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Synthesis of conjugated-bridged triphenylenes and application in OLEDs

Roland Freudenmann, Boris Behnisch and Michael Hanack*

Institut für Organische Chemie Lehrstuhl II, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: hanack@uni-tuebingen.de; Fax: +49-7071-295268; http://www.uni-tuebingen.de/hanack/index.html

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Novel conjugated-bridged triphenylene derivatives with electroluminescent properties were synthesized. A six step synthesis yields the cyanomethyltriphenylene derivatives (**7a–7d**). These were condensed by applying a Knoevenagel reaction with the alkoxy substituted dialdehyde **8** to PPV analogous short chain compounds **9a–9d**. The products **9a–9d** show bright orange to red photoluminescence. They are suitable as the emissive layer in organic light-emitting diodes (OLEDs), both in single and double layer arrangements with copper phthalocyanine as the hole transport layer.

Introduction

Since the discovery of light emission from poly-*p*-phenylenevinylene (PPV)[1] and analogous polymers,[2] organic light-emitting diodes (OLEDs) based on conjugated polymers are of wide research interest.[3] Substitution of the PPV backbone increases the solubility and allows tailoring of the electronic and optical properties in many directions. Besides the introduction of substituents, a partial or complete replacement of the phenylene rings in the PPV by different moieties (for example naphthalene, anthracene or heterocycles[3b]) offers the possibility of tuning the light-emitting properties in a controlled manner. Molecules with a low molecular weight are of special interest: due to easy thin layer fabrication by a high-vacuum deposition technique the processability is enhanced and the impurities that arise from polymerisation steps can be avoided.[4] Moreover, conjugated short-chain model compounds often show similar properties, when compared with the corresponding polymers.[5] Recently, the triphenylene system, especially hexaalkoxy substituted triphenylenes have gained increased interest in the construction of OLEDs. Not only the discotic properties of these compounds, but also their hole transporting properties have been investigated.[6–8] On the other hand, for a balanced electron flow in a light-emitting device there is also an additional layer with increased electron transport properties recommended. Alkoxy substituted PPV derivatives, containing electron withdrawing cyano groups (CN-PPV), are therefore suitable compounds.[2,9] Up to now, one had to take at least double or triple layer arrangements for an efficient OLED. A combination of hole and electron transporting properties within one single molecule should have a favourable effect on the preparation of an OLED.

In this paper we present for the first time the π-conjugated systems **9** (Scheme 2), containing a combination of the thermally stable and hole transporting triphenylene system with solubilizing alkoxy chains and a structural unit, that is part of the electron conducting and also light-emitting CN-PPV.[2]

Results and discussion

Most of the various syntheses of triphenylenes (Tp) lead to symmetric hexaalkoxy-substituted triphenylenes, which were obtained *e.g.* from *o*-dialkoxybenzenes by oxidative trimerisation with $FeCl_3$,[10] $MoCl_5$[11] or $VOCl_3$.[12]

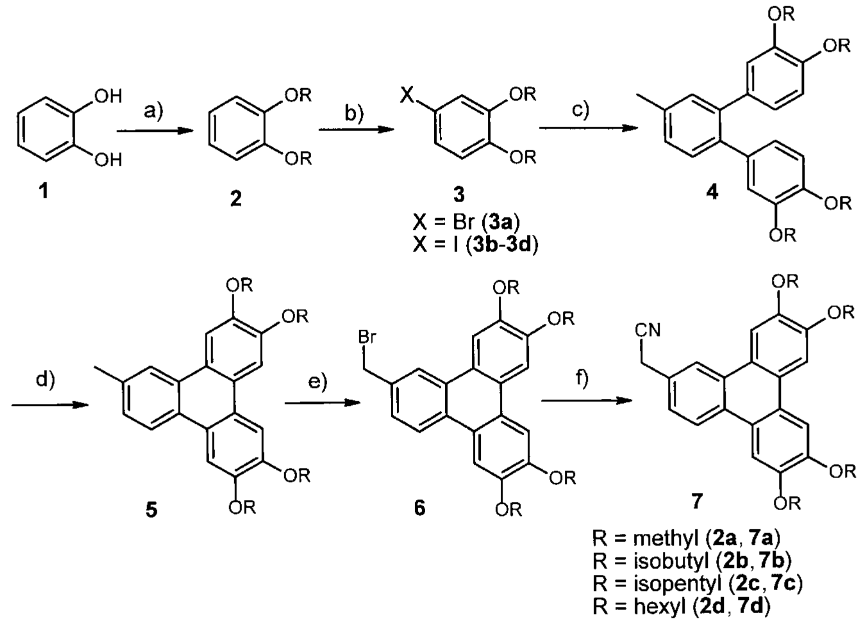
The synthesis of **9** requires a synthetic pathway for the preparation of an unsymmetrically substituted triphenylene (in our case the CH-acid cyanomethyl substituted triphenylenes **7a–7d**) which will be submitted to a Knoevenagel reaction with the terephthalaldehyde **8** (Scheme 2).

The synthesis of unsymmetrical Tps has been much less explored than the symmetrically substituted hexaalkoxy triphenylenes. A rational route involves the iodine promoted photocyclisation of *ortho*-terphenyls.[13] A selective coupling of a 3,3,4,4-tetraalkoxybiphenyl and a 1,2-dialkoxybenzene is also possible.[14] Another route to unsymmetrically substituted triphenylenes involves the oxidative coupling of unsymmetrically substituted terphenyls with $FeCl_3$,[15] monofunctionalised triphenylenes have also been synthesized by various methods starting from symmetrically substituted hexaalkoxytriphenylenes.[16,17]

For the synthesis of a conjugated bridged Tp **9**, a CN-PPV linked to two unsymmetrically substituted triphenylenes, we have chosen the route given in Scheme 1. This includes the synthesis of a methyl substituted triphenylene (**5**) which could be converted into the cyano derivative **7**. Due to its acetic hydrogens **7** would react in a Knoevenagel reaction with the dialdehyde **8** to then form the conjugated bridged Tp **9**.

Systems with high planarity and π-conjugation like **9** show a strong tendency for aggregation and are expected to be insoluble. This problem can be reduced by using alkoxy substituted triphenylenes in which the peripheral alkoxy substituents differ in their chain lengths. Thereby, the solubility of the compounds **9a–9d** in organic solvents with increasing chain lengths should become better. In addition the effect of luminescence properties of these conjugated systems can be studied depending upon different substituents.

