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$W(CO)_6$-Mediated desulfuroligomerization of bis-dithioacetals. New synthesis of substituted oligo(phenylene–vinylenes)

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Dedicated to Professor J.-F. Normant on the occasion of his 65th birthday

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Abstract

Treatment of bisdithioacetals of 1,4-diaroylbenzenes (**4**) with $W(CO)_6$ in refluxing chlorobenzene afforded the corresponding substituted oligophenylenevinylenes (OPVs) (**5**). Average molecular weights determined by GPC indicate that OPVs **5** have 5–13 repetitive substituted phenylenevinylene units with narrow polydispersities. Emission in the blue–green to green region was observed for these OPVs depending on the nature of the substituent. The electron-donating alkoxy substituent shifted the emission to the longer wavelength whereas the electron-withdrawing trifluoromethyl group caused a blue shift in the fluorescence spectra.

Keywords: Desulfuroligomerization; Bis-dithioacetals; Oligophenylenevinylenes (OPVs)

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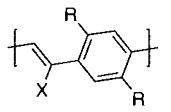
1. Introduction

Conjugated polymers have been demonstrated to exhibit diverse electroactive properties [1]. Poly(phenylene–vinylene) (PPV) (**1**) is known for its photoconductivity behavior and, more recently, electroluminescence phenomenon [2]. Modification of the structure of PPV has paved the way to furnish desired band gap in such a way that efficient multicolor display applications in the LED device could be achieved. For example, the alkoxy-substituted polymer **2** exhibits orange light emission [3]. The HOMO–LUMO energy gap can even be narrowed to the red light region by incorporating a cyano substituent onto the olefinic moiety (e.g. **3**) [4]. Soluble analogs of PPV with aryl substituents at the olefinic carbons have attracted much attention [5–10]. The Wittig reaction, McMurry reaction as well as dehydrochlorination and dehalogenation reactions have been employed for the synthesis of aryl-substituted PPVs.



1 R = X = H

2 R = alkoxy, X = H

3 R = H, X = CN

Various models suggest that the photophysical properties of certain conjugated polymers can be represented by those of a short fragment of the corresponding chromophores [11]. In other words, selective synthesis of certain conjugated oligomers having narrow polydispersity may furnish the desired band gap for efficient multicolor display applications [12]. About a decade ago, we disclosed a novel $W(CO)_6$-mediated desulfurdimerization of dithioacetals leading to the corresponding dimeric olefins (Eq. (1)) [13–15]. This reaction provides a new entry for the dimerization of carbonyl moiety under neutral conditions with tolerance to a variety of functional groups. It is envisaged that this reaction can be extended to the synthesis of substituted oligophenylenevinylenes (OPVs) **5** from the corresponding rigid bis-dithioacetals **4**. Described herein is a full

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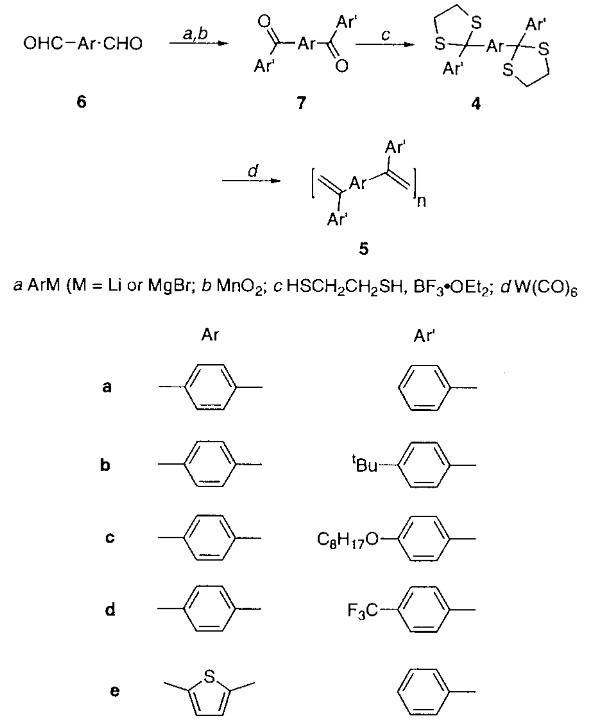
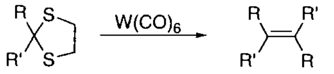


Scheme 1.

account of the new synthesis and properties of aryl-substituted OPVs [16].



