Synthesis and Electronic Spectra of Substituted *p*-Distyrylbenzenes for the Use in Light-Emitting Diodes

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Abstract. The influence of substitution on the absorption and Luminescence spectra of oligo(phenylenevinylene)s has been studied using distyrylbenzene (DSB) as a model compound. The degree, character, and pattern of substitution was varied systematically, altering the electronic properties of the DSB, the wavelength of the emitted light could be tuned over a range of 100 nm. The syntheses of **6b**–**h** were performed by twofold Wittig–Horner-olefinations of bisphoshonates **1a**, **b** with substituted benzaldehydes **2a**–**i**, **6i** *via* Heck-reaction of the dibromosulfonylbenzene **3**, **6k** by Siegrist-reaction of **4** with *N*-phenylbenzaldimine and the Knoevenagel-reaction of benzyl cyanide with **5** led to **6l**.

Poly(*p*-phenylenevinylene) and its derivatives are one of the preferred groups of materials for the use as emissive layer in organic polymer light emitting diodes [1–4]. Several groups investigated the photochemistry and particularly the photophysical behaviour of these polymers in order to establish knowledge of the fundamental properties that are responsible for the efficiencies of the devices as well as their amelioration [3–9]. However, the fact that the parent polymer is insoluble and intractable prevents its complete characterization so that systematic investigations on structure–property relationships are almost impossible. A part of this problem can be circumvented by the investigation of model compounds. This approach, the estimation of the properties of a polymer by investigation of oligomers as model compounds is widely used, especially in the field of conjugated polymers [10–15].

Oligo(phenylenevinylene)s are useful as model compounds for the corresponding polymers and as luminescent material in Organic Light Emitting Diodes (OLEDs). Herein, the synthesis and the electronic spectra of a series of substituted distyrylbenzenes (DSBs) with a great variety of position, number, and character of substituents is reported. In order to elucidate the influence of different substitution patterns on the absorption and emission spectra, electron donors like dimethylamino and alkoxy side chains, a well as electron withdrawing groups like sulfones or nitriles and combinations of them were studied. Electron-donating ether groups have been used extensively in the field of conjugated polymers, as they reduce the band gap and allow to attach solubilising side chains. Sulfones and nitriles on the other hand, are electron withdrawing, which is especially important for a balanced charge carrier injection into the emitting material in a LED [16, 17] and for the application of metals with higher work function as cathode [18]. To allow comparison of the influences of different substitution, the basic chromophore, DSB, remains unchanged.

Synthesis

Several reactions are suitable to synthesize 1,4-distyrylbenzenes with two identical styrene units. Besides aldol-type condensations like Knoevenagel and Siegrist, Heck and Wittig–Horner reactions are most versatile. For the latter one, the starting materials are terephthaldialdehydes or 1,4-bis(halomethyl)benzenes for the central ring and benzylic halides or benzaldehydes for the lateral units.

The majority of the distyrylbenzenes investigated here (**6a**–**h**) was synthesized starting with the Michaelis–Arbusov reaction of easily accessible 1,4-bis(chloromethyl) benzenes [19] to bisphosphonates **1a**, **1b** followed by PO-activated olefination with particular aldehydes **2a**–**e** (Scheme 1) [19]. The sulfonyl-substituted aldehyde **2c** was prepared in a three-step sequence from *p*-bromobenzaldehyde ethyleneacetal [20] and copper-(I)-hexylthiolate, followed by oxidation with hydrogen peroxide and subsequent hydrolysis.

Due to their specific substitution, the distyrylbenzenes **6i**–**l** were synthesized independently (Scheme 2). The starting materials **3**, **4** were prepared according to literature procedures [21, 22], 2,5-dipropoxyterephthaldialdehyde **5** from 1,4-dipropoxybenzene [23] by twofold bromination and Bouveault-reaction with butyl lithium and DMF [19, 24]. The Heck- and Knoevenagel-reactions of **3** and (**5**) with styrene or benzaldehyde, respectively [25, 26], gave the electron deficient DSBs **6i**, **6k**

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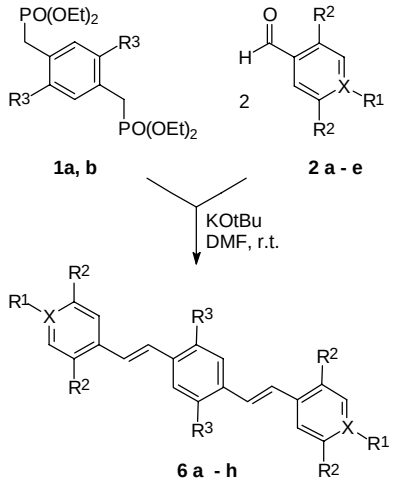
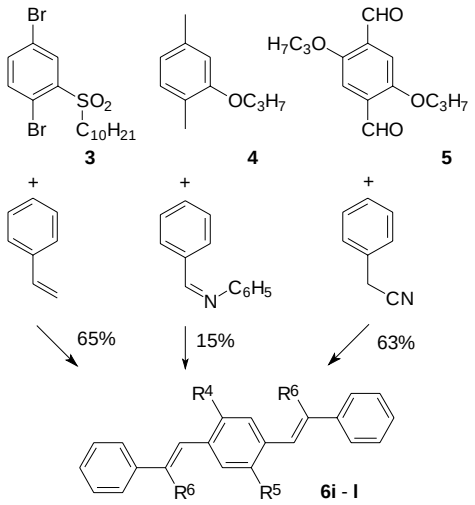