The first step of the synthetic route given in Schemes 1 and 2 is an ether synthesis of catechol (**1**) with an alkyl bromide in acetonitrile at 80 °C with K_2CO_3 as base giving **2b–2d** in yields of at least 90%. For the palladium catalysed step (**3**→**4**) it is necessary to have a halogen atom in the starting material **3a–3d**. As the bromination of **2b–2d** often leads to polybrominated products, we prefered to introduce iodine, which is possible in high yields (>90%) by using iodine/iodic acid.[18] Lithiation of **3a–3d** with butyllithium (**3a** is commercially available) at -78 °C, followed by transmetallization with $ZnCl_2$ leads to the

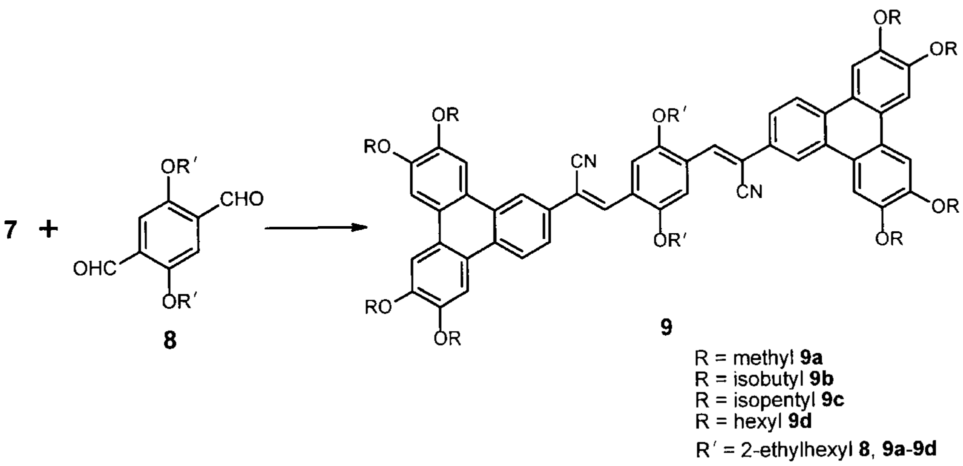


Scheme 1 Synthesis of the monocyanomethylene precursors **7a–7d**: a) ether synthesis, b) I_2/HIO_3, c) I) BuLi, II) $ZnCl_2$, III) 3,4-dibromotoluene, $[P(Ph)_3]_4Pd$, d) $FeCl_3$, e) NBS-bromination, f) $[(Et)_4N]CN/CH_2Cl_2$.

intermediate organozinc compound. Pd-catalysed coupling of the organozinc compound with 0.5 eq. dibromotoluene yields the substituted *o*-terphenyls **4a–4d**.[19] Side products (*e.g.* homo coupled biphenylenes) are removed by column chromatography. The products **4a–4d** were used without further purification. Cyclisation of **4a–4d** with $FeCl_3$ in dichloromethane at room temperature gives the unsymmetrically substituted triphenylenes **5a–5d** with yields for these two steps between 48 (**5a**) and 9% (**5d**). Longer alkyl chains in **3a–3d** give lower yields, because of the insolubility of the iodine derivatives at the low reaction temperature for the lithiation step. The subsequent bromination of **5a–5d** in CCl_4 with NBS and azoisobutyronitrile leads to the bromomethyl products **6a–6d** (yields > 60 %). Reaction of **6a–6d** with tetraethylammonium cyanide in dichloromethane at room temperature results in the desired monofunctional cyanomethyltriphenylenes **7a–7d** (yields: 70–80%). **7a–7d** and the substituted terephthalaldehyde **8** are precursors for the products **9a–9d**, by applying the Knoevenagel reaction (yields 48 to 54%).[2] All compounds are characterized by ^{1}H-NMR, ^{13}C-NMR (with exception of the bistriphenylenes **9a–9d** due to their low solubility), MS, IR and UV-spectroscopy (see Experimental).

Photophysical properties

The UV-absorption of symmetrical substituted hexaalkoxytriphenylenes is about 280 nm, the photoluminescence (PL) is at the edge of the visible area (380–420 nm).[17] They exhibit good hole transporting properties, when used in organic light-emitting diodes.[6–8] By extending the π-conjugated system as shown for the new bridged triphenylene **9a–9d**, the UV-absorption as well as the PL maxima in comparison to hexaalkoxytriphenylenes are strongly shifted to the red (see Fig. 1). **9a–9d** show strong orange to red photoluminescence that meets the requirements for the preparation of OLEDs. Therefore, we investigated the electroluminescent properties of the triphenylenes **9a–9d** by preparing single layer (ITO/TpPPV/Al) and double layer (ITO/PcCu/TpPPV/Al) organic light-emitting diodes. For controlling the electroluminescent capability, for an enhanced reproducibility and for a better comparison of the investigated compounds we carried out a screening test by preparing devices that contain 25 light-emitting segments. For the schematic assembly of a device see Fig. 2a. The commercially available ITO-glass substrate was cut into 5 cm × 5 cm plates, which is advantageous due to the



Scheme 2 Synthesis of the bridged triphenylenes **9a–9d** by Knoevenagel reaction (potassium *tert*-butoxide, THF).

