Oligo-2,6-naphthylenevinylenes – New Building Blocks for the Preparation of Photoluminescent Polymeric Materials

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Synthetic strategies towards appropriate symmetric and unsymmetric functionalization of the naphthalene ring are presented. By means of Knoevenagel and Wittig condensation reactions new fluorescent, differently functionalized oligo(2,6-naphthylenevinylene)s have been synthesized, the presence of terminal aldehyde or bromine substitution opening the way to the incorporation of the fluorescent trimers in a variety of polymeric materials. The effect of substituting the phenylene ring by the more bulky dialkoxynaphthalene system in arylenevinylene-type materials is studied from the structural point of view and the possibility to tune the emission color and the electron affinity through the introduction of naphthylenevinylene and cyano-substituted naphthylenevinylene units is also investigated.

Introduction

During the last decade an explosive growth of activity in the area of organic electroluminescence has occurred in both academia and industry, stimulated by the promise of light-emitting plastics for the fabrication of large, flexible, inexpensive, and efficient screens to be used in different applications.[1] Thus, a variety of organic materials have been investigated as active materials in a number of device structures in order to optimize device performances.[2−4]

Since the demonstration of light emission from a poly(*p*-phenylenevinylene) (PPV) thin film sandwiched between hole- and electron-injecting contacts,[5] several efforts have been directed to the development of PPV derivatives in order to optimize all the parameters which are involved in the fabrication of devices. Different modifications carried out in the skeleton of conjugated polymeric materials are depicted in Figure 1a.

By introducing long alkoxy chains soluble, easily processible materials can be obtained[6] and the emitting properties of the polymers can be tuned.[7] Especially interesting is the introduction of CN groups at the double bonds of PPV resulting in the obtention of high-electron-affinity polymers which can be used to manufacture light-emitting diodes (LEDs) with air-stable electrodes.[8] Another strategy involves the modification of the vinylene linkage like in poly(*p*-phenylene)s (PPPs) which can be seen as PPV derivatives in which the vinylene linkage has been suppressed. Apart from being very resistant organic materials, PPP derivatives are very interesting because they offer the possibility of tuning the color of the emission by the production of derivatives with different torsion angles between consecutive rings.[9] An extended strategy towards the design of conjugated polymers involves the variation of the arylene building block itself. Different carbo- and heterocyclic systems have been used to replace the phenylene moiety in PPV,[1,2,10] the development of new fluorophores to be used as building blocks for the preparation of either conjugated or non-conjugated materials having gained great attention.

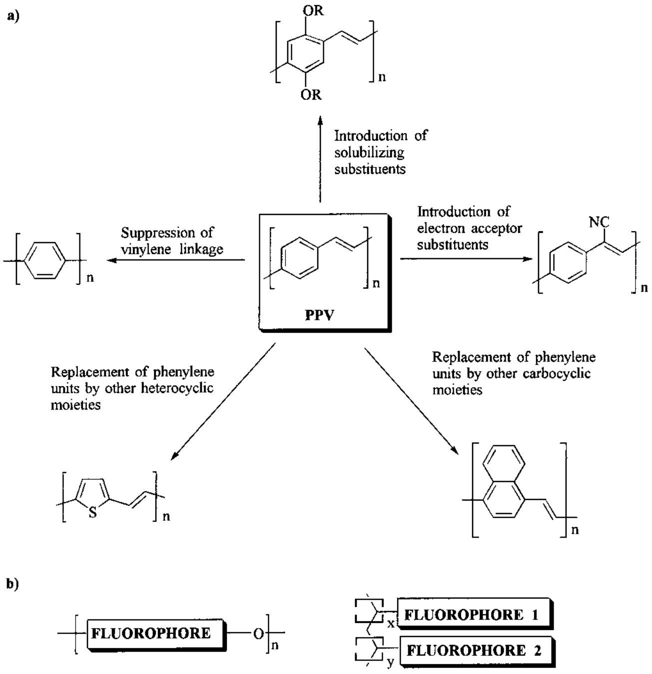

Figure 1. a) Modifications carried out in the skeleton of conjugated polymeric materials and b) non-conjugated polymeric materials bearing fluorophores as pendant groups or in the main chain

A common feature of conjugated polymers is that they inevitably contain randomly distributed defects, i.e., non-conjugated systems, which lead to a statistical distribution of lumophore lengths. In order to gain control over the conjugation length and subsequently over the band gap[11] while keeping the processibility properties of polymeric materials, copolymers bearing different fluorophores (oligophenylene, oligophenylenevinylene,[12] oligothiophene,[13] and others[14]) linked by flexible spacers either in the main

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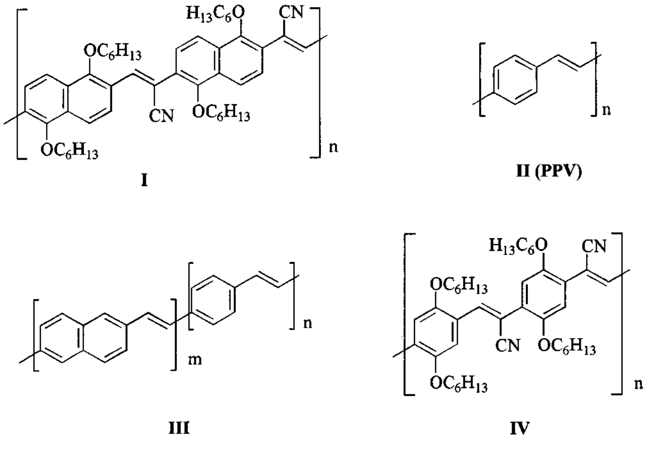
chain or as pendant groups (Figure 1b) have been synthesized and tested as luminescent materials. Thus, the conjugation length of conjugated-nonconjugated multiblock copolymers can be effectively tailored by choice of the appropriate fluorophores and spacers.[15−20] Furthermore, the block structure can also enhance the luminescence efficiency through confinement of the excitons in the small band-gap regions, hindering their migration to quenching sites.

In the present article we report the synthesis and study of new oligomeric materials containing appropriate functionalization to be attached to different spacers as main-chain chromophores in conjugated-nonconjugated multiblock copolymers. The new oligomers contain the very little studied 2,6-naphthylenevinylene unit; the effect of substituting phenylene units by naphthalene moieties on the electron affinity and on the emitting properties of these materials is investigated.

Results and Discussion

We have recently reported on the photo- and electroluminescent properties of a soluble poly(2,6-naphthylenevinylene) derivative[21,22] in which a blue shift of the emission color has been observed when compared with analogous phenylene-containing polymers.

