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Convergent/Divergent Synthesis and Photophysical Studies of Alternating Benzene–Furan Oligoaryls from Substituted Propargylic Dithioacetals

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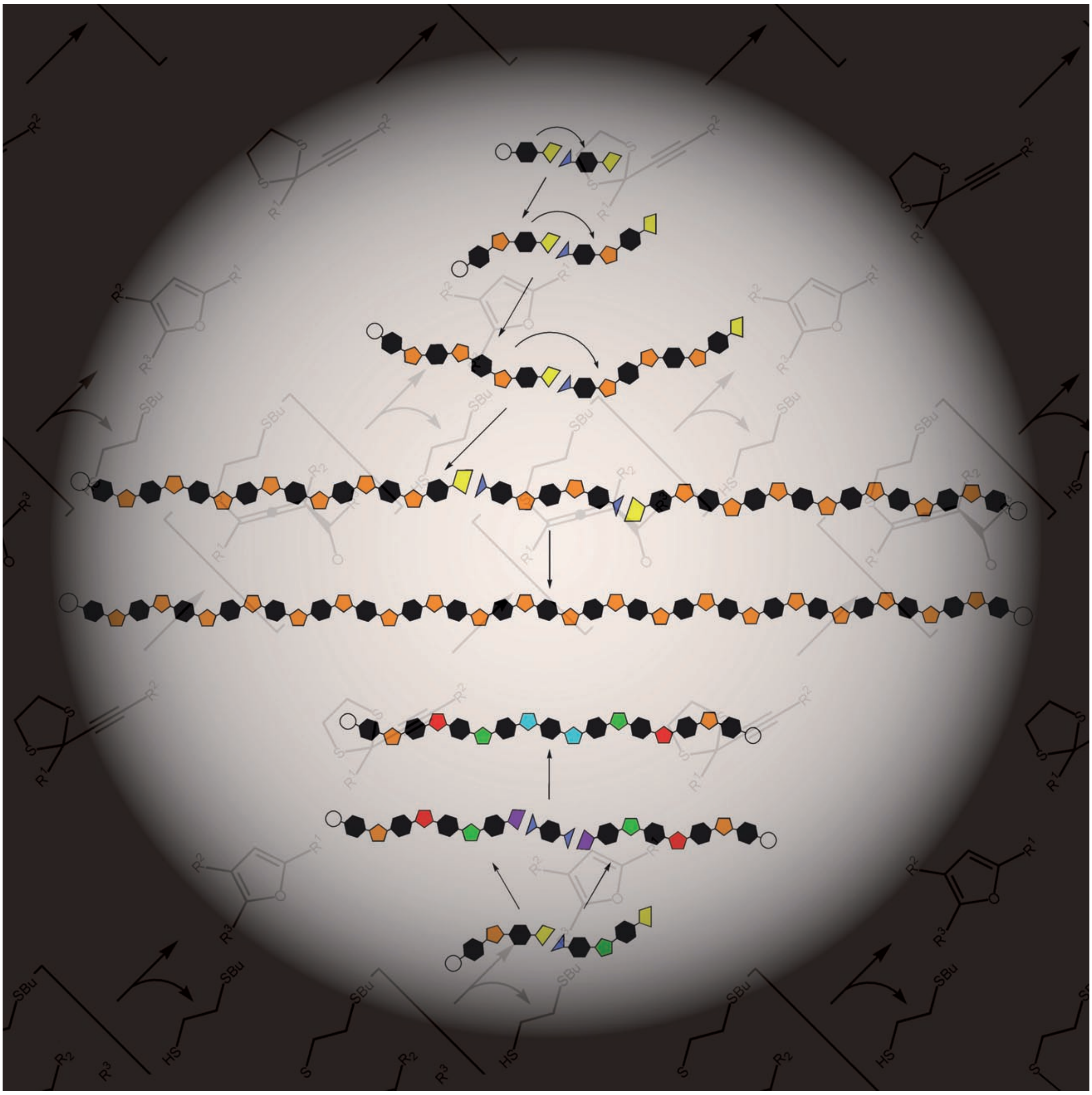
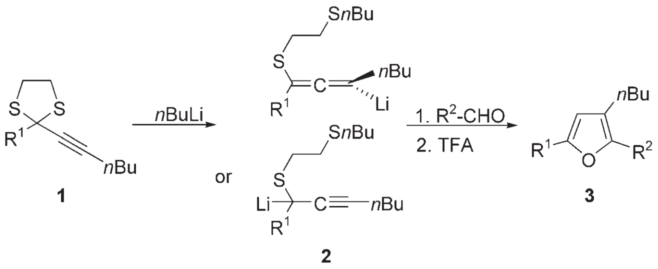


Abstract: A range of oligoaryls that contain alternating benzene–furan rings is synthesized by a rapid convergent/divergent method from the annulation of a propargylic dithioacetal and an aldehyde with a propargylic dithioacetal moiety as a substituent. These oligomers are fairly soluble in a range of organic solvents and can be easily purified by reprecipitation. The substituents on the furan rings can be varied according to the substituents in the starting propargylic dithioacetals. This route provides a useful procedure for the synthesis of alternating benzene–furan oligomers without repeated units. These furan-containing oligoaryls are highly fluorescent in the visible region and are electrochemically active. The band gaps of these oligomers appear to be less sensitive towards changes in conjugation length than those of oligofurans.

Keywords: annulation • band gaps • electrochemistry • fluorescence • oligomerization

Introduction

The incorporation of heteroaromatic rings into conjugated polymers is known to modify remarkably the photophysical and electronic properties of the polymers.[1] For example, polythiophenes[2] and polypyrroles[3] are extensively studied and widely used in optoelectronics. There is burgeoning interest in well-defined monodispersed oligomers of precise conjugation lengths as models for polymer analogues.[4] It is suggested that these nanoscale conjugated oligomers may fit nicely with the approximate size of present nanopattern probe gaps.[4] Various approaches are known in the synthesis of long conjugated oligoaryls. Coupling reactions and annulation protocols appear to be most commonly used in the construction of oligomer backbones. Oligothiophenes[5] and oligopyrroles[6] are conveniently synthesized by such methods. Relatively speaking, the corresponding furan analogues have only been sporadically explored.[7] Furan-containing conjugated polymers are photochemically labile in the presence of air (oxygen).[7a] Under inert atmosphere, however, furan rings in oligoaryls remain intact upon irradiation.[8] Indeed, alternating benzene–furan oligomers are used in electroluminescence as efficient hole-transporting materials with good charge mobility.[8] Furthermore, the bismercaptan derivatives of ter- and pentaaryls were shown to assemble on the gold (111) surface with significant π–π stacking.[9] By adopting an annulation protocol starting from the propargylic dithioacetal **1** and an aldehyde (Scheme 1),[10] oligomers **5** and/or **6** can be formed by bidirectional iterative synthesis from the corresponding dialdehyde and **4** (Scheme 2).[10b,c] However, each annulation in Scheme 2 can only introduce four aryl moieties, including two furan rings. A more expeditious protocol would be highly desirable to enable the rapid synthesis of higher homologues of furan-containing oligoaryls.



Scheme 1. Annulation protocol used as the basis for subsequent syntheses.

A range of functional groups, such as ester, ether linkage, trifluoromethyl, cyano, hydroxyl, and even aryl bromide, was shown to be stable under the annulation conditions in Scheme 1.[10] We therefore envisaged that an allenyl or propargylic lithium intermediate **7**, generated from **4**, might react with another molecule of aldehyde **8**, which contains a propargylic dithioacetal moiety, to give teraryl **9**. Notably, **9** thus produced may contain both a propargylic dithioacetal moiety and an ester group, and the latter may be converted into aldehyde **10** for further transformation. Accordingly, a similar combination of two teraryls **12** and **10** may furnish the corresponding heptamer **13** (Scheme 3).

The strategy shown in Scheme 3 would provide an efficient way to synthesize convergently a range of higher ho-

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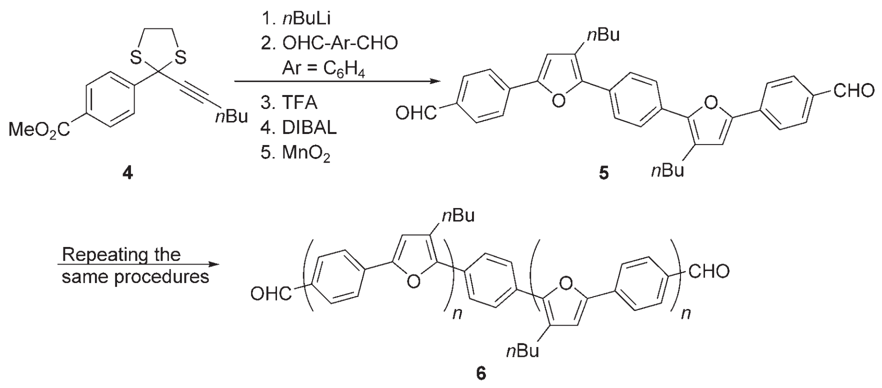
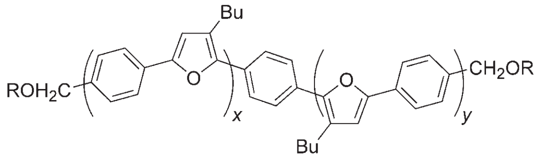


Scheme 2. Bidirectional iterative annulation of **4** to produce alternating benzene–furan oligoaryl **6**.

mologues of alternating benzene–furan oligoaryls in a selective manner. In this paper, we report a new iterative convergent/divergent[4b, 5c] synthesis of alternating benzene–furan oligoaryls **17** by a combination of the routes shown in Schemes 2 and 3. A preliminary investigation of the synthesis of monodispersed oligoaryls without repeated units is also presented. As these furan-containing oligoaryls are highly fluorescent,[8–10] the physical properties of these oligomers are systematically explored.

