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Alternating furanylene-meta-phenylene oligomers: synthesis and photophysics

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ABSTRACT

A range of alternating furanylene-*meta*-phenylene oligoaryls of different chain lengths is synthesized by a convergent/divergent protocol from the annulation of a propargylic dithioacetal and an aldehyde with a propargylic dithioacetal moiety as a substituent. The emission properties of these oligomers showed chain-length dependent in poor solvent such as cyclohexane. Time resolved fluorescence spectroscopic analyses indicate that there might be intramolecular interaction between the chromophores in **2c**-**e** and such interaction became more prominent as the chain-lengths increased from 9 to 21. Since oligomers **2** have *meta*-phenylene and 2,5-furnaylene linkages, the oligomers **2e**, may likely be folded to enable intrachain chromophore–chromophore interactions. In addition, these oligomers are electrochemically active and the first oxidation potentials are chain-length dependent.

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1. Introduction

Studies on well-defined oligomers with interesting optoelectronic properties remain to be rapidly burgeoning.¹ A variety of structurally sound scaffolds with diverse molecular architectures has been designed and synthesized. Incorporation of heteroaromatic rings into these systems will tune the optoelectronic properties of the oligomers, and studies on oligothiophenes or pyrroles and related compounds abound.^{1,2} Relatively speaking, investigations on furan-containing oligoaryls have been only sporadically explored.³⁻⁶ Indeed. alternating benzene-furan oligomers **1** have been used as efficient hole transporting materials with good charge mobility in electroluminescent applications.⁴ These furan containing oligoaryls are found to be stable towards sunlight in the absence of oxygen (air).⁴ In addition, the bismercaptan derivatives of alternating benzene-furan oligomers have been shown to assemble nicely on gold (111) surface with significant π - π stacking and conformational dependent conductivities of these oligoaryls by using STM break junction techniques were also reported.⁵ Bidirectional iterative or convergent-divergent^{3b,7} annulation of propargylic dithioacetals (Scheme 1) have been used for the synthesis of a range of these monodispersed alternating benzene-furan oligomers with or without repetitive units.8

Incorporation of *meta*-phenylene moiety into a conjugated system occasionally acts as interrupting blocks so that the



2a: m = 0, n = 1; **b**: m = n = 1; **c**: m = n = 2; **d**: m = n = 3; **e**: m = n = 5

Scheme 1.



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photophysical properties can be well controlled.⁹ On the other hand, the *meta*-connectivity furnishes a 120° angle, which can offer a unique geometry poised to fold upon amalgamation with appropriate linkers. To illustrate this, *m*-phenylene ethynylene oligomers of discrete length have been extensively examined, and their folding behavior through solvophobic π - π -stacking is well documented.^{10–12} The role of linear alkynyl spacer is to limit the conformational flexibility and, therefore, facilitate the foldability of the oligomers. Incorporation of six-membered heteroaromatic linkers, such as pyridine-pyrimidine and related helicity condons, where transoid conformation around the interheterocyclic bonds is imposed, has been shown to generate molecular helices.¹³ However, the use of five-membered heteroaromatic ring as the linker to tether meta-phenylene modules has not been explored. The folding behavior of these oligomers containing such five-membered heterocycles would, in general, be difficult to control. As shown in Scheme 1, our furan annulation protocol will introduce regioselectively an alkyl substituent at C₃ position of the furan ring. It is envisaged that the size and the nature of these alkyl group on furan rings may dictate the conformation of the carbon-carbon bond linking the furan and benzene rings in furanylene-meta-phenylene oligomers 2, and hence, the folding character of 2. In this paper, we report the synthesis and photophysical properties of a series of 2.

2. Results and discussion

2.1. Synthesis

Propargylic dithioacetal **3** was prepared according to Scheme 2. Sequential treatment of 1-hexyne with ^{*n*}BuLi and **4** followed by MnO_2 oxidation gave the corresponding ketone **5**, which was dithioacetalized with ethanedithiol in the presence of $BF_3(OEt_2)$ in



Scheme 2. Reagents and conditions: (a) (i) ⁿBuLi, THF, -78 °C; (ii) methyl 3-formylbenzoate (4), THF, -78 °C, rt; (iii) MnO₂, rt, 97%; (b) 1,2-ethanedithiol, BF₃(OEt₂), MeOH, -78 °C to rt, 52%; (c) DIBAL, 97%; (d) MnO₂, 92%; (e) NaH, Mel, 94%.

methanol to afford **3** in overall 50% yield. DIBAL reduction of **3** gave 97% yield of **6**, which was oxidized with MnO_2 to furnish aldehyde **7** in 92% yield. Methyl ether **8** was obtained from the reaction of **6** with NaH and Mel.

Sequential treatment of **8** with 1 equiv of ⁿBuLi, **7** and then TFA afforded **9** in 63% yield. Attempts to oxidize of **9** with DDQ was unsuccessful, no corresponding aldehyde **10** being obtained. In a similar manner, **6** was allowed to react with ⁿBuLi, **7** and TFA to give **11** in 63% yield. Oxidation of **11** with MnO₂ produced the **10** in 94% yield. Furan annulation procedure was repeated to couple **9** and **10** to furnish **12** in 52% yield (Scheme 3).



Scheme 3. Reagents and conditions: (a) (i) ⁿBuLi, -78 °C; (ii) **7**; (iii) TFA, Yield of **9**: 63%; (b) (i) 2 equiv ⁿBuLi, -78 °C; (ii) **7**; (iii) TFA, Yield of **11**: 63%; (c) MnO₂, 94%; (d) (i) ⁿBuLi, -78 °C; (ii) **10**; (iii) TFA, 52%.