Recent investigations[23] show that partially replacing the phenylene unit in PPV by a naphthalene system linked through the 1,4- or the 2,6-positions only show a significant effect in photoluminescence (PL) and electroluminescence (EL) emission maxima in the former case. Hückel molecular orbital calculations show that substitution of phenylene units in PPV (**II**, Figure 2) by unsubstituted naphthalene moieties linked through the 2,6-positions of the ring has little effect on the band structure and similar PL behavior is observed for polymer **III** (Figure 2) and PPV.[22][24]

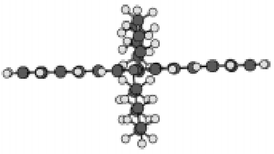
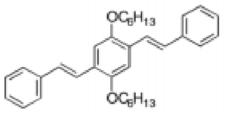
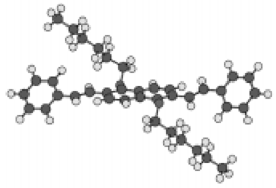
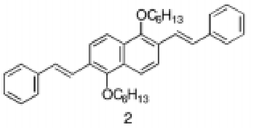


I **II (PPV)** **III** **IV**

Figure 2. Examples of replacement of phenylene units by naphthalene moieties in conjugated polymeric materials

In contrast to these observations we found that the PL emission of the poly(2,6-naphthylenevinylene) **I** (Figure 2) exhibits a strong blue shift relative to the phenylene-containing analogous polymer **IV** (PL emission maxima of 500 and 710 nm for **I** and **IV**, respectively). Since this effect can not be rationalized in terms of band structure, it may be ascribed to the steric hindrance of the more bulky dihexyloxynaphthalene ring, which induces torsion of the main chain and, consequently, reduces the planarity of the backbone. With this aim we have carried out geometry optimization using the Austin model 1 (AM1) semiempirical technique.[25] We chose this method because previous studies on phenylene and polyene chains have shown that the AM1 method gives good agreement for bond lengths and torsion angles with data obtained from experiment and Hartree-Fock ab initio calculations[26] and, recently, this method has been successfully used to perform theoretical studies of torsion and its effect on the structural and electronic properties of substituted poly(*p*-phenylenevinylene).[27] In Table 1 are depicted the AM1 equilibrium geometries optimized for oligomers **1** and **2** in which the central 1,4-dihexyloxybenzene moiety in **1** is replaced by a 1,5-dihexyloxynaphthalene unit linked through the 2- and 6-positions. While oligomer **1** presents a planar structure, the torsion angle between consecutive rings being approximately zero, oligomer **2** shows a distorted structure in which the peripheral benzene units out of the plane described by the naphthalene unit with torsion angles of 128 ± 1°. This lack of planarity in oligomer **2** induces a loss of conjugation which may be responsible for the blue shift of the PL emission of **2** (430 nm in dichloromethane solution) in relative to that of **1** (445 nm under analogous conditions).

Table 1. AM1-optimized geometries and fluorescence emission maxima of oligomeric model compounds **1** and **2**

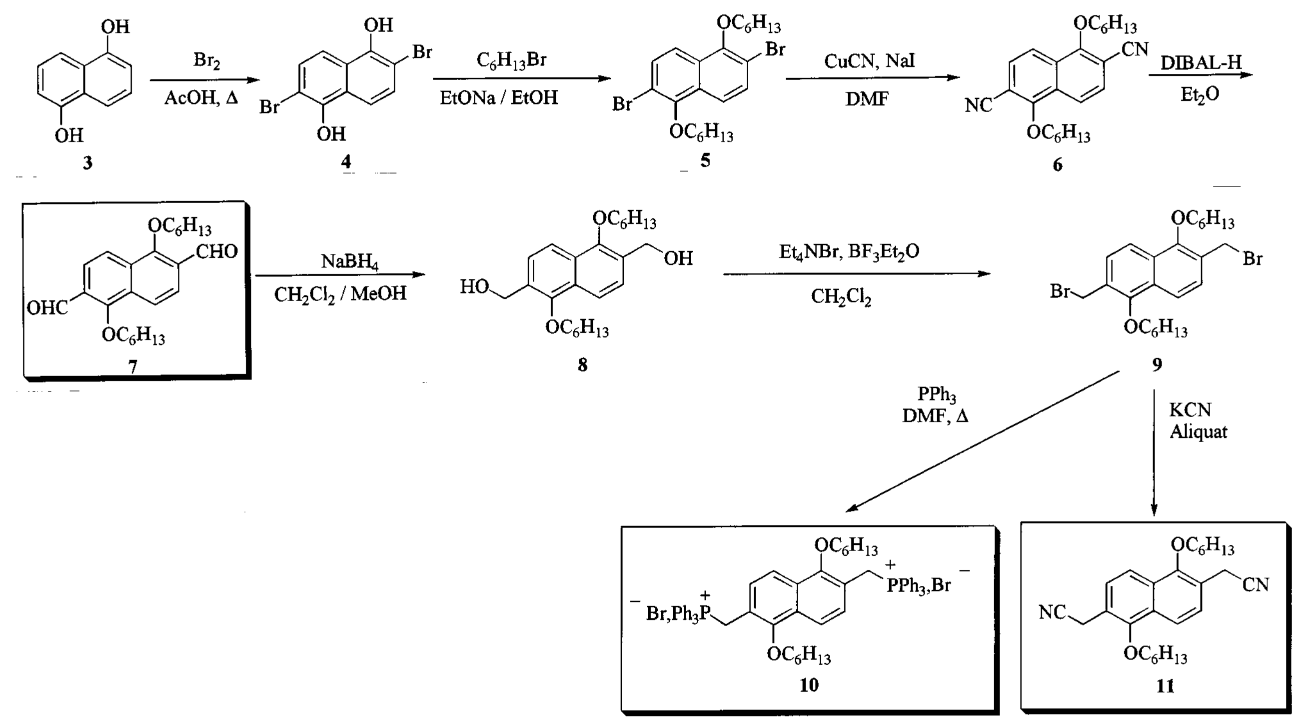
AM1-optimized geometries	Model compound	λ_{max} (PL)[a]
	 OC_6H_{13} OC_6H_{13} 1	445 nm
	 OC_6H_{13} OC_6H_{13} 2	430 nm

[a] In dichloromethane.

The possibility to induce torsion in the main chain, together with the intrinsic fluorescence of dialkoxynaphthalenes make functionalized naphthylenevinylenes suitable building blocks to be used in copolymerization reactions in order to tune the band gap in conjugated copolymers or to be incorporated in nonconjugated polymeric chains, thus having defined conjugation lengths.

Oligomer Syntheses

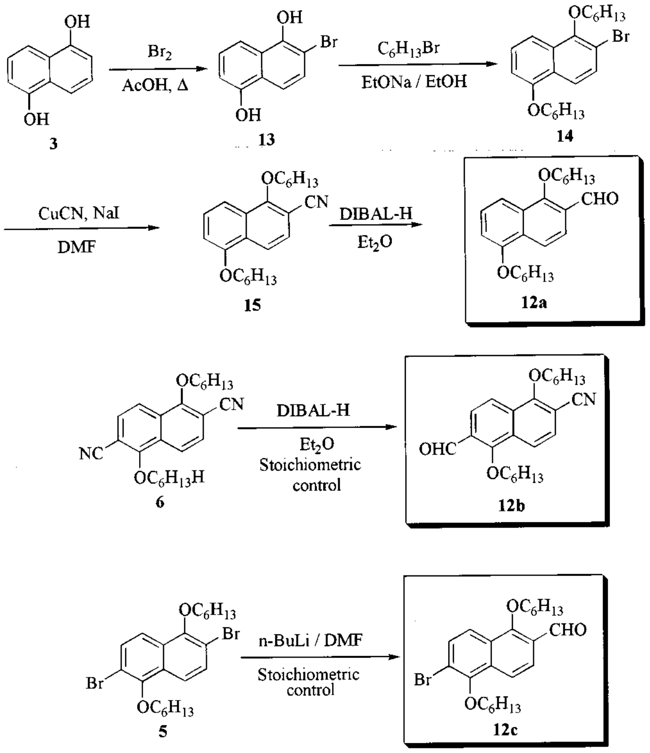
Previous attempts to synthesize oligo(2,6-naphthylenevinylene)s led to the obtention of highly insoluble materials



Scheme 1. Synthesis of symmetric monomeric units derived from naphthalene

which prevented appropriate spectroscopic and electrochemical characterization.[28] We have overcome this difficulty by synthesizing monomeric units containing hexyl chains as starting materials. The syntheses of the symmetric and unsymmetric monomeric units required for the preparation of the oligomeric materials involve the multistep processes which are depicted in Schemes 1 and 2, respectively.