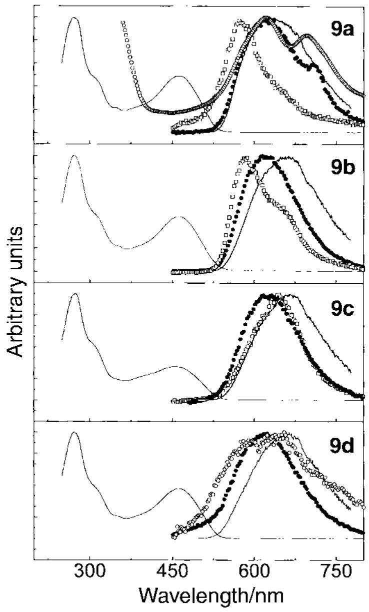


Fig. 1 UV-Vis absorption (solid line, measured in solution ($CHCl_3$)), photoluminescence (PL) (solid line, measured as thin film) and electroluminescence (EL) spectra of the bridged triphenylenes **9a–9d**. The single layer EL spectra are plotted as solid circles, the double layer spectra (ITO/PcCu/Emitter/Al) are shown as open squares. The UV-Vis spectra of a thin film of copper phthalocyanine (PcCu) is depicted in the first plot (open circles).

size-match to usual photo-type slides. A single light-emitting segment is approx. 0.4 cm × 0.8 cm (an image of a single light-emitting segment under forward current is shown in Fig. 2b). The way of structuring the ITO-layer was done in the easy and convenient way, which we have described earlier.[20] After several washing and cleaning steps the organic layers and the air-stable aluminium cathode were evaporated in high-vacuum (1×10^{-5} mbar, layer thickness PcCu 10–30 nm, emitter 40–80 nm). The EL spectra of all devices (single and double layer) are shown in Fig. 1 together with the corresponding PL spectra obtained from vacuum deposited thin films. The emission maxima are listed in Table 1.

Due to the longer alkyloxy chains the PL maxima of **9b–9d** are shifted 25 nm to the red, when compared with **9a**. The EL maxima of the single layer devices are in good agreement with the PL values (630 nm, orange–red), whereas the spectra of the double layer devices strongly differ from the PL spectra, which is caused by the additional PcCu layer. PcCu is a good and commonly used hole transport layer and enhances the long-term stability as well as the efficiency of the device,[21] but PcCu has two UV-absorption maxima at 624 and 695 nm (see Fig. 1). Reabsorption of the emitted light occurs and the spectra and the resulting emission color are changed, when compared to the single layer device. Depending on the thickness of PcCu the maxima can be shifted more than 60 nm to the blue, *e.g.* for **9a** (the optimized thickness of PcCu is discussed between 2 and 30 nm, see lit.[21a]).

Due to the preparation method (deposition of a relatively large emitting area (25 cm^2)) and the resulting natural gradient of the layer thickness of the different emitting segments, the determination of precise efficiency values is difficult. The efficiency and luminescence of several emitting segments were calculated according to literature by assuming a lambertian emission.[22] The values for the luminescence are between 0.5 and 2.5 cd m^{-2} (measured at 20 V) with the devices showing onset voltages around 8 V. The photograph (Fig. 2b) was taken at daylight with an applied voltage of 16 V. The obtained values for the new bridged triphenylenes are not optimized and can be improved by controlling the layer thicknesses of the hole transport layer as well as the emitter layer. Improvement of the electron injection by introducing an additional LiF layer[23] at the emitter/aluminium cathode interface to enhance the intensities is under investigation.

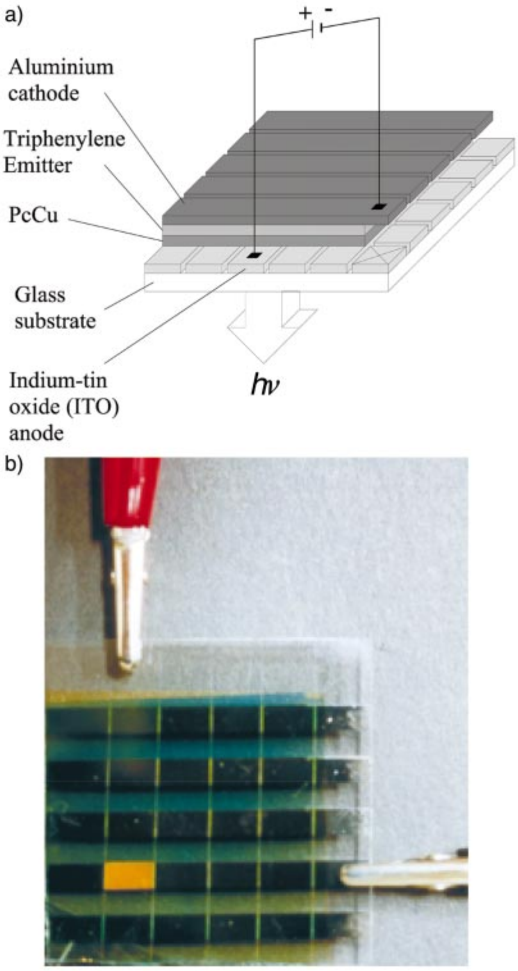


Fig. 2 a) Schematic set-up of the organic light-emitting diode, b) emission of TpPPV1 (**9a**) in a double layer arrangement with PcCu, measured at 16 V.

Conclusions

We have prepared new monofunctional triphenylene derivatives containing a methyl (**5a–5d**), bromomethyl (**6a–6d**) or a cyanomethyl group (**7a–7d**), which are useful for linking two triphenylene systems maintaining full π-conjugation. This was carried out by a double Knoevenagel reaction with the monofunctionalized cyanomethyltriphenylene derivatives (**7a–7d**) and a suitable terephthalaldehyde compound (**8**). The obtained bridged bistriphenylenes (**9a–9d**) are highly conjugated and exhibit strong orange to red photoluminescence ($\lambda_{max} \cong 630$ to 660 nm). They show a strong bathochromic shift of more than 250 nm when compared with a single triphenylene system. Up to now, triphenylenes were only used as a hole tranport material in organic light-emitting diodes. In an electroluminescent screening method by preparing single and double layer devices with 25 segments we have shown that highly conjugated triphenylenes are possible candidates for use in displays. The triphenylene derivatives **9a–9d** exhibit bright orange to red electroluminescence which is visible in daylight. The comparison of single layer devices with double layer devices showed a marked shift in the emission maxima, which is assigned to reabsorption of the hole transport layer copper phthalocyanine.

Table 1 Absorption and emission maxima. UV/Vis absorption, photoluminescence (PL) and electroluminescence (EL) maxima (wavelength units, nm) of the TpPPVs **9a–9d**.