(1)

2. Results and discussion

The monomeric starting materials **4** were conveniently synthesized according to the sequence outlined in Scheme 1. The details are described in Section 3. Treatment of **4** with W(CO)$_6$ in refluxing chlorobenzene for 48–60 h afforded the corresponding substituted OPVs **5**. The results are summarized in Table 1.

Average molecular weights determined by gel permeation indicate that OPVs **5a**–**d** have 5–13 repeating substituted phenylenevinylene units with quite narrow polydispersities. TGA investigations showed that OPVs **5a**–**c** are stable up to 300–350°C. A typical TGA curve is shown in Fig. 1. OPV **5d** having an electron-withdrawing CF$_3$ group was unstable above 200°C.

As can be seen in Table 1, only low molecular weight species **5e** (corresponding to three repeating thienylenevinylene units) was obtained. A TGA study showed that **5e** started to decompose at 100°C. The presence of the thiophene unit in the backbone apparently affects the stability. It is noteworthy that the OPVs **5** were synthesized under refluxing chlorobenzene conditions and it is therefore not surprising to find that the M_n for **5e** was lower than those for other OPVs.

It is interesting to note that no T_g was observed for **5c**. As described earlier [15], the methoxy-substituted analog exhibited much lower T_g (92°C) than those of other related OPVs. The long chain aliphatic alkoxy substituent may account for the discrepancy.

The ^{1}H-NMR spectra of **5** showed high field signals (ca δ 3.8–4.0), which may be attributed to the residual dithiolane moiety at the terminal units of the OPVs. However, the relative intensity of these peaks with respect to those in the aromatic region varies with the substrates in comparison with the average molecular weights of these OPVs. In order to solve this discrepancy, we have examined the spectroscopic properties of **5** in detail.

The infrared spectrum of **5a** showed a weak absorption at 1659 cm^{-1} which is characteristic for a diaryl ketone functionality. With the exception of **5c**, all other oligomers **5b**, **5d**, and **5e** behaved similarly, an absorption at 1650 cm^{-1} being observed. The mechanism of the Group 6 metal carbonyl-promoted desulfurdimerization of dithiolanes has been investigated [13b,d]. A thioketone intermediate has been isolated and a radical fragmentation has been suggested leading to a thioketone intermediate which may further react under the reaction conditions to afford the dimeric olefin (Scheme 2) [13b,d]. It is noteworthy that thioketals **4** can also serve as promoters for the Mo(CO)$_6$-catalyzed ring opening metathesis polymerization of norbornene derivatives [17]. It is also known that a thioketone moiety is susceptible to hydrolysis upon exposure to air or moisture. This may account for the carbonyl absorption in the infrared region. These observations indicate that the terminal dithiolane group may be transformed

Table 1
Synthesis and physical properties of oligomers **5**

5	% Yield	M_n	PDI	T_g	λ_{em} (nm)	Φ_f	$\sigma \times 10^{15}$ (Ω^{-1} cm^{-1})
a	80	3380	1.4	175	530	0.01	5
b	82	4330	1.2	188	530	0.02	1000
c	62	2740	1.8		543	0.03	2000
d	81	3010	1.5	134	500	0.02	2
e	67	990	1.2				1