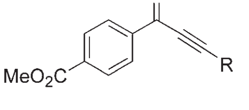


17a $x = 1, y = 0$, R = Me
17b $x = y = 1$, R = Me
17c $x = y = 3$, R = Me
17d $x = y = 4$, R = Me
17e $x = y = 9$, R = Me
17f $x = 1, y = 0$, R = H
17h $x = y = 1$, R = H
17g $x = y = 3$, R = H

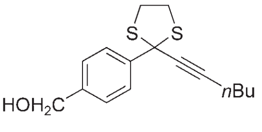
Results and Discussion

Synthesis

Propargylic dithioacetal **4** was obtained in 62% yield from the $BF_3 \cdot OEt$-promoted reaction of ynone **18a** with 1,2-ethanedithiol in methanol. The ester group in **4** was reduced by diisobutylaluminum hydride (DIBAL) to afford alcohol **19** in 97% yield. Oxidation of **19** with MnO_2 gave the corresponding aldehyde **8** in 92% yield. Sequential reaction of **4** with *n*BuLi, **8**, and trifluoroacetic acid (TFA) afforded the corresponding teraryl **9** in 56% overall yield. There are two interesting features in this reaction sequence. First, *n*-butyllithium reacted selectively with the sulfur moiety of the dithiolane functionality in **4** to give allenyl anion **7**, with the ester group remaining intact under the reaction conditions. Second, the allenyl or propargylic anion **7** reacted preferentially with the aldehyde group in **8** to give the corresponding annulation product **9**; the dithiolane group in **8** was stable under these conditions.



18a R = *n*Bu
18b R = *n*Hex



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Abstract in Chinese:

結合匯集法與分流法，利用炔丙基硫縮醛與有機鋰試劑反應，再與含炔丙基硫縮醛取代基之醛進行環化，可以迅速合成長鏈的苯環-呋喃環交替的共軛寡聚分子。利用這一策略，可以合成共軛寡聚分子不含重複基團，甚至可期合成單一分子量的高分子。本文也探討這些共軛寡聚分子的光物理和電化學性質。

Reduction of **9** with DIBAL gave **11**, which was then oxidized with MnO_2 to give **10** in 90% yield (two steps). Methylation of **11** with NaH and then MeI afforded the corresponding methyl ether **12** in 94% yield.

Attempts to annulate **9** with **10** under the conditions used for the synthesis of **9** gave the desired heptaaryl dithioacetal **14** in trace amounts. Interestingly, a significant amount of the ester group in **9** reacted with *n*BuLi under the reaction conditions. Presumably, an extension of conjugation would enhance the reactivity of the ester group toward *n*BuLi. Instead, treatment of **12** with *n*BuLi (1 equiv) followed by **10** and TFA afforded **13** in 73% yield. Oxidation of **13** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), however, gave the corresponding aldehyde **15** in very low yield (≈5%). Alternatively, treatment of **11** with *n*BuLi (2.2 equiv) followed by **10** and TFA in usual manner afforded **16** in 70% yield. Swern oxidation of **16** (dimethyl sulfox-

Editorial Board Member

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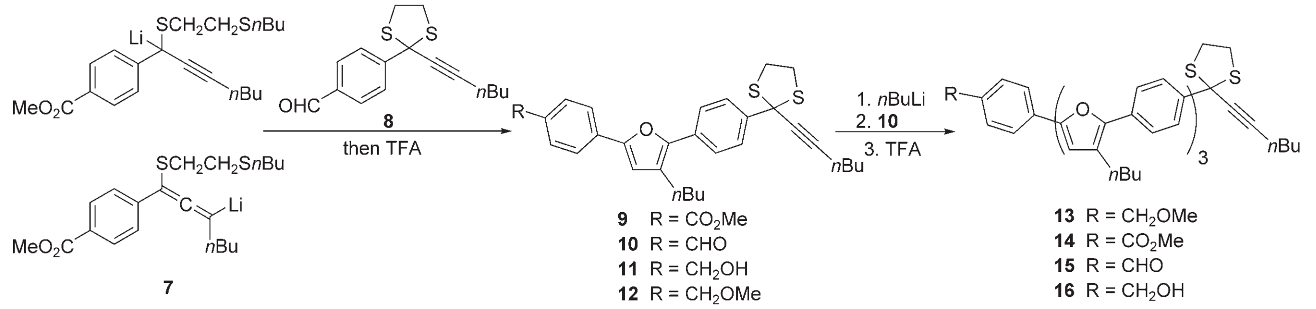
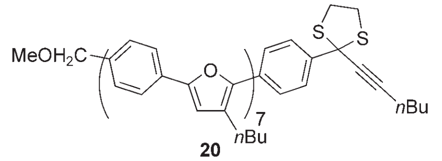


Scheme 3. Convergent synthesis of alternating benzene–furan heptamers from **7** and **8**.

ide (DMSO), Ac_2O) gave **15** in 78% yield. Further annulation of **13** with **15** under similar conditions produced the corresponding 15-mer dithioacetal **20** in 73% yield.



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This protocol apparently provided a rapid convergent synthesis of a range of well-defined monodispersed oligomers that contain alternating benzene–furan rings. Furthermore, the corresponding aldehyde functionality and propargylic dithioacetal groups were conveniently introduced by this reaction sequence.

The oligoaryl dithioacetals thus obtained were used for further annulations with a dialdehyde with the protocol described in Scheme 2. For example, reaction of **13** with *n*BuLi followed by terephthaldehyde ($^1/_2$ equiv) and the usual treatment afforded **17d** in 23% yield. Similarly, 37-mer **17e** was obtained in 77% yield from the annulation of **20** (2 equiv) with **5** under typical annulation conditions. As there are alkyl substituents on each of the furan rings, these oligomers are fairly soluble in organic solvents. Because the starting materials and the products have very different molecular weights, purification of the final products can be achieved easily by the typical reprecipitation commonly used in polymer chemistry.

As shown in Scheme 3, teraryl **9** is obtained from the reaction of propargylic dithioacetal **4**, which serves as the precursor of allenyl anion **7**, and another propargylic dithioacetal **8**, which has an electrophilic aldehyde group. We therefore envisaged that the substituents on the alkynyl carbons in **4** and **8** could be different, so that the substituent on C3 of the furan rings in **9** would be different from the substituent on the alkynyl carbon atom. By employing this strategy, synthesis of oligoaryls without repeated units would be feasible. We tested this hypothesis by synthesizing teraryls **24** and **26** (Scheme 4). Thus, reaction of the allenyl anion (like **7**, prepared from **21** and *n*BuLi) with **8** followed by treatment with TFA in the same manner as that described above afforded **24** in 53% yield. Similarly, reaction of **7** with **23** by the same method gave **26** in 50% yield.

Functional-group transformation of **24** afforded the corresponding aldehyde **28**. In a similar manner, **26** was converted into **29**, which was allowed to annulate with **28** to form heptaaryl **31** in 49% overall yield. Further reaction of **31** with terephthaldehyde in the usual manner afforded the corresponding 17-mer **33** in 45% yield. Dithioacetal **32** was obtained similarly in 68% yield from the annulation of **29** and **32**. Further annulation of **32** with **5** under similar conditions gave the 21-mer **34** in 66% yield. Notably, the substituents on the furan rings in **33** and **34** are different.

Photophysical and Electrochemical Investigations

Alternating benzene–furan oligoaryls showed strong absorption and emission in the visible region. Typical spectra for a series of symmetrical oligoaryls **17** and **34** are shown in

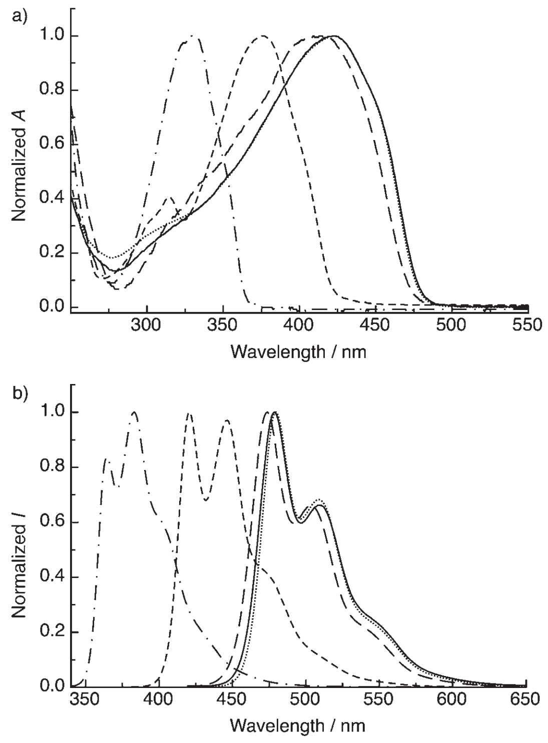
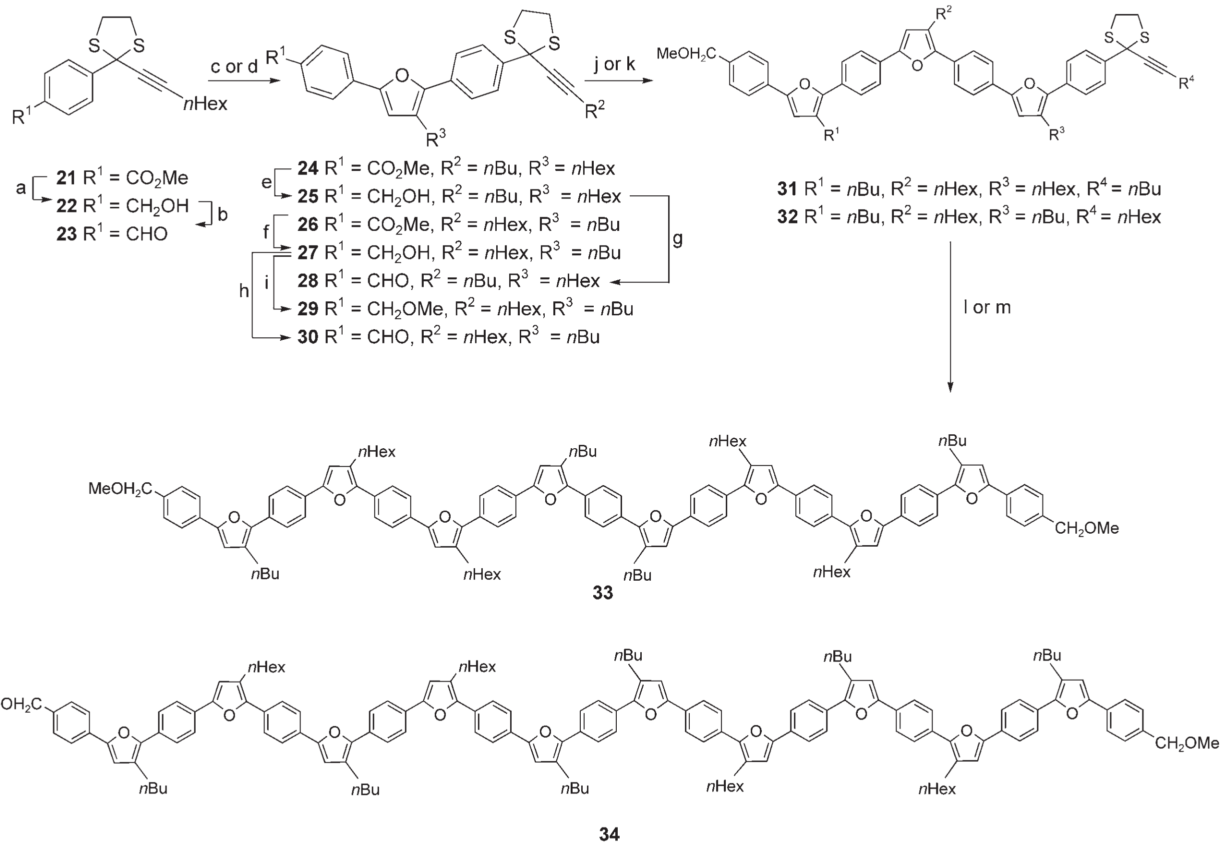


Figure 1. a) Absorption and b) emission spectra of **17a** (–•–•), **17b** (-----), **17c** (– – –), **34** (•••••) and **17e** (——) in THF.