	UV (sol., $CHCl_3$)	PL (thin film)	EL (single layer device)	EL (double layer with CuPc)
TpPPV1 (**9a**)	271, 458	635	631	571
TpPPVi4 (**9b**)	271, 458	660	632	586
TpPPVi5 (**9c**)	272, 461	660	632	645
TpPPV6 (**9d**)	272, 461	660	635	654

Experimental

Chemicals received from commercial sources (Aldrich and Fluka) were used without further purification. All reactions were performed under a dry nitrogen atmosphere. Solvents were dried according to standard procedures. The melting points are uncorrected. NMR spectra were recorded with a Bruker AC 250 spectrometer at 250 MHz (^1H) and 62.9 MHz (^{13}C) in $CDCl_3$ and internally referenced to $CHCl_3$ (^1H: $\delta = 7.24$, ^{13}C: $\delta = 77.00$). Infrared spectra were taken as KBr pellets or with NaCl carriers using a Bruker IFS 48 spectrometer. UV-Vis spectra were recorded in $CHCl_3$ solution with a Shimadzu UV-2102 PC. Mass spectra were recorded on a Finnigan ISQ 70 and a Varian MAT 711 A. Elemental analysis of the products was carried out with a VarioEL V, the E.A. of the precursors are in order. PL of evaporated thin films was measured with a SPEX fluorolog 112 in the 45° configuration. For EL measurements a HP 6030A voltage source was used together with a Keithley 171 DMM. The EL spectra were taken from devices with ITO/[copper phthalocyanine (PcCu)]/emitter/Al configuration with a waveguide diode array set-up in air at room temperature. The following compounds were prepared as described in the literature: the dialkyl ethers **2b–2d** were synthesized by ether synthesis of catechol (**1**) and alkyl bromides in acetonitrile at 80 °C with K_2CO_3 giving **2b–2d** in yields of over 90%. The spectroscopic data of **2b–2d** were described in the literature.[24] 2,5-Bis(2-ethylhexyloxy)terephthalaldehyde **8** was prepared according to the literature.[5d] Compound **3a** is commercially available.

General procedure for the preparation of the monoiodines 3b–3d

0.10 mol of **2b–2d** were added to a solution of 75 ml glacial acetic acid, 25 ml water and 2.0 ml conc. H_2SO_4. Before heating to 40 °C 40.3 mmol iodine was added. 24.5 mmol iodic acid was added in 3 parts, the first one following the addition of the iodine, the second and third after one and two hours, respectively. After 3.5 h the solution product was extracted with diethyl ether and washed with solutions of sodium hydrogensulfite and potassium carbonate. Drying in vacuum yielded the pure product **3b–3d**.

1,2-Diisobutoxy-4-iodobenzene (3b). Yield: 33.4 g, 96 mmol (96.4%); ^1H-NMR: 1.02 (d, $J = 6.46$ Hz, 12H), 2.10 (t sept, $J = 6.46$ Hz, 2H), 3.70 (d, $J = 6.46$ Hz, 4H), 6.59 (d, $J^3 = 8.36$ Hz, 1H), 7.11 (d, $J^4 = 2.04$ Hz, 1H), 7.16 (dd, $J^3 = 8.36$ Hz, $J^4 = 2.04$ Hz, 1H); ^{13}C-NMR: 19.2, 28.3, 28.3, 75.6, 75.7, 82.4, 115.7, 122.8, 129.7, 149.4, 150.3; IR (NaCl): 633, 798, 818, 829, 871, 889, 920, 982, 1003, 1015, 1055, 1138, 1071, 1218, 1250, 1290, 1321, 1367, 1387, 1429, 1474, 1501, 1582, 2648, 2719, 2870, 2932, 2956; MS: 348 (M^+), 292, 236, 222, 166, 110, 57, 43; UV-VIS: 285.

1,2-Bis(isopentyloxy)-4-iodobenzene (3c). Yield: 35.5 g, 94.8 mmol (94.5%); ^1H-NMR: 0.95 (d, $J = 6.57$ Hz, 12H), 1.67 (tt, 6.57 Hz, 4H) 1.82 (t sept, $J = 6.57$ Hz, 2H), 3.95 (d, $J = 6.57$ Hz, 4H), 6.52 (d, $J^3 = 8.42$ Hz, 1H), 7.17 (d, $J^4 = 2.22$ Hz, 1H), 7.20 (dd, $J^3 = 8.52$ Hz, $J^4 = 2.22$ Hz, 1H); ^{13}C-NMR: 22.5, 25.0, 37.8, 67.5, 67.6, 82.4, 115.5, 122.5, 129.7, 149.1, 150.0; IR (NaCl): 633, 798, 818, 839, 872, 889, 920, 982, 1003, 1015, 1055, 1138, 1171, 1219, 1250, 1290, 1321, 1367, 1387, 1429, 1474, 1501, 1582, 2569, 2646, 2719, 2870, 2932, 2955, 3074; MS: 376 (M^+), 306, 236, 110, 71, 55, 43; UV-VIS: 285.

1,2-Bis(hexyloxy)-4-iodobenzene (3d). Yield: 35.6 g, 88 mmol (88.0%); ^1H-NMR: 0.90 (t, $J = 6.53$ Hz, 6H), 1.21–1.47 (m, 12H), 1.78 (m, 4H), 3.95 (t, $J = 6.54$ Hz, 4H), 6.58 (d, $J^3 = 8.30$ Hz, 1H), 7.12 (d, $J^4 = 2.02$ Hz, 1H), 7.14 (dd, $J^3 = 8.30$ Hz, $J^4 = 2.02$ Hz, 1H); ^{13}C-NMR: 13.9, 22.5, 25.5, 25.6, 29.0, 29.2, 31.4, 31.5, 69.1, 69.2, 115.5, 122.5, 129.7, 149.1, 150.0; IR (NaCl): 631, 739, 795, 839, 868, 939, 1015, 1045, 1055, 1136, 1219, 1248, 1290, 1321, 1393, 1468, 1501, 1583, 2731, 2858, 2929, 2953; MS: 404, 278, 194, 110, 85, 55, 43; UV-VIS: 285.

