.22, H 3.43, N 7.13, S 16.15.

3-(5-{3-[4-(Hexyloxy)phenyl]benzo[*c*]thiophen-1-yl}thiophen-2-yl)-2-(thiophen-2-yl)acrylonitrile (16a): Monoaldehyde **13b** (0.2 g, 0.47 mmol) and thien-2-ylacetonitrile (0.064 g, 0.52 mmol) were condensed in the presence of *t*BuOK (0.064 g, 0.57 mmol) as base in dry ethanol. The reaction mixture was stirred at room temperature for 12 h. The solid was filtered, and the crude solid was purified by column chromatography (hexane/EA, 90:10). Yield: 0.15 g (60%). M.p. 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.8 Hz, 1 H), 7.76 (d, *J* = 8.8 Hz, 1 H), 7.57–7.59 (m, 2 H), 7.56 (s, 1 H), 7.35 (d, *J* = 3.9 Hz, 2 H), 7.32 (d, *J* = 3.8 Hz, 1 H), 7.27 (d, *J* = 3.9 Hz, 1 H), 7.20–7.23 (m, 1 H), 7.11–7.13 (m, 1 H), 7.04–7.08 (m, 1 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 4.01 (t, *J* = 6.6 Hz, 2 H), 1.82 (quint, *J* = 6.9 Hz, 2 H), 1.34–1.51 (m, 6 H), 0.90 (t, *J* = 7.0 Hz, 3 H) ppm. MS (EI): *m*/*z* (%) = 525 (24) $[M]^+$. $C_{31}H_{27}NOS_3$ (525.13): calcd. C 70.82, H 5.18, N 2.66, S 18.30; found C 70.75, H 5.20, N 2.60, S 18.36.

3-{5-[3-(3,4-Dimethoxyphenyl)benzo[*c*]thiophen-1-yl]thiophen-2-yl}-2-(thiophen-2-yl)acrylonitrile (16b): The cyano derivative **16b** was obtained in 55% yield accoding to a procedure similar to that used for **16a**. M.p. 166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9.2 Hz, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.52 (d, *J* = 3.8 Hz, 1 H), 7.42 (s, 1 H), 7.04–7.33 (m, 8 H), 6.98 (d, *J* = 8.3 Hz, 1 H), 3.95 (s, 6 H) ppm. $C_{27}H_{19}NO_2S_3$ (485.06): calcd. C 66.78, H 3.94, N 2.88, S 19.81; found C 66.70, H 3.90, N 2.96, S 19.90.

3-{5-[3-(4-Methoxyphenyl)benzo[*c*]thiophen-1-yl]thiophen-2-yl}-2-(thiophen-2-yl)acrylonitrile (16c): The cyano derivative **16c** was obtained in 61% yield according to a procedure similar to that used for **16a**. M.p. 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 6.3 Hz, 1 H), 7.75 (d, *J* = 6.9 Hz, 1 H), 7.52–7.57 (m, 3 H), 7.43 (s, 1 H), 7.21–7.33 (m, 4 H), 7.05–7.10 (m, 4 H), 3.88 (s, 3 H) ppm. MS (EI): *m*/*z* (%) = 455 (19) $[M]^+$. $C_{26}H_{17}NOS_3$ (439.05): calcd. C 68.54, H 3.76, N 3.07, S 21.11; found C 68.42, H 3.66, N 3.00, S 21.20.

Supporting Information (see footnote on the first page of this article): Emission spectra of selected benzo[*c*]thiophenes (**2d**, **4a**, **9a**, **9d**, **13b**, and **14d**) and cyclic voltammograms of selected benzo[*c*]-thiophenes (**4a**, **5a**, **9c**, **9d**, **9m**, and **15c**).

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