Scheme 4. Formation of alternating benzene–furan oligomers with different substituent groups. a) DIBAL, 98 %; b) MnO_2, 92 %; c) 1) **21**, *n*BuLi, −78 °C, 2) **5**, 3) TFA; yield of **24** = 53 %; d) 1) **6**, 2) TFA; yield of **26** = 50 %; e) DIBAL; yield of **25** = 93 %; f) DIBAL; yield of **27** = 90 %; g) MnO_2; yield of **28** = 91 %; h) MnO_2; yield of **30** = 90 %; i) NaH/MeI; yield of **29** = 93 %; j) 1) **29**, *n*BuLi (1.1 equiv), 2) **28**, 3) TFA; yield of **31** = 49 %; k) 1) **29**, *n*BuLi (1.1 equiv), 2) **30**, 3) TFA; yield of **32** = 68 %; l) **31**, *n*BuLi (1.1 equiv), 2) terephthaldehyde, 3) TFA; yield of **33** = 45 %; m) **32**, *n*BuLi (1.1 equiv), 2) **5**, 3) TFA; yield of **34** = 66 %.

Table 1. Photophysical and electrochemical parameters of benzene–furan oligomers.[a]

	n[b]	λ_{max} [nm]	λ_{em} (Φ_f) [nm]	E_{0-0} [eV]	$E_p^{1/2}$[c] [mV]	HOMO [eV]	LUMO [eV]
17a	12	328	364, 383, 404 (0.88)	3.47	622	−5.36	−1.89
17b	20	376	420, 446, 475 (0.84)	3.02	441	−5.20	−2.18
17c	52	414	474, 503, 536 (0.33)	2.71	206	−4.98	−2.27
34	84	422	478, 509, 544 (0.29)	2.66	98	−4.87	−2.21
17e	148	423	479, 509, 544 (0.23)	2.66	−21	−4.74	−2.08

[a] Absorption and fluorescence spectra were acquired in THF. [b] Total number of carbon atoms along the conjugated oligoaryl chain. [c] The potentials reported are referenced to the ferrocene/ferrocenium couple.

Figure 1, and their photophysical data are outlined in Table 1. As expected, the absorption maxima showed bathochromic shift as the conjugation lengths increased. These oligoaryls are also highly fluorescent with high quantum yield. The absorption and emission reached saturation in **34** (21-mer) and little change was observed in higher homologues (Table 1). As shown in Figure 1 b, the relative intensities of the emission due to 0–0 transition increased with increasing chain lengths. Interestingly, the quantum yield decreased with increasing molecular weights of the oligomers.

The first oxidation parameters, $E_p^{1/2}$, of **17** and **34** measured by cyclic voltammetry are also listed in Table 1. Notably, the oxidation potential continually shifted to the less-positive end as the molecular weights of the oligomers increased, and there is a significant difference (119 mV) in $E_p^{1/2}$ between the 21-mer and 37-mer compounds. Similar behavior was also observed in alternating ethynylene–thiophene oligomers.[11]

The energies of the highest occupied and lowest unoccupied molecular orbitals (HOMOs and LOMOs, respectively) of the alternating benzene–furan oligoaryls were estimated based on the photophysical and electrochemical data in Table 1 and are shown there. Plots of the HOMO and LUMO energies and the band gaps of **17** and **34** against $1/n$, where n is the total number of carbon atoms in the conjugated oligoaryl chain, are shown in Figure 2, and compared with those of oligothiophenes **35**,[5] oligofurans **36**,[7] and oligoethynylenethiophenes **37** [11] calculated from literature data. Surprisingly, replacement of alternating furan moieties along oligofuran chains by benzene rings may not significantly perturb the frontier orbital energies of oligofurans when the conjugation length is short ($n < 24$). However,

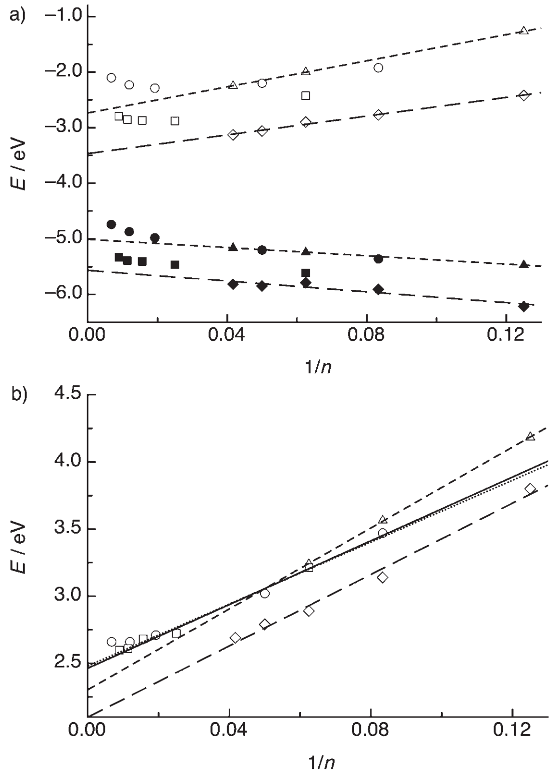
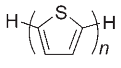


Figure 2. Plots of a) HOMO (solid) and LUMO (open) energies and b) of **17** and **34** (circle), **35** (diamond), **36** (triangle), and **37** (square) versus 1/*n*.



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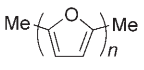

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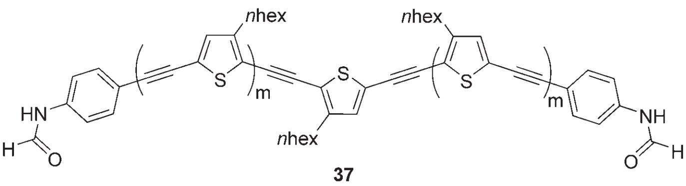

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when the conjugation length is increased, both the HOMO and LUMO energies of **17c–e** and **34** started to deviate from the linearly extrapolated values based on the smaller analogues of oligofurans.

Interestingly, the slope from the plot of the band gaps of **17** and **34** against 1/*n* was smaller than that from the plot of **36**. This observation indicates that the variation in band gap may be less sensitive towards the change in conjugation length. Similar results were also observed for **37**.[11]

Conclusions

In summary, we have demonstrated a rapid convergent/divergent approach for the synthesis of a range of oligoaryls that contain alternating benzene–furan rings. These oligomers are fairly soluble in a range of organic solvents, thus simplifying their purification. In particular, oligomers with relatively high molecular weights can be easily purified by reprecipitation. This advantage would allow convenient synthesis and isolation of the higher homologues. An extension towards the rapid synthesis of polymers with unity dispersity would therefore be feasible. Furthermore, since the syntheses involve stepwise procedures, the substituents on the furan rings can be varied depending on the substituents in the starting propargylic dithioacetals. This strategy would provide a promising route towards polymers without repeated units (Scheme 4). Since pyrrole derivatives can also be synthesized by this method,[10] incorporation of such nitrogen heterocycles could be possible.

These alternating benzene–furan oligoaryls are highly fluorescent in the visible region and electrochemically active. The band gaps of these oligomers appeared to be less sensitive towards changes in conjugation length than those of homo-oligomers such as **35** and **36**. Oligoethynylenethienylenes **37** behave similarly to the oligoaryls.[11] Our results indicate that insertion of benzene moieties into oligofurans may fine-tune the conjugated π-systems for further applications.

Experimental Section

Syntheses

4: $BF_3{\cdot}Et_2O$ (66.4 mL, 0.53 mol) and 1,2-ethanedithiol (37.8 mL, 0.45 mol) was added to a solution of **18a** (107.4 g, 0.44 mol) in MeOH (700 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 12 h. After quenching with NaOH (10 %, 400 mL), the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3×200 mL). The combined organic extracts were washed with NaOH (10 %, 5×300 mL) and brine (300 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane 1:9) to afford **4** as a pale yellow oil. The product was dissolved in pentane and cooled in the freezer, and pure **4** crystallized as colorless needles (87.4 g, 62 %). M.p.: 46–47 °C; IR (KBr): $\tilde{\nu}=2960$, 2934, 2870, 1726, 1610, 1437, 1408, 1280, 1193, 1111, 1021, 966, 869, 735, 496 cm^{-1}; ^1H NMR (400 MHz, CDCl3): $\delta=0.92$ (t, $^3J(H,H)=7.3$ Hz, 3 H), 1.43 (sext., $^3J(H,H)=7.3$ Hz, 2 H), 1.56 (tt, $^3J(H,H)=7.1$, 7.3 Hz, 2 H), 2.35 (t, $^3J(H,H)=7.1$ Hz, 2 H), 3.59–3.75 (m, 4 H), 3.89 (s, 3 H), 7.98 ppm (br s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.6$, 18.9, 22.0, 30.6, 41.4, 52.1, 61.7, 81.7, 88.7, 127.7, 129.4, 129.8, 145.1, 166.6 ppm; HRMS (EI): *m*/*z* calcd for $C_{17}H_{20}O_2S_2$: 320.0905; found: 320.0910; elemental analysis: calcd (%) for $C_{17}H_{20}O_2S_2$: C 63.72, H 6.29; found: C 63.68, H 5.89.