General procedure for the preparation of the 2,3,6,7-tetrakis(alkyloxy)-10-methyltriphenylenes 5a–5d

The reaction was carried out under nitrogen. To a solution of 45.0 mmol bromoveratrole (**3a**) or 1,2-bis(alkyloxy)-4-iodobenzene (**3b–3d**) in 100 ml THF, 32 ml of a 1.60 M solution of butyllithium (50.0 mmol) in hexane was added at −78 °C, immediately followed by a solution of 6.21 g dried zinc chloride (45.0 mmol) in 50 ml THF. The mixture was stirred for one more hour at −78 °C and refluxed for an additional hour. 15.0 mmol dibromotoluene were stirred together with 0.1 g tetrakis(triphenylphosphine)palladium in THF for 10 min before adding to the reaction mixture. The mixture was kept under reflux for 16 h. The resulting *o*-terphenyls **4a–4d** were extracted with diethyl ether. Byproducts were mainly removed by column chromatography. The crude product was cyclised with 45.0 mmol $FeCl_3$ in dichloromethane and 2 drops of conc. H_2SO_4. After stirring for 4 h the mixture was quenched with methanol. The solvents were removed. The crude product was purified by repeated column chromatography (silica gel; dichloromethane–petroleum ether eluents). The products **5a–5d** can be recrystallized from ethanol.

2,3,6,7-Tetramethoxy-10-methyltriphenylene (5a). White plates, mp 246–248 °C; yield: 2.59 g, 6.9 mmol (47.6% for 2 steps); ^1H-NMR: 2.60 (s, 3H), 4.09–4.11 (4s, 12H), 7.40 (d, $J = 8.39$ Hz, 1H), 7.74 (s, 2H), 7.92 (s, 1H), 7.94 (s, 1H), 8.23 (s, 1H), 8.34 (d, $J = 8.39$ Hz, 1H); ^{13}C-NMR: 21.8, 55.8, 103.8, 103.8, 104.1, 104.2, 122.5, 122.6, 123.1, 123.2, 123.4, 123.8, 126.4, 127.4, 128.8, 135.3, 148.4, 148.5, 148.7, 149.0; ^{13}C-NMR (DEPT-135): 21.8, 55.8, 103.8, 103.8, 104.1, 104.2, 122.5, 122.6, 127.4; IR (KBr): 627, 644, 777, 802, 843, 860, 928, 964, 1026, 1045, 1157, 1173, 1202, 1215, 1263, 1304, 1346, 1383, 1410, 1420, 1447, 1466, 1520, 1543, 1616, 2831, 2912, 2935, 2955, 3003; MS: 362 (M^+), 347, 333, 319, 304, 288, 181, 138; UV-VIS: 266, 275, 302, 341, 358.

2,3,6,7-Tetraisobutoxy-10-methyltriphenylene (5b). White plates, mp 166–167 °C, yield: 2.25 g, 4.2 mmol, (28.2% for 2 steps); ^1H-NMR: 1.15 (d, $J = 6.5$ Hz, 24H), 2.27 (d sept, $J = 6.5$ Hz, 4H) 2.61 (s, 3H), 4.02 (d, 12H), 7.39 (d, $J = 8.25$ Hz, 1H), 7.82 (s, 2H), 7.96 (s, 1H), 7.98 (s, 1H), 8.24 (s, 1H), 8.34 (d, $J = 8.25$ Hz, 1H); ^{13}C-NMR: 19.4, 21.8, 28.7, 75.7–76.1, 107.4, 122.8, 124.4, 127.5, 129.0, 135.3, 149.5; IR (KBr): 624, 762, 802, 839, 851, 860, 874, 924, 941, 955, 968, 1045, 1175, 1188, 1200, 1209, 1225, 1265, 1308, 1342, 1366, 1394, 1427, 1472, 1520, 1547, 1616, 2872, 2912, 2955, 3105; MS: 530 (M^+), 474, 418, 361, 318, 306, 277, 248, 57; UV-VIS: 267, 276, 302, 344, 361.

2,3,6,7-Tetrakis(isopentyloxy)-10-methyltriphenylene (5c). White plates, mp 119–120 °C, yield: 1.08 g, 1.85 mmol (12.3% for 2 steps); ^1H-NMR: 1.15 (d, $J = 6.4$ Hz, 24H), 1.80–2.03 (m, 12H) 2.60 (s, 3H), 4.28 (t, 6.0 Hz, 8H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.84 (s, 2H), 7.98 (s, 1H), 8.00 (s, 1H), 8.24 (s, 1H), 8.35 (d, $J = 8.3$ Hz, 1H); ^{13}C-NMR: 21.8, 22.6, 25.3, 38.1, 67.0, 67.8, 68.0, 68.1, 106.8, 107.0, 107.1, 107.2, 122.8, 122.9, 123.6, 123.7, 123.9, 124.3, 126.7, 127.5, 129.0, 135.5, 149.0, 149.1, 149.2, 149.4; IR (KBr): 623, 714, 761, 802 841, 860, 881, 920, 949, 982, 1018, 1061, 1171, 1184, 1211, 1225, 1263, 1302, 1367, 1385, 1425, 1468, 1518, 1541, 1614, 2363, 2870, 2932, 2955, 3101; MS: 586 (M^+), 516, 446, 376, 306, 71, 43; UV-VIS: 266, 276, 302, 343, 360.

2,3,6,7-Tetrakis(hexyloxy)-10-methyltriphenylene (5d). White plates, mp 115–117 °C, yield: 870 mg, 1.35 mmol (9.0% for 2 steps); ^{1}H-NMR: 0.85 (t, $J=6.7$ Hz, 12H), 1.09 (m, 16H), 1.49 (m, 8H), 1.85 (tt, $J=6.4$ Hz, 4H) 2.61 (s, 3H), 4.14 (t, $J=6.4$ Hz, 8H), 7.30 (d, $J=8.37$ Hz, 1H), 7.74 (s, 2H), 7.88 (s, 1H), 7.90 (s, 1H), 8.14 (s, 1H), 8.26 (d, $J=8.37$ Hz, 1H); ^{13}C-NMR: 14.1, 21.8, 22.7, 25.9, 29.5, 31.7, 69.4, 69.5, 69.8, 69.9, 107.3, 122.8, 123.8, 124.4, 126.7, 127.5, 129.0, 135.3, 149.2, 149.5; IR (KBr): 623, 725, 762, 802, 839, 860, 872, 924, 959, 1022, 1051, 1070, 1173, 1184, 1195, 1209, 1219, 1240, 1265, 1306, 1386, 1427, 1466, 1518, 1616, 2856, 2926, 2956, 3104; MS: 642, 558, 473, 389, 318, 305, 276, 247, 85, 55, 43; UV-VIS: 266, 276, 302, 345, 360.