By employing the same protocol, pentaaryl dialdehyde **14** was obtained in 41% overall yield from **6** and isophthaldehyde **15** followed by MnO₂ oxidation (Scheme 4).



Scheme 4. Reagents and conditions: (a) (i) ${}^{n}BuLi$, $-78 \,{}^{\circ}C$; (ii) isophthaldehyde (15); (iii) TFA, 43%; (b) MnO₂, 95%.

Annulation using different combinations of propargylic dithioacetals **8**, **9**, or **12**, and 3-methoxymethylbenzaldehyde (**16**) or **14** or **15** afforded the corresponding alternating furanylenemeta-phenylene oligomers **2** and results are summarized in Table 1.

Table 1

Photophysical	and electrochemical	parameters of	alternating f	furanylene	- <i>meta</i> -phenyl	lene oligomers 2

Dithioacetal	RCHO	2 (%yield)	$\lambda_{\max}^{a}(nm)$	$\lambda_{em} \left(nm \right) \left(\Phi_{f} ight)^{b}$	$\lambda_{em}^{c}(nm)$	τ^{c} (ps)	$E_p^{1/2d}$ (mV)
8	16	2a (65)	326	363, 382(0.87)	359, 378	1350	669
8	15	2b (55)	334	371, 386(0.55)	363, 381	1400	669
9	15	2c (35)	336	373, 389(0.23)	369, 387	1350, 200(1.5%)	619
9	14	2d (20)	337	374, 392(0.54)	371, 388	1350, 200(6.5%)	548
12	14	2e (40)	340	376, 392(0.65)	396	1350, 210(24%)	518

^a Absorption and fluorescence spectra were acquired at 10⁻⁵ M in CHCl₃, unless otherwise specified.

^b The quantum yield was determined in EtOAc (**2a**–**e**) by employing coumarin-1 ($\Phi_f = 0.99$ in EtOAc)¹⁴ as the reference.

^c Measured in cyclohexane.

^d Measured by differential pulse voltammetry with referenced to the Cp₂Fe/Cp₂Fe⁺ couple.

2.2. Photophysical investigations

The absorption and emission spectra of **2** are shown in Figure. 1 and the relevant spectroscopic data are summarized in Table 1. The absorption maxima showed bathochromic shift from **2a** to **2b** and almost reached the plateau as the chain lengths further increased from **2c** to **2e**. No significant solvent effects were recorded in these absorption properties, whereas the emission profiles were solvent dependent. As shown in Figure 1b, λ_{em} in CHCl₃ exhibited slightly bathochromic shift as the chain lengths increased from **2a** to **2e** and the spectra were structured. When cyclohexane was employed as the solvent, the emission curves for **2** were perturbed and differences in λ_{em} became more apparent. In particular, the spectrum for **2d** was less structured and that for **2e** was structureless (Fig. 1c). It is noteworthy that the emission profile of **2e** in cyclohexane was concentration independent.

The temperature dependent emission spectra of **2e** in hexane are shown in Figure. 1d. The λ_{em} shifted reversibly from 396 nm at 300 K to 407 nm at 220 K. Such slight bathochromic shifts suggest that there might be persistent chromophore–chromophore interaction in **2e** in nonpolar solvent such as hexane. Structurally, oligomers **2** have *meta*-phenylene and 2,5-furnaylene linkages. Oligomer **2e** might be expected to be somewhat folded.

Time resolved fluorescence spectroscopy was used to study the lifetimes (τ) of emission decay and the results are also outlined in Table 1. Single exponential decay was observed for **2a** and **2b** and the lifetimes were comparable. These results suggest that little conjugative interactions through *meta*-phenylene linkage might occur. For oligoaryls with longer chain lengths, two parameters were employed to fit the fluorescence decay. The longer lifetimes (1350 ps), which were comparable with that observed for **2a**, was attributed to the decay of diphenylfuran module. The shorter lifetimes (ca. 200 ps) were found in the emission of **2c–2e**. These fast decay may be arisen from the quenching due to chromophore–chromophore interactions.

Since the emission profiles were essentially concentration independent, it seemed likely that such interactions might occur intramolecularly. In other words, as the chain lengths increased, the chances for the diphenylfuran chromophores to meet through space might be enhanced in poor solvent like cyclohexane. The fact that the weight contribution of the short-life decay increased with increasing chain lengths would be consistent with the folding characters of furanylene-*meta*-phenylene oligomers.

2.3. Electrochemical investigations

Differential pulse voltammetry was employed to elucidate the oxidation behavior of 2 and the potentials were reported against Cp₂Fe/Cp₂Fe⁺ pair (Fig. 2). It is interesting to note that, as the number of furan moieties in **2** increases, the number of oxidation steps also increased. Thus, only one oxidation wave at 669 mV was observed for 2a. Oligomer 2b exhibited two oxidation waves at 669 and 890 mV. The same first oxidation potentials for 2a and 2b indicate that the extension of aryl chain at the meta-linkage might play little role in the electrochemical oxidation. Four electron transfer processes at 619, 719, 820, and 952 mV were clearly found for 2c, which contains four furan moieties. The first oxidation for 2c shifted 50 mV towards more negative potential in comparison with that for 2b. In addition, the differences in potentials between the each electron transfer processes for 2c were much smaller than that for 2b. In a similar manner, the first oxidation potentials for 2d (containing six furan rings) appeared at 548 mV, which was more negative than that of 2c. Three additional sequential oxidation processes at 618, 756, and 860 mV were observed and the separation between each oxidation steps was in the range of 70-130 mV. As to 2e having ten furan rings, no discrete oxidation potentials besides the first one at 518 mV were clearly identified. Again, the first oxidation for 2e required 30 mV less than that



Figure 1. Absorption and emission spectra (excitation at λ_{max}) of **2** (**a**, red, **b**, green, **c**, orange, **d**, blue and **e**, black) in (a, b) chloroform, (c) cyclohexane, and (d) Variable temperature emission spectra of **2e** in hexane (λ_{ex} , 331 nm).