19: DIBAL (150.0 mL, 1.0 M in hexane, 150.0 mmol) was added slowly with stirring to a solution of **4** (10.7 g, 33.5 mmol) in THF (120 mL) at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 2 h at room temperature, then saturated NH_4Cl (150 mL) was poured in slowly to quench the reaction. The gel-like organic layer was then acidified with HCl (6 M, 200 mL) and extracted with Et_2O (3×200 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (2×150 mL) and brine (200 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo to afford crude **19** (9.4 g, 97 %). Kugelrohr distillation (0.01 torr, 170 °C) afforded a pure colorless oil. IR (KBr): $\tilde{\nu}=3354$, 2956, 2928, 2870, 1507, 1458, 1414, 1209, 1043, 1016, 852, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=0.92$ (t, $^3J(H,H)=7.2$ Hz, 3 H), 1.43 (sext., $^3J(H,H)=7.2$ Hz, 2 H), 1.55 (quint., $^3J(H,H)=7.2$ Hz, 2 H), 1.60–1.78 (br s, 1 H), 2.35 (t, $^3J(H,H)=7.2$ Hz, 2 H), 3.58–3.74 (m, 4 H), 4.67 (s, 2 H), 7.32 (d, $^3J(H,H)=8.4$ Hz, 2H), 7.92 ppm (d, ^3J(H,H) = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 18.9, 22.0, 30.7, 41.2, 62.0, 64.9, 82.2, 88.1, 126.6, 127.8, 139.0, 140.9 ppm; elemental analysis: calcd (%) for $C_{16}H_{20}OS_2$: C 65.71, H 6.89; found: C 65.33, H 6.63.

8: A solution of **19** (34.9 g, 0.12 mol) in CH_2Cl_2 (200 mL) was added slowly to a suspension of activated MnO_2 (104.3 g, 1.20 mol) in CH_2Cl_2 (200 mL) at room temperature. The reaction mixture was stirred for 6 h, then passed through a silica-gel bed (5 cm) and washed with EtOAc (5 × 300 mL). The combined filtrate was evaporated in vacuo to afford crude **8** as an orange oil. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane 1:3) to afford **8** (32.0 g, 92%) as a pale yellow oil. IR (KBr): $\tilde{\nu}$ = 2957, 2929, 2870, 2860, 2734, 1701, 1603, 1574, 1417, 1387, 1303, 1208, 1169, 1015, 814, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, ^3J(H,H) = 7.3 Hz, 3H), 1.45 (sext., ^3J(H,H) = 7.3 Hz, 2H), 1.56 (tt, ^3J(H,H) = 7.0, 7.3 Hz, 2H), 2.35 (t, ^3J(H,H) = 7.0 Hz, 2H), 3.62–3.74 (m, 4H), 7.83 and 8.09 (AA′XX′, ^3J(H,H) = 8.0, 0.4, 1.9, 1.9 Hz, 4H), 10.00 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 18.9, 22.1, 30.6, 41.6, 61.7, 81.5, 89.0, 128.3, 129.5, 135.9, 146.9, 191.6 ppm; HRMS (EI): m/z calcd for $C_{16}H_{18}OS_2$: 290.0799; found: 290.0792; elemental analysis: calcd (%) for $C_{16}H_{18}OS_2$: C 66.16, H 6.25; found: C 66.02, H 6.09.

9: Under argon, *n*BuLi (13.2 mL, 2.5 M in hexane, 33.0 mmol) was introduced dropwise to a solution of **4** (9.6 g, 30.0 mmol) in THF (200 mL) at −78 °C, and the mixture was stirred at −78 °C for 50 min. A solution of **8** (7.2 g, 25.0 mmol) in THF (40 mL) was added at −78 °C, and the mixture was stirred at −78 °C for 1 h, then gradually warmed to room temperature. After further stirring for 1 h, TFA (5.5 mL, 60.0 mmol) was added, and the mixture was stirred at room temperature overnight. The reaction was then quenched with saturated NH_4Cl (150 mL), and the organic layer was extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (2 × 100 mL) and brine (100 mL), then dried over $MgSO_4$, filtered, and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane 1:3) to give **9** (7.32 g, 56%) as a pale yellow solid. M.p.: 98–99 °C; IR (KBr): $\tilde{\nu}$ = 2954, 2929, 2869, 1720, 1609, 1503, 1434, 1278, 1177, 1108, 933, 856, 771, 718, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J(H,H) = 7.3 Hz, 3H), 0.95 (t, ^3J(H,H) = 7.3 Hz, 3H), 1.37–1.52 (m, 4H), 1.53–1.72 (m, 4H), 2.37 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.69 (t, ^3J(H,H) = 7.8 Hz, 2H), 3.62–3.77 (m, 4H), 3.91 (s, 3H), 6.78 (s, 1H), 7.65 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.74 (d, ^3J(H,H) = 8.2 Hz, 2H), 8.00 (d, ^3J(H,H) = 8.2 Hz, 2H), 8.04 ppm (d, ^3J(H,H) = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 13.9, 18.9, 22.1, 22.6, 25.7, 30.8, 32.1, 41.3, 52.0, 62.1, 82.2, 88.3, 111.5, 123.2, 124.9, 125.3, 128.0, 128.3, 130.1, 131.1, 134.7, 138.4, 148.8, 150.9, 166.8 ppm; HRMS (FAB$^+$): m/z calcd for $C_{31}H_{35}O_3S_2$: 519.2028 [M^++H]; found: 519.2027; elemental analysis: calcd (%) for $C_{31}H_{34}O_3S_2$: C 71.78, H 6.61; found: C 71.65, H 6.58.

11: As with the preparation of **19**, **9** (4.0 g, 7.7 mmol) was treated with DIBAL (23.0 mL, 1.0 M in hexane, 23.0 mmol) to afford **11** (3.6 g, 97%) as a pale yellow solid. M.p.: 60–61 °C; IR (KBr): $\tilde{\nu}$ = 3244, 2954, 2925, 2856, 1605, 1505, 1456, 1421, 1364, 1289, 1188, 1047, 1014, 933, 843, 808, 708 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J(H,H) = 7.2 Hz, 3H), 0.95 (t, ^3J(H,H) = 7.3 Hz, 3H), 1.37–1.53 (m, 4H), 1.53–1.72 (m, 4H), 1.76–1.90 (br s, 1H), 2.37 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.68 (t, ^3J(H,H) = 7.8 Hz, 2H), 3.62–3.76 (m, 4H), 4.68 (s, 2H), 6.64 (s, 1H), 7.36 (d, ^3J(H,H) = 8.1 Hz, 2H), 7.65 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.69 (d, ^3J(H,H) = 8.1 Hz, 2H), 7.99 ppm (d, ^3J(H,H) = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.0, 18.9, 22.1, 22.6, 25.8, 30.7, 32.1, 41.3, 62.1, 65.1, 82.2, 88.2, 109.3, 123.8, 124.6, 125.0, 127.3, 127.9, 130.1, 131.4, 137.7, 139.8, 147.5, 151.8 ppm; HRMS (FAB$^+$): m/z calcd for $C_{30}H_{35}O_2S_2$: 491.2078 [M^++H]; found: 491.2068; elemental analysis: calcd (%) for $C_{30}H_{34}O_2S_2$: C 73.43, H 6.98; found: C 73.42, H 6.62.

10: As with the preparation of **8**, **11** (3.7 g, 7.7 mmol) was treated with activated MnO_2 (6.7 g, 77.1 mmol) to afford **10** (3.5 g, 93%) as a fluorescent yellow solid. M.p.: 68–70 °C; IR (KBr): $\tilde{\nu}$ = 2954, 2928, 2860, 2689, 1601, 1503, 1481, 1400, 1305, 1217, 1169, 931, 832, 764, 708, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^3J(H,H) = 7.1 Hz, 3H), 0.96 (t, ^3J(H,H) = 7.1 Hz, 3H), 1.38–1.52 (m, 4H), 1.53–1.72 (m, 4H), 2.37 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.70 (t, ^3J(H,H) = 7.8 Hz, 2H), 3.63–3.76 (m, 4H), 6.83 (s, 1H), 7.66 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.82 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.87 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.01 (d, ^3J(H,H) = 8.2 Hz, 2H), 9.97 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 13.9, 18.9, 22.1, 22.6, 25.7, 30.8, 32.1, 41.3, 62.1, 82.2, 88.3, 112.4, 123.7, 125.1, 125.4, 128.0, 130.3, 131.0, 134.8, 136.0, 138.7, 149.4, 150.6, 191.4 ppm; HRMS (FAB$^+$): m/z calcd for $C_{30}H_{33}O_2S_2$: 489.1922 [M^++H]; found: 489.1920; elemental analysis: calcd (%) for $C_{30}H_{32}O_2S_2$: C 73.73, H 6.60; found: C 73.57, H 6.53.

12: A solution of **11** (1.6 g, 3.3 mmol) in THF (30 mL) was introduced into a suspension of NaH (60% dispersion in mineral oil, 0.20 g, 4.9 mmol prewashed with hexane) in THF (30 mL) at room temperature under N_2 atmosphere. After 1 h of stirring, MeI (0.4 mL, 6.6 mmol) was added, and the reaction was stirred for 3 h at room temperature. The reaction mixture was poured into saturated NH_4Cl (50 mL) and the organic layer was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo to afford the residue, which was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane 1:3) to afford **12** (1.5 g, 94%) as a light yellow solid. M.p.: 75–76 °C; IR (KBr): $\tilde{\nu}$ = 2954, 2922, 2855, 1604, 1504, 1487, 1456, 1376, 1199, 1103, 1060, 970, 933, 846, 811, 791, 763, 710, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, ^3J(H,H) = 7.3 Hz, 3H), 0.95 (t, ^3J(H,H) = 7.3 Hz, 3H), 1.37–1.53 (m, 4H), 1.53–1.72 (m, 4H), 2.37 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.68 (t, ^3J(H,H) = 7.8 Hz, 2H), 3.38 (s, 3H), 3.62–3.76 (m, 4H), 4.45 (s, 2H), 6.64 (s, 1H), 7.34 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.64 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.68 (d, ^3J(H,H) = 8.2 Hz, 2H), 7.98 ppm (d, ^3J(H,H) = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.0, 18.9, 22.1, 22.6, 25.8, 30.8, 32.1, 41.3, 58.1, 62.2, 74.5, 82.2, 88.2, 109.3, 123.7, 124.6, 125.1, 127.9, 128.1, 130.2, 131.5, 137.2, 137.8, 147.6, 151.9 ppm; HRMS (FAB$^+$): m/z calcd for $C_{31}H_{36}O_2S_2$: 504.2157 [M^+]; found: 504.2169; elemental analysis: calcd (%) for $C_{31}H_{36}O_2S_2$: C 73.77, H 7.19; found: C 73.48, H 7.09.

