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Synthesis and optical characterization of unsymmetrical oligophenylenevinylenes

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Abstract—An efficient route to highly soluble unsymmetrical oligo(phenylenevinylenes) (OPVs) has been developed. The OPVs are end-substituted with donor alkoxy and acceptor sulfonyl groups for charge polarization and incorporate a methacrylate unit suitable for co-polymerization. The absorption and excitation spectra of the OPVs and their precursors have been examined; vibronic features are noted, and π-system lengthening and introduction of polarizing substituents red-shift the spectral maxima.

1. Introduction

Poly(*p*-phenylenevinylene) (PPV) is a π-conjugated polymeric material with a range of interesting and useful properties, such as large third-order nonlinearity,[1] efficient electroluminescence,[2] and laser emission.[3] However, the unsubstituted PPV is not soluble in organic solvents, which results in difficulties of processing. Various PPV derivatives and co-polymers have been synthesized to overcome the solubility problem[4–6] and a PPV-based material has been shown to have potential for application in optical signal processing.[7]

The third-order nonlinear optical properties of PPV originate from short π-conjugated segments,[8] so systematic investigation of the properties of oligomeric *p*-phenylenevinylenes (OPVs) are of significant interest.[5,9–11] However, useful routes into unsymmetrical OPVs are comparatively rare, and extant examples of OPVs often suffer from low solubility. We report herein a newly developed synthesis of highly soluble OPV derivatives with an electron-donating poly(alkeneoxy) group and an electron-accepting alkylsulfonyl substituent. This is an easier and more efficient method of introducing the polarizing substituents into the molecule than the method we described previously.[12] Replacement of the *n*-decyl chain utilized in our earlier work by a 2-ethylhexyl group results in vastly increased solubility of the oligo-PPV derivatives. The optical properties of the new and previously reported oligomers have been examined, the results from which are also described herein.

2. Results and discussion

2.1. Synthesis and characterization

We have previously reported the synthesis of $CH_2{=}CMe$-$C(O)O(CH_2)_2O(CH_2)_2O$–4-C_6H_4–(*E*)-CH=CH–4-C_6H_4–(*E*)-CH=CH–4-$C_6H_4SO_2$–*n*-$C_{10}H_{21}$ (**24**).[12] In an important step of this synthesis, 1,4-bis-*p*-xylene phosphonate diethyl ester **1** reacted with 4-(decylthio)benzaldehyde **2** in a 3:1 ratio under Wittig–Horner conditions to give the mono-substituted phosphonate **4**, a key intermediate en route to **24**. However, this reaction also afforded the undesired bis-substituted product **6**, which is sparingly soluble in all organic solvents (Scheme 1). Repeating the reaction in a 1:1 ratio of 1,4-bis-*p*-xylene phosphonate ester **1** and aldehyde **2** afforded none of the desired product **4**. Coupled to the low yields of **4** were its unsatisfactory processing properties. We therefore replaced the *n*-decyl chain with a 2-ethylhexyl unit. Repeating the above mentioned procedure with 1,4-bis-*p*-xylene phosphonate ester **1** and 4-(2-ethylhexylthio)benzaldehyde **3** in a ratio of 3:1 afforded less than 9% of the desired product **5** (Scheme 1); the symmetrical compound **7** was obtained in 54% yield, oxidation of which afforded **9** (Scheme 1). Product **7** with the 2-ethylhexyl chain is highly soluble in common organic solvents. The unsatisfactory yield of **5**, though, has necessitated development of a more efficient synthesis, described in Scheme 2.

The newly developed synthesis, which involved utilizing an

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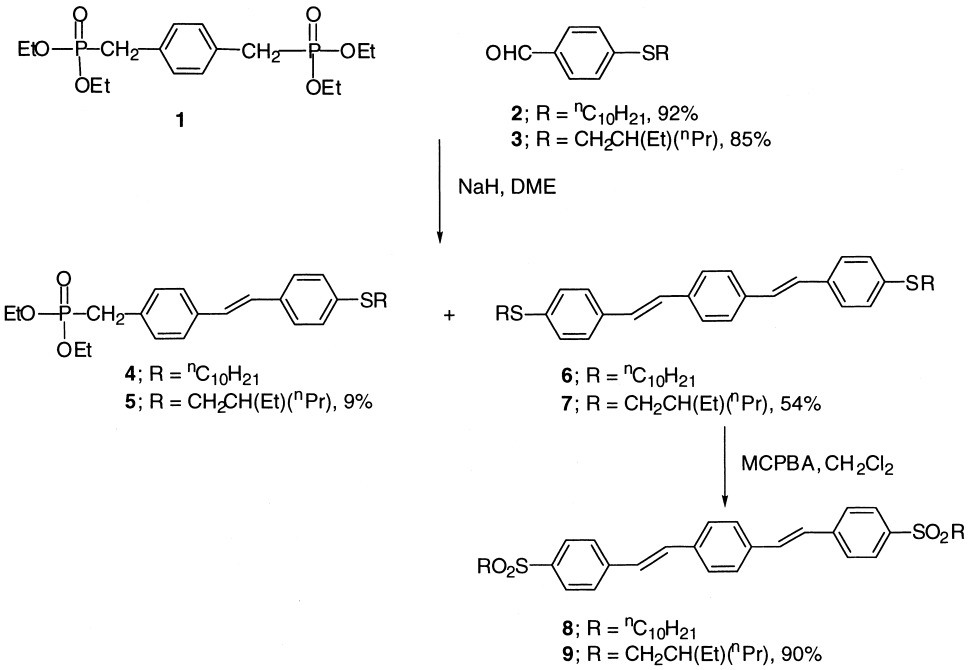


Scheme 1. Preparation of the symmetrically substituted OPVs **6**–**9**.

unsymmetrical precursor, methyl 4-(bromomethyl)benzoate **10** (commercially available), proceeded via several facile and high-yielding steps (Scheme 2). 4-(Diethoxyphosphonylmethyl)benzoic acid methyl ester **11** was prepared by a Michaelis–Arbuzov reaction of **10** and triethylphosphite. The aldehydes **2**, **3** and **21** were prepared by aromatic nucleophilic substitution of fluorobenzaldehyde with the appropriate thiol or ethylene glycol precursor in the presence of base. The thiol precursor for **3**, 2-ethylhexane thiol **12**, was prepared in high yields from the corresponding bromo derivative. A subsequent Wittig–Horner reaction of **11** with the aldehydes **2** or **3** afforded the *trans*-configured styrene derivatives **13** or **14**, respectively, in high yields.