General procedure for the preparation of the bromomethyltriphenylenes 6a–6d

2.5 mmol 2,3,6,7-tetrakis(alkyloxy)-10-methyltriphenylenes (**5a–5d**) were dissolved in 500 ml of dry CCl_4 under nitrogen atmosphere. After adding 2.5 mmol NBS and 0.10 g AIBN the reaction was kept under reflux for 16 h. The solvent was evaporated. The products **6a–6d** were purified by washing with methanol (3 × 50 ml).

2,3,6,7-Tetramethoxy-10-bromomethyltriphenylene (6a). White–yellowish powder, mp > 280 °C, yield: 660 mg, 1.5 mmol (60.2%); ^{1}H-NMR: 4.06–4.08 (4s, 12H), 4.76 (s, 2H), 7.56 (dd, $J^3=8.46$ Hz, $J^4=1.81$Hz, 1H), 7.56 (s, 1H), 7.59 (s, 1H), 7.74 (s, 1H), 7.86 (s, 1H), 8.32 (d, $J^3=8.39$ Hz, 1H), 8.34 (d, $J^4=1.81$ Hz, 1H); ^{13}C-NMR: 34.5, 55.9, 55.9, 56.0, 56.6, 103.8, 104.0, 104.3, 104.5, 122.8, 122.9, 123.2, 123.5, 123.9, 124.0, 126.6, 128.6, 128.7, 135.0, 148.7, 149.4, 149.5; IR (KBr): 633, 777, 804, 814, 822, 835, 1022, 1038, 1051, 1153, 1169, 1198, 1215, 1232, 1261, 1306, 1383, 1412, 1425, 1452, 1472, 1506, 1520, 1543, 1618, 2829, 2910, 2937, 2957, 2988; MS: 442 (M^+), 440, 361, 347, 332, 317, 304, 180, 96, 94, 82, 80, 40; UV-VIS: 281, 348, 365.

2,3,6,7-Tetraisobutoxy-10-bromomethyltriphenylene (6b). White–yellowish powder, mp 172–174 °C, yield: 960 mg, 1.59 mmol (63.5%); ^{1}H-NMR: 1.14 (d, $J=6.5$ Hz, 24H), 2.24 (m, 4H), 3.99 (d, $J=6.8$ Hz 12H), 4.77 (s, 2H), 7.58 (d, $J=8.52$ Hz, 1H), 7.79 (s, 2H), 7.93 (s, 2H), 8.41 (s, 1H), 8.43 (d, $J=8.52$ Hz, 1H); ^{13}C-NMR: 19.4, 28.6, 34.4, 75.6, 75.7, 75.9, 106.9, 107.0, 107.0, 107.1, 123.2, 123.2, 123.4, 123.7, 124.4, 124.5, 126.7, 128.9, 129.0, 135.0, 149.3, 149.4, 149.9, 150.0; IR (KBr): 633, 690, 719, 804, 839, 870, 922, 970, 1005, 1030, 1047, 1175, 1190, 1200, 1209, 1229, 1265, 1306, 1329, 1367, 1393, 1437, 1472, 1512, 1543, 1614, 2872, 2908, 2957, 3103; MS: 610 (M^+), 608, 530, 473, 417, 361, 317, 306, 277, 248, 231, 80, 82, 57, 43; UV-VIS: 281, 249, 366.

2,3,6,7-Tetrakis(isopentyloxy)-10-bromomethyltriphenylene (6c). Yellow powder, mp 165–167 °C, yield: 900 mg, 1.35 mmol (54.2%); ^{1}H-NMR: 1.04 (d, $J=6.45$ Hz, 24H), 1.79–1.97 (m, 12H), 4.24 (m, 8H), 4.76 (s, 2H), 7.58 (d, $J=8.24$ Hz, 1H), 7.81 (s, 2H), 7.96 (s, 2H), 8.41 (s, 1H), 8.43 (d, $J=8.24$ Hz, 1H); ^{13}C-NMR: 22.7, 25.3, 34.4, 38.0, 68.8, 67.9, 68.0, 106.8, 106.8, 106.9, 107.0, 123.2, 123.4, 123.7, 124.4, 126.7, 128.9, 129.0, 135.0, 149.1, 149.1, 149.7, 149.8; IR (KBr): 621, 633, 797, 808, 841, 918, 972, 984, 1015, 1059, 1123, 1175, 1188, 1198, 1211, 1229, 1267, 1311, 1331, 1367, 1389, 1429, 1443, 1466, 1522, 1543, 1614, 2866, 2928, 2553; MS: 666. (M^+), 642, 600, 586, 516, 445, 375, 305, 277, 248, 82, 80, 71, 43; UV-VIS: 282, 349, 368.

2,3,6,7-Tetrakis(hexyloxy)-10-bromomethyltriphenylene (6d). Yellow powder, mp 139–141 °C, yield: 1.14 g, 1.58 mmol (63.2%); ^{1}H-NMR: 0.92 (t, $J=5.9$ Hz, 12H), 1.39 (m, 16H), 1.57 (m, 8H), 1.90 (m, 4H), 4.23 (t, $J=5.68$ Hz, 8H), 4.75 (s, 3H), 7.57 (d, $J=8.48$ Hz, 1H), 7.79 (s, 2H), 7.94 (s, 2H), 8.33 (s, 1H), 8.34 (d, $J=8.48$ Hz, 1H); ^{13}C-NMR: 14.0, 22.6, 25.8, 29.3, 31.7, 34.4, 69.3, 69.4, 69.6, 106.9, 123.2, 123.4, 123.7, 124.4, 124.4, 126.7, 128.9, 129.0, 135.0, 149.1, 149.7, 149.8; IR (KBr): 633, 663, 725, 810, 839, 872, 881, 924, 962, 1020, 1049, 1072, 1175, 1184, 1204, 1228, 1242, 1265, 1310, 1329, 1389, 1427, 1443, 1466, 1512, 1543, 1614, 2854, 2928, 2952; MS: 724 (M^+), 720, 643, 557, 389, 317, 277, 148, 97, 82, 80, 71, 55, 53, 43; UV-VIS: 281, 368.