13: As with the preparation of **9**, **12** (504 mg, 1.0 mmol) was treated with *n*BuLi (0.5 mL, 2.5 M in hexane, 1.1 mmol), followed by **10** (391 mg, 0.8 mmol) and then TFA (0.3 mL, 3.3 mmol) to afford **13** as an orange yellow solid (658 mg, 73%). M.p.: 70–71 °C; IR (KBr): $\tilde{\nu}$ = 2954, 2927, 2857, 1666, 1601, 1503, 1465, 1378, 1185, 1101, 933, 839, 807, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, ^3J(H,H) = 7.3 Hz, 3H), 0.96 (t, ^3J(H,H) = 7.3 Hz, 3H), 0.97 (t, ^3J(H,H) = 7.3 Hz, 3H), 0.98 (t, ^3J(H,H) = 7.3 Hz, 3H), 1.38–1.54 (m, 8H), 1.54–1.64 (m, 2H), 1.65–1.78 (m, 6H), 2.38 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.64–2.80 (m, 6H), 3.40 (s, 3H), 3.63–3.76 (m, 4H), 4.46 (s, 2H), 6.66 (s, 1H), 6.68 (s, 1H), 6.69 (s, 1H), 7.36 (d, ^3J(H,H) = 8.1 Hz, 2H), 7.62–7.84 (m, 12H), 8.01 ppm (d, ^3J(H,H) = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.0, 18.9, 22.1, 22.6, 25.9, 26.0, 30.8, 32.1, 41.3, 58.1, 62.2, 74.5, 82.3, 88.2, 109.5, 109.7, 123.7, 123.8, 124.5, 124.7, 124.9, 125.1, 125.6, 127.9, 128.1, 128.9, 130.2, 130.5, 131.5, 137.2, 137.9, 147.7, 147.8, 147.9, 151.7, 151.8, 151.9 ppm; HRMS (FAB$^+$): m/z calcd for $C_{59}H_{65}O_4S_2$: 901.4324 [M^++H]; found: 901.4332; elemental analysis: calcd (%) for $C_{59}H_{64}O_4S_2$: C 78.63, H 7.16; found: C 78.33, H 6.99.

16: As with the preparation of **9**, **11** (2.4 g, 5.0 mmol) was treated with *n*BuLi (4.1 mL, 2.5 M in hexane, 10.2 mmol), followed by **10** (2.0 g, 4.2 mmol) and then TFA (1.35 mL, 15 mmol) to afford **16** as a yellow-orange solid (2.7 g, 70%). M.p.: 89–90 °C (Et_2O/pentane); IR (KBr): $\tilde{\nu}$ = 3391, 2955, 2928, 2869, 1610, 1503, 1465, 933, 840, 808, 758, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95–1.02 (m, 12H), 1.47–1.50 (m, 8H), 1.54–1.66 (m, 2H), 1.70–1.73 (m, 6H), 2.41 (t, ^3J(H,H) = 7.1 Hz, 2H), 2.73–2.75 (m, 6H), 3.71–3.75 (m, 4H), 4.71 (s, 2H), 6.68 (s, 1H), 6.70 (s, 1H), 6.71 (s, 1H), 7.39 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.68–7.80 (m, 12H), 8.02 ppm (d, ^3J(H,H) = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.0, 18.9, 22.1, 22.6, 25.8, 25.9, 30.8, 32.05, 32.09, 41.3, 62.2, 65.2, 82.2, 88.2, 109.5, 109.7, 123.8, 124.5, 124.7, 124.9, 125.1, 125.5, 127.4, 127.9, 128.9, 130.2, 130.39, 130.43, 131.5, 137.8, 139.8, 147.7, 147.8, 147.9, 151.71, 151.74, 151.9 ppm; HRMS (FAB$^+$): m/z calcd for $C_{58}H_{62}O_4S_2$: 886.4090 [M^+]; found: 886.4098.

15: A solution of **16** (786 mg, 0.89 mmol) in dry DMSO (40 mL) and acetic anhydride (5 mL) was allowed to stand for 3 days at room temperature and then carefully poured into saturated $NaHCO_3$ solution (200 mL). The mixture was stirred for 1 h and extracted with diethyl ether (3×100 mL). The combined organic extracts were washed with water (3×100 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated to afford **15** as a yellow-orange solid (615 mg, 78%). M.p.: 88–89 °C (Et_2O/pentane); IR (KBr): $\tilde{\nu}$ = 2955, 2928, 1697, 1650, 1602, 1504, 1464, 1427, 1164, 1125, 1091, 838 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95–1.01 (m, 12 H), 1.44–1.52 (m, 8 H), 1.58–1.64 (m, 2 H), 1.68–1.72 (m, 6 H), 2.40 (t, ^{3}J(H,H) = 7.1 Hz, 2 H), 2.70–2.77 (m, 6 H), 3.71–3.74 (m, 4 H), 6.71 (s, 1 H), 6.73 (s, 1 H), 6.87 (s, 1 H), 7.68 (d, ^{3}J(H,H) = 8.5 Hz, 2 H), 7.74–7.82 (m, 8 H), 7.86 (d, ^{3}J(H,H) = 8.2 Hz, 2 H), 7.91 (d, ^{3}J(H,H) = 8.2 Hz, 2 H), 8.02 (d, ^{3}J(H,H) = 8.5 Hz, 2 H), 10.00 ppm (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 13.96, 13.98, 18.9, 22.1, 22.6, 22.7, 25.7, 25.9, 26.0, 29.7, 30.8, 32.0,32.1, 41.3, 62.1, 82.2, 88.2, 109.6, 110.0, 112.4, 112.6, 123.7, 123.8, 124.7, 124.9, 125.0, 125.1, 125.6, 125.8, 127.9, 129.0, 129.5, 129.8, 130.3, 130.4, 131.5, 134.7, 136.0, 137.8, 147.7, 149.5, 150.4, 151.5, 151.8, 191.5 ppm; HRMS (FAB^{+}): m/z calcd for $C_{58}H_{60}O_4S_2$: 884.3937 [M^{+}]; found: 884.3933; elemental analysis: calcd (%) for $C_{58}H_{60}O_4S_2$: C 78.69, H 6.83; found: C 78.43, H 6.93.

20: As with the preparation of **9**, **13** (458 mg, 0.5 mmol) was treated with *n*BuLi (0.3 mL, 2.5 M in hexane, 0.7 mmol), followed by **15** (360 mg, 0.41 mmol) and then TFA (0.18 mL, 2.0 mmol) to afford **20** as an orange yellow solid (504 mg, 73%). M.p.: 131–133 °C; IR (KBr): $\tilde{\nu}$ = 2954, 2928, 2874, 2859, 1503, 933, 839 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92–1.05 (m, 24 H), 1.40–1.55 (m, 16 H), 1.55–1.66 (m, 2 H), 1.66–1.79 (m, 14 H), 2.40 (t, ^{3}J(H,H) = 7.2 Hz, 2 H), 2.70–2.85 (m, 14 H), 3.41 (s, 3 H), 3.67–3.80 (m, 4 H), 4.48 (s, 2 H), 6.65–6.78 (m, 7 H), 7.37 (d, ^{3}J(H,H) = 8.2 Hz, 2 H), 7.63–7.85 (m, 28 H), 8.01 ppm (d, ^{3}J(H,H) = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.0, 18.9, 22.1, 22.7, 25.9, 26.0, 30.8, 32.1, 41.3, 58.1, 62.2, 74.5, 82.2, 88.2, 109.5, 109.7, 123.7, 123.9, 124.5, 124.7, 124.9, 125.1, 125.6, 127.9, 128.1, 128.9, 130.2, 130.4, 131.5, 137.2, 137.8, 147.8, 147.9, 151.8 ppm; HRMS (FAB^{+}): m/z calcd for $C_{115}H_{120}O_8S_2$: 1692.8425 [M^{+}]; found: 1692.8451.

17a: As with the preparation of **12**, **17f**[9] (336 mg, 1.0 mmol) was treated with NaH (60% dispersion in mineral oil, 121 mg, 3.0 mmol) followed by MeI (0.25 mL, 4.0 mmol) to afford **17a** (335 mg, 92%) as a light yellow oil. IR (KBr): $\tilde{\nu}$ = 2927, 2858, 2821, 1616, 1509, 1492, 1456, 1380, 1192, 1100, 967, 934, 844, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, ^{3}J(H,H) = 7.3 Hz, 3 H), 1.43 (sext., ^{3}J(H,H) = 7.3 Hz, 2 H), 1.66 (tt, ^{3}J(H,H) = 7.3, 7.6 Hz, 2 H), 2.68 (t, ^{3}J(H,H) = 7.6 Hz, 2 H), 3.39 (s, 3 H), 3.40 (s, 3 H), 4.45 (s, 2 H), 4.48 (s, 2 H), 6.64 (s, 1 H), 7.34 (d, ^{3}J(H,H) = 8.3 Hz, 2 H), 7.38 (d, ^{3}J(H,H) = 8.3 Hz, 2 H), 7.66 (d, ^{3}J(H,H) = 8.3 Hz, 2 H), 7.68 ppm (d, ^{3}J(H,H) = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.6, 25.7, 32.1, 58.0, 58.1, 74.5, 109.2, 123.7, 124.1, 125.5, 128.0, 128.1, 130.3, 131.2, 136.7, 137.1, 147.8, 151.8 ppm; HRMS (EI): m/z calcd for $C_{24}H_{28}O_3$: 364.2038; found: 364.2030; elemental analysis: calcd (%) for $C_{24}H_{28}O_3$: C 79.09, H 7.74; found: C 79.03, H 7.53.