Bromination under acidic conditions[29] of the commercially available 1,5-dihydroxynaphthalene (**3**) yielded the corresponding 2,6-dibromo derivative **4**, which was subsequently hexylated by treatment with sodium ethoxide in ethanol and bromohexane to give **5**. Treatment of **5** with copper cyanide in dimethylformamide[30] led to the dicyano derivative **6**, which upon reduction with DIBAL-H yielded dialdehyde **7**. Reduction with sodium tetrahydroborate and treatment with boron trifluoride–diethyl ether and tetraethylammonium bromide in dichloromethane[31] afforded the dibromomethyl derivative **9** which was finally treated with triphenylphosphane (in refluxing DMF) to give the corresponding 1,5-dihexyloxy-2,6-bis[(triphenylphosphonio)methyl]naphthalene dibromide (**10**). Alternatively, solid-state reaction of **9** with potassium cyanide and aliquat[32] yielded 2,6-bis(cyanomethyl)-1,5-dihexyloxynaphthalene (**11**). By modifying the above synthetic route, unsymmetric monomeric units were obtained (Scheme 2).



Scheme 2. Synthesis of unsymmetric monomeric units derived from naphthalene

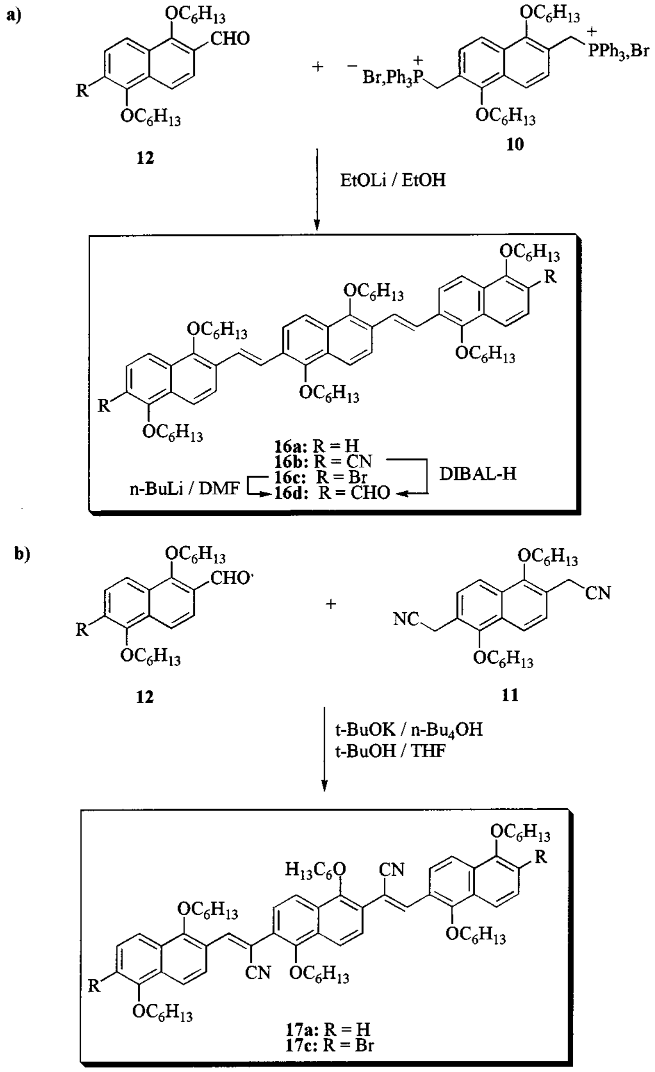
Direct formylation of dibromo derivative **5** with *n*-butyllithium and DMF as formylating reagent under stoichiometric control yielded the bromoaldehyde **12c** while reduction with DIBAL-H under stoichiometric control of the dicyano derivative **6** afforded 6-cyano-2-formyl-1,5-dihexyloxynaphthalene (**12b**). On the other hand, bromination under acidic conditions of the dihydroxynaphthalene **3** under stoichiometric control afforded a mixture of the monobromo and dibromo derivatives **13** and **4**, respectively, which after hexylation and cyanation yielded a mixture of the monocyano and dicyano derivatives **6** and **15** which could be separated by chromatography. Subsequent reduction of cyano derivative **15** with DIBAL-H gave the corresponding 2-formyl-1,5-dihexyloxynaphthalene (**12a**).

Wittig reactions of aldehydes **12** with bis[(triphenylphosphonio)methyl]naphthalene dibromide (**10**) using lithium ethoxide as the base[33] yielded the corresponding unsubstituted, dicyano-substituted and dibromo-substituted naphthylenevinylene derivatives **16a**, **16b**, and **16c**, respectively (Scheme 3a). Further reduction of the nitrile groups of **16b** with DIBAL-H gave the trimeric system functionalized with two aldehyde groups **16d**. This compound has also been obtained by direct formylation of the dibromo-substituted trimer **16c** with *n*-butyllithium and DMF as formylating reagent.

As the normal reaction of semistabilized triphenylphosphonium benzylides with aldehydes affords mixtures of (*Z*)- and (*E*)-alkenes nonstereoespecifically,[34] the oligonaphthylenevinylene series were obtained as a mixture of the *trans,trans* isomers together with the *cis,trans* and the *cis,cis* forms. Thus, it was necessary to isomerize the products by refluxing the mixture in toluene containing a trace of iodine to form the all-*trans* isomers in high yield. As the flexible side chains enhance the solubility of these compounds, it was possible to confirm this point by using high resolution NMR. A value of ^3J of 16 Hz corresponding to the vinylic protons of trimers **16** proves the *trans,trans* configuration.

The presence of the terminal aldehyde and bromine groups in this trimeric system make them especially attractive to be used as building blocks in a variety of polymerization reactions.[1,2,35]

By Knoevenagel condensation of aldehydes **12** with the bis(cyanomethyl)naphthalene **11** the corresponding trimeric analogues of **16** cyanated on the vinylene linkages **17** are obtained (Scheme 3b). The molecular structures of all intermediates and trimeric systems shown above were fully characterized by high-resolution ^{1}H-NMR and ^{13}C-NMR, IR spectroscopy, mass spectrometry, and elemental analyses.