Compd.	X	R^1	R^2	R^3
6a	C	H	H	H
6b	C	H	H	OC_3H_7
6c	C	H	OC_3H_7	H
6d	C	H	OC_3H_7	OC_3H_7
6e	C	$SO_2C_6H_{13}$	H	H
6f	C	$SO_2C_6H_{13}$	H	OC_3H_7
6g	C	NMe_2	H	OC_3H_7
6h	N	–	H	OC_3H_7

Scheme 1 Synthesis and substitution pattern of the distyrylbenzenes **6a**–**h**

in reasonable yields whereas the outcome of the Siegrist reaction [27] of **4** was only poor. The vicinal coupling constants of the vinylene protons of **6a**–**6k** indicated the *trans,trans*-configuration of the DSBs. This configuration for the vinylene substituted DSB **6l** was substantiated by nuclear Overhauser experiments: whereas the irradiation into the signal of the aromatic protons on the central ring caused a NOE only at the α-protons of the propyloxy group, the irradiation into the resonance of the olefinic proton gave a positive NOE only at the frequency of the ortho-protons of the terminal benzene rings, indicating the trans configuration of the phenyl rings at the vinylene linkage.



Compd.	R^4	R^5	R^6
6i	$SO_2C_{10}H_{21}$	H	H
6k	OC_3H_7	H	H
6l	OC_3H_7	OC_3H_7	CN

Scheme 2 Synthesis and substitution pattern of the distyrylbenzenes **6i**–**l**

Electronic Spectra

Table 1 summarizes the electronic properties of the various distyrylbenzene derivatives investigated in this paper. Listed are the values for the absorption maximum λ_{max}, the absorption band edge which is taken as the wavelength where $\varepsilon = 0.1\varepsilon_{max}$, and the emission maximum $\lambda_{em,max}$. All measurements were carried out in solution in $CHCl_3$.

Table 1 Electronic properties of the *various* compounds in solution ($CHCl_3$)

Cpd.	λ_{max}(nm)	λ_0 (nm)	ε (l mol^{-1} cm^{-1})	$\lambda_{em,max}$ (nm)
6a	356	390	50 000	417
6b	387	435	36 500	448
6c	379	422	56 700	452
6d	402	451	40 700	460
6e	369	409	62 500	435
6f	410	465	47 000	504
6g	417	469	38 000	494
6h	397	449	27 000	490
6i	350	396	31 000	430
6k	365	406	44 500	434
6l	425	489	21 000	509

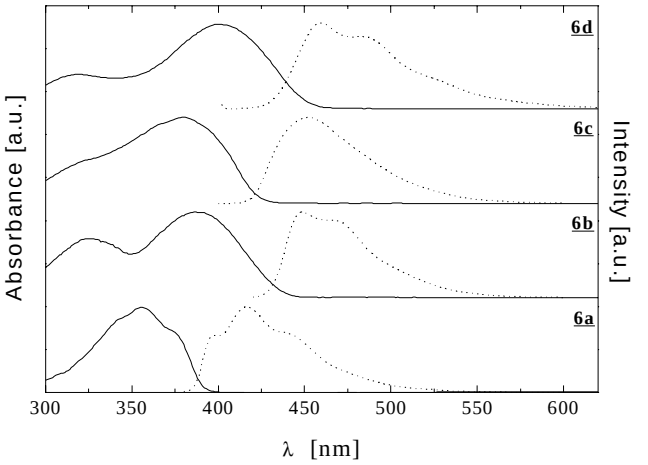


Fig. 1 Comparison of the electronic spectra of DSBs **6a**, **6b**, **6c**, **6d** ($CHCl_3$)

The electronic spectra of the 2,5-dipropyloxysubstituted DSBs **6b**–**d** and the parent compound **6a** are compared in Figure 1. Going from bottom to top, the chromo-

phore DSB is substituted at the central ring with two alkoxy groups (**6b**) or two at each outer ring (**6c**), respectively. Finally, compound **6d** comprises both patterns in carrying six alkoxy sidechains.

The electron-donating character of the ether groups provokes a bathochromic shift of both absorption and emission maxima. However, the comparison of **6b** and **6c** shows that this shift is less sensitive to the number, but more to the position of the substituents. Both maxima of **6c** are blue-shifted with respect to **6b**. As observed by Birckner, two alkoxy substituents at the central ring blur the vibrational structure of the absorption band accompanied by the buildup of a second, less intense absorption band [28]. Furthermore, the vibronic structure of the emission band vanishes completely for the fourfold substituted DSB **6c**. The absorption- and emission-bands are further shifted to lower energies upon addition of two more alkoxy groups. In going from **6a** to **6d**, the emission wavelength can be tuned over a range of more than 40 nm by the introduction of alkoxy side-chains.