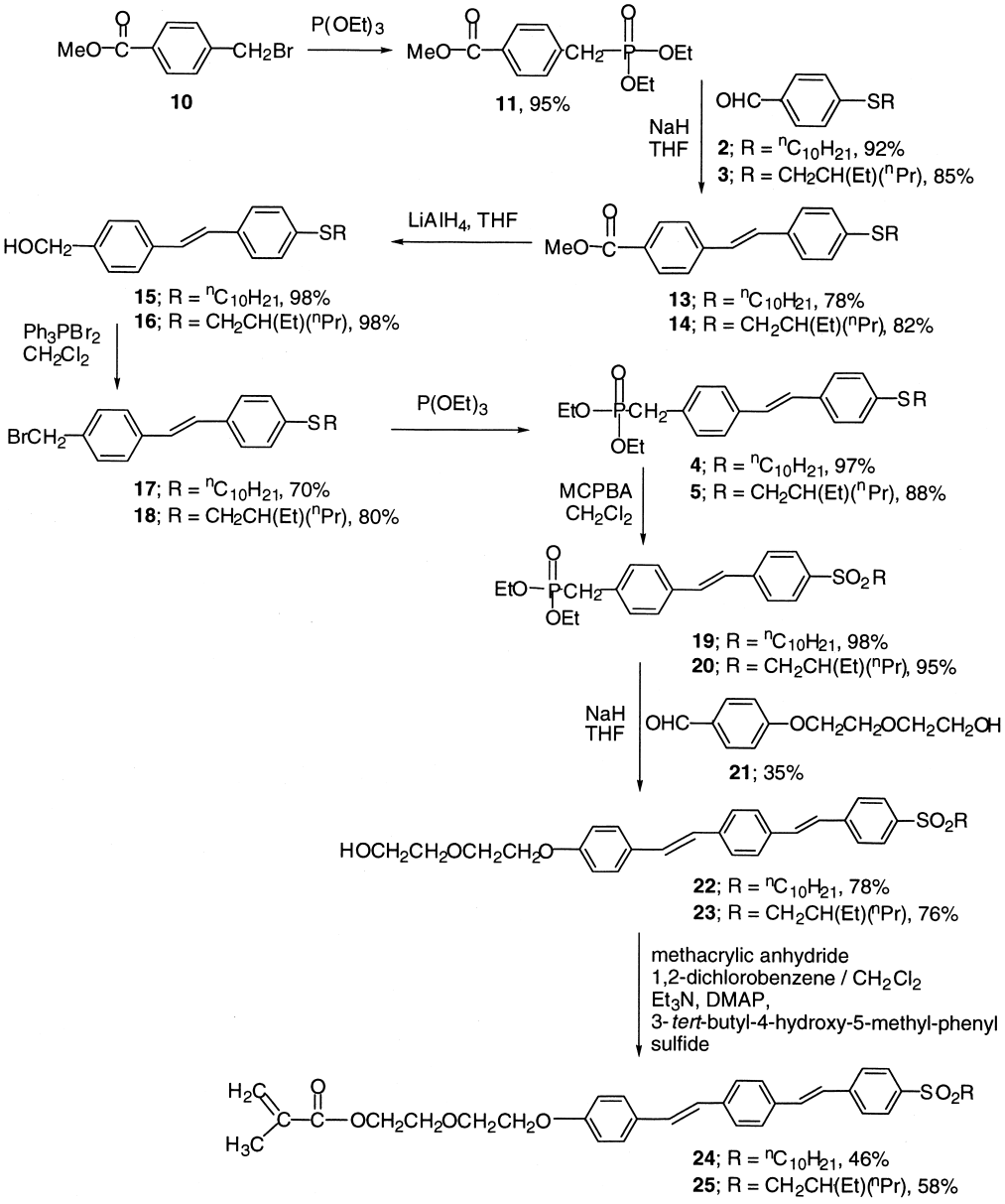
Reduction of the methyl ester group in **13** or **14** with $LiAlH_4$ gave the alcohol **15** or **16**, respectively, both in 98% yield. The hydroxy group in **15** or **16** was then converted into the bromomethyl groups in **17** or **18**, respectively, under mild conditions using freshly prepared triphenylphosphine dibromide.[13] Subsequent conversion to the phosphonate esters **4** or **5** proceeded easily with triethyl phosphite in nearly quantitative yield. The oxidation of the sulfanyl group in **4** or **5** was then achieved employing *m*-chloroperbenzoic acid (MCPBA) to give the sulfonyl-containing compounds **19** or **20**, respectively, in high yields. A second Wittig–Horner reaction, with the glycol-bearing substituted aldehyde **21**, was then used to synthesize the donor–acceptor substituted OPVs **22** and **23**. Compounds **22** or **23** reacted with methacrylic anhydride in the presence of dimethylaminopyridine (DMAP) as catalyst and triethylamine as base to afford the methacrylate-functionalized monomers **24** or **25**, respectively.

Compounds **22**–**25** are green-yellow and highly luminescent. Compounds **24** and **25** are chromophore-containing monomers which can, in principal, be co-polymerized with methyl methacrylate. However, ease of processing requires high solubility in organic solvents, and homogeneous distribution of chromophore in the putative polymeric matrix requires solubility in methyl methacrylate. The newly developed monomer **25** affords improved solubility in most common organic solvents compared to monomer **24**. For example, **25** is 34 and 45% w/w soluble in CH_2Cl_2 and THF, respectively, whereas **24** is 4 and 6% w/w soluble in these solvents, respectively. More importantly, **25** is about 1% w/w soluble in methyl methacrylate, unlike **24** which is insoluble; **25** is thus a suitable precursor for the preparation of homogeneous high-quality NLO chromophore-containing polymethylmethacrylate films.[14]

2.2. Spectroscopy

The optical properties of the OPVs prepared in the current studies have been assessed. The absorption, emission, and excitation spectra were recorded in chloroform solution in a 10 mm quartz cuvette; results are collected in Table 1, representative absorption spectra are displayed in Fig. 1, and a representative superposition of absorption, emission and excitation spectra for **25** is shown in Fig. 2.

A π–π^* transition dominates the absorption spectra of the compounds in the 300–400 nm region.[10] The wavelength of the absorption maximum of the stilbene derivatives is a function of the inductive and mesomeric effects of the *para* substituents. Thus, the methyl ester derivative **14** absorbs at 349 nm whereas the hydroxymethyl derivative **16** absorbs at higher energy (318 nm). Extending the π-system in proceeding to the three-ring phenylenevinylene compounds **23** and **25** results in a significant red-shift. These OPVs have UV–vis spectra which show vibronic features as shoulders on the broad absorption band. The vibronic features are more distinct on the spectra of the symmetrical compounds than on those of the unsymmetrical compounds.



Scheme 2. Preparation of the unsymmetrically substituted OPVs **22**–**25**.