Scheme 3. Synthesis of functionalized oligomeric units

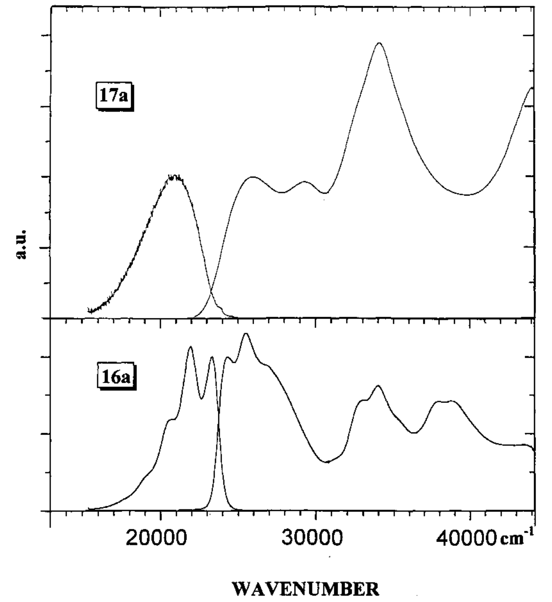


Figure 3. PL and absorption spectra of **16a** and **17a**

Absorption and Emission Spectra

Figure 3 shows the absorption and emission spectra of trimeric systems **16a** and **17a**. It is worth to note that the fluorescence spectrum of **16a** is clearly vibrationally structured while trimer **17a** shows unstructured fluorescence. This fact can be accounted for by the less-planarized carbon skeleton in **17a**. The close proximity of the cyano groups to the alkoxy chains prevents planarization due to steric hindrance even in the excited state.[36]

On the other hand, the presence of the cyano group on the vinylene moieties should lead to an overall stabilization of the HOMO and LUMO energy levels. The LUMO level is more affected upon substitution with electron-acceptor groups than the HOMO.[37] The asymmetry of this stabilization causes a decrease in the HOMO-LUMO gap and consequently a shift to longer wavelengths in the PL emission maxima. Thus, a bathochromic shift is observed when comparing the PL emission maxima of the cyano-substituted trimer **17a** [21000 cm^{-1} (476 nm)] with the corresponding unsubstituted analogue **16a** [22000 cm^{-1} (455 nm)]. This shift is smaller than that observed for other pairs of cyano-substituted materials and unsubstituted analogues (cyano-substituted dialkoxy-PPV[8] and the unsubstituted analogues[38] show emission maxima at aproximately 695 and 580 nm, respectively). This reduction of the observed bathochromic shift for compounds **16a** and **17a** can be rationalized in terms of the already mentioned steric effects. Steric hindrance of the bulky naphthalene and the cyano moiety will induce more torsion of the main chain in the cyano-substituted derivatives reducing the planarity of the backbone which induces a loss of conjugation. Thus, the shift to longer wavelength caused by the unsymmetric stabilization of the HOMO and LUMO levels upon cyano substitution is compensated by an opposite effect due to steric effects; the bathocromic shift observed is therefore smaller than expected.

The acceptor ability of the cyano group not only induces a shift to a longer wavelength of the PL emission but also leads to an increase of the electron affinity as demonstrated by the cyclic voltammetry measurements performed for **16a** and **17a**. Reversible cyclic voltammograms of the oligomers are obtained in dichloromethane solution with tetrabutylammonium perchlorate as supporting electrolyte, glassy carbon as the working electrode, and platinum and calomel electrodes as counter and reference electrodes, respectively. Introduction of electron-withdrawing groups leads to a positive shift of the potentials;[39] this trend is also observed for **16a** and **17a**. The anodic peak potentials of trimer **17a** (E^1_{pa} = 1.49 V and E^2_{pa} = 1.64 V) are anodically shifted, relative to those of **16a** (E^1_{pa} = 1.03 V and E^2_{pa} = 1.31 V) due to the presence of the cyano groups. The quasi-reversible reduction wave at E^1_{pc} = −1.64 V for **17a** is also shifted to a more positive potential relative to −2.05 V for **16a**. The cyclic voltammogram of trimer **17a** is depicted in Figure 4 and shows one reduction wave along with two oxidation waves.

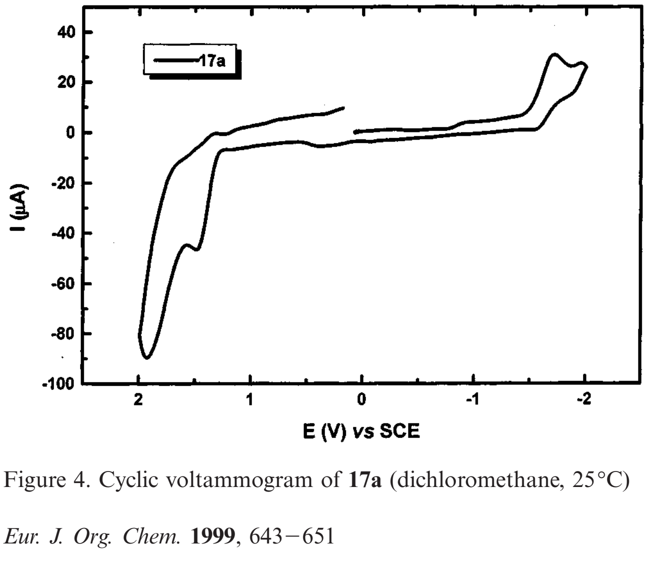


Figure 4. Cyclic voltammogram of **17a** (dichloromethane, 25°C)

Compounds **16** will therefore be more easily oxidized than the parent cyano-substituted analogues **17** and, by incorporating the appropriate trimeric unit in a polymeric chain, not only the emission properties but also the electron affinity can be tuned. To be able to tune the electron affinity of this type of materials is of great importance considering that improved efficiencies in light emission of LEDs come from an appropriate balance of charge injections between electrodes and luminescent materials.[1]

As the oxidation process corresponds to removal of charge from the HOMO energy level whereas the reduction cycle corresponds to electron addition to the LUMO, when the oxidation/reduction processes are measured with the same electrolyte/solvent system, the difference between the two onset potentials closely follows the optical band gap.[40] By determining the onset potentials from the intersection of the two tangents drawn at the rising current and background charging current of the CVs, ΔE values of 2.83 and 2.72 are found for **16a** and **17a**, respectively, showing a smaller HOMO-LUMO gap in the cyano-substituted trimer **17a**. Thus, the same conclusions emerged from structural changes and HOMO/LUMO energies as observed between structural changes and UV/Vis shifts.

Conclusions

We have developed synthetic strategies towards symmetric and unsymmetric functionalization of the naphthalene ring. By Wittig and Knoevenagel reactions we have prepared two series of naphthylenevinylene trimers functionalized in peripheral positions which allow them to be used as building blocks in a variety of polymerization reactions. The effect of substituting the phenylene ring by the more bulky dialkoxynaphthalene system has been studied from a structural point of view and the possibility to tune the emission color through the introduction of naphthylenevinylene units has been demonstrated. By incorporating the unsubstituted trimeric units or the dicyano-substituted analogues the emission properties can be tuned. In addition, the electron affinity, which is one important factor to take into account in the fabrication of light-emitting diodes, can also be finely modulated.

Experimental Section

All melting points were measured with a Gallenkamp melting-point apparatus and are uncorrected. − IR spectra were recorded as KBr pellets with a Perkin-Elmer 257 spectrometer. − Fluorescence spectra were recorded with a Spex-Fluorolog 222 and UV/Vis spectra were recorded with a Perkin-Elmer Lambda 3 instrument. − ^{13}C- and ^{1}H-NMR spectra were recorded with a Varian VXR-300 spectrometer (300 MHz and 75 MHz for ^{1}H and ^{13}C respectively). Chemical shifts are given as δ values (int. standard: TMS). − Elemental analyses were performed with a Perkin-Elmer CHN 2400 apparatus. − MS were recorded with a Finnigan 8430 (70 eV) spectrometer. − Semiempirical calculations (AM1) were performed using the program Hyperchem (version 3.0) from Hypercube Inc. with a PC compatible at 133 MHz. For each structure, the minimum energy was determined after reminimization. − Cyclic voltammetric measurements were performed with an EG & PAR Versastat potentiostat using 250 Electrochemical Analysis software. A Metrohm 6.0840.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies. − 1,5-Dihydroxynaphthalene is commercially available and was used without further purification. Diethyl ether, ethanol, and *t*BuOH were dried with sodium, tetrahydrofuran and dimethylformamide were dried with calcium hydride, and chloroform and dichloromethane were distilled from $CaCl_2$, and all were distilled before use. 2,6-Dibromo-1,5-dihydroxynaphthalene (**4**) was prepared according to the literature procedure.[29]