Figure 2. Differential pulse voltammograms of 2 (1 mM) in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 . Scan rate=5 mV s⁻¹.

for **2d**. The trend of decreasing first oxidation potentials from **2b** to **2e** was interesting.

From the resonance point of view, furan moiety can be considered as an electron donating substituent with a negative Hammett σ^+ value (-0.39).¹⁵ The presence of multiple furan moieties in the oligomer chain may raise the corresponding HOMO energies so that the oxidation would be easier as the chain length increased. Since *meta*-phenylene linker can be considered essentially as an insulator, no conjugation through this spacer being take place. The diphenylfuran modules in the oligoaryls would be more or less independent. Accordingly, the second oxidation might be easier as the chain lengths of **2** became longer, because the electrostatic interactions might be reduced. Similar situation might be expected in further oxidation potentials.

3. Conclusions

In summary, we have documented the synthesis and photophysical studies of a range of oligoaryls having alternating 2,5furanylene-meta-phenylene modules by convergent/divergent approach from the corresponding propargylic dithioacetals. The emission properties showed chain-length dependent. Time resolved fluorescence spectroscopic analyses indicate that there might be intramolecular interaction between the chromophores in 2c-e and such interaction became more prominent as the chain-lengths increased from 9 to 21. Because oligomers 2 have meta-phenylene and 2,5-furnaylene linkages, it seems likely that the oligomers **2e**, in particular, may be somewhat folded to enable intrachain chromophore-chromophore interactions. Electrochemical behavior showed that the first oxidation will gradually shift toward more negative potentials as the chain-length grows. In addition, the differences in potentials in the first and the second oxidation steps appeared to decrease with the increase in chain-length.

4. Experimental

4.1. General

4.1.1. 3-Hept-2-ynoyl-benzoic acid methyl ester (**5**). To a solution of 1-hexyne (37.0 mL, 0.32 mol) in THF (200 mL), stirred under N₂ atmosphere, was slowly added ⁿBuLi (132.0 mL of 2.5 M solution in hexane, 0.33 mol) at -78 °C. The reaction mixture was stirred for 30 min. Then a solution of **4** (53.0 g, 0.32 mol) in THF (400 mL) was added slowly and the mixture was stirred for 30 min at -78 °C,

then slowly warmed to rt and further stirred for 2 h. The mixture was quenched with saturated NH₄Cl (500 mL), and the organic layer was separated. The aqueous layer was extracted with Et₂O (300 mL×3). The combined organic extracts were dried (MgSO₄), filtered, and evaporated in vacuo to afford the crude alcohol, which was taken in CH₂Cl₂ (300 mL). The solution was added slowly to a suspension of activated MnO₂ (170 g, 1.95 mol) in CH₂Cl₂ (500 mL) at rt and the mixture was stirred for 6 h. After passing through a silica gel bed (5 cm) and washing with EtOAc (300 mL×5), the combined filtrate was evaporated in vacuo to afford **5** as an orange oil (77.0 g, 97%): ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, *J*=7.3 Hz, 3H), 1.46 (sext, *J*=7.3 Hz, 2H), 1.60 (tt, *J*=7.3, 7.1 Hz, 2H), 2.46 (t, J=7.1 Hz, 2H), 3.88 (s, 3H), 7.49 (t, J=7.8 Hz, 1H), 8.17 (d, J=7.8 Hz, 1H), 8.22 (d, J=7.8 Hz, 1H), 8.69 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 19.1, 22.2, 29.8, 52.5, 79.4, 97.9, 128.6, 130.5, 130.7, 133.1, 134.4, 137.0, 165.9, 177.0; IR (KBr) v 2957, 2872, 1728, 1649, 1601, 1431, 1303, 1234, 1127, 923, 718 cm⁻¹; HRMS (FAB) calcd for C₁₅H₁₇O₃ (M⁺+H): 245.1178; found: 245.1171.

4.1.2. 2-(2-Hex-1-ynyl)-2-(3-methoxycarbonylphenyl)-1,3-dithiolane (3). To a solution of 5 (77.0 g, 0.32 mol) in MeOH (500 mL) was added BF₃·Et₂O (41.0 mL, 0.32 mol) and 1,2-ethanedithiol (27.0 mL, 0.32 mol) at -78 °C. The mixture was slowly warmed to rt and stirred for 12 h. After quenching with NaOH (10%, 300 mL), the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (200 mL×3). The combined organic extracts were washed with 10% NaOH (300 mL×5), brine (300 mL), dried (MgSO₄), filtered, and evaporated in vacuo. The resulting residue was purified by flash column chromatography (silica gel, CH_2Cl_2 /hexane=2/3) to afford **3** as a pale yellow oil (53.4 g, 52%): ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, *J*=7.3 Hz, 3H), 1.45 (sext, *J*=7.3 Hz, 2H), 1.56 (tt, *J*=7.3, 7.0 Hz, 2H), 2.35 (t, J=7.0 Hz, 2H), 3.64-3.70 (m, 4H), 3.89 (s, 3H), 7.38 (t, J=7.8 Hz, 1H), 7.93 (d, J=7.8 Hz, 1H), 8.11 (d, J=7.8 Hz, 1H), 8.59 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.4, 19.6, 22.7, 31.3, 42.0, 52.6, 62.1, 82.1, 88.9, 128.1, 128.8, 129.3, 130.0, 132.1, 140.2, 166.3; IR (KBr) v 2954, 2929, 2870, 1724, 1437, 1275, 1203, 1141, 1104, 1082, 733, 690 cm⁻¹; HRMS (FAB) calcd for C₁₇H₂₁O₂S₂ (M⁺+H): 321.0983; found: 321.0976.