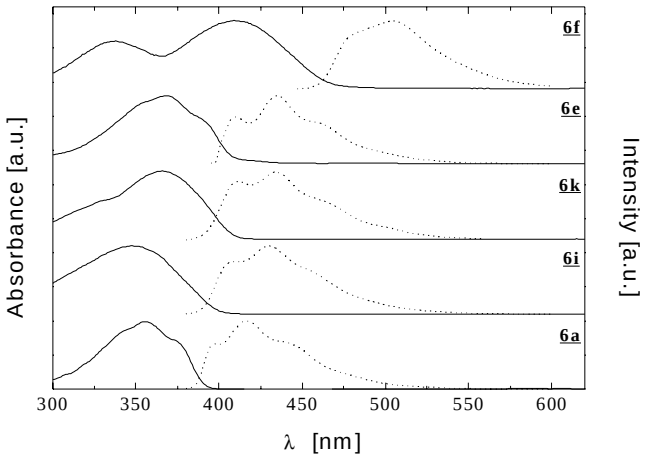


Fig. 2 Comparison of the electronic spectra of DSBs **6a**, **6e**, **6f**, **6i**, **6k** ($CHCl_3$)

The spectra of the sulfonyl-substituted DSBs are summarized in Fig. 2. Compared to DSB (**6a**), an electron-accepting sulfonyl group on the central ring of the chromophore (**6i**) causes a broadening and a slight hypsochromic shift (ca. 6 nm) of the absorption band but a bathochromic shift (ca. 13 nm) of the fluorescence, the vibronic structure is retained. Exchanging the electron withdrawing sulfone for an electron-donating ether (**6k**) slightly shifts the absorption (6 nm) and emission maxima (17 nm) to lower energies relative to the parent compound (**6a**). Nearly the same shifts are observed for a DSB with two sulfonyl groups, each in the *p*-position of the styrene unit (**6e**). These examples demonstrate that a tuning of the electron affinity of the chromophore is possible with only small alterations of the optical properties. This changes completely when the central ring is substituted with two propoxy groups (**6f**). Push–pull substitution and, predominant, this substitution pattern (*vide infra*) reduce the transition energies strongly.

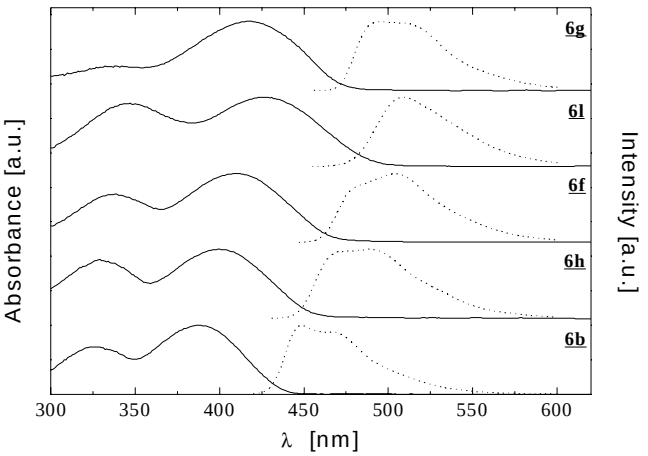


Fig. 3 Comparison of the electronic spectra of DSBs **6b**, **6f**, **6g**, **6h**, **6l** ($CHCl_3$)

Figure 3 presents the spectra of DSBs substituted with two alkoxy groups at the 2,5-positions of the central ring. The structure of the absorption and emission spectra in this group of DSBs is dominated by the spectral features of the parent chromophore **6b**, further substitution at both lateral *p*-positions (**6f**, **6g**, **6h**), regardless of electron donating or withdrawing character, shifts the wavelengths of excitation and fluorescence to the red. The structure of the emission bands, a maximum and a shoulder of similar intensity is retained, but differently weighted. Release of electron density (**6b**, **6g**) amplifies the blue part of the emission band whereas groups of –M character (**6f**, **6h**) strengthen the transition of lower energy. A comparison of the wavelengths of the "blue" and of the "red" fluorescence bands as well as of the absorption maxima establishes smaller shifts for substituents increasing the electron affinity of the chromophore. Finally, in DSB **6l** the electron accepting groups are attached to the ethylene unit. Compared with the other push–pull substituted chromophores, the absorption bands suffer the largest bathochromic shifts, but the structure is retained. Contrary, the red-shifted fluorescence becomes a sharpened single-maximum band, the loss of the shoulder reflects the drastic changes in the excited and ground states.

In conclusion, we have prepared a series of substituted 1,4-distyrylbenzenes. The variation of number, position, and electronic character of the substituents can alter the wavelength of the emitted light over a range of almost 100 nm. The electron-withdrawing sulfone has only small effects on the absorption and emission, on the outer rings as well as on the central ring. While a single alkoxy group on the central ring causes only a

small bathochromic shift, a medial 2,5-dialkoxyphenylene unit changes the electronic spectra drastically, only slight variations occur upon further substitution with electron-donating or withdrawing groups. Some of these model compounds have been used as emitting layer in electroluminescent devices [22] with promising optical results. DSB-type chromophores with electron-accepting substituents are interesting for electrooptical devices due to higher stability towards oxidation and, most notably, to their increased electron affinity, favouring balanced charge injection and transport. Additionally, the dimethylamino-substituted DSB **6g** seems to form J-type aggregates in thin films, which are known to be favourable for their high fluorescence quantum yields in the solid state [30].

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Experimental

IR-Spectra: in KBr, Beckman Acculab 4, NMR-Spectra: in $CDCl_3$ or DMSO-[D_6], Bruker AC 200 and AM 400, mass spectra: 70 eV, Varian MAT 711 (EI), MAT 95 (FD), UV-Vis: Perkin-Elmer, Lambda 15, Fluorescence spectra: Shimadzu RF5301 PC, elemental analyses were performed in the microanalytical laboratory of the Chemical Institute of the Johannes Gutenberg-Universität, Mainz, Germany, melting points: not corrected. – Eluent mixtures are v/v. Chemicals were used as received, solvents dried according to standard procedures and distilled.