2,6-Dibromo-1,5-dihexyloxynaphthalene (5): Under argon, 4.32 g of sodium was dissolved in 254 mL of dry ethanol. To the sodium ethoxide solution, 23.174 g (73 mmol) of the naphthalenediol **4** was added and the solution was refluxed. Afterwards, 26.4 mL (188 mmol) of hexyl bromide was added dropwise during a period of 10 min. The reaction was heated at reflux for 5 h. After this time, the solution was cooled to room temperature and poured into 254 mL of a 1 N solution of NaOH. The black solid formed was filtered off, dissolved in 1 L of dichloromethane and filtered to eliminate insoluble impurities. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane/dichloromethane, 9:1, as the eluent) to obtain 15 g of a yellow solid. Yield 43%, m.p. 62°C (from hexane/dichloromethane). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, 2 H), 7.64 (d, 2 H), 4.1 (t, 4 H, OCH_2), 1.91 (m, 4 H, CH_2), 1.58 (m, 4 H), 1.42 (m, 8 H), 0.95 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 131.0, 130.1, 119.3, 113.7, 74.6, 31.7, 30.2, 25.7, 22.6, 14.0. − IR: $\tilde{\nu}$ = 2951, 2928, 1572, 1489, 1472, 1414, 1018, 810 cm^{-1}. − MS *m*/*z*: 486 [M^+] (10), 318 (100), 238 (27). − $C_{22}H_{30}Br_2O_2$ (486.3): calcd. C 54.32, H 6.17, Br 32.92; found C 54.63, H 6.09, Br 33.26.

2,6-Dicyano-1,5-bis(hexyloxy)naphthalene (6): Under argon, 2.5 g (5.14 mmol) of dibromonaphthalene **5**, 1.39 g (15.42 mmol) of CuCN, and 0.05 g of sodium iodide were refluxed in dry DMF for 2 d. After this time, the mixture was poured into a solution of NH_3 (15% by weight) in water (86 mL) out of which a solid precipitated. The solid was filtered under vacuum and washed with another portion of the NH_3 solution (86 mL) and then with water (86 mL). The solid was dried in a desiccator over phosphorus pentoxide for 1 d at 0.13 mbar and the raw material was hot extracted with acetone in a Soxhlet apparatus (43 mL, 5 h) giving a yellow solution. After evaporation of the solvent, the residue was dissolved in chloroform (34 mL) and the resulting solution was filtered through silica gel. The pure compound was obtained by removal of the solvent under reduced pressure. Yield 60%; m.p. 88°C (from hexane/dichloromethane). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, 2 H), 7.52 (d, 2 H), 4.46 (t, 4 H, OCH_2), 1.95 (m, 4 H, CH_2), 1.56 (m, 4 H), 1.38 (m, 8 H), 0.92 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0, 130.6, 128.7, 118.1, 117.1, 101.5, 76.0, 31.5, 30.2, 25.5, 22.5, 14.0. − IR: $\tilde{\nu}$ = 2951, 2928, 2226 (CN), 1470, 1421, 1375, 1327, 1200, 1040, 829 cm^{-1}. − MS; *m*/*z*: 378 [M^+] (18), 294 (10), 210 (100). − $C_{24}H_{30}N_2O_2$ (378.5): calcd. C 76.19, H 7.93, N 7.41; found C 76.12, H 7.71, N 6.93.

2,6-Diformyl-1,5-bis(hexyloxy)naphthalene (7): Under argon, 756 mg (2 mmol) of **6** was dissolved in 55 mL of dry ether and then 3.02 mL of a 1.5 M solution of DIBAL-H in toluene was added dropwise and the solution was heated under reflux for 1 d. After that time, the reaction mixture was allowed to cool and carefully first methanol and then water was added while a white precipitate was formed. Then, over 1 h, small amounts of concentrated HCl were added until all the precipitate was redissolved and two layers could be observed. The two layers were separated, the aqueous layer was washed with ether and the combined ethereal layers were washed with water, with saturated $NaHCO_3$ solution, and again with water. Finally, it was dried with magnesium sulfate, the solvent was removed under vacuum, and the yellow oil thus obtained was purified by chromatography on silica gel (hexane/dichlorometane, 7:3, as the eluent) to obtain 652 mg of a yellow solid. Yield 85%; m.p. 69°C (from hexane/dichloromethane). − ^1H NMR (300 MHz, $CDCl_3$): 10.52 (s, 2 H, CHO), 7.97 (d, 2 H), 7.87 (d, 2 H), 4.07 (t, 4 H, OCH_2), 1.89 (m, 4 H, CH_2), 1.53 (m, 4 H), 1.28 (m, 8 H, 0.88 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5 (CHO), 161.5, 133.2, 127.5, 123.7, 119.5, 79.5, 31.6, 30.2, 25.6, 22.6,13.9. − IR: $\tilde{\nu}$ = 2947, 2920, 2869, 1683 (CHO), 1498, 1326, 1070, 823 cm^{-1}. − MS; *m*/*z*: 384 [M^+] (4), 216 (100), 210 (100). − $C_{24}H_{32}O_4$ (384.5): calcd. C 75.00, H 8.33; found C 74.66, H 8.41.

1,5-Dihexyloxy-2,6-bis(dihydroxymethyl)naphthalene (8): Under argon, a mixture of 8 mL of MeOH and 8 mL of dichloromethane was added to 56 mg (1.48 mmol) of sodium tetrahydroborate and the suspension was stirred for 5 min until a yellow solution was formed. Then, 257 mg (0.67 mmol) of dialdehyde **7** was added and the solution was stirred for 1 h at room temperature. After this time, the solution was diluted with dichloromethane, washed with saturated $NaHCO_3$ solution and then with water. Finally, the organic layer was dried with sodium sulfate and the solvent was removed under vacuum. 170 mg of a white solid was obtained and crystallized from hexane. Yield 65%; m.p. 63°C (from hexane). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, 2 H), 7.41 (d, 2 H), 4.78 (s, 4 H, CH_2OH), 3.90 (t, 4 H, OCH_2), 2.49 (br. s, 2 H, OH), 1.86 (m, 4 H, CH_2), 1.50 (m, 4 H), 1.32 (m, 8 H), 0.86 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 129.4, 126.7, 118.5, 75.8, 60.8, 31.7, 30.4, 25.8, 22.6,14.1. − IR: $\tilde{\nu}$ = 3279 (OH), 2953, 2926, 2869, 1605, 1499, 1468, 1377, 1234, 1040, 814 cm^{-1}. − MS: *m*/*z*: 388 [M^+] (19), 286(5), 184 (100). − $C_{24}H_{36}O_4$ (388.6): calcd. C 74.22, H 9.28; found C 74.05, H 8.56.