4.1.3. 2-(2-Hex-1-ynyl)-2-(3-hydroxymethylphenyl)-1,3-dithiolane (6). To a THF solution (120 mL) of 3 (10.7 g, 33.5 mmol), stirred under N2 atmosphere, was added DIBAL (150.0 mL, 1.0 M in hexane 0.15 mol) slowly at 0 °C and the reaction mixture was stirred for 2 h at rt, quenched by slowly pouring into saturated NH₄Cl (50 mL). After the remaining DIBAL was completely quenched, the gel-like organic layer was acidified with 6 M HCl (200 mL), and extracted with EtOAc (100 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (150 mL×2), brine (200 mL), dried (MgSO₄), filtered, and evaporated in vacuo to afford **6** as a pale yellow oil (9.4 g, 97%): ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, *J*=7.2 Hz, 3H), 1.45 (sext, J=7.2 Hz, 2H), 1.56 (tt, J=7.2, 7.0 Hz, 2H), 2.35 (t, J-7.0 Hz, 2H), 3.63-3.73 (m, 4H), 4.67 (d, J=6.0 Hz, 2H), 7.27-7.34 (m, 2H), 7.85 (d, *J*=8.0 Hz, 1H), 7.92 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 19.3, 22.4, 31.0, 41.4, 62.3, 65.3, 82.3, 88.1, 125.7, 126.3, 126.6, 127.9, 139.6, 140.4; IR (KBr) v 3363, 2956, 2927, 2869, 1601, 1580, 1482, 1460, 1430, 1275, 1177, 1018, 745, 698, 648 cm⁻¹; HRMS (FAB) calcd for $C_{16}H_{21}OS_2$ (M⁺+H): 293.1034; found: 293.1032; Anal. Calcd for C₁₆H₂₀OS₂: C 65.71, H 6.89; found: C 65.32, H 6.96.

4.1.4. 2-(2-Hex-1-ynyl)-2-(3-formylphenyl)-1,3-dithiolane (**7**). A solution of alcohol **6** (11.6 g, 40 mmol) in CH₂Cl₂ (100 mL) was added slowly to a suspension of activated MnO₂ (34.7 g, 400 mmol) in CH₂Cl₂ (150 mL) at rt. The reaction mixture was stirred for 6 h at rt. After passing through a silica gel bed (5 cm) and washing with EtOAc (100 mL×5), the combined filtrate was evaporated in vacuo to afford **7** as a pale yellow oil (10.7 g, 92%): ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J*=7.3 Hz, 3H), 1.44 (sext, *J*=7.3 Hz, 2H), 1.56 (tt,

J=7.3, 7.0 Hz, 2H), 2.36 (t, *J*=7.0 Hz, 2H), 3.66–3.73 (m, 4H), 7.48 (t, *J*=7.7 Hz, 1H), 7.78 (d, *J*=7.7 Hz, 1H), 8.19 (d, *J*=7.7 Hz, 1H), 8.43 (s, 1H), 10.01 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.6, 19.8, 22.9, 31.4, 42.2, 62.1, 82.0, 89.3, 128.9, 129.2, 129.5, 133.8, 136.3, 141.3, 191.5; IR (KBr) ν 2956, 2929, 2860, 2725, 1700, 1596, 1581, 1431, 1379, 1277, 1239, 1176, 1164, 1117, 807, 747, 685, 650 cm⁻¹; HRMS (FAB) calcd for C₁₆H₁₉OS₂ (M⁺+H): 291.0877; found: 291.0875.

4.1.5. 2-(Hex-1-ynyl)-2-(3-methoxymethylphenyl)-1,3-dithiolane (8). To a suspension of NaH (60% dispersion in mineral oil, 0.20 g, 4.9 mmol prewashed with hexane) in THF (20 mL) was introduced a THF solution (10 mL) of 7 (0.96 g, 3.3 mmol) at rt under N₂ atmosphere. After 1 h of stirring, MeI (0.4 mL, 6.6 mmol) was added and the mixture was stirred for 3 h at rt, poured into saturated NH₄Cl (50 mL) and extracted with CH₂Cl₂ (20 mL \times 3). The combined organic extracts were washed with brine (100 mL), dried (MgSO₄), filtered, and evaporated in vacuo to afford **8** as a pale yellow oil (0.95 g, 94%): ¹H NMR (300 MHz, CDCl₃) δ 0.92 (t, J=7.2 Hz, 3H), 1.44 (sext, J=7.2 Hz, 2H), 1.56 (tt, J=7.2, 7.0 Hz, 2H), 2.36 (t, J=7.0 Hz, 2H), 3.37 (s, 3H), 3.63-3.71 (m, 4H), 4.46 (s, 2H), 7.23–7.33 (m, 2H), 7.85 (d, J=7.8 Hz, 1H), 7.89 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 19.3, 22.4, 31.0, 41.4, 58.3, 62.2, 74.5, 82.2, 88.0, 126.5, 126.6, 127.1, 127.8, 137.6, 139.1; R (KBr) v 2955, 2926, 2869, 2819, 1652, 1558, 1540, 1456, 1429, 1375, 1361, 1275, 1191, 1102, 963, 890, 790, 746, 696 cm⁻¹; HRMS (FAB) calcd for C₁₇H₂₃OS₂ (M⁺+H): 307.1190; found: 307.1193.

