Synthesis, Absorption and Luminescence of a New Series of Soluble Distyrylbenzenes Featuring Cyano Substituents at the Peripheral Rings

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Dedicated to Professor Manfred Regitz on the occasion of his 65th birthday

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The synthesis of a complete series of nine soluble distyrylbenzenes (DSBs) with two (**2a**–**c**) and four cyano groups (**1a**–**f**) attached to the peripheral aromatic rings is reported. They were prepared by the Wittig reaction and characterized by ^{1}H and ^{13}C NMR, FT-IR, UV/Vis, PL, EL, mass spectra, and elemental analysis. The optical properties have been studied in detail to monitor structure–luminescence relationships as a function of the position of the cyano moieties. The DSBs with cyano substituents show bathochromic shifts in their absorption spectra when compared to the parent DSB (**30**). The extent of this red-shift depends on electronic and steric factors. The bis(*p*-cyano)-substituted compound **2c** exhibits a small Stokes shift and a remarkably high quantum yield of φ_F = 0.6–0.8 in the solid state. All the new distyrylbenzenes show electroluminescence when employed in devices with an ITO/PcCu/DSB/Al configuration and with colors ranging from red to green.

Introduction

Since the discovery of the electroluminescent properties of poly(1,4-phenylenevinylene) (PPV) in 1990[1] many new modified analogous compounds have been developed and applied as an emissive layer in organic light-emitting diodes (OLEDs).[2–4] Tuning of their properties, especially their photoluminescence (PL) and electroluminescence (EL) emissions, can be achieved by varying the structure and type of substituents. The systematic modification of the properties of light-emitting polymers or oligomers, plays an important role in optimizing OLED performances.

A typical OLED set-up consists of an emitting layer sandwiched between two electrodes. For high efficiencies of such devices, charge carrier injection as well as charge transport have to be balanced. However, in most emitting materials investigated so far, the injection and transport of holes is easier than that of electrons.[3] To improve the electron injection rate at the cathode, two main strategies have been followed: i) a low-work-function metal, for example Ca or Mg, can be used as the cathode material [5] (accepting its disadvantage of high susceptibility to atmospheric degradation), or ii) the electron affinity (EA) of the emitter can be increased by the introduction of electron-withdrawing groups (e.g. cyano groups).[6,7] The latter permits the construction of devices utilizing a higher work function and a more stable metal, such as aluminium. The first reported example of this work involved the preparation of poly-2,5-bis(hexyloxy)cyanoterephthalidene (PCTP) and its application in a heterostructure device in combination with PPV as the hole transporting layer.[7] Since this example, quite a number of related polymers[8] and oligomers[9] with cyano groups attached to the vinylene linkages have been synthesized, and their optical and electronic properties have been studied.

In previous studies we investigated the steric and electronic influence of cyano substituents attached to the vinylic double bonds of some PPV analogous short-chain model compounds.[10] For this purpose we found oligomeric systems to be advantageous because, owing to their well-defined structure, they are easy to characterize and allow predictions about the optical behavior of the corresponding polymers. In trimeric systems, when the cyano groups are attached to the vinylene double bonds there are just two possible positions (α-position: neighboring to the peripheral ring; β-position: neighboring to the central ring, see Figure 2). In contrast, the peripheral rings permit a wider variety of substitution patterns, thus leading to a greater number of possible regioisomers. However, there are only a few reports on PPV analogous polymers or oligomers with cyano groups at the aryl rings.[11]

A series of new distyrylbenzenes (DSBs) with cyano substituents in both of the peripheral phenyl rings were prepared (Figure 1). The aim of this work was to utilize the electron withdrawing, and thus, EA increasing character of the cyano groups and to systematically vary their positions within the peripheral phenyl rings, in order to investigate how these factors affect the optical properties of the corresponding compounds.

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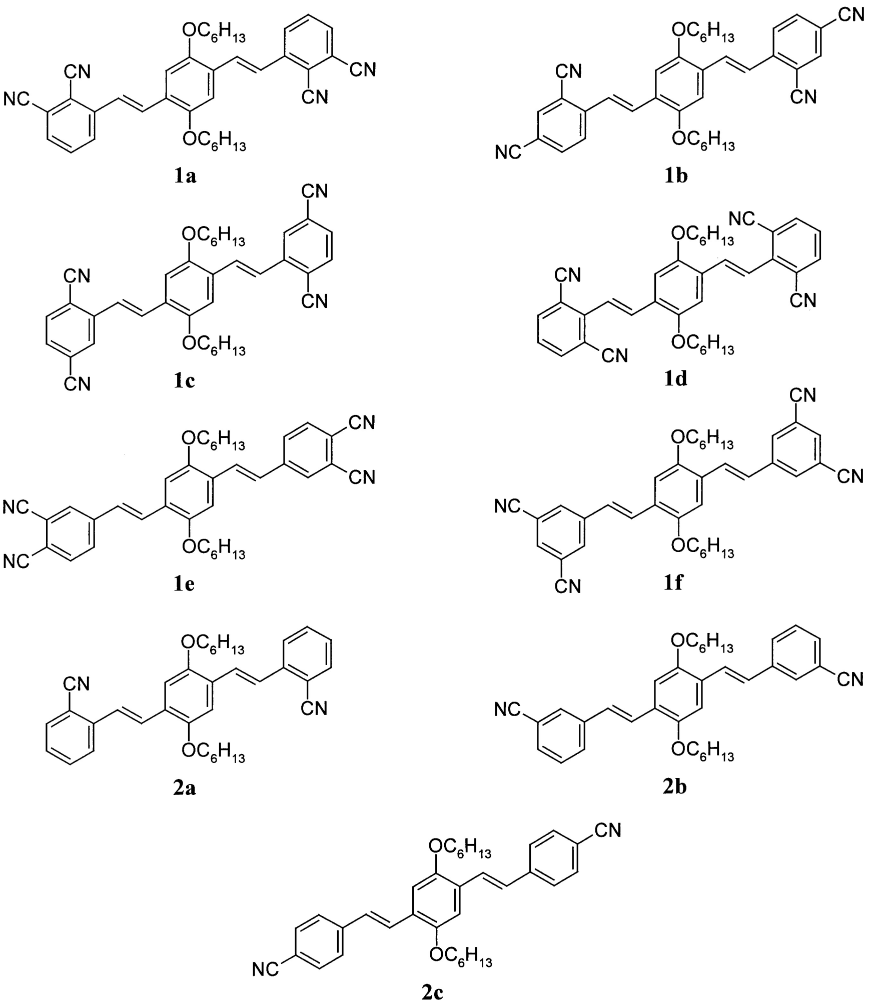


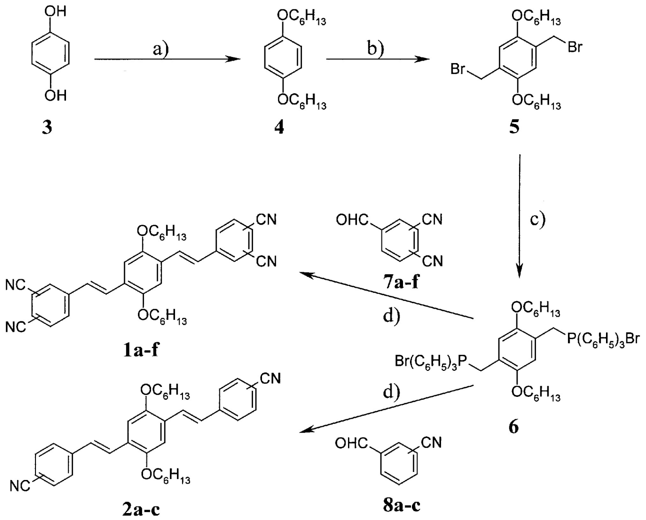
Figure 1. Arrangement of the new dicyanodistyrylbenzenes (DC-DSBs) **2a−c** and tetracyanodistyrylbenzenes (TC-DSBs) **1a−f**

The present study reports on the synthesis and characterization of these trimers. The influence of the withdrawing cyano substituents on absorption, PL and EL shifts is investigated and the capability of tuning the emission color by changing their positions is discussed.

Results and Discussion

In the case of dicyanodistyrylbenzenes with the cyano moieties attached to the peripheral rings there are three possibilities for their positions: *o*-(2-) (**2a**), *m*-(3-) (**2b**) and *p*-(4-) (**2c**) position relative to the vinylene double bond. For the tetracyanodistyrylbenzenes there are six possible regioisomers: *o*/*m*-(2,3-) (**1a**), *o*/*p*-(2,4-) (**1b**), *o*/*m*′-(2,5-) (**1c**), *o*/*o*′-(2,6-) (**1d**), *m*/*p*-(3,4-) (**1e**) and *m*/*m*′-(3,5-) (**1f**) substituted (Figure 1). For a systematic investigation of their properties the complete series was synthesized and characterized by IR, NMR, UV/Vis, PL and EL spectroscopy, and MS and elemental analysis. The dicyanodistyrylbenzenes will be abbreviated in the following text as DC-DSBs and the tetracyanodistyrylbenzenes as TC-DSBs.