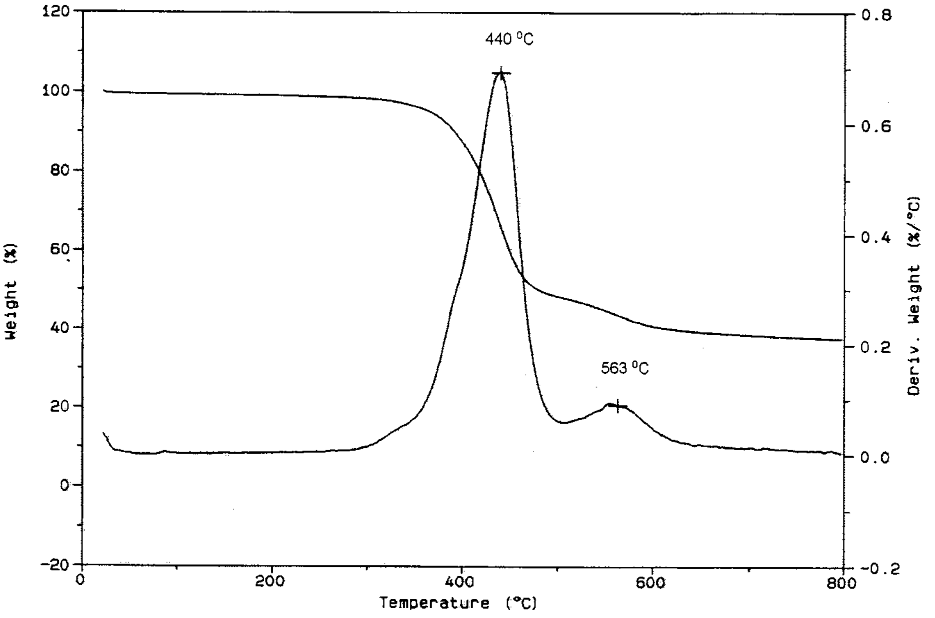


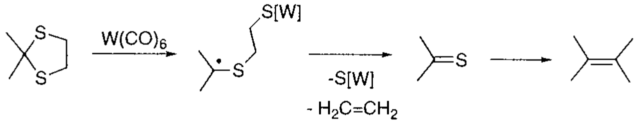
Fig. 1. TG curve of **5c**. TGA was performed under nitrogen flow at a heating rate of 10°C min^{-1}.

into the corresponding thioketone moiety which was then hydrolyzed during the work-up to generate the carbonyl functionality. Accordingly, the terminal groups of **5** may contain either dithiolane moiety or the carbonyl group. As shown in Section 3, the microanalysis data also showed that the carbon content is slightly less than the theoretical prediction[1].

The use of the ^{1}H-NMR provides an important tool in the elucidation of the structures of the polymers. As described in detail in Section 3, the relative chemical shifts for ortho protons in the starting dithioacetals and diketones are very characteristic and therefore can be employed as a reference for the end group of the polymers. Oligomer **5a** was chosen as an example to elucidate this point. The ^{1}H-NMR of **5a** exhibited residual absorptions at low field (at δ 7.75, br d $J = 6.0$ Hz) attributed to the aromatic ortho protons of the diaryl ketone moiety. The absorptions at δ 7.31–7.58 were assigned to the aromatic ortho protons of the dithiolane of the diaryl ketone functionality. The ratio of the intensities of the absorption at δ 7.75, the residual peaks of the dithiolane moiety (δ 3.70–3.90) and that of the absorptions for the other aromatic protons (δ 6.39–7.31) of **5a** was ca 1:1.3:59. There are four ortho protons for each aryl ketone moiety as well as for its corresponding dithiolane group. In addition, each of the internal diphenylvinylene-phenylene units contains 14 protons. These results indicate that OPV **5a** contains ca 16 units and are consistent with the GPC results (ca. 13 units).

It is known that the benzylic carbon–sulfur bond can be reduced upon treatment with Group 6 metal carbonyl in ethereal solvent. The α-hydrogen of such ethereal solvent may be responsible for this reduction and is presumably abstracted by a radical intermediate. The alkoxy substituent in **4c** contains such active hydrogen. During the course of the desulfurization process, it seems likely that the reduction of the carbon–sulfur bond may occur such that the yield of the corresponding thioketones may be affected. In other words, the relative quantity for the formation of the corresponding thioketones from **4c** might be less than those of related reactions. It is therefore not surprising to see that no residual ketone was detected in the reaction of **4c** under similar conditions.

Oligomers **5a**–**d** exhibit continuous absorptions in the UV and visible regions up to 450 nm. The red thiophene analog **5e** becomes transparent beyond 600 nm. The fluorescence spectra of **5a**–**d** and their quantum yields (Φ_f) were also measured (Table 1). Emission in the blue–green to green region was observed depending on the nature of the substituent. The electron-donating alkoxy substituent shifted the emission to the longer wavelength (543 nm) whereas the electron-withdrawing trifluoromethyl group caused a blue shift (500



Scheme 2.