General procedure for the preparation of the cyanomethyltriphenylenes 7a–7d

2.0 mmol 2,3,6,7-tetrakis(alkyloxy)-10-bromomethyltriphenylenes (**6a–6d**) were dissolved in 100 ml dichloromethane. A solution of 2.2 mmol tetraethylammonium cyanide in dichloromethane was added dropwise in 15 min. The reaction mixture was stirred for another 2 h at room temperature. The solution was washed with water, the organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product **7a–7d** was purified by column chromatography (silica gel; dichloromethane–petroleum ether).

2,3,6,7-Tetramethoxy-10-cyanomethyltriphenylene (7a). Yellow–brown powder, mp 233 °C, yield: 490 mg, 1.27 mmol (63.8%); ^{1}H-NMR: 3.94 (s, 2H), 4.07 (s, 12H), 7.42 (d, $J^3=7.18$ Hz, $J^4=1.50$ Hz 1H), 7.60 und 7.61 (2s, 2H), 7.75 (s, 1H), 7.79 (s, 2H), 8.31 (s, 1H), 8.36 (d, $J=7.18$ Hz, 1H); ^{13}C-NMR: 23.9, 55.9, 56.0, 56.6, 104.0, 104.0, 104.2, 104.4, 118.1, 122.0, 122.6, 122.8, 123.7, 123.9, 124.1, 125.2, 127.1, 128.2, 129.0, 148.8, 149.5, 149.6; IR (KBr): 619, 777, 802, 810, 824, 837, 1018, 1034, 1047, 1151, 1167, 1184, 1194, 1213, 1261, 1306, 1383, 1412, 1425, 1448, 1472, 1518, 1545, 1618, 2245, 2831, 2912, 2941, 2963, 2991, 3005; MS: 387 (M^+), 376, 361, 344, 330, 312, 304, 258, 215, 193, 152, 93; UV-VIS: 276, 302, 344, 361.

2,3,6,7-Tetraisobutoxy-10-cyanomethyltriphenylene (7b). Yellow–brown powder, mp 123–127 °C, yield: 920 mg, 1.65 mmol (82.7%); ^{1}H-NMR: 1.13 (d, $J=6.63$ Hz, 24H), 2.26 (sept t, $J=6.63$ Hz, 4H), 3.98 (d, $J=6.63$ Hz 12H), 3.99 (s, 2H), 7.47 (d, $J=8.56$ Hz, 1H), 7.79 (s, 2H), 7.91 (s, 1H), 7.96 (s, 1H), 8.34 (s, 1H), 8.43 (d, $J=8.56$ Hz, 1H); ^{13}C-NMR: 19.3, 23.9, 28.6, 75.6, 75.7, 75.9, 76.0, 106.8, 106.9, 107.0, 107.1, 118.1, 122.3, 122.9, 123.1, 124.0, 124.3, 124.5, 125.3, 127.1, 128.6, 129.3, 149.4, 150.0, 150.1; IR (KBr): 802, 839, 864, 874, 893, 905, 922, 943, 953, 972, 984, 1003, 1049, 1072, 1082, 1113, 1175, 1202, 1265, 1367, 1393, 1427, 1441, 1472, 1514, 1543, 1614, 2247, 2872, 2910, 2957; MS: 555, 530, 499, 473, 443, 416, 386, 361, 331, 306, 278, 248, 57, 41; UV-VIS: 277, 304, 345, 362.

2,3,6,7-Tetrakis(isopentyloxy)-10-cyanomethyltriphenylene (7c). Yellow–brown powder, mp 142–144 °C, yield: 830 mg, 1.36 mmol (68%); ^{1}H-NMR: 1.03 (d, $J=6.45$ Hz, 24H), 1.84–1.91 (m, 12H), 4.05 (s, 2H), 4.24 (t, $J=6.57$ Hz, 8H), 7.47 (d, $J=7.18$ Hz, 1H), 7.81 (s, 2H), 7.94 (s, 2H), 8.34 (s, 1H), 8.47 (d, $J=7.18$ Hz, 1H); ^{13}C-NMR: 22.7, 23.9, 25.3, 38.0, 67.8, 67.9, 68.0, 68.0, 106.8, 106.8, 106.9, 118.1, 122.3, 122.9, 123.1, 123.9, 124.3, 124.5, 125.3, 127.2, 128.5, 129.3, 149.2, 149.8, 149.9; IR (KBr): 804, 841, 972, 984, 1016, 1059, 1124, 1173, 1198, 1213, 1265, 1304, 1337, 1367, 1385, 1425, 1443, 1466, 1516, 1543, 1614, 1670, 1695, 1718, 2249, 2868, 2955, 3103; MS: 611, 586, 541, 400, 343, 331, 302, 235, 82, 80, 71, 43; UV-VIS: 277, 303, 344, 362.

2,3,6,7-Tetrakis(hexyloxy)-10-cyanomethyltriphenylene (7d). Yellow–brown powder, mp 105–107 °C, yield: 1.12 g, 1.68 mmol

(83.9%); ^{1}H-NMR: 0.92 (t, $J=6.5$ Hz, 12H), 1.38 (m, 16H), 1.57 (m, 8H), 1.93 (m, 8H), 3.97 (s, 2H), 4.22 (t, $J=6.35$ Hz, 8H), 7.47 (d, $J=8.38$ Hz, 1H), 7.80 (s, 2H), 7.93 (2s, 2H), 8.33 (s, 1H), 8.42 (d, $J=8.38$ Hz, 1H); ^{13}C-NMR: 14.0, 22.6, 23.9, 25.8, 29.3, 31.7, 69.4, 69.5, 69.6, 69.7, 106.9, 106.9, 107.0, 107.0, 118.1, 122.3, 122.9, 123.1, 123.9, 124.3, 124.5, 125.3, 127.1, 128.5, 129.3, 149.1, 149.7, 149.8; IR (KBr): 612, 725, 764, 802, 839, 872, 924, 941, 962, 1020, 1051, 1072, 1177, 1200, 1211, 1265, 1308, 1427, 1443, 1466, 1514, 1614, 1693, 2249, 2365, 2854, 2925, 2953, 3103; MS: 667 (M^{+}), 642, 583, 557, 499, 473, 414, 389, 331, 302, 277, 85, 55, 43; UV-VIS: 277, 305, 344, 361.