2,6-Bis(bromomethyl)-1,5-dihexyloxynaphthalene (9): A mixture of 582 mg (1.5 mmol) of the bis(hydroxymethyl)naphthalene **8**, 946 mg (4.5 mmol) of tetraethylammonium bromide and 0.5 mL of freshly distilled boron trifluoride−diethyl ether was refluxed for 3 h under argon in 5 mL of dry dichloromethane. After this time, the reaction mixture was allowed to cool and 3 mL of a saturated solution of $NaHCO_3$ was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed first with 10% aqueous sodium thiosulfate and then with brine solution and finally dried with sodium sulfate. Removal of the solvent yielded the crude product which was further purified by chromatography (silica gel, eluent hexane/dichloromethane, 8:2) to afford 640 mg of a white solid. Yield 83%; m.p. 62°C (from hexane/dichloromethane). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, 2 H), 7.42 (d, 2 H), 4.66 (s, 4 H, CH_2Br), 4.02 (t, 4 H, OCH_2), 1.92 (m, 4 H, CH_2), 1.54 (m, 4 H), 1.36 (m, 8 H), 0.87 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.9, 130.0, 128.4, 127.5, 119.3, 75.5, 31.7, 30.4, 28.3, 25.8, 22.7, 14.1. − IR: $\tilde{\nu}$ = 2950, 2933, 2859, 1600, 1377, 1336, 1242, 1043, 825 cm^{-1}. − MS; *m*/*z*: 514 [M^+] (24), 433 (11), 349 (27), 269 (10), 185 (82), 80 (50), 43 (100). − $C_{24}H_{34}Br_2O_2$ (514.3): calcd. C 56.03, H 6.61, Br 31.13; found C 56.09, H 6.44, Br 31.25.

1,5-Dihexyloxy-2,6-bis[triphenylphosphonio(methyl)]naphthalene Dibromide (10): A stirred solution of 336 mg (1.28 mmol) of triphenylphosphane and 257 mg (0.5 mmol) of the bis(bromomethyl)-naphthalene derivative **9** in 2 mL of dry dimethylformamide was heated under reflux for 4 h. The viscous mixture was allowed to cool and then the DMF was removed under vacuum. A greenish oil was obtained, which was chromatographed on silica gel eluting first with chloroform to remove the excess of triphenylphosphane and then with chloroform/MeOH (95:5) to afford 290 mg of a white solid. Yield 56%; m.p. 256 °C (from chloroform/MeOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83−7.20 (m, 34 H), 5.46 (d, 4 H, CH_2P, J = 14.5 Hz), 3.60 (t, 4 H, OCH_2), 1.75(m, 4 H, CH_2), 1.56 (m, 4 H), 1.18 (m, 8 H), 0.77 (t, 6 H, CH_3). − IR: ṽ = 3025, 2950, 1450, 1225, 1125, 775 cm^{-1}. − $C_{60}H_{64}Br_2O_2P_2$ (1038.9): calcd. C 69.63, H 6.16, Br 15.25; found C 69.25, H 6.45, Br 15.40.

2,6-Bis(cyanomethyl)-1,5-dihexyloxynaphthalene (11): A mixture of the bis(bromomethyl)naphthalene **9** (1.542 g, 3 mmol) and potassium cyanide (590 mg, 9 mmol) was thoroughly crushed in a mortar until a homogeneous solid was obtained. Afterwards, 0.12 mmol of tricaprylylmethylammonium chloride (Aliquat336) and three drops of water were added and the mixture was crushed again. The fine powder thus obtained was placed in a flask and was shaken for 1 d. After this time, the solid was extracted with diethyl ether and the solution filtered through silica gel to obtain 817 mg of a white solid. Yield 67%; m.p. 88 °C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, 2 H), 7.53 (d, 2 H), 3.99 (t, 4 H, OCH_2), 3.91 (t, 4 H, CH_2CN), 1.95 (m, 4 H, CH_2), 1.57 (m, 4 H), 1.43 (m, 8 H), 0.95 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.5, 129.6, 127.0, 119.8, 119.1, 117.9, 75.6, 31.8, 30.7, 25.8, 22.6, 18.4, 14.1. − IR: ṽ = 3078, 2952, 2925, 2252, 1604, 1367, 1251, 1045, 827 cm^{-1}. − MS; *m/z*: 406 [M$^+$] (13), 322 (4), 238 (100). − $C_{26}H_{34}N_2O_2$ (406.6): calcd. C 76.85, H 8.37, N 6.90; found C 76.56; H 8.52, N 6.85.

2-Cyano-1,5-dihexyloxynaphthalene (15): By following a similar three-step procedure to that used in the synthesis of **6** starting from 1,5-dihydroxynaphthalene but using a mixture of the monobromo and dibromo derivatives obtained in the first step, **15** was obtined after separation from the dicyano derivative **6** by chromatography (hexane/dichloromethane, 7:3); m.p. 41 °C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, 1 H), 7.69 (d, 1 H), 7.42 (dd, 1 H), 7.40 (d, 1 H), 6.83 (d, 1 H), 4.31 (t, 2 H, OCH_2), 4.03 (t, 2 H, OCH_2), 1.83 (m, 4 H, CH_2), 1.50 (m, 4 H), 1.36 (m, 8 H), 0.87 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3, 155.0, 128.7, 127.3, 126.3, 118.1, 118.0, 114.6, 114.6, 107.9, 99.8, 75.9, 68.6, 31.6, 30.3, 29.2, 25.9, 22.6, 14.0. − IR: ṽ = 2955, 2932, 2228 (CN), 1595, 1501, 1425, 1329, 1263, 1065 cm^{-1}. − MS; *m/z*: 353 [M$^+$] (4), 269 (11),185 (100). − $C_{23}H_{31}NO_2$ (353.5): calcd. C 78.19, H 8.78, N 3.97; found C 78.12, H 8.91, N 4.05.

2-Formyl-1,5-dihexyloxynaphthalene (12a): By following a similar procedure to that used in the synthesis of **7** but using 2-cyano-1,5-dihexyloxynaphthalene (**15**) as the starting material, **12c** was obtained as a slightly yellow oil in 91% yield; b.p. 295 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.50 (s, 1 H, CHO), 7.97 (d, 1 H), 7.84 (d, 1 H), 7.71 (dd, 1 H), 7.36 (d, 1 H), 6.86 (d, 1 H), 4.06 (t, 2 H, OCH_2), 4.04 (t, 2 H, OCH_2), 1.89(m, 4 H, CH_2), 1.51 (m, 4 H), 1.35 (m, 8 H), 0.86 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): 190.06 (CHO), 161.5, 155.3, 130.3, 129.4, 126.9, 125.5, 121.7, 118.7, 115.0, 108.1, 79.0, 68.5, 31.7, 31.6, 30.3, 29.2, 25.9, 25.7, 22.6, 14.0. − IR: ṽ = 2950, 2925, 2869, 1683, 1498, 1326, 1070 cm^{-1}. − MS; *m/z*: 356 [M$^+$] (6), 272 (10), 188 (100). − $C_{23}H_{32}O_3$ (356.5): calcd. C 77.53, H 8.99; found C 77.69, H 8.91.

6-Cyano-2-formyl-1,5-dihexyloxynaphthalene (12b): By following a similar procedure to that used in the synthesis of **7** but using stoichiometric amounts of dicyano derivative **6** and DIBAL-H, **12b** was obtained as a slightly yellow oil in 46% yield; m.p. 65 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): 10.50 (s, 1 H, CHO), 7.99 (d, 1 H), 7.88 (d, 1 H), 7.85 (dd, 1 H), 7.47 (d, 1 H), 4.39 (t, 2 H, OCH_2), 4.09 (t, 2 H, OCH_2), 1.89(m, 4 H, CH_2), 1.49 (m, 4 H), 1.33 (m, 8 H), 0.87 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): 189.3 (CHO), 161.1, 160.5, 132.0, 131.7, 128.3, 127.4, 124.1, 119.3, 118.4, 117.3, 101.7, 79.6, 76.0, 31.6, 31.5, 30.2, 29.2, 25.6, 25.5, 22.6, 14.0. − IR: ṽ = 2952, 2927, 2883, 2867, 2228 (CN), 1683 (CHO), 1589, 1375, 1234, 1068 cm^{-1}. − MS; *m/z*: 381 [M$^+$] (5), 297 (2), 213 (100). − $C_{24}H_{31}NO_3$ (381.5): calcd. C 75.59, H 8.14, N 3.67; found C 75.69, H 8.41, N 3.50.