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[1] As pointed by one reviewer, formation of a small amount of cyclic oligomers may account for the shortage of dithioacetal groups in the final material. Although we can not completely rule out this possibility, it seem less likely because oligomers **5** have relatively low molecular weights and their structures are quite rigid.

nm) in the fluorescence spectra. It is noteworthy that OPVs having a substituted aryl group will enhance the fluorescence quantum yields. Conductivity measurements for **5** doped with iodine indicate that these OPVs are poor conductors (Table 1). Presumably, the aryl-substituents may reduce the extension of conjugation because of the steric reason. In other words, the conjugated moieties become less planar than their unsubstituted PPV counterparts. Electron-donating substituents, however, slightly enhanced the conductivity.

In summary, we have demonstrated a new route for the synthesis of aryl-substituted oligo(phenylene–vinylenes) under neutral conditions in good yield. A variety of functional groups can survive under these conditions. Relatively narrow polydispersity was observed in most of these OPVs. The photophysical properties of these OPVs can be tuned by introducing substituents at the olefinic carbons.

3. Experimental

3.1. General procedure for the preparation of **7**

A mixture of **6** (one equivalent) and Grignard reagent or organolithium reagent (2.2 equivalents) in THF was stirred at room temperature (r.t.) for 12 h and quenched with NH_4Cl. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo to give a residue that was dissolved in CH_2Cl_2. MnO_2 was then added and the mixture was stirred at r.t. for 12 h. After filtration through silica gel, the solvent was removed in vacuo and the residue was recrystallized to give **7**.

*3.2. 1,4-Bis-(4-*tert*-butylbenzoyl)benzene (**7b**)*

In a manner similar to that described in the general procedure, **6a** (2.01 g, 15.0 mmol) in THF (50 ml) was allowed to react with 4-*tert*-butyl-phenylmagnesium bromide (32 ml, 1 M in ether, 32 mmol) to give the corresponding diol which was then treated with MnO_2 (3.10 g, 35 mmol) followed by usual work-up to give **7b** (4.41, 74%): m.p. 160–162°C (EtOAc–hexane); IR (KBr) ν 1645 (s), 1604 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.35 (s, 18 H), 7.50 (d, $J = 8.4$ Hz, 4 H), 7.77 (d, $J = 8.4$ Hz, 4 H), 7.85 (s, 4 H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 31.1, 35.2, 125.4, 129.6, 130.2, 134.2, 140.8, 156.8, 195.8; HRMS Calc. for $C_{28}H_{30}O_2$: 398.2245. Found: 398.2255. Anal. Calc.: C, 84.38; H, 7.59. Found: C, 83.18; H, 7.52%.

*3.3. 1,4-Bis-(4-octyloxybenzoyl)benzene (**7c**)*

In a manner similar to that described in the general procedure, **6a** (1.34 g, 10.0 mmol) in THF (50 ml) was treated with 4-octyloxyphenyllithium [prepared from *tert*-BuLi (2.2 M, 10 ml, 22 mmol) and 4-octyloxybromobenzene (5.7 g, 20.0 mmol)] in THF (20 ml) at −78°C for 3 h. The diol thus obtained was oxidized with MnO_2 (1.90 g, 21.0 mmol) to yield **7c** (4.3 g, 88%): m.p. 77–78°C (EtOAc–hexane); IR (KBr) ν 1639 (s), 1603 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, $J = 6.7$ Hz, 6 H), 1.27–1.50 (broad, 20 H), 1.80 (quint, $J = 6.5$ Hz, 4 H), 4.02 (t, $J = 6.5$ Hz, 4 H), 6.94 (d, $J = 8.5$ Hz, 4 H), 7.80 (s, 4 H), 7.82 (d, $J = 8.5$ Hz, 4 H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3, 114.2, 129.3, 129.4, 132.6, 141.1, 163.2, 194.9; HRMS Calc. for $C_{36}H_{46}O_4$: 542.3396. Found: 542.3384; Anal. Calc.: C, 79.65; H, 8.55. Found: C, 79.24; H, 8.35%.