Table 1. Absorption, emission and excitation data for compounds. All measurements as solutions in $CHCl_3$

Compound	Absorption λ_{max} (nm) (ε, [10^4 M^{-1} cm^{-1}])	Emission λ_{max} (nm) (λ_{ex} [nm])[a]	Excitation λ_{max} (nm) (λ_{em} [nm])[b]
5	327 (1.98)	393 (332)	
7	379 (7.06)	428/449/501 (379)	346/357/397/408 (428)
9	368 (6.56)	410/430/460/501 (365)	346/357/397 (430)
14	349 (3.72)	431 (349)	
16	318 (2.51)	394 (331)	
18	339 (4.05)	398 (340)	296/361 (395)
20	325 (2.59)	375 (325)	
23	374 (5.39)	464/501 (374)	357/397 (456)
25	372 (5.36)	466/501 (375)	355/395 (466)

[a] Excitation wavelength.
[b] Emission wavelength.

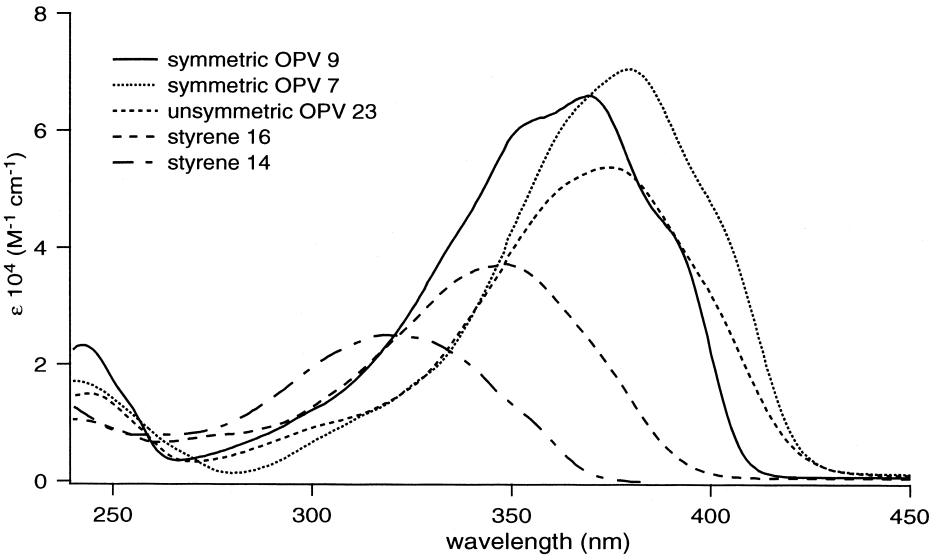


Figure 1. Representative absorption spectra for stilbene derivatives **14** and **16**, symmetrically substituted OPVs **7** and **9**, and unsymmetrically substituted OPV **23**.

The emission maxima vary with the electronic properties of the *para* substituents, and π-system lengthening, in a similar fashion to the absorption maxima. Thus, the stilbene compounds show emission bands below 400 nm whereas the OPVs **23** and **25** show strong emission bands at around 465 nm. The bromo derivative **18** and the sulfonyl-substituted phosphonate ester **20** afford typical fluorescence-quenched emission spectra with low quantum yield. The emission spectra of **23** and **25** (Fig. 2) are nearly identical and are independent of the excitation wavelength, confirming that the shoulder at 500 nm is compound-derived and not instrumental in origin; applying different excitation wavelengths in the shoulder regions of the absorption spectrum of **25** (360, 375, 400, 420 nm) afforded the same emission curve, but with varying intensity. The symmetrical OPVs **7** and **9** emit light at higher energy than the unsymmetrical OPVs **23** and **25**, introduction of polarizing substituents resulting in the expected shift to lower energy.

The excitation spectra of the unsymmetrical OPVs **23** and **25** show two distinct maxima at 368 and 397 nm. In contrast, the symmetrical OPV **7** shows four maxima at 346, 357, 397 and 408 nm in its excitation spectrum, and the symmetrical OPV **9** shows three distinct maxima at 346, 357 and 397 nm together with several shoulders in its excitation spectrum.

3. Conclusion

The studies detailed earlier have outlined an efficient synthetic procedure to highly soluble unsymmetrical OPV compounds. The generality of the synthetic procedure and solubilizing influence of the end-substituted 2-ethylhexyl unit suggests that soluble longer-chain OPVs should be readily accessible, without the need to attach side-substituted solubilizing groups which generally result in loss of co-planarity and hence loss of favourable electronic

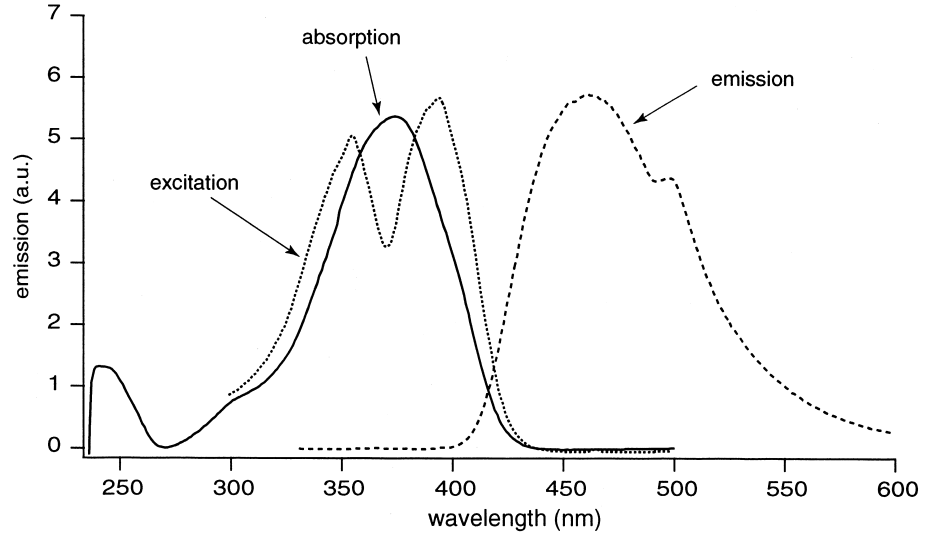


Figure 2. Absorption, emission and excitation spectra for **25**.

effects. The linear optical absorption, emission and excitation spectra of the OPVs and their precursors have been examined, and trends in spectral maxima rationalized. The extended π-conjugative pathway, polarizing substituents, and highly favourable solubility of **25** make it a promising precursor for incorporation into PMMA, to prepare processable films for electro-optic applications; studies directed towards addressing this issue will be the subject of a subsequent report.

4. Experimental

^1H and ^{13}C NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to residual $CHCl_3$ (at 7.24 ppm) and $CDCl_3$ (at 77.0 ppm), respectively. EI (electron impact) mass spectra (both unit resolution and high resolution (HR)) were recorded using a VG Autospec instrument (70 eV electron energy, 8 kV accelerating potential). Electronic absorption (UV–vis) spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. Fluorescence and excitation spectra were recorded using a SLM-Aminco 8100 Spectrofluorometer, OS-Version 1.09, 450 W Xenon arc lamp, scan rate 0.95 nm s^{-1}, voltage 1000 V, input and output slit: 2.0. Infrared spectra were recorded as dichloromethane solutions using a Perkin–Elmer system 2000 FT-IR spectrometer.