2-Bromo-6-formyl-1,5-dihexyloxynaphthalene (12c): 486 mg (1 mmol) of the dibromo derivative **5** was dissolved under argon in 10 mL of dry THF. The mixture was cooled to −78 °C and afterwards 0.62 mL of a 1.6 M solution of *n*BuLi in THF was added dropwise. The reaction was allowed to stay at −78 °C for 1 h and after this time, 0.618 mL (8 mmol) of dimethylformamide was added and the reaction was kept at −78 °C for another 30 min. Then, the reaction was allowed to reach room temperature and then was poured into 20 mL of water. The mixture was extracted three times with 10 mL of diethyl ether. The combined organic layers were washed with brine, dried with magnesium sulfate, and the solvent was finally removed under vacuum. The residual oil was chromatographed (hexane/dichloromethane, 7:3) to yield 260 mg of a yellowish solid. Yield 60%; m.p. 68 °C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.54 (s, 1 H, CHO), 7.89 (m, 3 H), 7.65 (d, 1 H), 4.16 (t, 2 H, OCH_2), 4.07 (t, 2 H, OCH_2), 1.97 (m, 4 H, CH_2), 1.63 (m, 4 H), 1.39 (m, 8 H), 0.93 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.6 (CHO), 161.9, 153.0, 133.9, 131.1, 128.9, 125.3, 123.7, 120.3, 118.6, 117.3, 79.5, 74.7, 31.7, 31.6, 30.3, 30.2, 25.7, 25.6, 22.6, 14.1. − IR: ṽ = 2950, 2925, 2842, 1683 (CHO), 1614, 1369, 1232, 1068, 1043 cm^{-1}. − MS; *m/z*: 436 [M$^+$] (29), 434 (28), 352 (9), 350 (8), 268 (100), 266 (100). − $C_{23}H_{31}BrO_3$ (435.4): calcd. C 63.59, H 7.14; found C 63.98, H 7.02.

Trimeric Systems Unsubstituted on the Vinylene Linkage. − Wittig Reactions: To a stirred solution of 0.26 mmol of bis[(triphenylphosphonio)methyl]naphthalene dibromide **10** and 0.52 mmol of naphthalenecarboxaldehyde **12** in 6 mL of a mixture of dry ethanol and dry chloroform (3:1) under argon was added at room temperature 0.62 mL of a 1 M solution of lithium ethoxide in ethanol. The mixture was stirred for 4 h and then 5 mL of water and 5 mL of ethanol were added. The organic layer was separated and the aqueous phase extracted several times with chloroform. The combined organic layers were dried with magnesium sulfate and the solvent was removed under vacuum. The yellow mixture was then refluxed for 4 h in toluene in the presence of a catalytic amount of iodine. After removal of toluene, a brown oil was obtained, which was chromatographed to obtain trimeric materials **2** and **16** as yellow solids. To synthesize **2**, benzaldehyde was used as the starting material. Yield 72%; m.p. 181 °C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, 2 H, arom.), 7.79 (d, 2 H), 7.67 (s, 1 H), 7.59 (m, 6 H), 7.35 (m, 4 H), 7.27 (m, 2 H), 7.18 (s, 1 H), 4.04 (t, 4 H, OCH_2), 1.99 (m, 4 H, CH_2), 1.67 (m, 4 H), 1.52 (m, 8 H), 0.93 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): 153.7, 138.2, 130.1, 130.0, 129.2, 128.1, 127.0, 126.9, 124.1, 123.6, 119.1, 76.1, 32.2, 31.0, 26.5, 23.1, 14.5. − IR: ṽ = 3061, 3024, 2952, 2925, 2867, 2850, 1598, 1495, 1466, 1402, 1346, 1265, 1047 cm^{-1}. − MS; *m/z*: 532 [M$^+$] (96), 448 (17), 364 (100), 259 (32), 231 (43). − $C_{38}H_{44}O_2$ (532.7): calcd. C 85.71, H 8.27; found C 85.56, H 8.34.

16a: Yield 35%; m.p. 150 °C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.079 (d, 2 H, J = 8 Hz.), 8.0−7.9 (m, 6 H), 7.81 (d, 2 H, J = 16 Hz, vinyl), 7.73 (d, 2 H, 16 Hz, vinyl), 7.72 (d, 2 H, J = 7 Hz), 7.39 (quasi-triplet, 2 H, J = 8 Hz), 6.80 (d, 2 H, J = 8 Hz), 4.15 (t, 4 H, OCH_2), 4.07 (t, 4 H, OCH_2), 4.05 (t, 4 H, OCH_2), 1.99 (m, 12 H, CH_2), 1.67 (m, 12 H), 1.52 (m, 24 H), 0.93 (t, 18 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3, 155.3, 152.9, 129.9, 126.9, 126.6, 126.3, 124.0, 123.7, 123.6, 122.3, 118.8, 118.4, 114.5, 105.3, 75.8, 75.6, 68.3, 31.7, 30.6, 29.3, 26.0, 22.7, 14.1. − IR: $\tilde{\nu}$ = 2923, 2854, 1605, 1345, 1070 cm^{-1}. − MS; *m*/*z*: 1032 [M$^+$] (19), 680 (26), 596 (41), 160 (100), 43 (67). − $C_{70}H_{96}O_6$ (1033.5): calcd. C 81.40, H 9.30; found C 81.72, H 9.18.

16b: Yield: 37%; m.p. 208°C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, 2 H, *J* = 9 Hz), 7.96 (m, 4 H), 7.95 (d, 2 H, *J* = 9 Hz) 7.90 (d, 2 H, *J* = 9 Hz), 7.87 (d, 2 H, *J* = 9 Hz), 7.82 (d, 2 H, *J* = 16 Hz, vinyl), 7.72 (d, 2 H, 16 Hz, vinyl), 7.50 (d, 2 H, *J* = 9 Hz), 4.05 (m, 12 H, OCH_2), 2.01 (m, 12 H, CH_2), 1.61 (m, 12 H), 1.43 (m, 24 H), 0.94 (t, 18 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.6, 153.8, 152.8, 132.1, 130.0, 129.8, 128.1, 127.7, 126.7, 125.5, 124.4, 123.5, 123.1, 119.1, 119.0, 118.1, 117.9, 99.0, 76.0, 75.9, 31.8, 30.5, 26.2, 25.6, 22.6, 14.1. − IR: $\tilde{\nu}$ = 2923, 2858, 2231 (CN), 1605, 1346, 1072, 1051 cm^{-1}. − $C_{72}H_{94}N_2O_6$ (1083.5): calcd. C 79.85, H 8.69, N 2.59; found C 79.76, H 8.83, N 2.76.