The key compounds within the synthetic approach to the desired DC-DSBs and TC-DSBs are the corresponding three monocyano- (**8a−c**) and the six dicyanobenzaldehydes (**7a−f**). A Wittig reaction in dry ethanol with 1,4-dihexyloxy-2,5-xylylene bis(triphenylphosphonium bro-



Scheme 1. Synthesis of the DC-DSBs **2a−c** and TC-DSBs **1a−f**: a) $C_6H_{13}Br$, K_2CO_3, b) HBr, $(HCHO)_n$, c) $P(C_6H_5)_3$, toluene, d) ethanol, KO*t*Bu

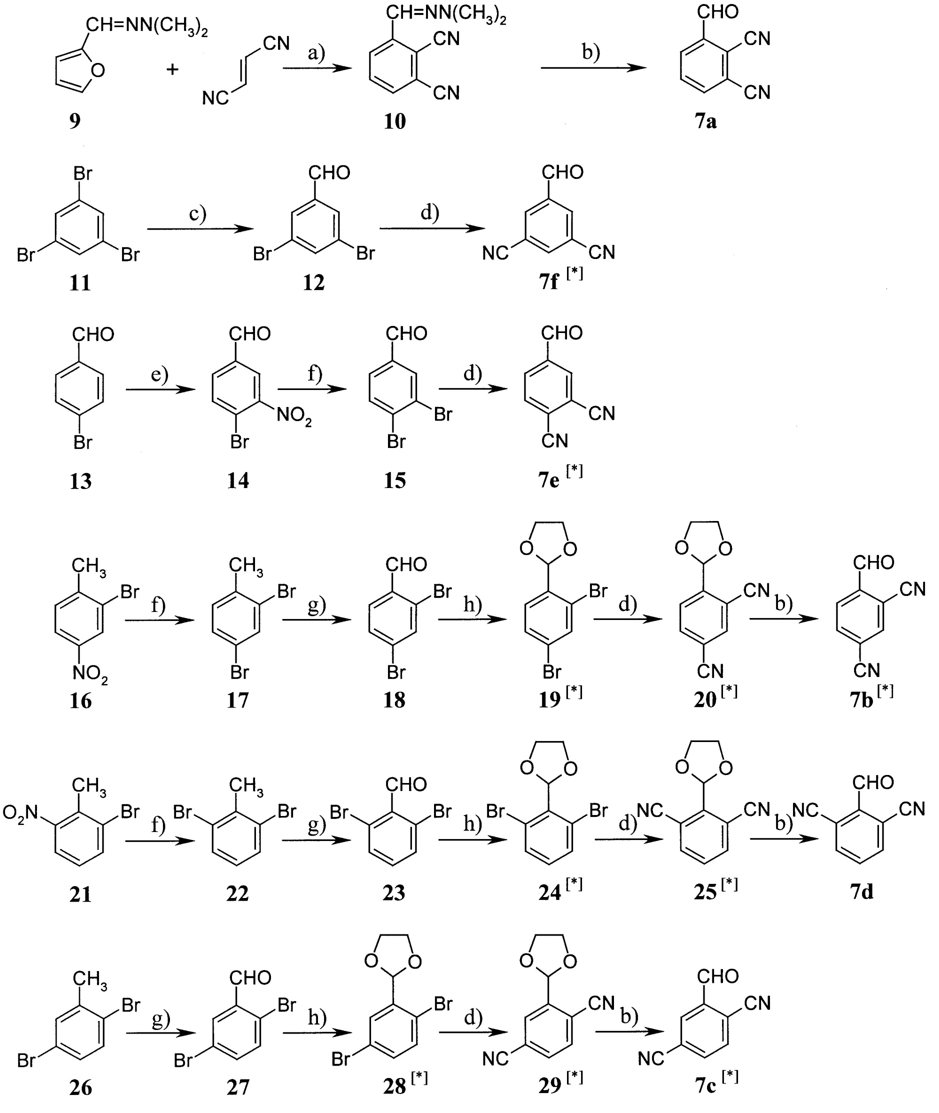
mide) (**6**)[12,13] gave **1a−f** and **2a−c** in moderate yields (Scheme 1). The products were isolated as mixtures of three isomers (*E*/*E*, *Z*/*Z* and *Z*/*E*).

In each case we were able to separate the required *E*/*E* isomer by recrystallization from ethyl acetate. The pure *E*/*E* isomer is evident from the ^{1}H NMR spectra due to a trans coupling constant $J > 16$ Hz for the vinylic protons and a single triplet signal at $\delta = 4.05-4.09$ for the OCH_2 protons of the hexyloxy substituents. The out-of-plane bending vibration of the −CH=CH− moieties appears in the IR spectrum in the range 960−980 cm^{-1}. Potassium *tert*-butoxide was used as the base for the Wittig reaction as it has several advantages over other commonly applied bases.[14] For the preparation of **6**, the hydroquinone **3** was converted into the corresponding dihexyloxy ether **4**. Bromomethylation and a subsequent reaction with triphenylphosphane resulted in the bisphosphonium salt **6**.[12,13]

The monocyanobenzaldehydes **8a−c** are commercially available. Different synthetic routes were used for the preparation of the dicyanobenzaldehydes **7a−f**, as depicted in Scheme 2.

2,3-Dicyanobenzaldehyde dimethylhydrazone (**10**) can be obtained in good yields from the Diels−Alder reaction of 2-furfuryl dimethylhydrazone with fumarodinitrile in the presence of tin(IV) chloride.[15,16] Hydrolysis of **10** with 2 N HCl gave the required 2,3-dicyanobenzaldehyde (**7a**). The reaction of 1,3,5-tribromobenzene (**11**) with butyl lithium at −78 °C resulted in the replacement of one bromo atom with lithium. A subsequent reaction with dimethylformamide (DMF) afforded 3,5-dibromobenzaldehyde (**12**).[17]

Nitration of the commercially available 4-bromobenzaldehyde (**13**) yielded the nitro derivative **14**.[18] 3,4-Dibromobenzaldehyde (**15**) was then formed by the reduction of **14** with tin(II) bromide, followed by diazotization and reaction with copper(I) bromide. These three steps can be readily performed in a one-pot reaction following a method described in the literature.[18] In a similar manner, 2-bromo-4-nitro- (**16**) and 2-bromo-6-nitrotoluene (**21**) were converted



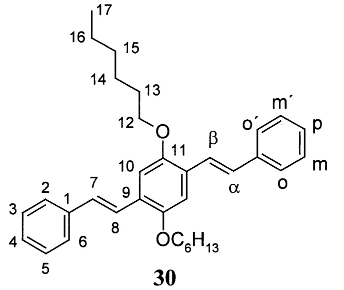
Scheme 2. Synthetic pathways to the dicyanobenzaldehydes **7a−f**: a) $SnCl_4$, $CHCl_3$, b) HCl, CH_3CN, c) I) BuLi, Et_2O, −78 °C, II) DMF, d) CuCN, DMF, 150 °C, e) $NaNO_3$, H_2SO_4, f) I) $SnBr_2$, II) $NaNO_2$, CuBr, g) I) CrO_3, H_2SO_4, AcOH, Ac_2O, II) H_2SO_4, ethanol, 80 °C, h) ethylene glycol, *p*-toluenesulfonic acid; new compounds are marked with [*]

Table 1. Fluorescence maxima ν_{max} (wavenumber units, cm^{-1}), Stokes shifts $\Delta\nu_{St}$, quantum yields φ and decay times τ of **30** and dicyano derivatives **2a−c** in thin films and in dichloromethane solutions

	Thin films ν_{max} (PL) / cm^{-1}	$\Delta\nu_{St}$ / cm^{-1} [a]	φ	τ / ns	CH_2Cl_2 solutions φ	τ / ns
30	17000	5000	0.15	21	0.66	1.6
2a	17000	4500	0.03−0.06	9.5	0.65	2.0
2b	18000	3700	0.04−0.08	2.3	0.72	1.9
2c	18950[b]	800[c]	0.6−0.8	0.5	0.81	1.8

[a] Spectral shifts against aggregate band **A**. − [b] Average $<\nu_F>$ of the fluorescence spectrum. − [c] Spectral shifts of (0 → 0) transitions of fluorescence and absorption against each other.

into the corresponding dibromo compounds **17** and **22**, respectively. The methyl groups of **17**, **22** and of the purchasable 2,5-dibromotoluene (**26**) can be oxidized with chromium(VI) oxide and sulfuric acid to form the dibromobenzaldehydes **18**, **23** and **27**, respectively.[19] In a Rosenmund−von Braun reaction, **12** and **15** can be converted directly into the dicyanobenzaldehydes **7f** and **7e**, respectively. In contrast, in compounds **18**, **23** and **27**, where at least one bromo atom is situated in an *ortho* position with respect to the aldehyde group, the exchange by the cyano group obviously takes place more slowly (TLC control) than the decomposition of the aldehyde function under the severe reaction conditions. Protection of the aldehyde moiety is therefore required. For this purpose we chose ethylene glycol as the reagent and this resulted in the formation of the dioxolane derivatives **19**, **24** and **28**, respectively. Additionally, the reaction times and the synthetic workup after the reaction were modified (see Experimental Section). After cyanation, the protection group of the dicyanodioxolane derivatives **20**, **25** and **29** can easily be cleaved to form the desired dicyanobenzaldehydes **7b**, **7d** and **7c**, respectively.