Methyl 4-(bromomethyl)benzoate **10** was purchased from Sigma–Aldrich and used without further purification.

4.1. General procedure for the synthesis of 2, 3 and 21

To an equimolar solution of 4-fluorobenzaldehyde (7.0 g, 56 mmol) and 2-ethylhexane thiol **12** in 100 mL DMSO were added 3 equiv. of freshly dried Na_2CO_3. The mixture was heated for 6 h at 160°C under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into water and extracted twice with CH_2Cl_2, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was then purified by silica gel chromatography using CH_2Cl_2 as eluent to give **3** in 85% yield. Similar reactions employing *n*-decane thiol using CH_2Cl_2 as eluent afforded **2**[12] in 92% yield and diethylene glycol using ethyl acetate afforded **21**[12] in 35% yield.

4.1.1. 4-(2-Ethylhexylthio)benzaldehyde 3. $C_{15}H_{22}OS$ (M=250 g mol^{-1}); colourless oil, HRMS (EI) calcd: 250.1391, found: 250.1391; ^1H NMR (δ, $CDCl_3$): 9.89 (s, 1H, CHO), 7.72 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.32 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 2.95 (d, J_{HH}=6.2 Hz, 2H, SCH_2), 1.70–1.20 (m, 9H, $CHCH_2$), 0.90 (m, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 147.7, 132.9 (2C, *i*-C_6H_4), 129.9, 126.2 (4C, CH, C_6H_4), 38.5 (1C, CH), 36.0 (1C, CH_2S), 32.4, 28.7, 25.6, 22.9 (4C, CH_2), 14.1, 10.7 (2C, CH_3); IR (CH_2Cl_2): 2962s, 2928s, 2866m, 2853m, 1697s (C=O), 1588m, 1561m, 1457w, 1381w, 1303w, 2118m, 1170m, 1085m, 837m, 817m cm^{-1}.

4.1.2. {{4-{2-[4-(Decylthio)phenyl]ethenyl}phenyl}methyl}-phosphonic acid diethylester 4 and {{4-{2-[4-(2-ethylhexylthio)phenyl]ethenyl}phenyl}methyl}phosphonic acid diethylester 5. 17 (0.75 g, 1.63 mmol) was suspended in triethylphosphite (1.0 g, 6 mmol) and the resultant mixture refluxed for 2 h. The triethylphosphite was then removed by distillation, and **4** was obtained in 97% yield as a colourless oil. Similar reaction of **18** (3.3 g, 7.9 mmol) afforded **5** in 88% yield, also as a colourless oil.

Compound **4**: $C_{29}H_{43}O_3PS$ (M=502 g mol^{-1}); HRMS (EI) calcd: 502.2670, found: 502.2671; ^1H NMR (δ, $CDCl_3$): 7.41 (d, J_{HH}=8.4 Hz, 4H, C_6H_4), 7.26 (d, J_{HH}=8.4 Hz, 4H, C_6H_4), 7.02 (s, 2H, =CH), 4.00 (m, 4H, $POCH_2$), 3.14 (d, J_{PH}=21.8 Hz, 2H, CH_2P), 2.91 (t, J_{HH}=7.4 Hz, 2H, SCH_2), 1.63 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.23 (m, 18H, CH_2, $POCH_2CH_3$), 0.85 (t, J_{HH}=6.6 Hz, 3H, CH_3).

Compound **5**: $C_{27}H_{39}O_3PS$ (M=474 g mol^{-1}); HRMS (EI) calcd: 474.2356, found: 474.2357; ^1H NMR (δ, $CDCl_3$): 7.42 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.39 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.26 (m, 4H, C_6H_4), 7.02 (s, 2H, =CH), 4.00 (m, 4H, $POCH_2$), 3.14 (d, J_{PH}=21.8 Hz, 2H, PCH_2), 2.89 (d, J_{HH}=6.1 Hz, 2H, SCH_2), 1.62–1.25 (m, 9H, $CHCH_2$), 1.23 (t, J_{HH}=8.2 Hz, 6H, $POCH_2CH_3$), 0.86 (t, J_{HH}=7.4 Hz, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 137.1, 135.9, 134.5, 130.7 (4C, *i*-C_6H_4), 130.0, 128.6 (4C, CH, C_6H_4), 127.9, 127.6 (2C, CH=CH), 126.8, 126.5 (4C, CH, C_6H_4), 62.2 (d, J_{PC}=6.4 Hz, 2C, CH_2OP), 38.8 (1C, CH), 37.8 (1C, CH_2–S), 33.4 (d, J_{PC}=130.6 Hz, 1C, CH_2P), 32.2, 28.7, 25.5, 22.9 (4C, CH_2), 16.3 (2C, CH_3CH_2O), 14.0, 10.9 (2C, CH_3); IR (CH_2Cl_2): 2969s, 2931s, 2855w, 1510m, 1241s (P=O), 1055s (P–O–C), 1029s (O–C–C), 966s (O–C–C), 841 cm^{-1}.

4.1.3. 1,4-Bis[4-(2-ethylhexylthio)styryl]benzene 7. 1,4-Bis-*p*-xylene phosphonate ester **1** (5.0 g, 13.2 mmol) was dissolved in 50 mL dimethoxyethane (DME) and cooled to 0°C. NaH (0.375 g, 15 mmol) was added and **3** (1.1 g, 4.4 mmol) in 30 mL DME was added dropwise to the solution. The solution was stirred for 1 h at 0°C and 1 h at room temperature. The unreacted NaH was quenched with water and the solution was extracted with CH_2Cl_2. The extracts were washed twice with water and dried over $MgSO_4$, filtered and the solvent evaporated. The product was purified by chromatography eluting with CH_2Cl_2/ethyl acetate to give 54% **7** as a yellow solid and 9% **5**.

Compound **7**: $C_{38}H_{50}S_2$ (M=570 g mol^{-1}); calcd: C 79.94, H 8.83, S 11.23, found: C 79.90, H 8.52, S 11.05; mp 144°C; ^1H NMR (δ, $CDCl_3$): 7.47 (s, 4H, C_6H_4), 7.41 (d, J_{HH}=8.5 Hz, 4H, C_6H_4), 7.27 (d, J_{HH}=8.5 Hz, 4H, C_6H_4), 7.05 (s, 4H, =CH), 2.90 (d, J_{HH}=6.2 Hz, 4H, SCH_2), 1.62–1.20 (m, 18H, $CHCH_2$), 0.83 (t, J_{HH}=6.7 Hz, 12H, CH_3), ^{13}C NMR (δ, $CDCl_3$): 137.2, 136.6, 134.6 (6C, *i*-C_6H_4), 128.6 (4C, CH, C_6H_4), 127.9, 127.7 (4C, CH=CH), 126.8, 126.7 (8C, CH, C_6H_4), 38.8 (2C, CH), 37.8 (2C, CH_2–SO_2), 32.4, 28.9, 25.6, 22.9 (8C, CH_2), 14.1, 10.8 (2C, CH_3); IR (CH_2Cl_2): 2959s, 2920s, 2865m, 2851m, 1512w, 1493w, 1465w, 909vs, 830s, 651w (S–C) cm^{-1}.