4-Hexylsulfonylbenzaldehyde **2c**

a) *4-Hexylsulfonylbenzaldehyde Ethylene Acetal*: 4-Bromobenzaldehyde ethylene acetal [20] (11.45 g, 0.05 mol) was dissolved in 50 mL of freshly distilled quinoline and 13.5 g (0.075 mol) of copper-(I)-hexylthiolate were added. The mixture was stirred and heated to 170 °C for 36 h. The bulk of the solvent was evaporated under reduced pressure, the residue mixed with toluene (50 mL), filtered, and the solution washed three times with 250 mL of water each. The organic layer was dried ($MgSO_4$), concentrated and filtered through a pad of silica gel. The solvent was stripped off and the oily residue was dissolved in a mixture of 30 mL of acetonitrile and 20 mL of chloroform. The vigorously stirred solution was heated to reflux, 0.8 g of sodium bicarbonate were added and 30 mL of a 30% solution of hydrogen peroxide were added carefully in six portions. Refluxing was continued for another 30 min. The cooled solution was diluted with water, the organic layer separated and the aqueous layer extracted twice with dichloromethane. The pooled organic solutions were washed with water and brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography using toluene/ethyl acetate as an eluent. Yield 10.3 g (69%). – IR (KBr): ν/cm^{-1} = 2 930, 2 900, 2 840, 1 445, 1 300, 1 135, 1 072. – ^{1}H NMR (CDCl3): δ/ppm = 0.76 (t, 3H, CH_3), 1.40 – 1.15 (m, 6H, CH_2), 1.62 (qui, 2H, CH_2), 2.99 (m, 2H, CH_2SO_2), 4.01 (m, 4H, OCH_2), 5.80 (s, 1H, OCHO), 7.63 (d, J = 7.2 Hz, 2H, arom. H), 7.84 (d, J = 7.2 Hz, 2H, arom. H). – ^{13}C NMR: δ/ppm = 13.9 (CH_3), 22.2, 22.6, 27.9, 31.1 (CH_2), 56.3 (SO_2CH_2), 65.4 (OCH_2), 102.4 (OCHO), 127.3, 128.1 (arom. CH), 139.7, 143.9 (arom. Cq). – EI-MS: m/z (%) = 298 (39) [M$^{\cdot+}$], 253 (9), 214 (16), 43 (100).

$C_{15}H_{22}SO_4$	Calcd.:	C 60.40	H 7.38	S 10.74
(298,3)	Found:	C 60.73	H 7.22	S 10.46

b) 4-Hexylsulfonylbenzaldehyde (**2c**): 4-Hexylsulfonylbenzaldehyde ethylene acetal (6 g, 0.02 mol) was dissolved in 30 mL of ether, water (10 mL), and 0.2 g of *p*-toluenesulfonic acid were added, and the mixture was heated to reflux for 6 h while stirring. After cooling to r.t., ether (50 mL) was added and the organic layer washed twice with a saturated solution of sodium bicarbonate, once with brine, and dried over Na_2SO_4. Recrystallization from petroleum ether. Yield: 4.6 g (91%); *m.p.* 45 °C. – IR (KBr): ν/cm^{-1} = 3 090, 2 930, 2 852, 1 698, 1 596, 1 575, 1 466, 1 405, 1 300, 1 202, 1 150, 1 086, 832, 771, 703. – ^{1}H NMR ($CDCl_3$): δ/ppm = 0.80 (t, 3H, CH_3), 1.04 – 1.15 (m, 6H, CH_2), 1.68 (m, 2H, CH_2), 3.09 (m, 2H, SO_2CH_2), 8.08 (s, 4H, arom. H), 10.10 (s, 1H, CHO). – ^{13}C NMR: δ/ppm = 13.8 (CH_3), 22.2, 22.4, 27.8, 31.0 (CH_2), 56.1 (SO_2CH_2), 128.8, 130.2 (arom. CH), 139.5, 144.1 (arom. Cq), 190.8 (CHO). – EI-MS: m/z (%) = 254 (1) [M$^{\cdot+}$], 184 (4), 171 (36), 43 (100).

$C_{13}H_{18}SO_3$	Calcd.:	C 61.41	H 7.09	S 12.60
(254,3)	Found:	C 61.66	H 7.47	S 12.26.

2,5-Dipropyloxy-terephthaldialdehyde **5**

a) 1,4-Dibromo-2,5-bispropyloxybenzene: A solution of 21 g (0,13 mol) of Br_2 in 60 mL of dry CCl_4 was added slowly to 10 g (0.052 mol) of 1,4-bispropyloxybenzene dissolved in 100 mL of dry CCl_4. After stirring overnight, the excess of bromine was destroyed with $Na_2S_2O_3$, the organic phase washed with water and dried with Na_2SO_4. The solvent was removed and the residue recrystallized from methanol. Yield: 16 g (88%), colourless crystals, *m.p.* 71°C. – IR (KBr): ν/cm^{-1} = 2 940, 2 860, 1 490, 1 460, 1 390, 1 360, 1 265, 1 210, 1 070, 1 050, 1 020, 910, 850, 810. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.03 (t, 6H, CH_3), 1.80 (m, 4H, CH_2), 3.89 (t, 4H, OCH_2), 7.06 (s, 2H, arom. H). – ^{13}C NMR: δ/ppm = 10.5 (CH_3), 22.5 (CH_2), 71.7 (OCH_2), 111.1 (arom. CH), 118.4, 150.0 (arom. Cq). – FD-MS: m/z (%) = 355 (5), 354 (50), 353 (12), 352 (100), 351 (5), 350 (50) [M$^{+\cdot}$].