16c: Yield: 39%; m.p. 145°C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, 2 H, *J* = 9 Hz.), 7.92−7.86 (m, 6 H), 7.82−7.78 (m, 6 H) 7.60 (d, 2 H, *J* = 9 Hz), 4.08 (m, 12 H, OCH_2), 2.02 (m, 12 H, CH_2), 1.65 (m, 12 H), 1.43 (m, 24 H), 0.96 (t, 18 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 153.2, 152.8, 130.4, 130.2, 129.7, 129.5, 127.0, 126.8, 124.1, 123.5, 123.4, 119.8, 118.7, 118.5, 113.6, 76.0, 75.9, 74.6, 32.0, 31.9, 31.8, 30.6, 30.5, 30.3, 26.2, 26.1, 25.8, 22.8, 22.7, 14.1. − IR: $\tilde{\nu}$ = 2923, 2856, 2667, 1605, 1465, 1344, 1272, 1070, 1047 cm^{-1}. − $C_{70}H_{94}Br_2O_6$ (1191.32): calcd. C 70.59, H 7.90; found C 70.83, H 8.02.

16d: This compound could be obtained by using two different synthetic procedures. − **Procedure a:** Under argon, 80 mg (0.074 mmol) of **16b** was dissolved in a refluxing mixture of 10 mL of dry ether and 10 mL of dry dichloromethane. To the refluxing mixture 0.1 mL of a 1.5 M solution of DIBAL-H in toluene was added dropwise and the solution heated under reflux for 1 d. After that time, the reaction mixture was allowed to cool and carefully first methanol and then water was added while a white precipitate formed. Then, over a period of 1 h, small amounts of concentrated HCl were added until all the precipitate was redissolved and two layers could be observed. The two layers were separated, the aqueous layer was washed with ether, and the combined ethereal layers were washed with water, saturated $NaHCO_3$ solution, and again with water. Finally, the ethereal solution was dried with magnesium sulfate, the solvent was removed under vacuum and the yellow solid thus obtained was purified by chromatography on silica gel (hexane/dichloromethane, 3:7, as the eluent) obtaining 46 mg of a yellow solid. Yield: 57%; m.p. 142°C (from hexane/dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, 2 H, *J* = 9 Hz), 7.97 (d, 2 H, *J* = 8 Hz), 7.95 (d, 2 H, *J* = 9 Hz) 7.90 (m, 6 H), 7.79 (d, 2 H, *J* = 16 Hz, vinyl), 7.75 (d, 2 H, 16 Hz, vinyl), 4.21 (t, 4 H, OCH_2), 4.06 (m, 8 H, OCH_2), 1.98 (m, 12 H, CH_2), 1.59 (m, 12 H), 1.41 (m, 24 H), 0.98 (t, 18 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.8 (CHO), 162.0, 153.7, 153.3, 133.6, 130.1, 129.8, 129.0, 126.7, 125.3, 125.2, 124.0, 123.5, 123.3, 123.1, 119.5, 119.0, 79.3, 76.1, 76.0, 31.9, 31.8, 30.6, 30.5, 29.8, 26.2, 25.7, 22.8, 14.1. − IR: $\tilde{\nu}$ = 2922, 2854, 2331, 1683 (CHO), 1612, 1363, 1072 cm^{-1}. − $C_{72}H_{96}O_8$ (1089.6): calcd. C 79.41, H 8.82; found C 79.36, H 8.67, N 2.85. − **Procedure b:** 119 mg (0.1 mmol) of the dibromo derivative **16c** was dissolved under argon in 5 mL of dry THF. The mixture was cooled at −78°C and afterwards 0.125 mL of a 1.6 M solution of *n*BuLi in THF was added dropwise. The reaction was kept at −78°C for 1 h and after this time, 0.12 mL (1.6 mmol) of dimethylformamide was added and the reaction was kept at −78°C for another 30 min. The reaction was allowed to reach room temperature and then poured into 20 mL of water. The mixture was extracted three times with 10 mL of diethyl ether. The combined organic layers were washed with brine, dried with magnesium sulfate and the solvent was finally removed under vacuum. The residual solid was chromatographed (hexane/dichloromethane, 3:7) to yield 35 mg of a yellow solid. Yield 15%. Physical and spectroscopical data of this compound are identical to those observed for the product obtained by procedure a.

Trimeric Systems Cyano-Substituted on the Vinylene Linkage. − Knoevenagel Reactions: A mixture of substituted naphthalenecarboxaldehyde **12** (0.15 mmol) and 2,6-bis(cyanomethyl)-1,5-dihexyloxynaphthalene **(11)** (0.07 mmol) in *t*BuOH (1.2 mL) and THF (0.4 mL) was stirred under argon at 50°C. Potassium *tert*-butoxide (1.7 mg) and 0.02 mL of a 1 M solution of tetrabutylammonium hydroxide in methanol were added quickly while the mixture was vigorously stirred at 50°C. The solution was stirred at 50°C for another 20 min during which time a yellow precipitate was formed. Filtration under vacuum of the precipitate led to trimeric materials **17** as yellow solids.

17a: Yield 80%; m.p. 164°C (from THF/*t*BuOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, 2 H, *J* = 9 Hz), 8.17 (s, 2 H, vinyl), 8.11 (d, 2 H, *J* = 9 Hz), 7.98 (d, 2 H, *J* = 9 Hz), 7.62 (m, 4 H), 7.36 (t, 4 H, *J* = 8 Hz), 6.83 (d, 2 H, *J* = 8 Hz), 4.08 (t, 4 H, OCH_2), 3.99 (m, 8 H, OCH_2), 1.86 (m, 4 H, CH_2), 1.6−1.2 (m, 12 H), 0.9 (m, 18 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 155.2, 153.6, 142.5, 130.3, 129.2, 128.2, 126.9, 126.6, 125.6, 123.6, 123.0, 119.2, 118.6, 118.2, 114.7, 108.1, 106.5, 75.3, 68.3, 31.5, 30.2, 29.1, 25.8, 22.5, 13.9. − IR: $\tilde{\nu}$ = 2932, 2870, 2210 (CN), 1593, 1504, 1466, 1423, 1373, 1261, 1080, 1057 cm^{-1}. − MS (field desorption); *m*/*z*: 1083.8, 519.6. − $C_{72}H_{94}N_2O_6$ (1083.6): calcd. C 79.85, H 8.69, N 2.59; found C 80.05, H 8.63, N 2.85.

17c. Yield: 68%; m.p.: 168°C (from THF/*t*BuOH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, 2 H, *J* = 9 Hz), 8.21 (s, 2 H, vinyl), 8.06 (d, 2 H, *J* = 9 Hz), 8.01 (2 H, *J* = 9 Hz), 7.81 (d, 2 H, *J* = 9 Hz), 7.69 (d, 2 H, *J* = 9 Hz), 7.65 (d, 2 H, *J* = 9 Hz), 4.12 (t, 4 H, OCH_2), 4.00 (m, 8 H, OCH_2), 1.93 (m, 4 H, CH_2), 1.6−1.2 (m, 12 H), 0.98 (t, 6 H, CH_3), 0.81 (t, 6 H, CH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 155.2, 153.6, 142.5, 130.3, 129.2, 128.2, 126.9, 126.6, 125.6, 123.6, 123.0, 119.2, 118.6, 118.2, 114.7, 108.1, 106.5, 75.3, 68.3, 31.5, 30.2, 29.1, 25.8, 22.5, 13.9. − IR: $\tilde{\nu}$ = 2932, 2870, 2210 (CN), 1593, 1504, 1466, 1423, 1373, 1261, 1080, 1057 cm^{-1}. − MS (field desorption): 1083.8, 519.6. − $C_{72}H_{92}Br_2N_2O_6$ (1241.3): calcd. C 69.68, H 7.42, N 2.26; found C 69.82, H 7.56, N 2.15.

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