4.1.4. 1,4-Bis[4-(2-ethylhexylsulfonyl)styryl]benzene 9. Similar reaction with **7** (0.20 g, 0.35 mmol) as for **4** and **5** afforded **9** in 90% yield as yellow solid.

Compound **9**: $C_{38}H_{50}S_2O_2$ (M=602 g mol^{-1}); calcd: C 71.88, H 7.94, S 10.10, found: C 71.65, H 7.77, S 9.92;

mp 201°C; ^{1}H NMR (δ, $CDCl_3$): 7.86 (d, J_{HH}=8.5 Hz, 4H, C_6H_4), 7.66 (d, J_{HH}=8.5 Hz, 4H, C_6H_4), 7.55 (s, 4H, C_6H_4), 7.24 (d, J_{HH}=16.3 Hz, 2H, =CH), 7.14 (d, J_{HH}=16.3 Hz, 2H, =CH), 3.01 (d, J_{HH}=6.0 Hz, 4H, SO_2CH_2), 1.91 (m, 2H, CH), 1.50–1.12 (m, 16H, CH_2), 0.83 (m, 12H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 142.4, 138.5, 136.6 (6C, *i*-C_6H_4), 131.8 (4C, CH=CH), 128.4, 127.4, 127.0 (12C, CH, C_6H_4), 59.9 (2C, CH_2–SO_2), 34.4 (2C, CH), 32.4, 28.2, 25.7, 22.7 (8C, CH_2), 14.1, 10.2 (4C, CH_3); IR (CH_2Cl_2): 2963s, 2932s, 2871m, 2862m, 1593s, 1465w, 1309s (SO_2), 1146s (SO_2), 1088m, 967m, 839m, 674 cm^{-1}.

4.1.5. 4-(Diethoxyphosphonylmethyl)benzoic acid methyl ester 11. A mixture of methyl 4-(bromomethyl)benzoate **10** (12.5 g, 54.5 mmol) and triethylphosphite (20 mL, 110 mmol) was stirred at 160°C under nitrogen atmosphere for 2 h. The excess triethylphosphite was removed by distillation in vacuum. The product **11** was purified by flash chromatography (CH_2Cl_2/gradient methanol, 5%)[15] to afford 95% yield as a colourless oil.

Compound **11**: $C_{13}H_{19}O_5P$ (M=286 g mol^{-1}); ^{1}H NMR (δ, $CDCl_3$): 7.97 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.36 (dd, J_{HH}=8.4 Hz, J_{PH}=2.5 Hz, 2H, C_6H_4), 4.00 (m, 4H, OCH_2), 3.89 (s, 3H, OCH_3), 3.18 (d, J_{PH}=22.1 Hz, 2H, CH_2P), 1.23 (t, J_{HH}=8.2 Hz, 6H, $POCH_2CH_3$).

4.1.6. 2-Ethylhexane thiol 12. KOH (33.66 g, 600 mmol) was dissolved in 300 mL EtOH and H_2S was bubbled through the solution for 30 min. 2-Ethylhexyl bromide (72.49 g, 375 mmol) was added to the reaction mixture dropwise while H_2S was continuously bubbled through. The mixture was then warmed to 53°C over 2 h. The reaction mixture was diluted with water and acidified with 1 M HCl and extracted with diethyl ether. The ether extracts were combined and dried with $MgSO_4$ and the ether was evaporated. The product was distilled at 38°C (0.1 mmHg) to give **12** in 68% yield as a colourless liquid.

Compound **12**: $C_8H_{18}S$ (M=146 g mol^{-1}); HRMS (EI) calcd: 146.2927, found: 146.2926; ^{1}H NMR (δ, $CDCl_3$): 2.52 (d, J_{HH}=8.07 Hz, 1H, SCH_2), 2.50 (d, J_{HH}=8.07 Hz, 1H, SCH_2), 1.45–1.20 (m, 9H, $CHCH_2$), 0.87 (m, 6H, CH_3), ^{13}C NMR (δ, $CDCl_3$): 41.6 (1C, CH), 31.5 (1C, CH_2–S), 28.8, 28.0, 24.7, 22.9 (4C, CH_2), 14.1, 10.8 (2C, CH_3); IR (CH_2Cl_2): 2962s, 2930s, 2873m, 2860m, 2584w SH, 1459m, 1379w, 617w (C–S) cm^{-1}.

4.1.7. 4-[2-(Decylthio)phenylethenyl]benzoic acid methyl ester 13 and 4-{2-[4-(2-ethylhexyl)thio]phenylethenyl}-benzoic acid methyl ester 14. To a solution of **11** (5.0 g, 5.5 mmol) in THF under nitrogen atmosphere was added sodium hydride (0.65 g, 26 mmol). After cooling the mixture to 0°C, 4-(decylthio)benzaldehyde **2** (4.86 g, 5.5 mmol) in 50 mL THF was carefully added dropwise. The reaction mixture was stirred for 1 h at room temperature and then quenched with water. After neutralization with 2 M HCl, a white solid was obtained which was washed twice with petroleum spirit and dried under high vacuum to give **13** in 78% yield as a white solid. Similar reaction with **3** (5.15 g, 20.6 mmol) afforded **14** in 82% yield as a white solid.

Compound **13**: $C_{26}H_{34}SO_2$ (M=410 g mol^{-1}); calcd: C 76.05, H 8.35, S 7.81, found: C 75.94, H 8.30, S 7.67; mp 134°C; ^{1}H NMR (δ, $CDCl_3$): 8.02 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.55 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.44 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.29 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.15 (d, J_{HH}=16.5 Hz, 1H, =CH), 7.08 (d, J_{HH}=16.5 Hz, 1H, =CH), 3.92 (s, 3H, OMe), 2.94 (t, J_{HH}=7.4 Hz, 2H, SCH_2), 1.66 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.26 (m, 12H, CH_2), 0.87 (t, J_{HH}=6.7 Hz, 3H, CH_3).