$C_{12}H_{16}Br_2O_2$	Calcd.:	C 40.94	H 4.58	Br 45.39
(352,07)	Found:	C 40.87	H 4.48	Br 45.44.

b) 2,5-Bispropyloxy-terephthaldialdehyde (**5**): 1,4-Dibromo-2,5-bispropyloxybenzene (2 g, 5,7 mmol), dissolved in 80 mL of dry ether, was cooled to –15 °C under an argon atmosphere and 8 mL of a solution of *n*-butyllithium in hexane (1.6M) were added *via* syringe. Upon addition, the solution changed its colour to yellow. After stirring for 30 minutes, 2 mL of dry DMF were added *via* syringe, and the cooling bath was removed. The yellow solution was stirred for another 30 minutes and quenched with 5 mL of concentrated hydrochloric acid. The organic layer was separated and the aqueous phase extracted with a small portion of ether. Washing of the pooled solutions three times with water was followed by drying with Na_2SO_4 and evaporation of the solvent.

The residue was purified by chromatography (silica gel, 5×10, toluene) and recrystallized from *n*-hexane to yield 1.05 g (74%) of yellow crystals, *m.p.* 75–76 °C. – IR (KBr): ν/cm^{-1} = 2 960, 2 940, 2 870, 1 680, 1 480, 1 465, 1 420, 1 400, 1 380, 1 270, 1 210, 1 120, 1 040, 1 015, 910, 875. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.03 (t, 6H, CH_3), 1.83 (m, 4H, CH_2), 4.02 (t, 4H, OCH_2), 7.39 (s, 2H, arom. H), 10.49 (s, 2H, CHO). – ^{13}C NMR: δ/ppm = 10.5 (CH_3), 22.5 (CH_2), 70.8 (OCH_2), 111.8 (arom. CH), 129.4, 155.3 (arom. Cq), 189.3 (CHO). – EI-MS: *m/z* (%) = 251 (4), 250 (27) [M$^{\cdot+}$], 166 (100), 138 (78), 43 (24).

$C_{14}H_{18}O_4$	Calcd.:	C 67.18	H 7.25
(250,3)	Found:	C 66.76	H 7.26.

Synthesis of Distyrylbenzenes *via* Wittig–Horner-Reaction (General Procedure)

In a three-necked round bottom flask dry DMF and KO*t*Bu were added together with 0.1 g of 18-crown-6, and the connected dropping funnel was charged with the aldehyde **2a**–**e** and the bisphosphonate **1a**, **b** dissolved in dry DMF. After the apparatus was evacuated and flushed with argon several times, the mixture was added slowly to the stirred solution of the base at room temperature, and stirring was continued for 2 h. The reaction was quenched by pouring onto crushed ice/hydrochloric acid. The precipitate was collected, washed with water first and then ethanol and subsequently recrystallized.

(E,E)-2,5-Bispropyloxy-1,4-distyrylbenzene (**6b**)

Synthesis according to the general procedure, using 0.5 g (4.7 mmol) benzaldehyde (**2a**), 1.05 g (2.1 mmol) bisphosphonate **1b**, 1 g potassium-*tert*-butylate and 50 mL of DMF. Recrystallization from ethanol yields 0.56 g (67%) of a yellow solid, *m.p.* 177–178 °C. – IR (KBr): ν/cm^{-1} = 3 048, 2 967, 2 934, 1 597, 1 498, 1 424, 1 256, 1 206, 1 062, 990, 978. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.14 (t, 6H, CH_3), 1.92 (m, 4H, CH_2), 4.04 (t, 4H, OCH_2), 7.15 (s, 2H, arom. H), 7.16 (AB, J = 16.5 Hz, 2H, olef. H), 7.26 (m, 2H, arom. H), 7.38 (m, 4H, arom. H), 7.52 (AB, J = 16.5 Hz, 2H, olef. H), 7.55 (m, 4H, arom. H). – ^{13}C NMR: δ/ppm = 10.8 (CH_3), 22.9 (CH_2), 71.2 (OCH_2), 111.0, 123.6, 126.5, 127.4, 128.7, 128.9 (olef., arom. CH), 127.1, 138.1, 151.2 (arom. Cq). – FD-MS: *m/z* (%) = 400 (9), 399 (60), 398 (100) [M$^{\cdot+}$], 199 (26), 199.5 (2) [M^{2+}]. – UV ($CHCl_3$): λ_{max}= 387 nm; ε = 36 500 l mol^{-1} cm^{-1}.

$C_{28}H_{30}O_2$	Calcd.:	C 84.38	H 7.59
(398,55)	Found:	C 84.32	H 7.59.