*3.4. 1,4-Bis-(4-trifluoromethylbenzoyl)benzene (**7d**)*

In a manner similar to that described in the general procedure, the reaction of **6a** (0.48 g, 3.5 mmol) with 4-trifluoromethylphenylmagnesium bromide (1 M, 7.1 ml, 7.1 mmol) followed by oxidation with MnO_2 (0.65 g, 7.20 mmol) to afford **7d** (1.20 g, 81%): m.p. 209–210°C (EtOAc–hexane); IR (KBr) ν 1650 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, $J = 7.9$ Hz, 4 H), 7.92 (d, $J = 7.9$ Hz, 8 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 123.5 (q, $J = 1083$ Hz), 125.6 (q, $J = 15.2$ Hz), 130.0, 130.2, 134.3 (q, $J = 130.8$ Hz), 139.8, 140.2, 194.76; MS (FAB) m/z (rel. intensity) 523 ($M^+ + 1$, 33), 307 (100), 289 (49), 273 (9); HRMS Calc. for $C_{22}H_{12}O_2F_6$: 422.0741. Found: 422.0753; Anal. Calc.: C, 62.57; H, 2.86. Found: C, 62.33; H, 2.89%.

*3.5. 2,5-Bisbenzoylthiophene (**7e**)*

In a manner similar to that described in the general procedure, the reaction of **6e** (1.45 g, 10 mmol) with PhMgBr (1 M, 20.0 ml in ether, 20.0 mmol) was followed by oxidation with MnO_2 (1.9 g, 20 mmol) to give **7e** (2.11 g, 72%): m.p. 108–109°C (EtOAc–hexane); IR (KBr) ν 1632 (s), 1596 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.45–7.62 (m, 6 H), 7.64 (s, 2 H), 7.87 (dt, $J = 6.83$, 1.56 Hz, 4 H); ^{13}C ($CDCl_3$, 50 MHz) δ 128.5, 129.2, 132.9, 133.7, 137.1, 148.4, 188.0; HRMS Calc. for $C_{18}H_{12}O_2S$: 292.0558. Found: 292.0564; Anal. Calc.: C, 73.95; H, 4.14. Found: C, 73.97; H, 4.30%.

3.6. General procedure for the preparation of bisdithioacetal **4**

A $CHCl_3$ solution of **7** (one equivalent) and 1,2-ethanedithiol (three equivalents) in the presence of a catalytic amount of $BF_3{\cdot}Et_2O$ was refluxed for 10 h. The mixture was poured into 10% NaOH and the layers were separated. The organic layer was washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was recrystallized from hexane–ethyl acetate to give **4**.

3.6.1. *Bisdithioacetal* ***4a***

91%: m.p. 213–214°C ($CHCl_3$–hexane); ^{1}H-NMR ($CDCl_3$, 200 MHz) 3.38 (s, 8 H), 7.10–7.30 (m, 6 H), 7.47 (s, 4 H), 7.59 (d, $J = 6.0$ Hz, 4 H); ^{13}C (50 MHz, $CDCl_3$) δ 40.1, 76.5, 127.2, 127.8, 127.9, 128.0, 143.2, 143.4, 144.4. Anal. Calc. for $C_{24}H_{22}S_4$: C, 65.71, H, 5.05. Found: C, 65.84, H, 4.94%.

3.6.2. *Bisdithioacetal* ***4b***

68%: m.p. 270–272°C ($CHCl_3$–hexane); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.27 (s, 18 H), 3.37 (s, 8 H), 7.26 (d, $J = 8.6$ Hz, 4 H), 7.48 (s, 4 H), 7.49 (d, $J = 8.6$ Hz, 4 H); ^{13}C (50 MHz, $CDCl_3$) δ 31.3, 34.4, 40.1, 76.4, 124.9, 127.81, 127.87, 141.2, 143.5, 150.1; HRMS Calc. for $C_{32}H_{38}S_4$ 550.1856. Found: 550.1842. Anal. Calc.: C, 69.77; H, 6.95. Found: C, 69.86; H, 6.90%.