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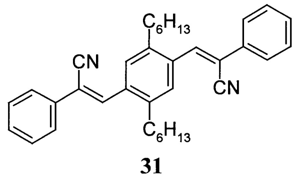

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Figure 2. Chemical structures of **30** and **31** and labelling of dihexyloxy-substituted DSBs: the numbers denote the hydrogen and carbon atoms for NMR assignments, α and β the possible positions of the cyano groups at the vinylene double bonds and o, m, p, m′ and o′, the positions at the peripheral rings

Table 1 summarizes the fluorescence maxima (ν_{max}), Stokes shifts ($\Delta\nu_{St}$), quantum yields (φ) and decay times (τ) of the cyano-free DSB **30** (see Figure 2) and the DC-DSBs **2a−c** in thin films and in dichloromethane solutions. Figure 3 presents UV/Vis absorption and fluorescence spectra of the dicyano-substituted series **2a−c** in vapor deposited films on glass substrates. The film spectra of **2c** are clearly vibronically structured, and fluorescence is only slightly Stokes-shifted relative to the lowest energetic absorption band. In contrast to **2c**, the film spectra of **2a**, **2b** and the tetracyano-substituted series **1b−f** are broad and unstructured, and the fluorescence maxima are strongly Stokes-shifted relative to the first absorption maxima. These features are also found for the cyano-free compound **30**.[10d]

The lowest energetic absorption maxima of all the cyano derivatives are red-shifted relative to the cyano-free molecule **30**. This is in accordance with the increased effective π-conjugation lengths and the asymmetric stabilization of the frontier orbital levels owing to the electron-withdrawing cyano groups.[6] In solution, the energetic order of the ab-

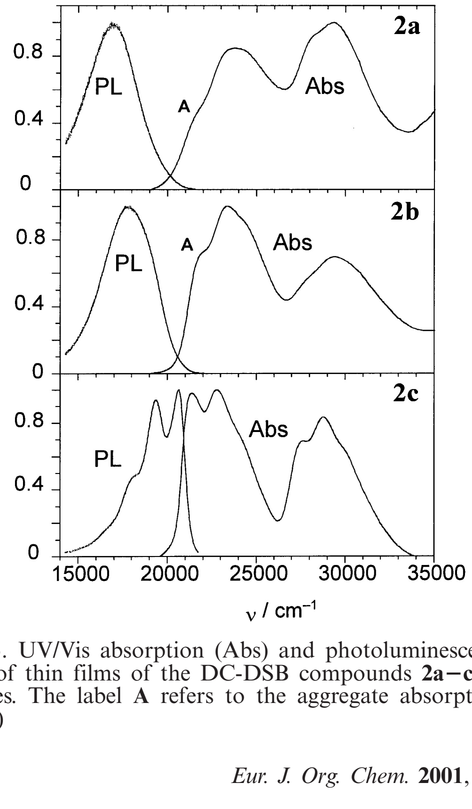

Figure 3. UV/Vis absorption (Abs) and photoluminescence (PL) spectra of thin films of the DC-DSB compounds **2a−c** on glass substrates. The label **A** refers to the aggregate absorption band (see text)

Table 2. UV/Vis absorption, photoluminescence (PL) and electroluminescence (EL) maxima (wavelength units, nm) of the DC-DSBs and TC-DSBs in different environments

	CH_2Cl_2 solutions		ITO/PcCu/DSB/Al devices			Films on glass	
	Abs. nm	PL nm	EL nm (ITO side)	PL nm (ITO side)	PL nm (Al side)	Abs. nm	PL nm
1a	422	506	532	–	–	442	524
1b	438	532	547	–	–	437	591
1c	426	512	534	–	–	440	577
1d	422	524	521	–	–	445	584
1e	435	533	662	–	–	467	616
1f	413	492	552	–	–	439	566
2a	407	488	544	550	573	421	588
2b	396	459	538	533	570	428	559
2c	409	491	515	516	531[a]	439	527[a]

[a] Spectral shifts against aggregate band **A**.

sorption maxima follows chemical experience, i.e. **30** > **2b** (*meta*) > **2a** (*ortho*) > **2c** (*para*). In the films the complete series of absorption maxima is bathochromically shifted by an additional 1000−3000 cm^{-1}, and the energetic order changes to **30** > **2a** (*ortho*) > **2b** (*meta*) > **2c** (*para*). The reasons for the solid state shifts are dipole−dipole interactions between the highly polarizable conjugated molecules and the increase of the effective conjugation lengths by reduction of the phenylene−vinylene dihedral angles. The latter effect may explain the interchange of energetic order, since **2a** is sterically more hindered against planarization than **2b**. In general, the band positions of the TC-DSB films are shifted to lower energies relative to the DC-DSB films, but the decrements are not additive. Even an energetic inversion is possible, as in the case of **1b** (*ortho*/*para*) > **2c** (*para*), since the effective conjugation of **2c** is reduced by additional CN substituents in the sterically unfavorable *ortho* positions. In **1e** (*meta*/*para*), these steric restrictions are absent, and consequently the films of **1e** absorb at the lowest energy of all the compounds discussed in this paper (Table 2).

The energetic order of the photoluminescence (PL) spectra of the films does not follow the order of the absorption spectra of the corresponding films (see Figure 3 and Table 2). Obviously, only **2c**, and to some extent **1a**, exhibit fluorescence behavior like molecules in solution, with small Stokes shifts, well-resolved vibrational structures, high quantum yields and short lifetimes (Table 1). Films of **2c** show bright fluorescence with a quantum yield of $\varphi_F \approx 0.6$, which is exceptionally high for oligophenylenevinylenes (OPVs) in the condensed state. Usually, the fluorescence yields of OPVs are low in films because of intermolecular excitonic side-by-side interactions.[20] Exceptions are films of **31** (Figure 2) or similar, where adjacent molecules are arranged in a head-to-tail configuration (J-aggregates) that makes fluorescence highly allowed and minimizes the Stokes shift.[20] The films of **2c** seem to produce a similar arrangement or, at least, there is sufficient intermolecular separation to suppress excitonic side-by-side coupling. The other representatives of Figure 3 and Table 2 exhibit fluorescence spectra that are strongly modified by intermolecular side-by-side interactions. The PL quantum yields are much lower than in solution, but the lifetimes are longer. Thus, fluorescence of the films is a weakly allowed process with radiative lifetimes in the order of τ_r = 100 ns (against τ_r = 2−3 ns in solution). The origin of the fluorescence must be ascribed to the shoulder **A** in the red part of the absorption spectra ("aggregate band"), since this part is polarized differently in the fluorescence excitation spectra than the main first band. The position of fluorescence is therefore determined by the position of the aggregate absorption band and an additional excited dimer (excimer) stabilization energy that enters into the Stokes shift. Since the stabilization energy depends strongly on π-overlap and intermolecular distances, it is difficult to predict the position of fluorescence from the aggregate absorption band and the absorption spectra of films that exhibit structureless fluorescence spectra, i.e. **30**, **1b−f**, **2a** and **2b**.