(E,E)-1,4-Bis(2,5-bispropyloxystyryl)benzene (**6c**)

Synthesis according to the general procedure, using 0.95 g (4.3 mmol) 2,5-bispropyloxybenzaldehyde (**2c**), 0.82 g (2.1 mmol) bisphosphonate **1a**, 1 g KO*t*Bu and 50 mL DMF. Yield 0.61 g (54%); *m.p.* 144–145 °C (methanol). – IR (KBr): ν/cm^{-1} = 3 049, 2 970, 2 937, 2 875, 1 607, 1 578, 1 511, 1 494, 1 466, 1 432, 1 390, 1 281, 1 240, 1 210, 1 122, 1 070, 1 053, 1 038, 983, 968. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.06 (t, 6H , CH_3), 1.10 (t, 6H, CH_3), 1.84 (m, 8H, CH_2), 3.93 (t, 4H, OCH_2), 3.94 (t, 4H, OCH_2), 6.77 (dd, J = 2.9 Hz, J = 8.9 Hz, 2H, arom. H), 6.82 (d, J = 8.9 Hz, 2H, arom. H), 7.13 (AB, J = 16.5 Hz, 2H, olef. H), 7.18 (d, J = 2.9 Hz, 2H, arom. H), 7.50 (AB, J = 16.5 Hz, 2H, olef. H), 7.52 (s, 4H, arom. H). – ^{13}C NMR: δ/ppm = 10.5, 10.7 (CH_3), 22.8, 22.9 (CH_2), 70.3, 71.1 (OCH_2), 112.5, 114.0, 114.6, 126.9 (arom. CH), 123.4, 128.8 (olef. CH), 127.7, 137.2, 151.1, 153.4 (arom. Cq). – FD-MS: *m/z* (%) = 516 (4), 515 (25), 514 (100) [M$^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 379 nm; ε = 56 700 l mol^{-1} cm^{-1}.

$C_{34}H_{42}O_4$	Calcd.:	C 79.34	H 8.22
(514,7)	Found:	C 79.55	H 8.20.

(E,E)-1,4-Bis-(4-hexylsulfonylstyryl)benzene (**6e**)

Synthesis according to the general procedure, using 0.66 g (1.8 mmol) of bisphosphonate **1a**, 0.5 g of KO*t*Bu and 1.07 g (4.2 mmol) of 4-hexylsulfonylbenzaldehyde (**2c**) dissolved in 30 mL of DMF. After workup, the solid residue was purified by chromatography using toluene/ethyl acetate as an eluent. Yield 0.55 g (53%), *m.p.* 262 °C. – IR (KBr): ν/cm^{-1} = 2 955, 2 934, 2 858, 1 593, 1 467, 1 405, 1 317, 1 281, 1 147, 1 089, 967, 843. – ^{1}H NMR ($CDCl_3$): δ/ppm = 0.84 (m, 6H, CH_3), 1.30–1.70 (m, 16H, CH_2), 3.09 (m, 4H, SO_2CH_2), 7.18, 7.22 (AB, J = 15.8 Hz, 4H, olef. H), 7.56 (s, 4H, arom. H), 7.69, 7.88 (AB, J = 7.7 Hz, 8H, arom. H). – ^{13}C NMR: δ/ppm = 13.9 (CH_3), 22.3, 22.6, 27.9, 31.1 (CH_2), 56.4 (SO_2CH_2), 127.0, 128.6, 131.8 (arom. CH), 127.4 (olef. CH), 136.6, 137.6, 143.5 (arom. Cq). – EI-MS: *m/z* (%) = 581 (5), 580 (18), 579 (41), 578 (100) [M$^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 369 nm; ε = 62 500 l mol^{-1} cm^{-1}.

$C_{34}H_{42}O_4S_2$	Calcd.:	C 70.55	H 7.31	S 11.08
(578,84)	Found:	C 70.32	H 7.44	S 10.75.

(E,E)-1,4-Bis-(4-hexylsulfonyl-styryl)-2,5-bispropyloxybenzene (**6f**)

By applying the general procedure to 0.36 g (0,7 mmol) of bisphosphonate **1b**, 0.37 g (1.5 mmol) of aldehyde **2c**, 1 g KO*t*Bu, and 50 mL DMF, **6f** (0.2 g, 40%) was obtained as a yellow solid, *m.p.* 179–180 °C (ethanol). – IR (KBr): ν/cm^{-1} = 3 053, 2 961, 2 932, 2 874, 1 592, 1 502, 1 466, 1 421, 1 317, 1 284, 1 205, 1145, 1 089, 980. – ^{1}H NMR ($CDCl_3$): δ/ppm = 0.84 (t, 6H, CH_3), 1.11 (t, 6H, CH_3), 1.24–1.90 (m, 20H, CH_2), 3.07 (m, 4H, SO_2CH_2), 4.03 (t, 4H, OCH_2), 7.11 (s, 2H, arom. H), 7.18, 7.60 (AB, J = 16.4 Hz, 4H, olef. H), 7.66, 7.85 (AB, J = 8.5 Hz, 4H, arom. H). – ^{13}C NMR: δ/ppm = 10.7, 10.8 (CH_3), 22.2, 22.7, 22.8, 27.9, 31.1 (CH_2), 56.4 (SO_2CH_2), 71.0 (OCH_2), 111.0, 126.9, 128.5 (arom. CH), 127.3 (olef. CH), 126.9, 137.4, 143.2, 151.4 (arom. Cq). – FD-MS: *m/z* (%) = 697 (5), 696 (22), 695 (44), 694 (100) [M$^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 410 nm; ε = 47 000 l mol^{-1} cm^{-1}.

$C_{40}H_{54}O_6S_2$	Calcd.:	C 69.13	H 7.83	S 9.23
(695,00)	Found:	C 69.08	H 7.95	S 9.17.