General procedure for the preparation of the bistriphenylenes 9a–9d

The reaction was carried out under nitrogen. 0.50 mmol 2,3,6,7-tetrakis(alkyloxy)-10-cyanomethyltriphenylenes (**7a–7d**) and 0.22 mmol 2,5-bis(2-ethylhexyloxy)terephthalaldehyde (**8**) were dissolved in dry THF and heated to 40 °C. 0.50 mmol potassium *tert*-butanolate and 4 drops of a methanolic solution of tetra-*n*-butylammonium hydroxide were added. After 30 min the products **9a–9d** precipitated and were centrifuged after addition of methanol. The product was washed with methanol (3 ×) and recrystallized from chloroform.

1,4-Bis(2-ethylhexyloxy)-2,5-bis[2′-cyano-2′-(2″,3″,6″,7″-tetramethoxytriphenylen-10-yl)ethenyl]benzene (9a). Orange–red plates, mp > 330 °C, yield: 94 mg, 0.08 mmol (37.7%); ^{1}H-NMR: 0.86 (t, 6.20 Hz, 3H), 0.97 (t, 7.03 Hz), 1.20–1.80 (m, 18H), 4.14 (m, 28 H), 7.85 (s, 4H), 7.89 (d, 9.37 Hz, 2H), 8.01 (s, 2H), 8.07 (s, 2H), 8.10 (s, 2H), 8.26 (s, 2H), 8.54 (d, 9.37 Hz, 2H), 8.83 (s, 2H); IR (KBr): 714, 777, 802, 870, 901, 1022, 1049, 1159, 1202, 1248, 1265, 1319, 1421, 1468, 1541, 1576, 1670, 2208, 2835, 2872, 2957, 2995; MS: 1128 (M^{+}), 1116, 770, 659, 546, 386, 313, 193, 99, 70, 57, 43; UV-VIS: 271, 458; EA: calculated for $C_{72}H_{76}N_2O_{10}$, C 76.60, H 6.74, N 2.48; found: C 75.71, H 6.40, N 2.52.

1,4-Bis(2-ethylhexyloxy)-2,5-bis[2′-cyano-2′-(2″,3″,6″,7″-tetraisobutoxytriphenylen-10-yl)ethenyl]benzene (9b). Red plates, mp > 330 °C, yield: 155 mg, 0.10 mmol (48.0%); ^{1}H-NMR: 0.85 (t, 7.37 Hz, 3H), 0.97 (t, 7.55 Hz, 6H), 1.14 (d, 6.70 Hz, 48H), 1.20–1.70 (m, 16H), 1.86 (m, 2H), 2.26 (d sept, 8.87 Hz, 8H), 4.03 (m, 16H), 4.10 (d, 5.55 Hz, 4H), 7.82 (s, 4H), 7.86 (d, 9.37 Hz, 2H), 7.98 (s, 2H), 8.05 (s, 2H), 8.07 (s, 2H), 8.23 (s, 2H), 8.52 (d, 9.04 Hz, 2H), 8.77 (s, 2H); IR (KBr): 613, 802, 814, 824, 839, 852, 870, 903, 912, 922, 932, 943, 972, 1024, 1049, 1177, 1217, 1248, 1267, 1317, 1367, 1393, 1429, 1472, 1516, 1541, 1614, 2208, 2874, 2930, 2959; MS (FD): 1464; UV-VIS: 271, 458; EA: calculated for $C_{96}H_{124}N_2O_{10}$, C 78.69, H 8.47, N 1.91; found: C 78.29, H 8.05, N 1.79.

1,4-Bis(2-ethylhexyloxy)-2,5-bis{2′-cyano-2′-[2″,3″,6″,7″-tetrakis(isopentyloxy)triphenylen-10-yl]ethenyl}benzene (9c). Red plates, mp > 330 °C, yield: 160 mg, 0.10 mmol (42.9%); ^{1}H-NMR: 0.85 (t, 7.37 Hz, 3H), 0,97 (t, 7.55 Hz, 6H), 1.14 (d, 6.55 Hz, 48H), 1.20–1.70 (m, 16H), 1.70–2.10 (m, 26H), 4.11 (d, 5.35 Hz, 4H), 4.28 (t, 5.95 Hz, 16H), 7.85 (s, 4H), 7.90 (d, 9.04 Hz, 2H), 8.01 (s, 2H), 8.05 (s, 2H), 8.09 (s, 2H), 8.24 (s, 2H), 8.50 (d, 9.04 Hz, 2H), 8.78 (s, 2H); IR (KBr): 802, 841, 870, 884, 903, 922, 951, 972, 982, 1013, 1061, 1177, 1219, 1248, 1267, 1319, 1367, 1385, 1427, 1466, 1516, 1541, 1614, 2208, 2870, 2932, 2954; MS: 1576; UV-VIS: 275, 454; EA: calculated for $C_{104}H_{140}N_2O_{10}$, C 79.19, H 8.88, N 1.78; found: C 78.13, H 8.39, N 1.64.

1,4-Bis(2-ethylhexyloxy)-2,5-bis{2′-cyano-2′-[2″,3″,6″,7″-tetrakis(hexyloxy)triphenylen-10-yl]ethenyl}benzene (9d). Dark red plates, mp > 330 °C, yield: 160 mg, 0.09 mmol (54.0%); ^{1}H-NMR: 0.88 (m, 30H), 1.20–1.70 (m, 64H), 1.70–2.10 (m, 18H), 4.11 (d, 5.35 Hz, 4H), 4.25 (t, 5.95 Hz, 16H), 7.84 (s, 4H), 7.90 (d, 9.40 Hz, 2H), 8.01 (s, 2H), 8.05 (s, 2H), 8.09 (s, 2H), 8.24 (s, 2H), 8.50 (d, 9.05 Hz, 2H), 8.78 (s, 2H); IR (KBr): 802, 824, 839, 872, 924, 932, 953, 960, 972, 1013, 1022, 1032, 1049, 1070, 1111, 1221, 1178, 1219, 1248, 1267, 1319, 1385, 1429, 1466, 1514, 1541, 1616, 2208, 2858, 2928, 2955; MS (FD): 1688 (M^{+}); UV-VIS: 272, 461; EA: calculated for $C_{112}H_{156}N_2O_{10}$, C 79.62, H 9.24, N 1.66; found: C 76.92, H 8.84, N 1.56.

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