4.1.6. Dithioacetal (9). Under argon. ⁿBuLi (0.88 mL, 2.5 M in hexane. 2.2 mmol) was introduced dropwise to a solution of $\mathbf{8}$ (0.61 g. 2.0 mmol) in THF (50 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of 7 (0.57 g, 2.0 mmol) in THF (10 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 1 h at rt, TFA (0.3 mL, 3.3 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (20 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (20 mL×3), brine (30 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2 /hexane=1/4) to give **9** as a pale yellow oil (845 mg, 65%): ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, *J*=7.2 Hz, 3H), 0.96 (t, *J*=7.2 Hz, 3H), 1.40-1.46 (m, 4H), 1.48-1.61 (m, 2H), 1.62-1.71 (m, 2H), 2.38 (t, J=7.4 Hz, 2H), 2.71 (t, J=7.8 Hz, 2H), 3.41 (s, 3H), 3.69–3.72 (m, 4H), 4.49 (s, 2H), 6.67 (s, 1H), 7.21 (d, J=7.8 Hz, 1H), 7.35-7.41 (m, 2H), 7.61–7.66 (m, 3H), 7.82 (d, J=7.8 Hz, 1H), 8.26 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 14.5, 19.4, 22.5, 23.1, 26.2, 31.1, 32.5, 41.5, 58.3, 62.3, 74.6, 82.1, 88.1, 109.3, 122.57, 122.63, 124.0, 124.5, 124.9, 125.6, 126.1, 128.0, 128.3, 130.5, 131.1, 138.1, 139.4, 147.3, 151.2; IR (KBr) ν 2955, 2927, 2859, 1597, 1455, 1194, 1102, 787, 695 cm⁻¹; HRMS (FAB) calcd for C₃₁H₃₆O₂S₂: 504.2157; found: 504.2163.

4.1.7. *Dithioacetal* (**10**). A solution of alcohol **11** (490 mg, 1.0 mmol) in CH₂Cl₂ (20 mL) was added slowly to a suspension of activated MnO₂ (867 mg, 10.0 mmol) in CH₂Cl₂ (10 mL) at rt. The reaction mixture was stirred for 6 h at rt. After passing through a silica gel bed (5 cm) and washing with EtOAc (10 mL×5), the combined filtrate was evaporated in vacuo to afford aldehyde **10** as a pale yellow oil (458 mg, 94%): ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, *J*=7.2 Hz, 3H), 0.96 (t, *J*=7.6 Hz, 3H), 1.40–1.50 (m, 4H), 1.55–1.61 (m, 2H), 1.62–1.72 (m, 2H), 2.39 (t, *J*=7.0 Hz, 2H), 2.72 (t, *J*=7.8 Hz, 2H), 3.66–3.77 (m, 4H), 6.76 (s, 1H), 7.41 (t, *J*=7.8 Hz, 1H), 7.53 (t, *J*=7.8 Hz, 1H), 7.63 (d, *J*=7.8 Hz, 1H), 7.73 (d, *J*=7.8 Hz, 1H), 7.86 (d, *J*=7.8 Hz, 1H), 7.94 (d, *J*=7.8 Hz, 1H), 8.17 (s, 1H), 8.27 (s, 1H), 10.04 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 14.5, 19.3, 22.5, 23.0, 26.1, 31.1, 32.4, 41.5, 62.3, 82.1, 88.2, 110.3, 124.2, 124.6, 125.0, 126.0, 127.8, 128.1, 128.7,

129.0, 130.7, 131.3, 136.3, 139.5, 148.0, 149.8, 191.3; IR (KBr) ν 2955, 2927, 2859, 2729, 1698, 1666, 1463, 1453, 1161, 794, 692 cm $^{-1}$; HRMS (FAB) calcd for C_{30}H_{32}O_2S_2: 488.1844; found: 488.1833.

4.1.8. Dithioacetal (11). Under argon, ⁿBuLi (0.88 mL, 2.5 M in hexane. 2.2 mmol) was introduced dropwise to a solution of $\mathbf{6}$ (290 mg, 1.0 mmol) in THF (30 mL) at -78 °C and the mixture was stirred at -78 °C for 70 min. A solution of 7 (270 mg, 0.93 mmol) in THF (10 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 3 h at rt, TFA (0.27 mL, 3.0 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc ($20 \text{ mL} \times 3$). The combined organic extracts were washed with saturated NaHCO₃ $(20 \text{ mL}\times3)$, brine (30 mL), dried $(MgSO_4)$, filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (CHCl₃) to give **11** as a pale yellow oil (308 mg, 63%): 1 H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J*=7.2 Hz, 3H), 0.98 (t, *J*=7.2 Hz, 3H), 1.43-1.52 (m, 4H), 1.58-1.63 (m, 2H), 1.65-1.74 (m, 2H), 2.08-2.16 (br, 1H), 2.38 (t, J=7.4 Hz, 2H), 2.73 (t, J=7.8 Hz, 2H), 3.66-3.77 (m, 4H), 4.72 (s, 2H), 6.69 (s, 1H), 7.23 (d, J=8.0 Hz, 1H), 7.37 (t, *J*=8.0 Hz, 1H), 7.42 (t, *J*=8.0 Hz, 1H), 7.65 (d, *J*=8.0 Hz, 1H), 7.70 (s, 1H), 7.88 (d, *J*=8.0 Hz, 1H), 8.29 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 14.1, 19.0, 22.2, 22.7, 25.9, 30.8, 32.2, 41.3, 62.2, 65.1, 82.1, 88.1, 109.4, 121.9, 122.7, 124.2, 124.7, 125.0, 125.5, 125.8, 128.2, 128.7, 130.8, 131.2, 139.7, 141.1, 147.5, 151.4; IR (KBr) v 3376, 2956, 2927, 2869, 1597, 1464, 1378, 1265, 1199, 1024, 788, 738, 699 cm⁻¹; HRMS (FAB) calcd for C₃₀H₃₄O₂S₂: 490.2000; found: 490.1996.