All the compounds in Table 2 show electroluminescence (EL) when sandwiched in an ITO/PcCu/DC-DSB or TC-DSB/Al configuration (Figure 4). The set-up of the devices is illustrated in Figure 5.[21]

The emission colors range from pure red in **1e** to green in **2c**. The EL maxima are summarized in Table 2, and for the DC-DSB series, the whole spectra are displayed together with the PL spectra in Figure 4. The correspondence of the general spectral shapes and the band positions are quite good. However, the spectra in Figure 4 are very different from the PL spectra of the films on glass substrates in Figure 3. These differences arise from the fact that the EL and PL of the devices have been measured from the ITO side, where the emission is filtered by the copper phthalocyanine (PcCu) hole transporting layer before leaving the sample. The PcCu layer shows Q-band absorption maxima at $\nu_1 = 16300\ cm^{-1}$ and $\nu_2 = 14400\ cm^{-1}$ (in the **2b** device the PcCu layer thicknesses were different for the PL and EL measurements, thus large intensity differences are obtained in the region of the main PcCu absorption). If the PL is detected from the Al side (between the Al stripes), no inner filter effect has to be considered, and the PL spectra are now identical or at least very similar to the films on glass substrates. The small remaining variation of $\Delta\nu \approx 500$

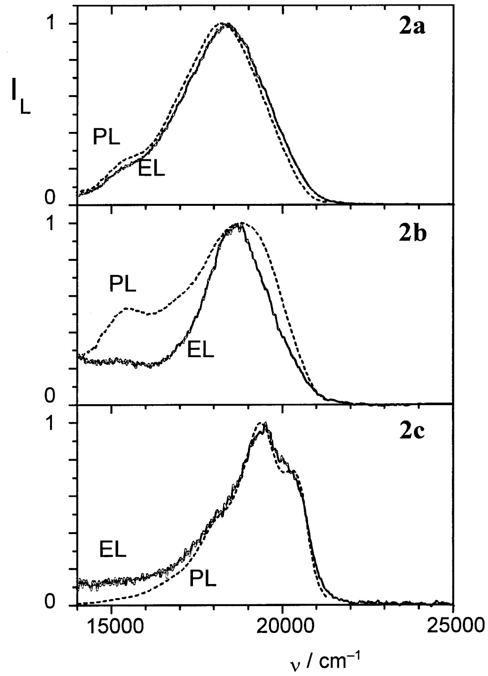

Figure 4. Normalized EL (−) and PL (− − −) spectra of **2a−c** in ITO/PcCu/DC-DSB/Al devices, detected from the ITO side

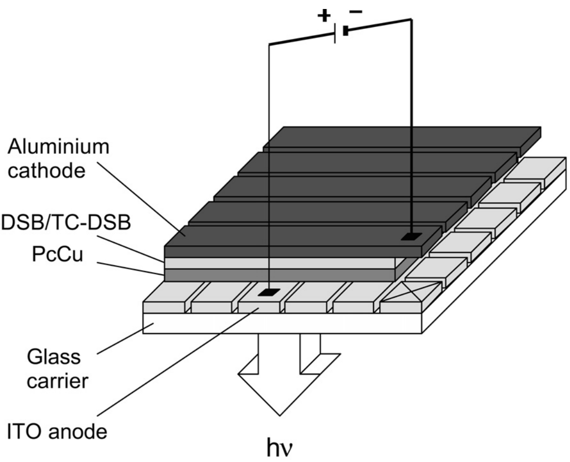

Figure 5. Set-up of the EL devices

cm^{-1} in the PL maxima of samples with excimer emission is expected to arise from different film morphologies on glass and on PcCu.

Conclusions

We have synthesized a new series of dihexyloxy-substituted distyrylbenzenes with two (DC-DSBs **2a−c**) and four (TC-DSBs **1a−f**) cyano groups attached to the peripheral phenylene rings. These new compounds were synthesized by the Wittig reaction and characterized by ^{1}H and ^{13}C NMR, FT-IR, UV/Vis, PL and EL spectroscopy, mass spectra, and elemental analysis. Several synthetic pathways have been described for the preparation of the dicyanobenzaldehydes **7a−f**, which represent the precursors for the TC-DSBs. Within the DSB series, the positions of the cyano substituents were systematically varied and their influence on the absorption and fluorescence spectra was investigated. The electron-withdrawing nature of the cyano groups causes a bathochromic shift in the corresponding spectra relative to the cyano-free molecule **30**. This is dependent on the number and position of the cyano groups within the molecule. In thin films, the fluorescence of nearly all the compounds is determined by intermolecular side-by-side aggregation, leading to small quantum yields and high Stokes shifts. An exception is noted with 2,5-bis(*p*-cyanostyryl)-1,4-dihexyloxybenzene (**2c**), which shows a small Stokes shift and a fluorescence quantum yield of $\varphi_F = 0.6-0.8$. This is unusually high for oligophenylenevinylenes in the solid state.[20] EL spectra were obtained for all the new DC-DSBs and TC-DSBs in ITO/PcCu/DC-DSB or TC-DSB/Al devices, with the emission color ranging from red (**1e**) to green (**2c**). By simply changing the cyano positions, the EL maxima could be tuned over a 130 nm range. However, other parameters, such as reabsorption of the hole transporting layer, layer thickness, and device preparation still have to be optimized to fabricate high performance OLEDs.

Experimental Section

General: Chemicals received from commercial sources (Aldrich and Fluka) were used without further purification. All solvents were dried according to standard procedures. All reactions were performed under dry nitrogen. The melting points are uncorrected. − IR: Bruker IFS 48, KBr pellets. − UV/Vis: Perkin−Elmer Lambda 2, in CH_2Cl_2 as well as thin films on glass carriers. − PL: SPEX fluorolog 112, in CH_2Cl_2 as well as thin films. − EL: HP 6030A voltage source together with a Keithley 171 DMM, spectra were taken from devices with an ITO/PcCu/DSB/Al configuration with a customized waveguide diode array set-up in air at room temperature. − NMR: Bruker AC 250 at 250 MHz (^{1}H) and 62.9 MHz (^{13}C) in $CDCl_3$ and internally referenced to $CHCl_3$ (^{1}H: $\delta = 7.24$; ^{13}C: $\delta = 77.00$). For assignments, the labelling is given in Figure 2. − Elemental analyses were carried out on a VarioEL V.

General Procedure for the Acetalization of the Aldehyde Group: A mixture of the dibromobenzaldehyde [**18** (9.60 g, 36.4 mmol), **23** (2.00 g, 7.60 mmol) or **27** (2.94 g 11.2 mmol)], 1.5 equiv. of ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid was stirred under reflux overnight in 250 mL of toluene. After cooling to room temperature, the solution was washed with water, dried (Na_2SO_4), and the solvent was removed in vacuo. The residue was then purified by column chromatography (silica gel, CH_2Cl_2) to yield the desired acetals **19**, **24** and **28**.

2-(2,4-Dibromophenyl)-1,3-dioxolane (19): Yield: 7.06 g (63%), colorless liquid. − IR (KBr): $\tilde{\nu} = 3084$ cm^{-1}, 2955, 2887, 1732, 1582, 1558, 1468, 1391, 1375, 1285, 1246, 1207, 1138, 1094, 1082, 1036 (C−O−C), 972, 943, 868, 816, 768, 735, 689. − ^{1}H NMR ($CDCl_3$): $\delta = 4.01-4.15$ (m, 4 H, OCH_2 dioxolane), 6.01 (s, 1 H, *CH* dioxolane), 7.44 (s, 1 H, 5-H), 7.45 (s, 1 H, 6-H), 7.71 (t, *J* = 1.06 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): $\delta = 65.5$ (O*C*H$_2$ dioxolane), 102.1 (*C*H dioxolane), 123.5, 123.6 (C-2, C-4), 129.0 (C-5), 130.6 (C-6), 135.3 (C-3), 135.9 (C-1). − MS (EI, 70 eV): *m*/*z* (%) = 306.7 (39) [M$^+$], 262.7 (67) [M$^+$ − C_2H_4O], 235.8 (30), 226.8 (33) [M$^+$ − Br], 184.7 (13), 168.6 (30), 154.7 (16), 117.8 (6), 88.0 (16), 72.9 (100). − $C_9H_8Br_2O_2$ (308.0): calcd. C 35.10, H 2.62, Br 51.89; found C 34.82, H 2.87, Br 51.28.