17b: As with the preparation of **12**, **17g**[9] (51.4 mg, 0.1 mmol) was treated with NaH (60% dispersion in mineral oil, 12.1 mg, 0.3 mmol) followed by MeI (0.025 mL, 0.4 mmol) to afford **17b** (48 mg, 90%) as a light yellow solid. M.p.: 125–126 °C; IR (KBr): $\tilde{\nu}$ = 2952, 2925, 2856, 2819, 1613, 1508, 1487, 1456, 1380, 1299, 1190, 1101, 1057, 933, 834, 811 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, ^{3}J(H,H) = 7.3 Hz, 6 H), 1.46 (sext., ^{3}J(H,H) = 7.3 Hz, 4 H), 1.69 (tt, ^{3}J(H,H) = 7.3, 7.8 Hz, 4 H), 2.73 (t, ^{3}J(H,H) = 7.8 Hz, 4 H), 3.39 (s, 6 H), 4.46 (s, 4 H), 6.67 (s, 2 H), 7.35 (d, ^{3}J(H,H) = 8.1 Hz, 4 H), 7.71 (d, ^{3}J(H,H) = 8.1 Hz, 4 H), 7.75 ppm (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.7, 25.9, 32.1, 58.1, 74.5, 109.4, 123.7, 124.5, 125.4, 128.1, 129.9, 130.2, 137.1, 147.7, 151.8 ppm; HRMS (EI): m/z calcd for $C_{38}H_{42}O_4$: 562.3083; found: 562.3080; elemental analysis: calcd (%) for $C_{38}H_{42}O_4$: C 81.10, H 7.52; found: C 80.95, H 7.46.

17c: As with the preparation of **12**, **17h**[10b] (133 mg, 0.1 mmol) was treated with NaH (60% dispersion in mineral oil, 12.1 mg, 0.3 mmol) followed by MeI (0.025 mL, 0.4 mmol) to afford **17c** (115 mg, 85%) as a light yellow solid. M.p.: 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95–1.01 (m, 18 H), 1.44–1.48 (m, 12 H), 1.62–1.74 (m, 12 H), 2.70–2.78 (t, 12 H), 3.39 (s, 6 H), 4.46 (s, 4 H), 6.66 (s, 2 H), 6.70 (s, 2 H), 6.72 (s, 2 H), 7.35 (d, ^{3}J(H,H) = 8.1 Hz, 4 H), 7.69–7.79 ppm (m, 24 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (d), 22.7 (d), 25.9 (d), 32.1 (d), 58.1, 74.5, 109.5, 109.7, 123.7, 123.8, 124.5, 124.7, 125.4, 125.5, 128.1, 128.9 (d), 129.9, 130.2, 130.4, 137.1, 147.7, 147.8, 151.7 ppm.

17d: Under an Ar atmosphere, *n*BuLi (0.21 mL, 2.5 M in hexane, 0.53 mmol) was added in one portion to a solution of **13** (446 mg, 0.49 mmol) in THF (100 mL) at −78 °C, and the mixture was stirred for 3 h. A solution of terephthaldehyde (26.8 mg, 0.20 mmol) in THF (10 mL) was then added slowly at the same temperature. The mixture was stirred for 30 min at −78 °C and allowed to warm to 0 °C slowly. Then TFA (0.30 mL, 3.3 mmol) was added at 0 °C, and the resulting solution was stirred at 30 °C overnight. The mixture was washed with saturated $NaHCO_3$ (3×100 mL), dried over $MgSO_4$, and concentrated. Further purification by silica-gel chromatography with hexane/ethyl acetate (10:1) afforded **17d** as an orange yellow solid (81 mg, 23%). M.p.: 109–110 °C; IR (KBr): $\tilde{\nu}$ = 2955, 2928, 2858, 1600, 1504, 1464, 1455, 1379, 1181, 1101, 933, 839, 808 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (m, 24 H), 1.50 (m, 16 H), 1.72 (m, 16 H), 2.75 (m, 16 H), 3.41 (s, 6 H), 4.48 (s, 4 H), 6.67 (s, 1 H), 6.71 (s, 1 H), 6.73 (s, 1 H), 6.74 (s, 1 H), 7.37 (d, ^{3}J(H,H) = 8.0 Hz, 4 H), 7.75 ppm (m, 32 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.7, 25.9, 26.0, 32.1, 58.1, 74.5, 109.5, 109.7, 123.7, 123.9, 124.5, 124.7, 125.5, 125.6, 128.1, 128.9, 130.0, 130.2, 130.4, 137.2, 147.7, 147.9, 151.8 ppm; HRMS (FAB^{+}): m/z calcd for $C_{122}H_{126}O_{10}$: 1750.9351 [M^{+}+H]; found: 1750.9352.

17e: Under Ar atmosphere, *n*BuLi (0.2 mL, 2.5 M in hexane, 0.5 mmol) was added in one portion to a solution of **20** (507 mg, 0.3 mmol) in THF (200 mL) at −65 °C, and the mixture was stirred for 90 min. A solution of **5** (53 mg, 0.1 mmol) in THF (10 mL) was then added slowly at the same temperature. The mixture was stirred for 1 h at −65 °C, and allowed to warm slowly to 0 °C. TFA (0.18 mL, 2.0 mmol) was then added at 0 °C, and the resulting solution was stirred at 30 °C overnight, washed with saturated $NaHCO_3$ (3×100 mL), dried over $MgSO_4$, and concentrated. The resulting residue was recrystallized from $CHCl_3$ to afford **17e** as an orange yellow solid (288 mg, 77%). M.p.: 181–182 °C; IR (KBr): $\tilde{\nu}$ = 2956, 2932, 2870, 2853, 1607, 1503, 1101, 932, 837, 759, 746, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–1.07 (m, 54 H), 1.42–1.60 (m, 36 H), 1.63–1.80 (m, 36 H), 2.70–2.85 (m, 36 H), 3.41 (s, 6 H), 4.47 (s, 4 H), 6.60–6.75 (m, 18 H), 7.36 (d, ^{3}J(H,H) = 7.9 Hz, 4 H), 7.68–7.84 ppm (m, 72 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.0, 22.7, 26.0, 32.0, 58.0, 74.4, 109.5, 109.6, 123.6, 123.7, 124.6, 125.5, 130.3, 137.1, 147.7, 147.8, 151.7 ppm; MS (MALDI-TOF): m/z calcd for $C_{262}H_{266}O_{20}$: 3734.9 [M^{+}+H]; found: 3735.7.

21: As with the preparation of **4**, **18b** (120.2 g, 0.44 mol) was treated with $BF_3{\cdot}Et_2O$ (66.4 mL, 0.53 mol) and 1,2-ethanedithiol (37.8 mL, 0.45 mol) to afford **21** as a white solid (62.8 g, 41%). M.p.: 75–77 °C; IR (KBr): $\tilde{\nu}$ = 2929, 2857, 1931, 1724, 1607, 1435, 1406, 1277, 1191, 1109, 1019, , 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^{3}J(H,H) = 6.8 Hz, 3 H), 1.30–1.32 (m, 4 H), 1.41–1.45 (m, 2 H), 1.55–1.60 (m, 2 H), 2.36 (t, ^{3}J(H,H) = 7.1 Hz, 2 H), 3.64–3.75 (m, 4 H), 3.92 (s, 3 H), 8.00 ppm (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.1, 22.5, 28.4, 28.5, 31.2, 41.4, 52.1, 61.7, 81.7, 88.7, 127.6, 129.3, 129.7, 145.0, 166.6 ppm; HRMS (FAB^{+}): m/z calcd for $C_{19}H_{25}O_2S_2$: 349.1296 [M^{+}+H]; found: 349.1290; elemental analysis: calcd (%) for $C_{19}H_{24}O_2S_2$: C 65.48, H 6.94; found: C 65.71, H 6.77.

22: As with the preparation of **19**, **21** (11.6 g, 33.5 mmol) was treated with DIBAL (150.0 mL, 1.0 M in hexane, 150 mmol) to afford **22** as colorless oil (10.5 g, 98%). IR (KBr): $\tilde{\nu}$ = 3399, 2954, 2927, 2856, 1902, 1660, 1535, 1503, 1459, 1413, 1372, 1213, 1044, 1016, 812, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^{3}J(H,H) = 6.8 Hz, 3 H), 1.30–1.33 (m, 4 H), 1.41–1.45 (m, 2 H), 1.57–1.60 (m, 2 H), 1.65 (t, ^{3}J(H,H) = 6.0 Hz, 1 H), 2.36 (t, ^{3}J(H,H) = 7.1 Hz, 2 H), 3.65–3.73 (m, 4 H), 4.69 (d, ^{3}J(H,H) = 6.0 Hz, 2 H), 7.33 (d, ^{3}J(H,H) = 8.3 Hz, 2 H), 7.94 ppm (d, ^{3}J(H,H) = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.2, 22.6, 28.6, 31.3, 41.2, 62.0, 65.0, 82.3, 88.2, 126.7, 127.9, 139.0, 140.9 ppm; HRMS (FAB^{+}): m/z calcd for $C_{18}H_{25}OS_2$: 321.1347 [M^{+}+H]; found: 321.1352.

23: As with the preparation of **8**, **22** (38.4 g, 0.12 mol) was treated with activated MnO_2 (104.3 g, 1.20 mol) to afford **23** as a pale yellow oil (35.1 g, 92%). IR (KBr): $\tilde{\nu}$ = 2961, 2927, 2856, 2732, 1702, 1603, 1574, 1463, 1416, 1389, 1301, 1208, 1168, 1017, 813, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, ^{3}J(H,H) = 7.0 Hz, 3 H), 1.29–1.32 (m, 4 H), 1.39–1.52 (m, 2 H), 1.56–1.60 (m, 2 H), 2.36 (t, ^{3}J(H,H) = 7.0 Hz, 2 H), 3.66–3.74 (m, 4 H), 7.83 (d, ^{3}J(H,H) = 8.4 Hz, 2 H), 8.10 (d, ^{3}J(H,H) =

8.3 Hz, 2H), 10.00 ppm (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 19.1, 22.5, 28.4, 28.6, 31.1, 41.5, 61.7, 81.5, 89.0, 128.3, 129.4, 135.9, 146.8, 191.6 ppm; HRMS (FAB$^+$): m/z calcd for $C_{16}H_{23}OS_2$: 319.1190 [M^++H]; found: 319.1183.