4.1.9. Dithioacetal (12). Under argon, ⁿBuLi (0.44 mL, 2.5 M in hexane, 1.1 mmol) was introduced dropwise to a solution of 9 (520 mg, 1.03 mmol) in THF (40 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of 10 (439 mg, 0.9 mmol) in THF (10 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 1 h at rt, TFA (0.18 mL, 2.0 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc ($30 \text{ mL} \times 3$). The combined organic extracts were washed with saturated NaHCO3 (20 mL×3), brine (30 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, ether/hexane=1/4) to give **12** as a pale yellow oil (468 mg, 52%): ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, *J*=7.2 Hz, 3H), 0.91-1.27 (m, 9H), 1.43-1.63 (m, 8H), 1.63-1.68 (m, 2H), 1.68-1.80 (m, 6H), 2.38 (t, J=7.0 Hz, 2H), 2.74-2.81 (m, 6H), 3.44 (s, 3H), 3.65-3.77 (m, 4H), 4.52 (s, 2H), 6.71 (s, 1H), 6.73 (s, 1H), 6.75 (s, 1H), 7.24 (d, J=8.0 Hz, 1H), 7.37-7.50 (m, 4H), 7.60-7.72 (m, 7H), 7.87 (d, J=7.6 Hz, 1H), 8.05 (s, 2H), 8.31 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 14.47, 14.51, 19.4, 22.5, 23.05, 23.11, 26.2, 31.1, 32.51, 32.54, 41.5, 58.3, 62.4, 74.6, 82.1, 88.1, 109.28, 109.34, 120.4, 121.8, 122.6, 122.7, 124.0, 124.1, 124.5, 124.8, 125.7, 126.2, 128.0, 128.4, 128.5, 128.6, 130.5, 130.60, 130.65, 131.1, 131.6, 138.2, 139.5, 147.3, 147.4, 151.2, 151.3; IR (KBr) v 2955, 2928, 2869, 1597, 1465, 1378, 1275, 1194, 1103, 958, 889, 788, 753, 696 cm⁻¹; HRMS (FAB) calcd for C₅₉H₆₄O₄S₂: 900.4246; found: 900.4258.

4.1.10. Bismethanol (13). Under argon, ⁿBuLi (4.4 mL, 2.5 M in hexane, 11.0 mmol) was introduced dropwise to a solution of **6** (1.45 g, 5.0 mmol) in THF (150 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of **15** (301 mg, 2.25 mmol) in THF (20 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 3 h at rt, TFA (1.35 mL, 15.0 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched

with saturated NH₄Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (50 mL \times 3). The combined organic extracts were washed with saturated NaHCO₃ (50 mL×3), brine (50 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, EtOAc/hexane=2/3) to give **13** as a white solid (516 mg, 43%): mp 117–118 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (t, J=7.2 Hz, 6H), 1.47 (sext, J=7.2 Hz, 4H), 1.71 (tt, J=7.2, 7.6 Hz, 4H), 1.81–1.98 (br, 2H), 2.75 (t, *J*=7.6 Hz, 4H), 4.73 (s, 4H), 6.70 (s, 2H), 7.23 (d, J=8.4 Hz, 2H), 7.37 (t, J=7.6 Hz, 2H), 7.47 (t, J=8.4 Hz, 1H), 7.59 (d, J=7.6 Hz, 2H), 7.64 (d, J=7.6 Hz, 2H), 7.75 (s, 2H), 8.03 (s, 1H): ¹³C NMR (100 MHz, CDCl₃) δ 14.8, 23.4, 26.5, 32.8, 65.6, 109.6, 122.0, 122.5, 122.9, 123.8, 124.3, 125.7, 128.7, 128.8, 130.9, 131.8, 141.2, 147.6, 151.5; IR (KBr) v 3332, 2954, 2927, 2869, 1599, 1483, 1453, 1378, 1209, 1016, 952, 896, 787, 693 cm⁻¹; HRMS (FAB) calcd for C₃₆H₃₈O₄: 534.2770; found: 534.2780.

4.1.11. Bisaldehyde (14). A solution of 13 (534 mg, 1.0 mmol) in CH₂Cl₂ (30 mL) was added slowly to a suspension of activated MnO₂ (1.7 g, 20.0 mmol) in CH₂Cl₂ (10 mL) at rt. The reaction mixture was stirred for 6 h at rt. After passing through a silica gel bed (5 cm) and washing with EtOAc (10 mL \times 5), the combined filtrate was evaporated in vacuo to afford 14 as a pale yellow solid (503 mg, 95%): mp 131–132 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (t, J=7.2 Hz, 6H), 1.48 (sext, J=7.2 Hz, 4H), 1.74 (tt, J=7.2, 7.4 Hz, 4H), 2.77 (t, J=7.4 Hz, 4H), 6.80 (s, 2H), 7.50-7.65 (m, 3H), 7.64 (d, J=7.2 Hz, 2H), 7.74 (d, J=8.2 Hz, 2H), 7.97 (d, J=8.2 Hz, 2H), 8.01 (s, 1H), 8.20 (s, 2H), 10.01 (s, 2H); 13 C NMR (100 MHz, CDCl₃) δ 14.5, 23.0, 26.2, 32.4, 110.3, 122.4, 124.0, 124.15, 124.22, 128.0, 128.6, 128.8, 129.1, 131.3, 136.4, 148.0, 150.0, 191.3; IR (KBr) v 3056, 2955, 2928, 2869, 2859, 2724, 1697, 1600, 1466, 1454, 1377, 1299, 1205, 1161, 957, 893, 790, 686 cm⁻¹; HRMS (FAB) calcd for C₃₆H₃₄O₄: 530.2457; found: 530.2458; Anal. Calcd for C₃₆H₃₄O₄: C 81.48, H 6.46; found: C 80.92, H 6.53.