2-(2,6-Dibromophenyl)-1,3-dioxolane (24): Yield: 1.73 g (74%), colorless, wax-like solid, m.p. 55−57 °C. − IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1}, 2893, 1575, 1555, 1439, 1394, 1263, 1215, 1192, 1144, 1105 (C−O−C), 1061, 1030, 982, 966, 941, 779, 723, 714. − ^1H NMR ($CDCl_3$): δ = 4.00−4.36 (m, 4 H, OCH_2 dioxolane), 6.38 (s, 1 H, *CH* dioxolane), 7.03 (t, *J* = 8.00 Hz, 1 H, 4-H), 7.55 (d, *J* = 8.00 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 65.9 (OCH_2 dioxolane), 104.2 (*C*H dioxolane), 124.9 (C-2, C-6), 131.4 (C-4), 132.6 (C-1), 133.6 (C-3, C-5). − MS (EI, 70 eV): *m/z* (%) = 306.9 (12) [M^+], 262.9 (8) [$M^+ - C_2H_4O$], 226.9 (4) [M^+ − Br], 198.9 (2), 183.0 (2) [$M^+ - C_2H_4O$ − Br], 169.0 (10), 156.1 (3), 118.1 (4), 89.2 (3), 73.1 (100). − $C_9H_8Br_2O_2$ (308.0): calcd. C 35.10, H 2.62, Br 51.89; found C 34.72, H 2.40, Br 53.94.

2-(2,5-Dibromophenyl)-1,3-dioxolane (28): Yield: 3.19 g (93%), colorless needles, m.p. 71−72 °C. − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2887, 1458, 1391, 1252, 1202, 1138, 1082, 1026 (C−O−C), 970, 943, 881, 810. − ^1H NMR ($CDCl_3$): δ = 4.02−4.15 (m, 4 H, OCH_2 dioxolane), 6.01 (s, 1 H, *CH* dioxolane), 7.32 (dd, *J* = 8.46 Hz, *J* = 2.41 Hz, 1 H, 4-H), 7.41 (d, *J* = 8.48 Hz, 1 H, 3-H), 7.70 (d, *J* = 2.39 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 65.6 (OCH_2 dioxolane), 102.0 (*C*H dioxolane), 121.5 (C-5), 121.5 (C-2), 131.0 (C-4), 133.5 (C-3), 134.4 (C-6), 138.7 (C-1). − MS (EI, 70 eV): *m/z* (%) = 307.0 (11) [M^+], 262.8 (8) [$M^+ - C_2H_4O$], 227.0 (19) [M^+ − Br], 182.9 (3) [$M^+ - C_2H_4O$ − Br], 168.8 (4), 88.1 (8), 73.1 (100). − $C_9H_8Br_2O_2$ (308.0): calcd. C 35.10, H 2.62, Br 51.89; found C 35.37, H 2.60, Br 51.80.

General Procedure for the Rosenmund−von Braun Reaction: A mixture of the dibromo compound [**12** or **15**: 4.30 g (16.2 mmol); **19**, **24** or **28**: 5.00 g (16.2 mmol)] and copper cyanide (5.80 g, 64.8 mmol) in 70 mL of dry DMF was stirred for 2−4 h at 150 °C until the reaction was complete (TLC control). The dark brown mixture was then cooled to room temperature.
a) Dicyanobenzaldehydes (**7e** and **7f**): the solvent was removed in vacuo, and the residue was purified by column chromatography (silica gel, CH_2Cl_2) to yield the desired dicyanobenzaldehydes.

3,4-Dicyanobenzaldehyde (7e): Yield: 1.15 g (46%), colorless crystals, m.p. 137−138 °C. − IR (KBr): $\tilde{\nu}$ = 2878 cm^{-1} [C(O)H], 2233 (CN), 1711 [C(H)O], 1630, 1381, 1229, 1096, 945, 851, 752. − ^1H NMR ($CDCl_3$): δ = 8.01 (d, *J* = 7.97 Hz, 1 H, 5-H), 8.22 (dd, *J* = 8.00 Hz, *J* = 1.57 Hz, 1 H, 6-H), 8.29 (d, *J* = 1.51 Hz, 1 H, 2-H), 10.10 (s, 1 H, C*H*O). − ^{13}C NMR ($CDCl_3$): δ = 114.3 (*m*-*C*N), 114.5 (*p*-*C*N), 117.3 (C-3), 120.3 (C-4), 133.2 (C-5), 133.7 (C-2), 134.5 (C-6), 138.8 (C-1), 188.2 (*C*HO). − MS (EI, 70 eV): *m/z* (%) = 155.1 (100) [M^+], 127.0 (35) [M^+ − CO], 100.1 (17) [M^+ − CO − CN], 75.1 (13) [M^+ − CO − 2 CN]. − $C_9H_4N_2O$ (156.1): calcd. C 69.23, H 2.58, N 17.94; found C 69.49, H 3.33, N 17.70.

3,5-Dicyanobenzaldehyde (7f): Yield: 1.06 g (42%), colorless crystals, m.p. 193−194 °C. − IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1}, 2860 [C(O)H], 2245 (CN), 1715, 1709 [C(H)O], 1591, 1450, 1389, 1279, 1163, 1146, 970, 905, 710, 675. − ^1H NMR ($CDCl_3$): δ = 8.16 (t, *J* = 1.50 Hz, 1 H, 4-H), 8.36 (d, *J* = 1.50 Hz, 2 H, 2-H, 6-H), 10.06 (s, 1 H, C*H*O). − ^{13}C NMR ($CDCl_3$): δ = 115.5 (C-3, C-5, *m*-*C*N, *m'*-*C*N), 136.1 (C-2, C-6), 137.6 (C-1), 139.6 (C-4), 187.5 (*C*HO). − MS (EI, 70 eV): *m/z* (%) = 155.0 (100) [M^+], 127.1 (58) [M^+ − CO], 100.0 (62) [M^+ − CO − CN], 75.0 (64) [M^+ − CO − 2 CN]. − $C_9H_4N_2O$ (156.1): calcd. C 69.23, H 2.58, N 17.94; found C 68.81, H 2.59, N 18.13.

b) Dicyanodioxolanes (**20**, **25** and **29**): the reaction mixture was poured into 400 mL of concentrated aqueous ammonia solution, and air was bubbled through the mixture overnight. The precipitate was filtered, washed thoroughly with water and dried in vacuo. The pure product was obtained by column chromatography (silica gel, CH_2Cl_2).

2-(2,4-Dicyanophenyl)-1,3-dioxolane (20): Yield: 1.43 g (44%), colorless crystals, m.p. 119−120 °C. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2926 (CH_2), 2899, 2854 (CH_2), 2241 (CN), 2233 (CN), 1744, 1485, 1477, 1400, 1385, 1313, 1229, 1211, 1134, 1121, 1082 (C−O−C), 1024, 966, 945, 908, 860, 818, 712, 694, 621. − ^1H NMR ($CDCl_3$): δ = 4.05−4.27 (m, 4 H, OCH_2 dioxolane), 5.99 (s, 1 H, C*H* dioxolane), 7.76 (d, *J* = 8.11 Hz, 1 H, 6-H), 7.86 (dd, *J* = 8.09 Hz, *J* = 1.57 Hz, 1 H, 5-H), 7.96 (d, *J* = 1.51 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 66.2 (O*C*H_2 dioxolane), 101.0 (*C*H dioxolane), 113.1 (C-2), 114.3 (C-4), 115.0 (*o*-*C*N), 116.4 (*p*-*C*N), 128.8 (C-6), 135.8 (C-3), 136.7 (C-5), 145.8 (C-1). − MS (EI, 70 eV): *m/z* (%) = 200.1 (52) [M^+], 199.0 (100), 174.0 (2) [M^+ − CN], 156.9 (47) [$M^+ - OC_2H_3$], 154.9 (63) [$M^+ - OC_2H_5$], 142.1 (45), 128.1 (27), 115.1 (31), 99.8 (5), 73.0 (56). − $C_{11}H_8N_2O_2$ (200.2): calcd. C 65.99, H 4.03, N 13.99; found C 66.28, H 3.22, N 14.23.

2-(2,6-Dicyanophenyl)-1,3-dioxolane (25): Yield: 1.91 g (59%), colorless crystals, m.p. 161−162 °C. − IR (KBr): $\tilde{\nu}$ = 3086 cm^{-1}, 3003, 2978, 2955, 2908, 2237 (CN), 1583, 1481, 1466, 1404, 1352, 1292, 1244, 1229, 1207, 1182, 1140, 1099 (C−O−C), 1078, 1061, 1016, 991, 966, 947. − ^1H NMR ($CDCl_3$): δ = 4.11−4.44 (m, 4 H, OCH_2 dioxolane), 6.20 (s, 1 H, C*H* dioxolane), 7.61 (t, *J* = 7.81 Hz, 1 H, 4-H), 7.90 (d, *J* = 7.83 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 66.7 (O*C*H_2 dioxolane), 100.4 (*C*H dioxolane), 113.9 (C-2, C-6), 115.3 (*o*-*C*N, *o'*-*C*N), 130.5 (C-4), 137.3 (C-3, C-5), 144.4 (C-1). − MS (EI, 70 eV): *m/z* (%) = 201.1 (9) [M^+], 199.1 (19), 172.9 (21), 157.0 (100), 141.9 (40), 129.1 (10), 114.9 (33), 99.8 (10), 73.0 (44). − $C_{11}H_8N_2O_2$ (200.2): calcd. C 65.99, H 4.03, N 13.99; found C 65.52, H 3.97, N 13.68.