(E,E)-1,4-Bis[4-(N,N-dimethylamino)styryl]-2,5-bispropyloxybenzene (**6g**)

Synthesis from aldehyde **2d** (0.45 g, 3.4 mmol), bisphosphonate **1b** (0.61 g, 1.2 mmol), KO*t*Bu (1 g), and 50 mL of DMF according to the general procedure, however, the hydrochloric acid for the quenching process was omitted. The precipitate was recrystallized from methanol to yield 0.45 g (75%) of a yellow powder, *m.p.* 232–233 °C. – IR (KBr): ν/cm^{-1} = 3 043, 2 960, 2 934, 2 873, 1 608, 1 526, 1 420, 1 363, 1 260, 1 221, 1 200, 1 188, 1 037, 962. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.09 (t, 6H, CH_3), 1.88 (m, 4H, CH_2), 2.94 (s, 12H, NCH_3), 4.00 (t, 4H, OCH_2), 6.76, 7.42 (AB, J = 8.5 Hz, 8H, arom. H), 7.05, 7.30 (AB, J = 16.5 Hz, 4H, olef. H), 7.09 (s, 2H, arom. H). – ^{13}C NMR: δ/ppm = 10.8 (CH_3), 23.0 (CH_2), 40.6

(NCH_3), 71.3 (OCH_2), 110.6, 112.6, 119.5, 127.4, 128.7, 128.9 (arom. CH), 127.1, 138.1, 151.2 (arom. Cq). – FD-MS: *m/z* (%) = 486 (6), 485 (37), 484 (100) [$M^{\cdot+}$], 242 (4) [M^{2+}]. – UV ($CHCl_3$): λ_{max} = 417 nm; ε = 38 000 l mol^{-1} cm^{-1}.

$C_{32}H_{40}N_2O_2$	Calcd.:	C 79.30	H 8.32	N 5.78
(484,69)	Found:	C 79.17	H 8.34	N 5,84.

(E,E)-1,4-Bis(pyrid-4-yl-ethenyl)-2,5-bispropyloxybenzene (**6h**)

Synthesis from bisphosphonate **1b** (0.34 g, 0.7 mmol), 0.28 g (2.6 mmol) of pyridine-4-carbaldehyde (**2e**), KO*t*Bu (1 g) and 50 mL of DMF according to the general procedure. After one hour, the reaction was quenched with brine, and the mixture was extracted three times with small portions of CH_2Cl_2. After drying with Na_2SO_4, the solvent was evaporated and the residue purified by chromatography (silica gel, 5×10, acetone). Recrystallization from *n*-hexane yielded 0,2 g (73%) of an orange solid, *m.p.* 190 °C. – IR (KBr): ν/cm^{-1} = 3 054, 3 023, 2 965, 2 940, 2 878, 1 628, 1 595, 1 501, 1 474, 1 427, 1 393, 1 351, 1 327, 1 264, 1 211, 1 048, 1 029, 990, 968, 851. – ^{1}H NMR (DMSO-[D_6]): δ/ppm = 1.07 (t, 6H, CH_3), 1.84 (m, 4H, CH_2), 4.07 (t, 4H, OCH_2), 7.39, 7.67 (AB, *J* = 16.5 Hz, 4H, olef. H), 7.39 (s, 2H, arom. H), 7.50, 8.56 (AB, *J* = 5.9 Hz, 8 H, arom. H). – ^{13}C NMR: δ/ppm = 10.5 (CH_3), 22.1 (CH_2), 70.4 (OCH_2), 111.6, 120.6, 150.1 (arom. CH), 127.0, 127.2 (olef. CH), 126.2, 144.6, 150.9 (arom. Cq). – FD-MS: *m/z* (%) = 402 (8), 401 (49), 400 (100) [$M^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 397 nm; ε = 27 000 l mol^{-1} cm^{-1}.

$C_{26}H_{28}O_2N_2$	Calcd.:	C 77.97	H 7.05	N 6.99
(400,52)	Found:	C 77.88	H 7.02	N 6.72.

(E,E)-1,4-Bis-styryl-2-(3,7-dimethyloctylsulfonyl)benzene (**6i**)

A mixture of 228 mg (2.2 mmol) of freshly distilled styrene, 440 mg (1 mmol) of 2,5-dibromo-(3,7-dimethyloctylsulfonyl)benzene (**3**) and 0.5 g of triethylamine in 3 mL of dry DMF was purged with argon and 0.9 mg (4 µmol) of palladium acetate and 2.5 mg (8 µmol) of tris-*o*-tolylphosphine were added. The solution was kept under argon and heated to 105 °C for 6 h while stirring. The cooled mixture was poured into hydrochloric acid (0,1M), extraction with ethyl acetate (3×) and washing of the pooled organic solutions (2×) with brine was followed by drying with $MgSO_4$ and chromatography on silica gel with toluene/ethyl acetate as an eluent. Yield 316 mg (65%), *m.p.* 81°C. – IR (KBr): ν/cm^{-1} = 3 059, 2 954, 2 927, 2 867, 1 634, 1 597, 1 497, 1 449, 1 322, 1 302, 1 149, 1 133, 1 053, 989, 972, 963, 824. – ^{1}H NMR ($CDCl_3$): δ/ppm = 0.88 (m, 9H, CH_3), 0.99–1.08 (m, 6H, CH_2), 1.30–1.78 (m, 4H, CH_2, CH), 3.17 (m, 2H, SO_2CH_2), 7.08 (d, *J* = 16 Hz, 1H, olef. H), 7.12 (d, *J* = 16 Hz, 1H, olef. H), 7.22 (d, *J* = 16 Hz, 1H, olef. H), 7.29–7.41 (m, 6H, aromat. H), 7.54 (d, *J* = 7.2 Hz, 2H, aromat. H), 7.57 (d, *J* = 7.2 Hz, 2H, aromat. H), 7.74 (dd, *J* = 8.0 Hz, *J'* = 1.8 Hz, 1H, aromat. H), 7.76 (d, *J* = 8.0 Hz, 1H, aromat. H), 8.09 (d, *J* = 16 Hz, 1H, olef. H), 8.19 (d, *J* = 1.8 Hz, 1H, aromat. H). – ^{13}C NMR: δ/ppm = 19.1, 22.5, 22.5 (CH_3), 24.4, 29.0, 36.4, 39.0 (CH_2), 27.8, 31.6 (CH), 53.7 (SO_2CH_2), 124.0, 126.7, 127.1, 127.8, 128.1, 128.2, 128.7, 130.9, 131.1 (arom. CH, olef. CH), 133.9, 136.2, 136.5, 136.6, 137.1 (arom. Cq). – EI-MS: *m/z* (%) = 486.3 (100) [$M^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 350 nm; ε = 31 000 l mol^{-1} cm^{-1}.