Compound **14**: $C_{24}H_{30}SO_2$ (M=382 g mol^{-1}); calcd: C 75.35, H 7.90, S 8.38, found: C 75.05, H 7.69, S 7.99; mp 91°C; ^{1}H NMR (δ, $CDCl_3$): 8.01 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.53 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.41 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.28 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.14 (d, J_{HH}=16.4 Hz, 1H, =CH), 7.05 (d, J_{HH}=16.4 Hz, 1H, =CH), 3.90 (s, 3H, OMe), 2.91 (d, J_{HH}=6.1 Hz, 2H, SCH_2), 1.62–1.20 (m, 9H, $CHCH_2$), 0.88 (t, J_{HH}=6.7 Hz, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 167.0 (1C, C=O), 141.9, 139.1, 134.0, 130.7 (4C, *i*-C_6H_4), 130.1, 128.4, 127.3 (6C, CH, C_6H_4), 126.9, 126.8 (2C, CH=CH), 126.3 (2C, CH, C_6H_4), 52.2 (1C, CH_3O), 38.9 (1C, CH), 37.6 (1C, CH_2–S), 32.4, 28.8, 25.6, 23.0 (4C, CH_2), 14.1, 10.8 (2C, CH_3); IR (CH_2Cl_2): 2962s, 2928s, 2866m, 2853m, 1717vs (C=O), 1605s, 1506m, 1492m, 1436m, 1284vs (C–O), 1180m, 1107m, 1091m, 969m, 845m, 810m cm^{-1}.

4.1.8. 1-Hydroxymethyl-{4-[2-(4-decylthio)phenyl]ethenyl}-benzene 15 and 1-hydroxymethyl-{4-{2-[4-(2-ethylhexyl)-thio]phenyl}ethenyl}benzene 16. 13 (4.56 g, 11.1 mmol) in 70 mL THF was carefully added to a suspension of $LiAlH_4$ (0.456 g, 12 mmol) in 100 mL THF under nitrogen atmosphere. The reaction mixture was refluxed for 4 h. After cooling to room temperature, the mixture was carefully quenched with a THF/water mixture to destroy remaining $LiAlH_4$. The mixture was then poured into water and the solid was separated, washed with methanol and dried under reduced pressure. The reduction of the methyl ester group afforded **15** in 98% yield as a pale yellow solid. Similar reaction of **14** (7.8 g, 20.4 mmol) gave **16** in 98% yield, also as a pale yellow solid.

Compound **15**: $C_{25}H_{34}OS$ (M=382 g mol^{-1}); calcd: C 78.48, H 8.96, S 8.38, found: C 78.25, H 8.64, S 8.27; mp 151°C; ^{1}H NMR (δ, $CDCl_3$): 7.49 (d, J_{HH}=8.3 Hz, 2H, C_6H_4), 7.40 (d, J_{HH}=8.3 Hz, 2H, C_6H_4), 7.37 (d, J_{HH}=8.3 Hz, 2H, C_6H_4), 7.26 (d, J_{HH}=8.3 Hz, 2H, C_6H_4), 7.05 (s, 2H, =CH), 4.68 (d, J_{HH}=6.0 Hz, 2H, CH_2OH), 2.91 (t, J_{HH}=6.4 Hz, 2H, SCH_2), 1.64 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.23 (m, 12H, CH_2), 0.85 (t, J_{HH}=6.7 Hz, 3H, CH_3).

Compound **16**: $C_{23}H_{30}SO$ (M=354 g mol^{-1}); calcd: C 77.92, H 8.53, S 9.04, found: C 77.72, H 8.44, S 9.03; mp 96°C; ^{1}H NMR (δ, $CDCl_3$): 7.48 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.39 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.33 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.26 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.04 (s, 2H, =CH), 4.67 (s, 2H, CH_2OH), 2.89 (d, J_{HH}=6.2 Hz, 2H, SCH_2), 1.62–1.28 (m, 9H, $CHCH_2$), 0.87 (t, J_{HH}=7.2 Hz, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 145.5, 140.1, 136.8, 134.4 (4C, *i*-C_6H_4), 128.7 (2C, CH, C_6H_4), 128.2, 127.7 (2C, CH=CH), 127.4, 126.9, 126.7 (6C, CH, C_6H_4), 65.2 (1C, CH_2–OH), 38.9 (1C, CH), 37.9 (1C, CH_2–S), 32.4, 28.8, 25.6, 23.0 (4C, CH_2), 14.2, 10.8 (2C, CH_3); IR (CH_2Cl_2):

3596w (OH), 2956s, 2925s, 2875m, 2857m, 1210s (C–O), 1093m, 1037m, 1009m, 966m, 827m cm^{-1}.

4.1.9. 1-Bromomethyl-{4-[2-(4-decylthio)phenyl]ethenyl}-benzene 17 and 1-bromomethyl-{4-{2-[4-(2-ethylhexyl)-thio]phenyl}ethenyl}benzene 18. Triphenylphosphine (0.84 g, 3.2 mmol) was dissolved in CH_2Cl_2 and the solution cooled to 0°C. An equimolar amount of bromine was carefully added to the solution to give Ph_3PBr_2.[13] A suspension of **15** (1.0 g, 2.6 mmol) in CH_2Cl_2 was added dropwise to the Ph_3PBr_2 solution. The resultant mixture was then refluxed for 2 h. After the reaction was complete 10 mL of MeOH were added dropwise to the mixture to destroy the unreacted Ph_3PBr_2. The solvent was removed by evaporation and the crude product dissolved in EtOH, heated for 10 min and then hot filtered. A pale yellow solid **17** was obtained in 70%. Similar reaction of **16** (5.0 g, 14.1 mmol) afforded **18**, which was washed three times with MeOH and dried to give pure **18** in 80% yield, also as a pale yellow solid.

Compound **17**: $C_{25}H_{33}BrS$ (M=445 g mol^{-1}); calcd: C 67.40, H 7.47, Br 5.94, S 7.20, found: C 67.33, H 7.80, Br 5.68, S 6.95; mp 124°C; ^{1}H NMR (δ, $CDCl_3$): 7.47 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.41 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.37 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.28 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.06 (s, 2H, =CH), 4.51 (s, 2H, CH_2Br), 2.93 (t, J_{HH}=7.4 Hz, 2H, SCH_2), 1.65 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.26 (m, 12H, CH_2), 0.87 (t, J_{HH}=6.7 Hz, 3H, CH_3).

Compound **18**: $C_{23}H_{29}BrS$ (M=417 g mol^{-1}); calcd: C 66.18, H 7.00, Br 19.14, S 7.68, found: C 66.33, H 6.66, Br 19.26, S 7.63; mp 86°C; ^{1}H NMR (δ, $CDCl_3$): 7.45 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.39 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.35 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.27 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.04 (s, 2H, =CH), 4.50 (s, 2H, CH_2Br), 2.90 (d, J_{HH}=6.1 Hz, 2H, SCH_2), 1.64–1.20 (m, 9H, $CHCH_2$), 0.87 (t, J_{HH}=7.3 Hz, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 137.5, 136.8, 134.2, 132.1 (4C, *i*-C_6H_4), 129.4 (2C, CH, C_6H_4), 128.7, 128.5 (2C, CH=CH), 127.2, 126.8, 126.7 (6C, CH, C_6H_4), 38.8 (1C, CH), 37.7 (1C, CH_2–S), 33.5 (1C, CH_2Br), 32.3, 28.7, 25.5, 22.9 (4C, CH_2), 14.2, 10.8 (2C, CH_3); IR (CH_2Cl_2): 2962s, 2928s, 2866m, 2853m, 1560m, 1513m, 1492m, 1279s (CH_2–Br), 1229m, 1087m, 966m, 830m, 599s (CH_2Br) cm^{-1}.