2-(2,5-Dicyanophenyl)-1,3-dioxolane (29): Yield: 454 mg (14%), colorless crystals, m.p. 111−112 °C. − IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1}, 2978, 2899, 2241 (CN), 2233 (CN), 1497, 1437, 1418, 1396, 1373, 1285, 1261, 1246, 1227, 1196, 1159, 1124, 1097 (C−O−C), 1078, 1018, 995, 972, 949, 920, 854, 839, 619. − ^1H NMR ($CDCl_3$): δ = 4.05−4.27 (m, 4 H, OCH_2 dioxolane), 5.99 (s, 1 H, C*H* dioxolane), 7.74 (dd, *J* = 7.99 Hz, *J* = 1.54 Hz, 1 H, 4-H), 7.81 (d, *J* = 7.96 Hz, 1 H, 3-H), 7.91 (d, *J* = 0.90 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 66.1 (O*C*H_2 dioxolane), 100.7 (*C*H dioxolane), 115.4 (C-5), 115.6 (C-2), 116.5 (*m'*-*C*N), 116.9 (*o*-*C*N), 131.1 (C-4), 132.9 (C-6), 134.1 (C-3), 142.9 (C-1). − MS (EI, 70 eV): *m/z* (%) = 200.0 (14) [M^+], 199.0 (47), 172.9 (2), 157.0 (30) [$M^+ - OC_2H_3$], 154.9 (24) [$M^+ - OC_2H_5$], 142.0 (20), 128.1 (10), 115.1 (19), 100.0 (10), 73.0 (100). − $C_{11}H_8N_2O_2$ (200.2): calcd. C 65.99, H 4.03, N 13.99; found C 63.55, H 3.97, N 13.07.

General Procedure for the Cleavage of the Acetal Group: For the deprotection, the dioxolane compound [**20**, **25** or **29**: 600 mg (3.00 mmol)] was dissolved in 100 mL of acetonitrile and 50 mL of 2 N HCl was added dropwise, whilst the mixture was stirred at room temperature. After 15 min. the solution was quenched with 500 mL of CH_2Cl_2. The organic phase was washed with aqueous $NaHCO_3$ solution and water, dried (Na_2SO_4), and the solvent was evaporated. The crude product (**7b**, **7d** or **7c**, respectively) was purified by column chromatography (silica gel, CH_2Cl_2).

2,4-Dicyanobenzaldehyde (7b): Yield: 258 mg (55%), colorless crystals, m.p. 150−151 °C. − IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1}, 2885 [C(O)H], 2243 (CN), 2232 (CN), 1705 [C(H)O], 1562, 1385, 1296, 1204, 920, 854, 797. − ^1H NMR ($CDCl_3$): δ = 8.04 (dd, *J* = 8.10 Hz, *J* = 1.52 Hz, 1 H, 5-H), 8.11 (d, *J* = 1.48 Hz, 1 H, 3-H), 8.17 (d, *J* = 8.05 Hz, 1 H, 6-H), 10.40 (s, 1 H, C*H*O). − ^{13}C NMR ($CDCl_3$): δ = 113.9 (C-2), 115.1 (*o*-*C*N), 115.7 (*p*-*C*N), 118.3 (C-4), 130.1

(C-6), 136.4 (C-3), 137.1 (C-5), 138.8 (C-1), 186.9 (*C*HO). − MS (EI, 70 eV): *m*/*z* (%) = 154.9 (20) [M$^+$], 128.1 (100) [M$^+$ − CO], 101.1 (27) [M$^+$ − CO − CN], 75.1 (19) [M$^+$ − CO − 2 CN]. − $C_9H_4N_2O$ (156.1): calcd. C 69.23, H 2.58, N 17.94; found C 67.20, H 2.54, N 17.67.

2,5-Dicyanobenzaldehyde (7c): Yield: 272 mg (58%), colorless crystals, m.p. 134−135 °C. − IR (KBr): $\tilde{\nu}$ = 3082 cm^{-1}, 2924, 2233 (CN), 1724, 1707 [C(H)O], 1599, 1481, 1394, 1288, 1273, 1219, 1190, 1148, 941, 930, 870, 781. − ^{1}H NMR ($CDCl_3$): δ = 7.96 (d, *J* = 7.91 Hz, 1 H, 3-H), 8.01 (dd, *J* = 8.09 Hz, *J* = 1.50 Hz, 1 H, 4-H), 8.30 (d, *J* = 1.42 Hz, 1 H, 6-H), 10.35 (s, 1 H, C*H*O). − ^{13}C NMR ($CDCl_3$): δ = 114.3 (*m*′-*C*N), 116.0 (C-5), 117.4 (*o*-*C*N), 117.6 (C-2), 132.8 (C-3), 134.6 (C-6), 136.8 (C-4), 137.3 (C-1), 186.2 (*C*HO). − MS (EI, 70 eV): *m*/*z* (%) = 155.0 (17) [M$^+$], 128.1 (100) [M$^+$ − CO], 101.1 (46) [M$^+$ − CO − CN], 75.1 (26) [M$^+$ − CO − 2 CN]. − $C_9H_4N_2O$ (156.1): calcd. C 69.23, H 2.58, N 17.94; found C 68.84, H 2.41, N 18.09.

General Procedure for the Wittig Reaction: The monocyano- (**8a−c**; 1.00 g, 7.60 mmol) or the dicyanobenzaldehyde (**7a−f**; 200 mg, 1.30 mmol) was added under nitrogen to a solution of 1,4-dihexyloxy-2,5-xylylene bis(triphenylphosphonium bromide) (**6**; 0.5 equiv.) in 40 mL of dry ethanol. Potassium *tert*-butoxide (1.5 equiv.) was added in portions, and the mixture was stirred for 5 h at room temperature. Water (ca. 10 mL) was then added and the yellow to orange precipitate filtered, washed with water and dried in vacuo. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) and then recrystallized from ethyl acetate to obtain the pure *E*/*E* isomer.

2,5-Bis(2′,3′-dicyanostyryl)-1,4-dihexyloxybenzene (1a): Yield: 129 mg (34%), orange crystals, m.p. 247−249 °C. − IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (CH_3), 2928 (CH_2), 2885 (CH_3), 2856 (CH_2), 2233 (CN), 1626, 1582, 1499, 1462, 1427, 1393, 1346, 1294, 1263, 1209 (C−O−C), 1057, 1032, 962 (=C−H trans), 847, 798, 735. − ^{1}H NMR ($CDCl_3$): δ = 0.86−0.92 (m, 6 H, 17-H), 1.34−1.53 (m, 12 H, 14-H, 15-H, 16-H), 1.83−1.91 (m, 4 H, 13-H), 4.07 (t, *J* = 6.49 Hz, 4 H, 12-H), 7.13 (s, 2 H, 10-H), 7.51 (d, *J* = 16.26 Hz, 2 H, 7-H, 8-H), 7.69 (d, *J* = 16.58 Hz, 2 H, 7-H, 8-H), 7.62−7.71 (m, 4 H, 5-H, 6-H), 8.03 (dd, *J* = 6.90 Hz, *J* = 2.41 Hz, 2 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.3 (C-13), 31.5 (C-15), 69.6 (C-12), 111.1 (C-10), 113.8 (C-2), 114.7 (C-3), 115.7 (*o*-*C*N), 116.8 (*m*-*C*N), 123.3 (C-7, C-8), 126.6 (C-9), 129.1 (C-7, C-8), 130.7 (C-6), 131.7 (C-4), 132.7 (C-5), 143.0 (C-1), 151.7 (C-11). − MS (FD): *m*/*z* (%) = 582.1 (100) [M$^+$]. − UV/Vis: λ_{max} = 422 nm, 341 (CH_2Cl_2), 442, 357 (solid state). − $C_{38}H_{38}N_4O_2$ (582.7): calcd. C 78.32, H 6.57, N 9.61; found C 79.11, H 6.83, N 9.84.