$C_{30}H_{38}O_2S$	Calcd.:	C 77.88	H 8.28	S 6.93
(462,70)	Found:	C 77.76	H 7.93	S 6.64.

(E,E)-1,4-Distyryl-2-propyloxybenzene (**6k**)

In an argon atmosphere, a solution of 1.5 g (8.28 mmol) of *N*-phenylbenzaldimine and 0.5 g (3.05 mmol) of 1,4-dimethyl-2-propyloxybenzene (**4**) in 25 mL of dry DMF was added to KO*t*Bu (2 g) dissolved in 25 mL of dry DMF and the reaction mixture was heated to 60 °C for one hour and then poured onto 200 g of crushed ice containing 10 mL of concentrated hydrochloric acid. The product was isolated by extraction with three small portions of $CHCl_3$. Drying with Na_2SO_4, evaporation and chromatography (silica gel, 5×15, petroleum ether/ ether 5:1) yielded 0,15 g (15%) of a colourless solid, *m.p.* 125 °C. – IR (KBr): ν/cm^{-1} = 3 022 , 2 963, 2 929, 2 874, 1 595, 1 555, 1 505, 1 425, 1 267, 1 244, 1 115, 1 073, 1 028, 964, 815. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.14 (t, 3H, CH_3), 1.93 (m, 2H, CH_2), 4.06 (t, 2H, OCH_2), 7.03 (d, 1H), 7.10 (d, 2H), 7.13 (m, 1H), 7.19 (AB, *J* = 16.5 Hz, 1H), 7.26 (m, 2H), 7.36 (m, 4H), 7.50 (m, 1H), 7.53 (m, 4H), 7.58 (d, 1H) (arom. H, olef. H). – ^{13}C NMR: δ/ppm = 10.8 (CH_3), 22.8 (CH_2), 70.1 (OCH_2), 110.1, 119.3, 123.5, 126.5, 126.8, 127.3, 127.6, 128.6, 128.7, 128.7, 128.9 (arom. CH, olef. CH), 126.3, 137.4, 137.9, 138.2, 156.8 (arom. Cq). – FD-MS: *m/z* (%) = 342 (3), 341 (24), 340 (100) [$M^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 365 nm; ε = 44 500 l mol^{-1} cm^{-1}.

$C_{25}H_{24}O$	Calcd.:	C 88.20	H 7.11	
(340,47)	Found:	C 87.86	H 7.50.	

(Z,Z)-1,4-Bis(α-cyanostyryl)-2,5-bispropyloxybenzene (**6l**)

Potassium-*tert*-butylate (0.35 g, 3.2 mmol) was dissolved in 8 mL of dry *tert*-butanol under an argon atmosphere. Dialdehyde **5** (0.39 g, 1,6 mmol) and benzylcyanide (0.37 g, 3.2 mmol), dissolved in 20 mL of dry THF, were added quickly *via* syringe, the solution turned green. After stirring for 15 minutes at room temperature, the reaction was quenched by the addition of 60 mL of methanol containing 2 mL of concentrated hydrochloric acid. An orange solid precipitated which was recrystallized from *n*-hexane. Yield 0.45 g (63%), *m.p.* 194–196 °C. – IR (KBr): ν/cm^{-1} = 3 069, 2 965, 2 935, 2 876, 2 209, 1 589, 1 502, 1 428, 1 368, 1 249, 1 216, 1 069, 1 018, 981, 904. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.07 (t, 6H, CH_3), 1.87 (m, 4H, CH_2), 4.08 (t, 4H, OCH_2), 7.38 (m, 2H, arom. H), 7.44 (m, 4H, arom. H), 7.69 (m, 4H, arom. H), 7.88 (s, 2H, olef. H), 8.03 (s, 2H, arom. H). – ^{13}C NMR: δ/ppm = 10.6 (CH_3), 22.6 (CH_2), 70.9 (OCH_2), 111.5, 126.1, 129.1, 129.2 (arom. CH), 111.9 (olef. Cq), 118.3 (CN), 136.1 (olef. CH), 125.9, 134.8, 151.6 (arom. Cq). – FD-MS: *m/z* (%) = 450 (5), 449 (32), 448 (100) [$M^{\cdot+}$]. – UV ($CHCl_3$): λ_{max} = 425 nm; ε = 21 000 l mol^{-1} cm^{-1}.

$C_{30}H_{28}N_2O_2$	Calcd.:	C 80.33	H 6.29	N 6.25
(448,57)	Found:	C 80.04	H 6.01	N 6.07.

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