4.1.10. {{4-{2-[4-(Decylsulfonyl)phenyl]ethenyl}phenyl}-methyl}phosphonic acid diethylester 19 and {{4-{2-[4-(2-ethylhexylsulfonyl)phenyl]ethenyl}phenyl}methyl}phosphonic acid diethylester 20. 4 (0.84 g, 1.67 mmol) in CH_2Cl_2 was cooled to 0°C and *m*-chloroperbenzoic acid (MCPBA) (0.574 g, 3.34 mmol) in CH_2Cl_2 was added slowly. After 2 h the resultant solid was isolated, washed twice with Na_2CO_3 solution, and dried over $MgSO_4$. The solvent was removed by evaporation and the sulfonyl compound **19** was obtained in 98% yield as a colourless oil. Similar reaction with **5** (3.7 g, 7.8 mmol) afforded **20** in 95% yield, also as a colourless oil.

Compound **19**: $C_{29}H_{43}O_5PS$ (M=534 g mol^{-1}); HRMS (EI) calcd: 534.3569, found: 534.3570; ^{1}H NMR (δ, $CDCl_3$): 7.85 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.63 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.47 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.32 (dd, J_{HH}=8.4 Hz, J_{HH}=2.4 Hz, 2H, C_6H_4), 7.21 (d, J_{HH}=5.3 Hz, 1H, =CH), 7.09 (d, J_{HH}=5.3 Hz, 1H, =CH), 4.02 (m, 4H, $POCH_2$), 3.16 (d, J_{PH}=21.8 Hz, 2H, PCH_2), 3.06 (t, J_{HH}=7.0 Hz, 2H, SO_2CH_2), 1.69 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 1.24 (m, 18H, CH_2, $POCH_2CH_3$), 0.86 (t, J_{HH}=6.7 Hz, 3H, CH_3).

Compound **20**: $C_{27}H_{39}O_5PS$ (M=506 g mol^{-1}); HRMS (EI) calcd: 506.2256, found: 506.2256; ^{1}H NMR (δ, $CDCl_3$): 7.85 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.63 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.47 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.29 (dd, 2H, J_{HH}=8.4, 2.4 Hz, C_6H_4), 7.19 (d, J_{HH}=16.6 Hz, 1H, =CH), 7.08 (d, J_{HH}=16.6 Hz, 1H, =CH), 4.02 (m, 4H, $POCH_2$), 3.14 (d, J_{PH}=21.8 Hz, 2H, PCH_2), 3.00 (d, J_{HH}=6.9 Hz, 2H, SO_2CH_2), 1.90 (m, 1H, CH), 1.50–1.12 (m, 8H, CH_2), 1.23 (t, J_{HH}=7.2 Hz, 6H, $POCH_2CH_3$), 0.80 (m, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 142.6, 138.3, 135.0, 132.2 (4C, *i*-C_6H_4), 130.3, 130.2 (2C, CH=CH), 128.4, 127.1, 126.9, 126.5 (8C, CH, C_6H_4), 62.2 (d, J_{PC}=6.7 Hz, 2C, CH_2OP), 59.9 (1C, CH_2SO_2), 34.4 (1C, CH), 33.6 (d, J_{PC}=126.7 Hz, 1C, CH_2P), 32.4, 28.2, 25.7, 22.7 (4C, CH_2), 16.3 (2C, CH_3CH_2O), 14.0, 10.2 (2C, CH_3); IR (CH_2Cl_2): 2963s, 2931s, 2873m, 2862m, 1593m, 1512m, 1464m, 1404m, 1394m, 1308s (SO_2), 1238s (P=O), 1143s (C–SO_2), 1089m, 1051s (P–O–C), 1028vs (O–C–C), 966s (O–C–C), 848m cm^{-1}.

4.1.11. 1-{4-[2-(2-Hydroxyethoxy)ethoxy]styryl}-4-(4-decyl-sulfonylstyryl)benzene 22 and 1-{4-[2-(2-hydoxy-ethoxy)ethoxy]styryl}-4-(4-(2-ethylhexylsulfonyl-styryl) benzene 23. 19 (0.89 g, 1.67 mmol) in 50 mL THF was stirred under nitrogen atmosphere at 0°C. NaH (0.08 g, 3.2 mmol) was carefully added, and then aldehyde **21** (0.35 g, 1.67 mmol) in 40 mL THF was added dropwise to the reaction mixture. The reaction mixture was stirred for 2 h at room temperature, and then quenched with water, extracted twice with CH_2Cl_2 and washed twice with 1 M HCl, and dried over $MgSO_4$. The solvent was evaporated and the remaining solid was dried. The yellow-green solid **22** was obtained in 78% yield. Similar reaction with **20** (3.0 g, 5.9 mmol) afforded **23** in 76% yield as a yellow-green solid, purified by precipitation with petrol from a CH_2Cl_2 solution.

Compound **22**: $C_{36}H_{46}O_5S$ (M=590 g mol^{-1}); calcd: C 73.19, H 7.85, S 5.43, found: C 72.99, H 7.65, S 5.24; mp 260°C; ^{1}H NMR (δ, $CDCl_3$): 7.84 (d, J_{HH}=8.2 Hz, 2H, C_6H_4), 7.64 (d, J_{HH}=8.2 Hz, 2H, C_6H_4), 7.50 (s, 4H, C_6H_4), 7.45 (d, J_{HH}=8.2 Hz, 2H, C_6H_4), 7.23 (d, J_{HH}=16.3 Hz, 1H, =CH), 7.11 (d, J_{HH}=16.3 Hz, 1H, =CH), 7.09 (d, J_{HH}=16.3 Hz, 1H, =CH), 6.97 (d, J_{HH}=16.3 Hz, 1H, =CH), 6.91 (d, J_{HH}=8.2 Hz, 2H, C_6H_4), 4.15 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.87 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.77 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.67 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.07 (t, J_{HH}=5.7 Hz, 2H, SO_2CH_2), 1.69 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 1.24 (m, 12H, CH_2), 0.86 (t, J_{HH}=6.7 Hz, 3H, CH_3).