4.1.12. Oligomer (2a). Under argon, ⁿBuLi (2.2 mL, 2.5 M in hexane, 5.5 mmol) was introduced dropwise to a solution of 8 (1.53 g, 5.0 mmol) in THF (100 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of 16 (675 mg, 4.5 mmol) in THF (15 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 2 h at rt, TFA (0.67 mL, 7.5 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (50 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (50 mL×3), brine (50 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2 /hexane=1/2) to give **2a** as a pale yellow oil (1.06 g, 65%): ¹H NMR (400 MHz, CDCl₃) δ 0.99 (t, *J*=7.2 Hz, 3H), 1.47 (sext, *J*=7.2 Hz, 2H), 1.70 (tt, *J*=7.2, 7.8 Hz, 2H), 2.72 (t, *J*=7.8 Hz, 2H), 3.42 (s, 3H), 3.45 (s, 3H), 4.52 (s, 2H), 4.55 (s, 2H), 6.70 (s, 1H), 7.23 (d, J=7.6 Hz, 1H), 7.27 (d, J=7.6 Hz, 1H), 7.38 (t, J=7.6 Hz, 1H), 7.42 (t, J=7.6 Hz, 1H), 7.62 (d, J=7.6 Hz, 1H), 7.66-7.71 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 22.7, 25.8, 32.1, 58.13, 58.15, 74.55, 74.62, 109.3, 122.8, 122.9, 124.1, 124.6, 124.7, 126.0, 126.4, 128.5, 128.6, 130.7, 131.6, 138.3, 138.4, 147.6, 151.5; IR (KBr) v 2954, 2926, 2858, 2819, 1611, 1467, 1450, 1378, 1193, 1103, 959, 788, 699 cm⁻¹; HRMS (FAB) calcd for C₂₄H₂₈O₃: 364.2083; found: 364.2046; Anal. Calcd for C₂₄H₂₈O₃: C 79.09, H 7.74; found: C 79.63, H 7.88.

4.1.13. Oligomer (**2b**). Under argon, ⁿBuLi (2.2 mL, 2.5 M in hexane, 5.5 mmol) was introduced dropwise to a solution of **8** (1.53 g, 5.0 mmol) in THF (100 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of **15** (290 mg, 2.2 mmol) in THF (20 mL) was added at -78 °C and the mixture was stirred at -78 °C

for 1 h, then gradually warmed to rt. After further stirring for 2 h at rt, TFA (0.67 mL, 7.5 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (50 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (50 mL×3), brine (50 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel. CH_2Cl_2 /hexane=1/1) to give **2b** as a pale vellow oil (680 mg, 55%): ¹H NMR (400 MHz, CDCl₃) δ 1.00 (t, *J*=7.4 Hz, 6H), 1.51 (sext, *J*=7.4 Hz, 4H), 1.76 (tt, J=7.4, 7.6 Hz, 4H), 2.80 (t, J=7.6 Hz, 4H), 3.45 (s, 6H), 4.53 (s, 4H), 6.74 (s, 2H), 7.25 (d, *J*=8.2 Hz, 2H), 7.40 (t, *J*=8.2 Hz, 2H), 7.52 (t, J=7.7 Hz, 1H), 7.64 (d, J=7.7 Hz, 2H), 7.69 (d, J=8.2 Hz, 2H), 7.72 (s, 2H), 8.03 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 22.8, 25.9, 32.2, 58.2, 74.6, 109.3, 122.4, 122.7, 122.8, 123.8, 124.2, 126.4, 128.6, 128.7, 130.7, 131.7, 138.4, 147.6, 151.6; IR (KBr) v 2955, 2928, 2858, 2819, 1600, 1484, 1467, 1453, 1379, 1194, 1110, 959, 888, 787, 694 cm⁻¹; HRMS (FAB) calcd for C₃₈H₄₂O₄: 562.3083; found: 562.3074; Anal. Calcd for C₃₈H₄₂O₄: C 81.10, H 7.52; found: C 80.61, H 7.60.

4.1.14. Oligomer (**2c**). Under argon, ^{*n*}BuLi (0.22 mL, 2.5 M in hexane, 0.55 mmol) was introduced dropwise to a solution of 9 (252 mg, 0.5 mmol) in THF (30 mL) at $-78\ ^\circ\text{C}$ and the mixture was stirred at -78 °C for 50 min. A solution of **15** (27 mg, 0.2 mmol) in THF (5 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 2 h at rt, TFA (0.09 mL, 1.0 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH_4Cl (20 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (20 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (20 mL×3), brine (20 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, EtOAc/hexane=1/9) to give **2c** as a white solid (67 mg, 35%): mp 79–80 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.95–1.00 (m, 12H), 1.45– 1.53 (m, 8H), 1.68-1.78 (m, 8H), 2.73-2.82 (m, 8H), 3.43 (s, 6H), 4.51 (s, 4H), 6.70 (s, 2H), 6.75 (s, 2H), 7.24 (d, J=7.7 Hz, 2H), 7.38 (t, J=7.7 Hz, 2H), 7.46 (t, J=7.7 Hz, 2H), 7.52 (t, J=7.7 Hz, 1H), 7.59 (d, J=7.7 Hz, 2H), 7.65–7.71 (m, 9H), 8.04 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.5, 23.1, 26.2, 26.3, 32.5, 58.3, 74.6, 109.3, 120.4, 121.8, 122.2, 122.6, 122.7, 123.6, 124.1, 126.2, 128.4, 128.5, 130.5, 130.6, 131.6, 131.7, 138.2, 147.3, 147.4, 151.3; IR (KBr) v 2954, 2927, 2859, 1597, 1482, 1466, 1453, 1378, 1193, 1102, 943, 886, 788, 691 cm⁻¹; HRMS (FAB) calcd for C₆₆H₇₀O₆: 958.5172; found: 958.5164.