2,5-Bis(2′,4′-dicyanostyryl)-1,4-dihexyloxybenzene (1b): Yield: 239 mg (63%), orange crystals, m.p. 209−210 °C. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (CH_3), 2935 (CH_2), 2872 (CH_3), 2232 (CN), 1622, 1597, 1502, 1483, 1427, 1402, 1344, 1317, 1290, 1213 (C−O−C), 1059, 1038, 957 (=C−H trans), 893, 856, 829, 721. − ^{1}H NMR ($CDCl_3$): δ = 0.86−0.92 (m, 6 H, 17-H), 1.34−1.47 (m, 12 H, 14-H, 15-H, 16-H), 1.83−1.94 (m, 4 H, 13-H), 4.08 (t, *J* = 6.49 Hz, 4 H, 12-H), 7.13 (s, 2 H, 10-H), 7.54 (d, *J* = 16.32 Hz, 2 H, 7-H, 8-H), 7.73 (d, *J* = 16.32 Hz, 2 H, 7-H, 8-H), 7.79 (dd, *J* = 8.46 Hz, *J* = 1.45 Hz, 2 H, 5-H), 7.91 (d, *J* = 8.33 Hz, 2 H, 6-H), 7.91 (d, *J* = 1.73 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.2 (C-13), 31.5 (C-15), 69.5 (C-12), 111.2 (C-10), 111.3 (C-2), 112.3 (C-4), 116.0 (*o*-*C*N), 116.9 (*p*-*C*N), 123.6 (C-7, C-8), 125.9 (C-9), 126.7 (C-7, C-8), 131.8 (C-6), 135.4 (C-3), 136.7 (C-5), 145.0 (C-1), 151.9 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 582.3 (21) [M$^+$], 498.1 (4) [M$^+$ − C_6H_{13}], 444.3 (7), 414.0 (71) [M$^+$ − 2 C_6H_{13}], 360.1 (5), 276.1 (30). − UV/Vis: λ_{max} = 438 nm, 354 (CH_2Cl_2), 437, 370 (solid state). − $C_{38}H_{38}N_4O_2$ (582.7): calcd. C 78.32, H 6.57, N 9.61; found C 77.77, H 5.72, N 9.49.

2,5-Bis(2′,5′-dicyanostyryl)-1,4-dihexyloxybenzene (1c): Yield: 170 mg (45%), orange crystals, m.p. 226−227 °C. − IR (KBr): $\tilde{\nu}$ = 2947 cm^{-1} (CH_3), 2932 (CH_2), 2918, 2872 (CH_3), 2856 (CH_2), 2235 (CN), 2224 (CN), 1626, 1597, 1547, 1516, 1483, 1410, 1396, 1364, 1256, 1240, 1219, 1204 (C−O−C), 1032, 980, 968 (=C−H trans), 829, 818. − ^{1}H NMR ($CDCl_3$): δ = 0.87−0.92 (m, 6 H, 17-H), 1.35−1.41 (m, 12 H, 14-H, 15-H, 16-H), 1.88−1.94 (m, 4 H, 13-H), 4.09 (t, *J* = 6.56 Hz, 4 H, 12-H), 7.12 (s, 2 H, 10-H), 7.52 (d, *J* = 16.34 Hz, 2 H, 7-H, 8-H), 7.64 (d, *J* = 16.31 Hz, 2 H, 7-H, 8-H), 7.56 (dd, *J* = 8.01 Hz, *J* = 1.45 Hz, 2 H, 4-H), 7.74 (d, *J* = 8.02 Hz, 2 H, 3-H), 8.06 (d, *J* = 1.17 Hz, 2 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.2 (C-13), 31.5 (C-15), 69.5 (C-12), 111.4 (C-10), 114.8 (C-2), 116.5 (C-5), 116.8 (*o*-*C*N), 117.3 (*m*′-*C*N), 123.2 (C-7, C-8), 126.5 (C-9), 129.8 (C-7, C-8), 129.9 (C-6), 130.9 (C-4), 133.8 (C-3), 142.3 (C-1), 151.8 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 582.4 (44) [M$^+$], 498.3 (9) [M$^+$ − C_6H_{13}], 444.3 (4), 414.1 (100) [M$^+$ − 2 C_6H_{13}], 357.2 (4), 275.9 (13). − UV/Vis: λ_{max} = 426 nm, 338 (CH_2Cl_2), 467, 441, 350 (solid state). − $C_{38}H_{38}N_4O_2$ (582.7): calcd. C 78.32, H 6.57, N 9.61; found C 77.44, H 6.40, N 9.47.

2,5-Bis(2′,6′-dicyanostyryl)-1,4-dihexyloxybenzene (1d): Yield: 140 mg (37%), orange crystals, m.p. 190−191 °C. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (CH_3), 2922 (CH_2), 2872 (CH_3), 2854 (CH_2), 2232 (CN), 1624, 1580, 1514, 1499, 1468, 1456, 1437, 1393, 1259, 1236, 1227, 1211 (C−O−C), 1188, 1057, 1028, 968 (=C−H trans), 845, 804, 743, 673. − ^{1}H NMR ($CDCl_3$): δ = 0.87−0.90 (m, 6 H, 17-H), 1.32−1.52 (m, 12 H, 14-H, 15-H, 16-H), 1.83−1.94 (m, 4 H, 13-H), 4.08 (t, *J* = 6.47 Hz, 4 H, 12-H), 7.13 (s, 2 H, 10-H), 7.41 (t, *J* = 7.83 Hz, 2 H, 4-H), 7.55 (d, *J* = 16.56 Hz, 2 H, 7-H, 8-H), 7.88 (d, *J* = 7.82 Hz, 4 H, 3-H, 5-H), 8.07 (d, *J* = 16.59 Hz, 2 H, 7-H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.8 (C-14), 29.3 (C-13), 31.6 (C-15), 69.6 (C-12), 111.6 (C-10), 112.1 (C-2, C-6), 117.0 (*o*-*C*N, *o*′-*C*N), 122.2 (C-7, C-8), 126.8 (C-9), 127.2 (C-4), 135.0 (C-7, C-8), 137.7 (C-3, C-5), 144.1 (C-1), 152.1 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 582.4 (29) [M$^+$], 498.2 (4) [M$^+$ − C_6H_{13}], 414.1 (100) [M$^+$ − 2 C_6H_{13}], 357.2 (7), 155.0 (19). − UV/Vis: λ_{max} = 422 nm, 341 (CH_2Cl_2), 445, 356 (solid state). − $C_{38}H_{38}N_4O_2$ (582.7): calcd. C 78.32, H 6.57, N 9.61; found C 77.60, H 6.06, N 9.30.

2,5-Bis(3′,4′-dicyanostyryl)-1,4-dihexyloxybenzene (1e): Yield: 163 mg (43%), red crystals, m.p. 294−295 °C. − IR (KBr): $\tilde{\nu}$ = 2928 cm^{-1} (CH_2), 2870 (CH_3), 2856 (CH_2), 2228 (CN), 1711, 1628, 1591, 1551, 1506, 1489, 1466, 1429, 1381, 1346, 1323, 1294, 1263, 1238, 1211 (C−O−C), 968 (=C−H trans), 960, 851, 824. − ^{1}H NMR ($CDCl_3$): δ = 0.88−0.94 (m, 6 H, 17-H), 1.37−1.55 (m, 12 H, 14-H, 15-H, 16-H), 1.83−1.94 (m, 4 H, 13-H), 4.06 (t, *J* = 6.50 Hz, 4 H, 12-H), 7.08 (s, 2 H, 10-H), 7.14 (d, *J* = 16.35 Hz, 2 H, 7-H, 8-H), 7.60 (d, *J* = 16.39 Hz, 2 H, 7-H, 8-H), 7.74 (d, *J* = 8.32 Hz, 2 H, 6-H), 7.79 (d, *J* = 8.56 Hz, 2 H, 5-H), 7.87 (s, 2 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.3 (C-13), 31.5 (C-15), 69.4 (C-12), 110.9 (C-10), 113.2 (C-4), 115.4 (C-3), 115.6 (*p*-*C*N), 116.5 (*m*-*C*N), 125.6 (C-7, C-8), 126.5 (C-9), 129.6 (C-7, C-8), 130.2 (C-2), 131.0 (C-6), 133.8 (C-5), 143.1 (C-1), 151.6 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 582.3 (36) [M$^+$], 498.1 (4) [M$^+$ − C_6H_{13}], 413.9 (84) [M$^+$ − 2 C_6H_{13}], 178.2 (5), 155.0 (19), 141.0 (5). − UV/Vis: λ_{max} = 435 nm, 348 (CH_2Cl_2), 467, 363 (solid state). − $C_{38}H_{38}N_4O_2$ (582.7): calcd. C 78.32, H 6.57, N 9.61; found C 78.16, H 6.36, N 9.49.