3.6.3. *Bisdithioacetal* ***4c***

91%: m.p. 162–164°C ($CHCl_3$–hexane); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, $J = 6.9$ Hz, 6 H), 1.25–1.50 (m, 20 H), 1.73 (quint, $J = 6.4$ Hz, 4 H), 3.36 (s, 8 H), 3.90 (t, J = 6.4 Hz, 4 H), 6.76 (d, $J = 8.7$ Hz, 4 H), 7.47 (d, $J = 8.7$ Hz, 8 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.0, 22.6, 26.0, 29.2, 29.3, 31.7, 40.0, 67.9, 76.3, 113.6, 127.7, 129.4, 135.9, 143.5, 158.2; HRMS Calc. for $C_{40}H_{54}O_2S_4$: 694.3006. Found: 694.3002; Anal. Calc.: C, 69.12; H, 7.83. Found: C, 68.88; H, 7.80%.

3.6.4. *Bisdithioacetal* ***4d***

90%: m.p. 156–157°C ($CHCl_3$–hexane); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.30–3.50 (m, 8 H), 7.43 (s, 4 H), 7.52 (d, $J = 8.4$ Hz, 4 H), 7.73 (d, $J = 8.4$ Hz, 4 H); ^{13}C ($CDCl_3$, 100 MHz), 40.5, 75.8, 124.0 (q, $J = 1083.2$ Hz), 124.96 (q, $J = 15.2$ Hz), 127.9, 128.6, 129.4 (q, $J = 130.4$ Hz), 142.9, 148.7; HRMS Calc. for $C_{26}H_{20}F_6S_4$: 574.0352. Found: 574.0371; Anal. Calc.: C, 54.34; H, 3.51. Found: C, 54.42; H, 3.61%.

3.6.5. *Bisdithioacetal* ***4e***

80%: m.p. 137–138°C ($CHCl_3$–hexane); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.37–3.57 (m, 8 H), 6.60 (s, 2 H), 7.22–7.33 (m, 6 H), 7.68 (d, $J = 6.2$ Hz, 4 H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 40.5, 72.7, 127.0, 127.5, 127.8, 127.9, 143.2, 151.5; HRMS Calc. for $C_{22}H_{20}S_5$: 444.0168. Found: 444.0166; Anal. Calc.: C, 59.42; H, 4.13. Found: C, 59.07; H, 4.57%.

3.7. *General procedure for desulfuroligomerization of* ***4***

Under N_2 atmosphere, a mixture of **4** (one equivalent) and excess $W(CO)_6$ (four equivalents) in chlorobenzene was refluxed for 48–60 h. After cooling to room temperature, the black mixture was filtered and the residue was washed with ethyl acetate. The filtrate was evaporated in vacuo. The residue was evacuated at r.t. under vacuum to remove the excess $W(CO)_6$ and then taken up in chloroform. Methanol was added to precipitate **5** which was filtered and evacuated under vacuum.

3.8. *OPV* ***5a***

In a manner similar to that described in the general procedure, a mixture of **4a** (1.13 g, 2.58 mmol) and $W(CO)_6$ (3.6 g, 10.2 mmol) in chlorobenzene (20 ml) was refluxed for 48 h followed by usual work-up to afford **5a** (0.51 g, 78%): ^{1}H-NMR ($CDCl_3$, 200 MHz): δ (ratio) 3.70–3.95 (1), 6.50–7.90 (46). $M_n = 3380$ (PDI = 1.4).

3.9. *OPV* ***5b***

In a manner similar to that described in the general procedure, a mixture of **4b** (0.91 g, 1.65 mmol) and $W(CO)_6$ (2.3 g, 6.6 mmol) in chlorobenzene (20 ml) was refluxed for 48 h followed by usual work-up to afford **5b** (0.25 g, 82%): ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ratio) 1.18–1.42 (132), 3.85–3.92 (1), 6.7–7.08 (80); IR (KBr) ν 3083, 3054, 3030, 2965, 2907, 2870, 1908, 1664, 1606, 1511, 1474, 1464, 1406, 1396, 1364, 1270, 1202, 1109, 1020, 834, 798, 697, 565 cm^{-1}. $M_n = 6167$ (PDI = 1.07); Anal. Calc. for $(C_{28}H_{30})_n$: C, 91.80; H, 8.30. Found: C, 89.49; H, 8.42%; quantum yield = 2.1%.