Compound **23**: $C_{34}H_{42}O_5S$ (M=562 g mol^{-1}); calcd: C 72.57, H 7.52, S 5.70, found: C 72.33, H 7.50, S 5.66; mp 243°C; ^{1}H NMR (δ, $CDCl_3$): 7.85 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.64 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.49 (s, 4H, C_6H_4), 7.44 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.22 (d,

J_{HH}=16.5 Hz, 1H, =CH), 7.09 (d, J_{HH}=16.5 Hz, 1H, =CH), 7.07 (d, J_{HH}=16.5 Hz, 1H, =CH), 6.96 (d, J_{HH}=16.5 Hz, 1H, =CH), 6.91 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 4.15 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.87 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.74 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.67 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.01 (d, J_{HH}=6.0 Hz, 2H, SO_2CH_2), 1.91 (m, 1H, CH), 1.50–1.12 (m, 8H, CH_2), 0.81 (m, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 158, 142.6 (2C, *i*-C_6H_4), 138.8, 138.7 (2C, CH=CH), 135.2, 132.0, 130.2, 128.6 (4C, *i*-C_6H_4), 128.3, 127.8, 127.3, 126.8, 126.6 (10C, CH, C_6H_4), 126.1, 126.0 (2C, CH=CH), 114.8 (2C, CH, C_6H_4), 72.6 (1C, CH_2–OH), 69.6, 67.4, 61.7 (3C, CH_2–O), 59.9 (1C, CH_2–SO_2), 34.3 (1C, CH), 32.3, 28.1, 25.7, 22.6 (4C, CH_2), 14.0, 10.1 (2C, CH_3); IR (CH_2Cl_2): 3687w (O–H), 3598w (O–H), 2967s, 2931s, 2874m, 1592m, 1514s, 1305s (SO_2), 1248s (C–O), 1170m (C–O–C), 1143s (SO_2), 1138s (C–O–C), 966m, 834m cm^{-1}.

4.1.12. 2-Methyl-2-propenoic acid 2-{2-{4-{2-{4-{2-[4-(decylsulfonyl)phenyl]ethenyl}phenyl}ethenyl}phenoxy}-ethoxy}ethyl ester 24 and 2-methyl-2-propenoic acid 2-{2-{4-{2-{4-{2-[4-(2-ethylhexylsulfonyl)phenyl]ethenyl}-phenyl}ethenyl}phenoxy}ethoxy}ethyl ester 25. Freshly distilled methacrylic anhydride (0.075 g, 0.49 mmol), **22** (0.23 g, 0.39 mmol) and 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (0.015 g, 0.0419 mmol) were dissolved in 60 mL anhydrous 1,2-dichlorobenzene. Triethylamine (0.49 g, 4.8 mmol) and a catalytic amount of *N*,*N*-dimethylaminopyridine (DMAP, 0.0062 g, 0.049 mmol) in 40 mL 1,2-dichlorobenzene were slowly added at room temperature. The reaction mixture was stirred for 12 h at room temperature, extracted three times with water and dried over $MgSO_4$ and the solvent was evaporated. The solid was washed with diethyl ether and dried, to give **24** in 46% yield as a yellow-green solid. Similar reaction with **23** (1.16 g, 1.84 mmol) in CH_2Cl_2, and precipitation from a CH_2Cl_2 solution with petrol afforded **25** in 58% yield as a yellow-green solid.

Compound **24**: $C_{40}H_{50}O_6S$ (M=658 g mol^{-1}); calcd: C 72.95, H 7.60, S 4.86, found: C 72.66, H 7.45, S 4.71; mp 198°C; ^{1}H NMR (δ, $CDCl_3$): 7.84 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.64 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.50 (s, 4H, C_6H_4), 7.45 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.23 (d, J_{HH}=16.3 Hz, 1H, =CH), 7.10 (d, J_{HH}=16.3 Hz, 1H, =CH), 7.08 (d, J_{HH}=16.3 Hz, 1H, =CH), 6.95 (d, J_{HH}=16.3 Hz, 1H, =CH), 6.90 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 6.12 (broad s, 1H, =CH_2), 5.56 (broad s, 1H, =CH_2), 4.15 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.87 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.77 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.67 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.07 (t, J_{HH}=6.0 Hz, 2H, SO_2CH_2), 1.93 (s, 3H, CH_3), 1.69 (m, 2H, CH_2), 1.24 (m, 14H, CH_2), 0.86 (t, J_{HH}=6.7 Hz, 3H, CH_3).

Compound **25**: $C_{38}H_{46}O_6S$ (M=646 g mol^{-1}); calcd: C 72.38, H 7.30, S 5.08, found: C 72.31, H 7.33, S 4.99; mp 179°C; ^{1}H NMR (δ, $CDCl_3$): 7.86 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.64 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.50 (s, 4H, C_6H_4), 7.43 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 7.12 (d, J_{HH}=16.4 Hz, 1H, =CH), 7.10 (d, J_{HH}=16.4 Hz, 1H, =CH), 7.09 (d, J_{HH}=16.4 Hz, 1H, =CH), 6.95 (d, J_{HH}=16.4 Hz, 1H, =CH), 6.90 (d, J_{HH}=8.4 Hz, 2H, C_6H_4), 6.12 (broad s, 1H, =CH_2), 5.56 (broad s, 1H, =CH_2), 4.32 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 4.14 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.86 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.81 (t, J_{HH}=4.8 Hz, 2H, OCH_2), 3.01 (d, J_{HH}=6.0 Hz, 2H, SO_2CH_2), 1.93 (s, 3H, CH_3), 1.89 (m, 1H, CH), 1.50–1.10 (m, 8H, CH_2), 0.83 (m, 6H, CH_3); ^{13}C NMR (δ, $CDCl_3$): 167.3 (1C, C=O), 158.4, 142.6 (2C, *i*-C_6H_4), 138.1, 137.9 (2C, CH=CH), 136.0 (1C, *C*=CH_2), 135.1, 132.0, 130.4, 128.7 (4C, *i*-C_6H_4), 128.3, 127.7, 127.2, 126.8, 126.6 (10C, CH, C_6H_4), 126.0 (1C, *C*H_2=C), 125.9, 125.8 (2C, CH=CH), 114.8 (2C, CH, C_6H_4), 69.6, 69.3, 67.4, 63.7 (4C, CH_2–O), 59.9 (1C, CH_2–SO_2), 34.3 (1C, CH), 32.3, 28.1, 25.6, 22.6 (4C, CH_2), 18.3 (1C, *C*H_3–C=CH_2), 14.0, 10.1 (2C, CH_3); IR (CH_2Cl_2): 2962m, 2928m, 2866w, 2853w, 1717s (C=O), 1635s (C=C–O), 1591s (C_6H_4), 1514s (C_6H_4), 1299s (SO_2), 1246s (C–O), 1176s (C–O–C), 1142s (SO_2), 1139s (C–O–C), 965m (C=C conjug.), 836 (1,4-C_6H_4) cm^{-1}.

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