2,5-Bis(3′,5′-dicyanostyryl)-1,4-dihexyloxybenzene (1f): Yield: 155 mg (41%), yellow crystals, m.p. 267−268 °C. − IR (KBr): ṽ = 3072 cm^{-1}, 2930 (CH_2), 2856 (CH_2), 2235 (CN), 1630, 1585, 1502, 1468, 1421, 1406, 1348, 1323, 1269, 1246, 1211 (C−O−C), 1061, 1030, 997, 976 (=C−H trans), 899, 879, 687, 665, 646. − ^{1}H NMR ($CDCl_3$): δ = 0.89−0.94 (m, 6 H, 17-H), 1.36−1.44 (m, 8 H, 15-H, 16-H), 1.50−1.60 (m, 4 H, 14-H), 1.84−2.15 (m, 4 H, 13-H), 4.06 (t, J = 6.55 Hz, 4 H, 12-H), 7.07 (s, 2 H, 10-H), 7.11 (d, J = 16.40 Hz, 2 H, 7-H, 8-H), 7.53 (d, J = 16.58 Hz, 2 H, 7-H, 8-H), 7.76 (s, 2 H, 4-H), 7.95 (d, J = 1.35 Hz, 4 H, 2-H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.3 (C-13), 31.5 (C-15), 69.4 (C-12), 110.9 (C-10), 114.5 (C-3, C-5), 116.7 (*m*-*C*N, *m'*-*C*N), 124.9 (C-7, C-8), 126.3 (C-9), 128.7 (C-7, C-8), 132.9 (C-4), 133.3 (C-2, C-6), 140.7 (C-1), 151.5 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 582.5 (17) [M$^+$], 498.2 (2) [M$^+$ − C_6H_{13}], 414.2 (37) [M$^+$ − 2 C_6H_{13}], 154.9 (5). − UV/Vis: λ_{max} = 413 nm, 335 (CH_2Cl_2), 439, 349 (solid state). − $C_{38}H_{38}N_4O_2$ (582.7): calcd. C 78.32, H 6.57, N 9.61; found C 77.59, H 6.28, N 9.41.

2,5-Bis(2′-cyanostyryl)-1,4-dihexyloxybenzene (2a): Yield: 1.68 g (83%), yellow crystals, m.p. 110−111 °C. − IR (KBr): ṽ = 2984 cm^{-1}, 2953 (CH_3), 2932 (CH_2), 2868 (CH_3), 2218 (CN), 1630, 1593, 1506, 1470, 1448, 1427, 1387, 1344, 1323, 1292, 1285, 1258, 1209 (C−O−C), 1069, 1047, 1020, 960 (=C−H trans), 841, 754. − ^{1}H NMR ($CDCl_3$): δ = 0.86−0.92 (m, 6 H, 17-H), 1.34−1.54 (m, 12 H, 14-H, 15-H, 16-H), 1.85−1.93 (m, 4 H, 13-H), 4.07 (t, J = 6.43 Hz, 4 H, 12-H), 7.16 (s, 2 H, 10-H), 7.30 (t, J = 7.57 Hz, 2 H, 4-H), 7.49 (d, J = 16.40 Hz, 2 H, 7-H, 8-H), 7.56 (t, J = 7.98 Hz, 2 H, 5-H), 7.63 (d, J = 7.87 Hz, 2 H, 6-H), 7.64 (d, J = 16.28 Hz, 2 H, 7-H, 8-H), 7.81 (d, J = 8.04 Hz, 2 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.3 (C-13), 31.6 (C-15), 69.6 (C-12), 110.9 (C-10), 111.2 (C-2), 118.1 (*o*-*C*N), 124.5 (C-7, C-8), 125.2 (C-7, C-8), 126.8 (C-9), 127.3 (C-6), 128.1 (C-4), 132.7 (C-5), 133.1 (C-3), 141.2 (C-1), 151.5 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 532.4 (72) [M$^+$], 448.3 (10) [M$^+$ − C_6H_{13}], 364.2 (100) [M$^+$ − 2 C_6H_{13}]. − UV/Vis: λ_{max} = 408 nm, 335 (CH_2Cl_2), 420, 340 (solid state). − $C_{36}H_{40}N_2O_2$ (532.7): calcd. C 81.17, H 7.57, N 5.26; found C 80.91, H 7.16, N 5.36.

2,5-Bis(3′-cyanostyryl)-1,4-dihexyloxybenzene (2b): Yield: 1.80 g (89%), yellow crystals, m.p. 169−170 °C. − IR (KBr): ṽ = 2951 cm^{-1} (CH_3), 2934 (CH_2), 2870 (CH_3), 2856 (CH_2), 2228 (CN), 1630, 1593, 1578, 1506, 1481, 1474, 1423, 1406, 1385, 1344, 1325, 1288, 1265, 1238, 1213 (C−O−C), 1061, 1042, 997, 970, 960 (=C−H trans), 897, 864, 783, 685. − ^{1}H NMR ($CDCl_3$): δ = 0.88−0.94 (m, 6 H, 17-H), 1.36−1.56 (m, 12 H, 14-H, 15-H, 16-H), 1.84−1.93 (m, 4 H, 13-H), 4.05 (t, J = 6.50 Hz, 4 H, 12-H), 7.08 (s, 2 H, 10-H), 7.09 (d, J = 16.47 Hz, 2 H, 7-H, 8-H), 7.43 (t, J = 7.63 Hz, 2 H, 5-H), 7.49 (d, J = 16.39 Hz, 2 H, 7-H, 8-H), 7.50 (dt, J = 7.63 Hz, J = 1.45 Hz, 2 H, 6-H), 7.71 (dt, J = 7.62 Hz, J = 1.52 Hz, 2 H, 4-H), 7.76 (s, 2 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.4 (C-13), 31.6 (C-15), 69.5 (C-12), 110.7 (C-10), 112.9 (C-3), 118.8 (*m*- *C*N), 126.0 (C-7, C-8), 126.5 (C-7, C-8), 126.7 (C-9), 129.4 (C-5), 129.9 (C-6), 130.4 (C-4), 130.5 (C-2), 139.1 (C-1), 151.2 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 532.5 (84) [M$^+$], 448.2 (13) [M$^+$ − C_6H_{13}], 364.1 (100) [M$^+$ − 2 C_6H_{13}]. − UV/Vis: λ_{max} = 398 nm, 328 (CH_2Cl_2), 429, 340 (solid state). − $C_{36}H_{40}N_2O_2$ (532.7): calcd. C 81.17, H 7.57, N 5.26; found C 80.99, H 7.50, N 5.77.

2,5-Bis(4′-cyanostyryl)-1,4-dihexyloxybenzene (2c): Yield: 1.70 g (84%), yellow crystals, m.p. 211−212 °C. − IR (KBr): ṽ = 3051 cm^{-1}, 2941 (CH_3), 2918 (CH_2), 2874 (CH_3), 2854 (CH_2), 2222 (CN), 1624, 1599, 1508, 1502, 1493, 1470, 1423, 1400, 1342, 1323, 1286, 1256, 1209 (C−O−C), 1175, 1030, 980 (=C−H trans), 868, 824. − ^{1}H NMR ($CDCl_3$): δ = 0.88−0.93 (m, 6 H, 17-H), 1.54−1.35 (m, 12 H, 14-H, 15-H, 16-H), 1.84−1.92 (m, 4 H, 13-H), 4.05 (t, J = 6.45 Hz, 4 H, 12-H), 7.10 (s, 2 H, 10-H), 7.13 (d, J = 16.33 Hz, 2 H, 7-H, 8-H), 7.56 (d, J = 16.31 Hz, 2 H, 7-H, 8-H), 7.57 (d, J = 8.51 Hz, 4 H, 2-H, 6-H), 7.62 (d, J = 8.55 Hz, 4 H, 3-H, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (C-17), 22.6 (C-16), 25.9 (C-14), 29.4 (C-13), 31.6 (C-15), 69.5 (C-12), 110.4 (C-10), 110.8 (C-4), 119.1 (*p*-*C*N), 126.7 (C-7, C-8), 126.8 (C-2, C-6), 127.1 (C-7, C-8), 127.3 (C-9), 132.5 (C-3, C-5), 142.3 (C-1), 151.4 (C-11). − MS (EI, 70 eV): *m*/*z* (%) = 532.4 (100) [M$^+$], 448.1 (17) [M$^+$ − C_6H_{13}], 364.0 (95) [M$^+$ − 2 C_6H_{13}]. − UV/Vis: λ_{max} = 415 nm, 341 (CH_2Cl_2), 469, 439, 348 (solid state). − $C_{36}H_{40}N_2O_2$ (532.7): calcd. C 81.17, H 7.57, N 5.26; found C 80.85, H 7.58, N 5.24.

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