24: As with the preparation of **9, 21** (10.4 g, 30.0 mmol) was treated with *n*BuLi (13.2 mL, 2.5 M in hexane, 33.0 mmol), followed by **8** (7.2 g, 25.0 mmol) and then TFA (5.5 mL, 60.0 mmol) to afford **24** (7.2 g, 53 %) as a pale yellow solid. M.p.: 72–73 °C; IR (KBr): $\tilde{\nu}=2959$, 2932, 2846, 1722, 1611, 1434, 1282, 1110, 670.21 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.90$ (t, ^{3}J(H,H)=6.8 Hz, 3H), 0.95 (t, ^{3}J(H,H)=7.3 Hz, 3H), 1.33–1.34 (m, 4H), 1.40–1.48 (m, 4H), 1.57–1.68 (m, 4H), 2.39 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.70 (t, ^{3}J(H,H)=7.7 Hz, 2H), 3.68–3.75 (m, 4H), 3.93 (s, 3H), 6.80 (s, 1H), 7.66 (d, ^{3}J(H,H)=8.4 Hz, 2H), 7.75 (d, ^{3}J(H,H)=8.3 Hz, 2H), 8.01 (d, ^{3}J(H,H)=8.4 Hz, 2H), 8.05 ppm (d, ^{3}J(H,H)=8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=13.6$, 14.1, 18.9, 22.1, 22.6, 26.0, 29.2, 29.9, 30.7, 31.7, 41.3, 52.0, 62.1, 82.1, 88.3, 111.5, 123.2, 125.0, 125.3, 128.0, 128.3, 130.1, 131.1, 134.7, 138.4, 148.7, 150.9, 166.8 ppm; HRMS (FAB$^+$): m/z calcd for $C_{33}H_{39}O_3S_2$: 547.2341 [M^++H]; found: 547.2332.

25: As with the preparation of **19**, **24** (4.2 g, 7.7 mmol) was treated with DIBAL (23.0 mL, 1.0 M in hexane, 23.0 mmol) to afford **25** (3.7 g, 92 %) as a pale yellow solid. M.p.: 72–73 °C; IR (KBr): $\tilde{\nu}=3371$, 2959, 2927, 2861, 1613, 1502, 1460, 1424, 1010, 851, 804 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.91$ (t, ^{3}J(H,H)=7.3 Hz, 3H), 0.95 (t, ^{3}J(H,H)=7.3 Hz, 3H), 1.32–1.34 (m, 4H), 1.43–1.50 (m, 4H), 1.56–1.70 (m, 4H), 2.39 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.70 (t, ^{3}J(H,H)=7.8 Hz, 2H), 3.69–3.75 (m, 4H), 4.71 (d, ^{3}J(H,H)=5.0 Hz, 2H), 6.64 (s, 1H), 7.39 (d, ^{3}J(H,H)=7.8 Hz, 2H), 7.65 (d, ^{3}J(H,H)=8.2 Hz, 2H), 7.71 (d, ^{3}J(H,H)=8.0 Hz, 2H), 7.99 ppm (d, ^{3}J(H,H)=8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=13.6$, 14.0, 18.9, 22.1, 22.6, 26.1, 29.2, 29.9, 30.7, 31.7, 41.3, 62.1, 65.2, 82.2, 88.2, 109.3, 123.8, 124.7, 125.1, 127.4, 127.9, 130.2, 131.4, 137.7, 139.8, 147.5, 151.8 ppm; HRMS (FAB$^+$): m/z calcd for $C_{32}H_{39}O_2S_2$: 519.2391 [M^++H]; found: 519.2386.

26: As with the preparation of **9, 4** (9.61 g, 30.0 mmol) was treated with *n*BuLi (13.2 mL, 2.5 M in hexane, 33.0 mmol), followed by **23** (7.9 g, 25.0 mmol) and then TFA (5.5 mL, 60.0 mmol) to afford **26** (6.8 g, 50 %) as a pale yellow solid. M.p.: 63–64 °C; IR (KBr): $\tilde{\nu}=2955$, 2928, 2857, 2734, 1698, 1604, 1308, 1213, 1166, 937, 832, 765, 712 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.92$ (t, ^{3}J(H,H)=6.8 Hz, 3H), 0.97 (t, ^{3}J(H,H)=7.3 Hz, 3H), 1.32–1.35 (m, 4H), 1.42–1.48 (m, 4H), 1.59–1.68 (m, 4H), 2.37 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.71 (t, ^{3}J(H,H)=7.8 Hz, 2H), 3.70–3.74 (m, 4H), 3.93 (s, 3H), 6.80 (s, 1H), 7.75 (d, ^{3}J(H,H)=8.4 Hz, 2H), 7.85 (d, ^{3}J(H,H)=8.5 Hz, 2H), 8.02 (d, ^{3}J(H,H)=8.5 Hz, 2H), 8.05 ppm (d, ^{3}J(H,H)=8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=13.9$, 14.0, 19.2, 22.5, 22.6, 25.7, 28.6, 31.3, 32.0, 41.3, 52.0, 62.0, 82.1, 88.3, 111.5, 123.2, 124.9, 125.2, 128.0, 128.3, 130.1, 131.1, 134.6, 138.3, 148.7, 150.9, 166.8 ppm; HRMS (FAB$^+$): calcd for $C_{33}H_{38}O_3S_2$): 547.2338 [M^++H]; found: 547.2341; elemental analysis: calcd (%) for $C_{33}H_{38}O_3S_2$: C 72.49, H 7.00; found: C 72.58, H 6.94.

27: As with the preparation of **19**, **26** (4.2 g, 7.7 mmol) was treated with DIBAL (23.0 mL, 1.0 M in hexane, 23.0 mmol) to afford **27** (3.6 g, 90 %) as a pale yellow oil. IR (KBr): $\tilde{\nu}=3450$, 2954, 2927, 2857, 1912, 1603, 1504, 1464, 1422, 1378, 1185, 1050, 1015, 934, 844, 808 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.91$ (t, ^{3}J(H,H)=6.7 Hz, 3H), 0.97 (t, ^{3}J(H,H)=7.3 Hz, 3H), 1.32–1.34 (m, 4H), 1.44–1.48 (m, 4H), 1.59–1.70 (m, 4H), 2.38 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.70 (t, ^{3}J(H,H)=7.7 Hz, 2H), 3.70–3.75 (m, 4H), 4.72 (s, 2H), 6.66 (s, 1H), 7.39 (d, ^{3}J(H,H)=8.1 Hz, 2H), 7.66 (d, ^{3}J(H,H)=8.5 Hz, 2H), 7.71 (d, ^{3}J(H,H)=8.1 Hz, 2H), 8.01 ppm (d, ^{3}J(H,H)=8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 19.2, 22.6, 25.8, 28.6, 31.3, 32.1, 41.3, 62.1, 65.2, 82.2, 88.3, 109.4, 123.9, 124.6, 125.1, 127.4, 127.9, 130.2, 131.5, 137.8, 139.8, 147.6, 151.8 ppm; HRMS (FAB$^+$): m/z calcd for $C_{32}H_{39}O_2S_2$: 519.2391 [M^++H]; found: 519.2386.

28: As with the preparation of **8**, **25** (3.9 g, 7.7 mmol) was treated with activated MnO$_2$ (6.7 g, 77.1 mmol) to afford **28** (3.6 g, 91 %) as a fluorescent yellow solid. M.p.: 42–43 °C; IR (KBr): $\tilde{\nu}=2959$, 2932, 2860, 1700, 1606, 1429, 1415, 1168, 834 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.88$–0.92 (t, ^{3}J(H,H)=7.1 Hz, 3H), 0.96 (t, ^{3}J(H,H)=7.1 Hz, 3H), 1.38–1.52 (m, 4H), 1.53–1.72 (m, 4H), 2.37 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.70 (t, ^{3}J(H,H)=7.8 Hz, 2H), 3.63–3.76 (m, 4H), 6.83 (s, 1H), 7.66 (d, ^{3}J(H,H)=8.2 Hz, 2H), 7.82 (d, ^{3}J(H,H)=8.4 Hz, 2H), 7.87 (d, ^{3}J(H,H)=8.4 Hz, 2H), 8.01 (d, ^{3}J(H,H)=8.2 Hz, 2H), 9.97 ppm (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=13.6$, 14.1, 18.9, 22.5, 26.1, 29.2, 29.9, 30.7, 31.7, 41.3, 62.0, 82.1, 88.3, 112.4, 123.7, 125.2, 125.3, 128.0, 130.4, 130.9, 134.7, 136.0, 138.5, 149.3, 150.6, 191.5 ppm; HRMS (FAB$^+$): m/z calcd for $C_{32}H_{37}O_2S_2$: 517.2235 [M^++H]; found: 517.2227.

29: As with the preparation of **12**, **27** (1.7 g, 3.2 mmol) was treated with NaH (60 % dispersion in mineral oil, 0.2 g, 4.9 mmol) followed by MeI (0.4 mL, 6.5 mmol) to afford **29** (1.6 g, 92 %) as a light yellow solid. M.p.: 57–58 °C; IR (KBr): $\tilde{\nu}=2955$, 2928, 2857, 2230, 1906, 1597, 1505, 1490, 1465, 1379, 1186, 1101, 930, 847, 808, 709 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.92$ (t, ^{3}J(H,H)=6.9 Hz, 3H), 0.98 (t, ^{3}J(H,H)=7.3 Hz, 3H), 1.34–1.35 (m, 4H), 1.45–1.48 (m, 4H), 1.60–1.68 (m, 4H), 2.39 (t, ^{3}J(H,H)=7.0 Hz, 2H), 2.71 (t, ^{3}J(H,H)=7.9 Hz, 2H), 3.41 (s, 3H), 3.70–3.75 (m, 4H), 4.48 (s, 2H), 6.66 (s, 1H), 7.36 (d, ^{3}J(H,H)=8.2 Hz, 2H), 7.66 (d, ^{3}J(H,H)=8.6 Hz, 2H), 7.70 (d, ^{3}J(H,H)=8.2 Hz, 2H), 8.01 ppm (d, ^{3}J(H,H)=8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 19.2, 22.6, 25.8, 28.6, 31.3, 32.1, 41.2, 58.0, 62.1, 74.4, 82.2, 88.2, 109.3, 123.7, 124.6, 125.0, 127.9, 128.1, 130.1, 131.5, 137.2, 137.8, 147.5, 151.9 ppm; HRMS (FAB$^+$): m/z calcd for$C_{33}H_{41}O_2S_2$: 533.2548 [M^++H]; found: 533.2554; elemental analysis: calcd (%) for $C_{33}H_{40}O_2S_2$: C 74.39, H 7.57; found: C 74.47, H 7.69.