3.10. *OPV* ***5c***

In a manner similar to that described in the general procedure, a mixture of **4c** (0.66 g, 1.0 mmol) and $W(CO)_6$ (1.4 g, 4.0 mmol) in chlorobenzene (15 ml) was converted to **5c** (0.41 g, 62%). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ (ratio) 0.85 (3), 1.25–1.50 (12), 1.6–1.7 (2), 3.6–4.0 (7), 6.58– 6.90 (2); IR (KBr) ν 2930, 2859, 1608, 1512, 1471, 1392, 1288, 1246, 1176, 1112, 1032, 831, 752, 724, 618, 523 cm^{-1}; Anal. Calc. for $(C_{22}H_{20}O_2)_n$: C, 84.7; H, 9.08. Found: C, 74.30; H, 8.65%. $M_n = 5848$; PDI = 1.02; quantum yield = 3.2%.

3.11. *OPV* ***5d***

In a manner similar to that described in the general procedure, a mixture of **4d** (0.42 g, 0.7 mmol) and $W(CO)_6$ (1.0 g, 2.9 mmol) in chlorobenzene (15 ml) was transformed into **5d** (0.32 g, 81%): ^{1}H-NMR ($CDCl_3$, 200 MHz): δ (ratio) 3.80–3.90 (1), 6.72–7.94 (62), 7.75 (d, $J = 8.0$ Hz, 3.4), 7.90–7.94 (4.7); IR (KBr) ν 3034, 3052, 2931, 2859, 2020, 1981, 1924, 1729, 1670, 1618, 1510, 1467, 1412, 1327, 1266, 1168, 1127, 1114, 1068, 1019, 979, 958, 931, 861, 843, 805, 764, 701, 640, 630, 601, 506 cm^{-1}; Anal. Calc. for $(C_{22}H_{12}F_6)_n$: C, 67.70; H, 3.10. Found: C, 66.57; H, 4.02%. $M_n = 6205$; PDI = 1.06. quantum yield = 1.8%.

3.12. Oligomer **5e**

In a manner similar to that described in the general procedure, a mixture of **4e** (0.31 g, 0.7 mmol) and $W(CO)_6$ (1.0 g, 2.9 mmol) in chlorobenzene (15 ml) was transformed into **5e** (0.2 g, 67%): ^{1}H-NMR ($CDCl_3$, 200 MHz): δ (ratio) 3.86–4.04 (1), 6.54–7.59 (22); IR (KBr) ν 3060, 3028, 2956, 2924, 2855, 1651, 1633, 1601, 1493, 1444, 1245, 1159, 1106, 1073, 1028, 916, 761, 734, 698, 570 cm^{-1}. $M_n = 990$ (PDI = 1.2); Anal. Calc. for $(C_{18}H_{12}S)_n$: C, 83.04; H, 4.65. Found: C, 80.46; H, 5.55%.

3.13. Fluorescence measurements

An Aminco-Bowman Series 2 luminescence spectrometer was employed for the measurements. Fluorescence quantum yields of **5** were measured by the optically dense measurement method at 22°C using the same spectrometer. A solution of quinine sulfate (Aldrich, USA) in 1.0 (N) H_2SO_4 ($< 10^{-5}$ M conc.) was used as a standard ($\phi_f = 0.52$) for all quantum yield measurement experiments. A solution of OPV **5** in spectroscopic grade $CHCl_3$ (10^{-5} M conc.) was used for the measurement. Excitation wavelengths of all the OPVs and of the standard were determined by a Shimadzu UV–vis spectrophotometer (1601PC) with an absorbance value ranging between 0.1 and 0.2. Experiments were conducted under identical conditions of emission bandpass and the wavenumber integrated value of the emission spectrum was calculated.

3.14. DC electrical conductivity measurement

The oligomer was coated as a film on glass and the d.c. electrical resistance was measured by a voltage measurement unit (Keithley Model 236). The thickness of the film was measured by surface profile measurement (DEKTAK 3030ST). The conductivity was obtained by the equation, $\sigma = \text{length}/(\text{resistance} \times \text{area})$ in units of $\Omega^{-1}\ \text{cm}^{-1}$.

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