4.1.15. Oligomer (2d). Under argon, ⁿBuLi (0.32 mL, 2.5 M in hexane, 0.8 mmol) was introduced dropwise to a solution of 9 (380 mg, 0.75 mmol) in THF (30 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of 14 (146 mg, 0.32 mmol) in THF (5 mL) was added at $-78 \degree$ C and the mixture was stirred at $-78 \degree$ C for 1 h, then gradually warmed to rt. After further stirring for 2 h at rt, TFA (0.14 mL, 1.5 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (20 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (20 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (20 mL×3), brine (20 mL), dried (MgSO₄), filtered and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, EtOAc/hexane=1/9) to give **2d** as a white solid (86 mg, 20%): mp 107–108 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.93–0.98 (m, 18H), 1.45– 1.51 (m, 12H), 1.68-1.76 (m, 12H), 2.72-2.80 (m, 12H), 3.42 (s, 6H), 4.50 (s, 4H), 6.68 (s, 2H), 6.71 (s, 2H), 6.73 (s, 2H), 7.22 (d, J=7.7 Hz, 2H), 7.37 (t, J=7.7 Hz, 2H), 7.43-7.52 (m, 5H), 7.58-7.70 (m, 15H), 8.04 (s, 2H), 8.06 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.15, 14.17, 22.8, 26.0, 26.05, 32.25, 32.29, 58.2, 74.6, 109.4, 109.5, 120.6, 122.0, 122.4, 122.8, 122.9, 123.7, 124.22, 124.29, 124.32, 124.40, 126.4, 128.6, 128.8, 130.76, 130.82, 130.88, 131.8, 131.90, 131.94, 138.4, 147.56, 147.62, 147.68, 151.6; IR (KBr) ν 2955, 2926, 2857, 1596, 1481, 1467, 1451, 1378, 1194, 1103, 944, 813, 786, 688 cm $^{-1}$; HRMS (FAB) calcd for C94H98O8: 1354.7262; found: 1354.7278.

4.1.16. Oligomer (2e). Under argon, ⁿBuLi (0.16 mL, 2.5 M in hexane, 0.4 mmol) was introduced dropwise to a solution of **12** (350 mg. 0.39 mmol) in THF (15 mL) at -78 °C and the mixture was stirred at -78 °C for 50 min. A solution of 14 (73 mg, 0.16 mmol) in THF (5 mL) was added at -78 °C and the mixture was stirred at -78 °C for 1 h, then gradually warmed to rt. After further stirring for 3 h at rt, TFA (0.07 mL, 0.8 mmol) was added and the mixture was stirred at rt overnight. The reaction mixture was quenched with saturated NH₄Cl (20 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (20 mL×3). The combined organic extracts were washed with saturated NaHCO₃ (20 mL \times 3), brine (20 mL), dried (MgSO₄), filtered and evaporated in vacuo. The resulting residue was recrystallized from ether/pentane (3/10) to afford **2e** as a white solid (139 mg, 40%): mp 135–136 $^{\circ}$ C; ¹H NMR (400 MHz, CDCl₃) δ 0.94–0.97 (m, 30H), 1.45–1.48 (m, 20H), 1.67– 1.70 (m, 20H), 2.72-2.78 (m, 20H), 3.42 (s, 6H), 4.50 (s, 4H), 6.68-6.70 (m, 10H), 7.23 (d, J=7.6 Hz, 2H), 7.30-7.50 (m, 11H), 7.58-7.70 (m, 21H), 8.03–8.07 (m, 10H); 13 C NMR (100 MHz, CDCl₃) δ 14.0, 22.7, 22.9, 25.9, 26.0, 32.1, 58.1, 74.6, 109.6, 120.6, 120.7, 122.1, 122.9, 123.0, 124.1, 124.4, 124.5, 126.5, 128.8, 128.9, 130.9, 131.0, 131.9, 132.1, 138.6, 147.8, 151.7, 151.8; IR (KBr) v 2952, 2923, 2853, 1593, 1455, 1374, 1243, 1095, 943, 786, 739, 687 cm⁻¹; HRMS (FAB) calcd for C₁₅₀H₁₅₄O₁₂: 2147.1440; found: 2147.1448.

4.2. Electrochemical measurements

A conventional three-electrode system with a potentiostat/galvanostat (EG&G PAR 273A) 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 AgNO₃) and a Pt wire was used as the counter electrode. Samples are dissolved in CH₂Cl₂ containing 0.1 M tetrabutylammonia hexafluorophosphate as the electrolyte, and the solution was purged with Ar for at least 15 min before electrochemical experiments.

4.3. Time-resolved fluorescence experiments

A mode-locked Ti:sapphire laser (wavelength: 850 nm; repetition rate: 76 MHz; pulse width: <200 fs) passed through an optical parametric amplifier to produce 425 nm pulse laser. The fluorescence of sample was reflected by a grating (150 g/mm; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. The sample was prepared with 1×10^{-5} M concentration in cyclohexane, and using ultra-micro cuvette with 1 mm pathlength to maintain the excitation at the same time. The signal was collected for twenty times to decrease signal to noise ratio.

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Supplementary data

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