30: As with the preparation of **8, 27** (2.0 g, 3.9 mmol) was treated with activated MnO$_2$ (3.0 g, 34.5 mmol) to afford **30** as a fluorescent yellow solid (1.8 g, 90 %). M.p.: 62–64 °C; IR (KBr): $\tilde{\nu}=2953$, 2927, 2851, 1698, 1603, 1433, 1213, 1165, 833 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.91$ (t, ^{3}J(H,H)=6.9 Hz, 3H), 0.96 (t, ^{3}J(H,H)=7.3 Hz, 3H), 1.34 (m, 4H), 1.47 (m, 4H), 1.61 (m, 2H), 1.68 (m, 2H), 2.39 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.72 (t, ^{3}J(H,H)=7.9 Hz, 2H), 3.72 (m, 4H), 6.86 (s, 1H), 7.68 (d, ^{3}J(H,H)=8.6 Hz, 2H), 7.84 (d, ^{3}J(H,H)=8.2 Hz, 2H), 7.90 (d, ^{3}J(H,H)=8.2 Hz, 2H), 8.03 (d, ^{3}J(H,H)=8.6 Hz, 2H), 9.99 ppm (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$ (d), 19.2, 22.6 (d), 25.7, 28.6 (d), 31.3, 32.1, 41.3, 62.1, 82.2, 88.4, 112.4, 123.7, 125.1, 125.4, 128.0, 130.4, 131.0, 134.7, 136.0, 138.6, 149.3, 150.6, 191.5 ppm; HRMS (FAB$^+$): m/z calcd for $C_{32}H_{37}O_2S_2$: 517.2235 [M^++H]; found: 517.2227; elemental analysis: calcd (%) for $C_{32}H_{36}O_2S_2$: C 74.38, H 7.02; found: C 74.73, H 7.05.

31: As with the preparation of **9, 29** (532 mg, 1.00 mmol) was treated with *n*BuLi (0.44 mL, 2.5 M in hexane, 1.1 mmol), followed by **28** (413 mg, 0.80 mmol) and then TFA (0.30 mL, 3.3 mmol) to afford **31** as an orange yellow solid (376 mg, 49.2 %). M.p.: 63–64 °C; IR (KBr): $\tilde{\nu}=2959$, 2933, 2861, 2361, 1560, 1543, 1508 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.85$–1.03 (m, 12H), 1.30–1.38 (m, 8H), 1.45–1.54 (m, 8H), 1.59–1.79 (m, 8H), 2.40 (t, ^{3}J(H,H)=7.2 Hz, 2H), 2.69–2.82 (m, 6H), 3.41 (s, 3H), 3.65–3.80 (m, 4H), 4.49 (s, 2H), 6.68 (s, 1H), 6.71 (s, 1H), 6.73 (s, 1H), 7.37 (d, ^{3}J(H,H)=7.9 Hz, 2H), 7.67–7.84 (m, 12H), 8.02 ppm (d, ^{3}J(H,H)=8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$, 14.1, 19.3, 22.6, 22.7, 25.9, 26.0, 26.3, 28.6, 28.7, 29.3, 29.9, 30.9, 31.3, 31.8, 32.1, 32.2, 41.3, 58.1, 62.2, 74.5, 82.3, 88.3, 109.5, 109.7, 123.7, 123.8, 124.5, 124.8, 124.9, 125.1, 125.6, 127.9, 128.1, 128.9, 130.2, 130.4, 131.5, 137.2, 137.8, 147.6, 147.7, 147.8, 151.7, 151.8, 151.9 ppm; HRMS (FAB$^+$): m/z calcd for $C_{63}H_{72}O_4S_2$: 956.4872 [M^+]; found: 956.4874.

32: As with the preparation of **9, 29** (532 mg, 1 mmol) was treated with BuLi (0.44 mL, 2.5 M in hexane, 1.1 mmol), followed by **30** (413 mg, 0.80 mmol) and then TFA (0.30 mL, 3.3 mmol) to afford **32** as an orange yellow solid (522 mg, 68 %). M.p.: 107–109 °C; IR (KBr): $\tilde{\nu}=2955$, 2928, 2857, 1906, 1660, 1601, 1504, 1465, 1380, 1192, 1102, 930, 840, 809 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.92$ (t, ^{3}J(H,H)=6.0 Hz, 6H), 0.99 (t, ^{3}J(H,H)=7.4 Hz, 6H), 1.35 (m, 8H), 1.45 (m, 8H), 1.60 (m, 2H), 1.72 (m, 6H), 2.39 (t, ^{3}J(H,H)=7.1 Hz, 2H), 2.75 (m, 6H), 3.41 (s, 3H), 3.72 (m, 4H), 4.48 (s, 2H), 6.68 (s, 1H), 6.70 (s, 2H), 6.71 (ds, 2H), 7.37 (d, ^{3}J(H,H)=8.2 Hz, 2H), 7.68–7.81 (m, 12H), 8.02 ppm (d, ^{3}J(H,H)=8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$ (d), 14.1, 19.2, 22.6 (d), 25.9 (d), 26.3, 28.6 (d), 29.3, 29.9, 31.3, 31.7, 32.1 (d), 41.3, 58.1, 62.2, 74.5, 82.3, 88.3, 109.5, 109.6, 123.7, 123.8, 124.5, 124.7, 124.8, 125.0, 125.5, 127.9, 128.1, 128.9, 130.2, 130.4, 131.5, 137.1, 137.8, 147.7 (d), 147.8, 151.7, 151.8, 151.9 ppm; HRMS (FAB$^+$): m/z calcd for $C_{563}H_{72}O_4S_2$: 956.4872

[M^++H]; found: 956.4863; elemental analysis: calcd (%) for $C_{59}H_{64}O_4S_2$: C 79.04, H 7.58; found: C 78.50, H 7.55.

33: As with the preparation of **9, 31** (287 mg, 0.30 mmol) was treated with *n*BuLi (0.20 mL, 2.5 M in hexane, 0.5 mmol), followed by terephthaldehyde (13.4 mg, 0.10 mmol) and then TFA (0.18 mL, 2.0 mmol) to afford **33** as an orange yellow solid (84 mg, 45%). M.p.: 80–81 °C; IR (KBr): $\tilde{\nu}$ = 2966, 2933, 2860, 1603, 1514, 934, 840, 811 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92–1.04 (m, 24 H), 1.28–1.40 (m, 16 H), 1.40–1.54 (m, 16 H), 1.67–1.82 (m, 16 H), 2.63–2.83 (m, 16 H), 3.41 (s, 6 H), 4.48 (s, 4 H), 6.68–6.74 (m, 8 H), 7.37 (d, ^3J(H,H) = 8.1 Hz, 4 H), 7.71–7.87 ppm (m, 32 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 14.0, 22.0, 22.7, 26.0, 26.3, 29.3, 29.9, 31.8, 32.1, 58.1, 74.5, 109.5, 109.7, 123.7, 123.9, 124.5, 124.8., 125.1, 125.6, 128.2, 128.9, 130.0, 130.2, 130.4, 137.1, 147.7, 147.9, 151.8 ppm; HRMS (FAB$^+$): *m*/*z* calcd for $C_{130}H_{142}O_{10}$: 1863.0603 [M^+]; found: 1863.0618.

34: As with the preparation of **9**, **32** (547 mg, 0.57 mmol) was treated with *n*BuLi (0.25 mL, 2.5 M in hexane, 0.63 mmol), followed by **5** (106 mg, 0.20 mmol) and then TFA (0.18 mL, 2.0 mmol) to afford **34** as an orange yellow solid (300 mg, 66%). M.p.: 165–166 °C; IR (KBr): $\tilde{\nu}$ = 2956, 2929, 2870, 1660, 1600, 1503, 1465, 1415, 1379, 1262, 1217, 1180, 1101, 933, 839, 809, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (m, 12 H), 1.00 (m, 18 H), 1.37 (m, 16 H), 1.47 (m, 20 H), 1.72 (m, 20 H), 2.75 (m, 20 H), 2.75 (m, 6 H), 3.41 (s, 6 H), 4.48 (s, 4 H), 6.70 (m, 10 H), 6.70 (s, 1 H), 6.71 (s, 1 H), 7.37 (d, ^3J(H,H) = 8.2 Hz, 2 H), 7.68–7.81 (m, 12 H), 8.02 ppm (d, ^3J(H,H) = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.7, 26.0 (d), 26.3, 29.3, 29.9, 31.7, 32.1 (d), 58.1, 74.5, 109.5, 109.7, 123.7, 123.8, 124.5, 124.7 (d), 125.4, 125.5, 128.1, 128.9, 129.9, 130.2, 130.4, 137.1, 147.7, 147.8, 151.8 ppm; HRMS (FAB$^+$): *m*/*z* calcd for $C_{158}H_{170}O_{12}$: 2259.2692 [M^++H]; found: 2259.2637.

Electrochemical Measurements

A conventional three-electrode system with a potentiostat/galvanostat (EG&G PAR 273 A) was employed for electrochemical experiments. The working electrode is a Pt disc with a diameter of 3 mm, the reference electrode is Ag/Ag$^+$ (10 mM $AgNO_3$), and a Pt wire was used as the counter electrode. Samples were dissolved in CH_2Cl_2 containing tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte, and the solutions were purged with Ar for at least 15 min before electrochemical experiments.

Photophysical Measurements

Absorption and emission spectra were measured with a Hitachi U-3310 spectrometer and a Hitachi F-4500 fluorescence spectrometer, respectively. Spectrometric-grade solvents and quartz cells (1×1 cm^2) were used. The molar concentration of the sample solution was about 10^{-5} M. The fluorescence quantum yields were obtained by using the Parker–Reas method.[12] The quantum yield of the oligomers was calculated by Equation (1), in which Φ is the quantum yield, I is the integrated intensity, A is the absorbance at the excitation wavelength, and n is the refractive index. The subscripts f and ref refer to the oligomers and coumarin 1 (Φ_{ref} = 0.99 in EtOAc), respectively.

$$\Phi_{\text{f}} = \Phi_{\text{ref}} \times (I_{\text{f}}/I_{\text{ref}}) \times (A_{\text{ref}}/A_{\text{f}}) \times (n_{\text{f}}/n_{\text{ref}})^2 \qquad (1)$$

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