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Photo- and electroluminescent properties of cyano-substituted styryl derivatives and synthesis of CN–PPV model compounds containing an alkoxy spacer for OLEDs

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Abstract—The series of cyano-substituted model compounds **18**–**20** for organic light emitting diodes (OLEDs) was prepared through Knoevenagel condensation reactions between the dialdehydes **3**,**6**,**9** and the differently substituted acetonitrile derivatives **11**,**16**,**17**. The influence of the different substituents on the optical properties of the resulting α-cyanostyryl compounds **18**–**20** was investigated. Another series of dimeric cyano-substituted styryl compounds **26**–**28** were prepared, in which a flexible, nonconjugated spacer is present between the two cyanostyryl moieties. The spacer isolates the π-conjugated portions of dimeric compounds **26**–**28**, improves their solubility in common organic solvents, and decreases their tendency to crystallize. These features are favorable for producing efficient luminescent films in OLEDs devices.

1. Introduction

During the last decade the application of organic materials in the area of optoelectronic technology has received great interest in academia and industry due to the easier fabrication in comparison to inorganic semiconductors and their easily tunable optical properties. The discovery of light emitting properties in electroluminescent (EL) devices based on poly(*p*-phenylenevinylene) (PPV) became a milestone in the development of organic light emitting materials,[1] and numerous efforts have been directed to the development of PPV derivatives in order to produce highly efficient organic EL devices as commercial products.[2,3] In particular, the introduction of electron-withdrawing groups on the polymer backbone (e.g., CN–PPV) results in a high electron affinity polymer, which can be used to manufacture organic light emitting diodes (OLEDs) with air-stable electrodes and produces a strong red-shift in the photo- and electroluminescent spectra.[4] The tuning of color emission in OLEDs can be accomplished by including functional groups in the polymer backbone or by changing the polymer repeat units.[5,6] Polymers in electronic applications show some disadvantages such as lack of efficient purification procedures, ill-defined structure, and generally scarce processability. For these reasons much interest arose for developing new materials in electronic applications with low molecular mass. In addition, short chain model compounds, which have electronic properties similar to those of their polymeric analogues were synthesized and studied in order to understand the mechanism of light emission in OLEDs.[7] Recently, a white-light-emitting electroluminescent device based on a single-emitting-component with a carbazyl moiety has been reported.[8]

Furthermore, a number of PPV derivatives containing nonconjugated blocks as spacer have been also studied.[9] The interruption of π-conjugation by spacers in the luminescent materials results in a blue-shift of their PL and EL spectra compared to fully conjugated materials and the nonconjugated spacer increases the solubility of the materials.

In this work, we present the synthesis and the characterization of CN–PPV model compounds **18**–**20** containing phenyl-, naphthyl-, and carbazyl units (Fig. 1). Upon variation of the substituents R, the influence on the photoluminescent and electroluminescent characteristics is investigated. Moreover, the synthesis and optical properties of CN–PPV model compounds **26**–**28** (Fig. 1) containing the alkoxy spacer, –O$(CH_2)_6$O–, was also accomplished in order to study their optical properties. The synthesis of **26**–**28** had the purpose of increasing the solubility and the processability of these compounds in the process of film preparation.

Keywords: Organic light emitting diodes; Photoluminescence; Electroluminescence; CN–PPV; Knoevenagel condensation; Spacer.
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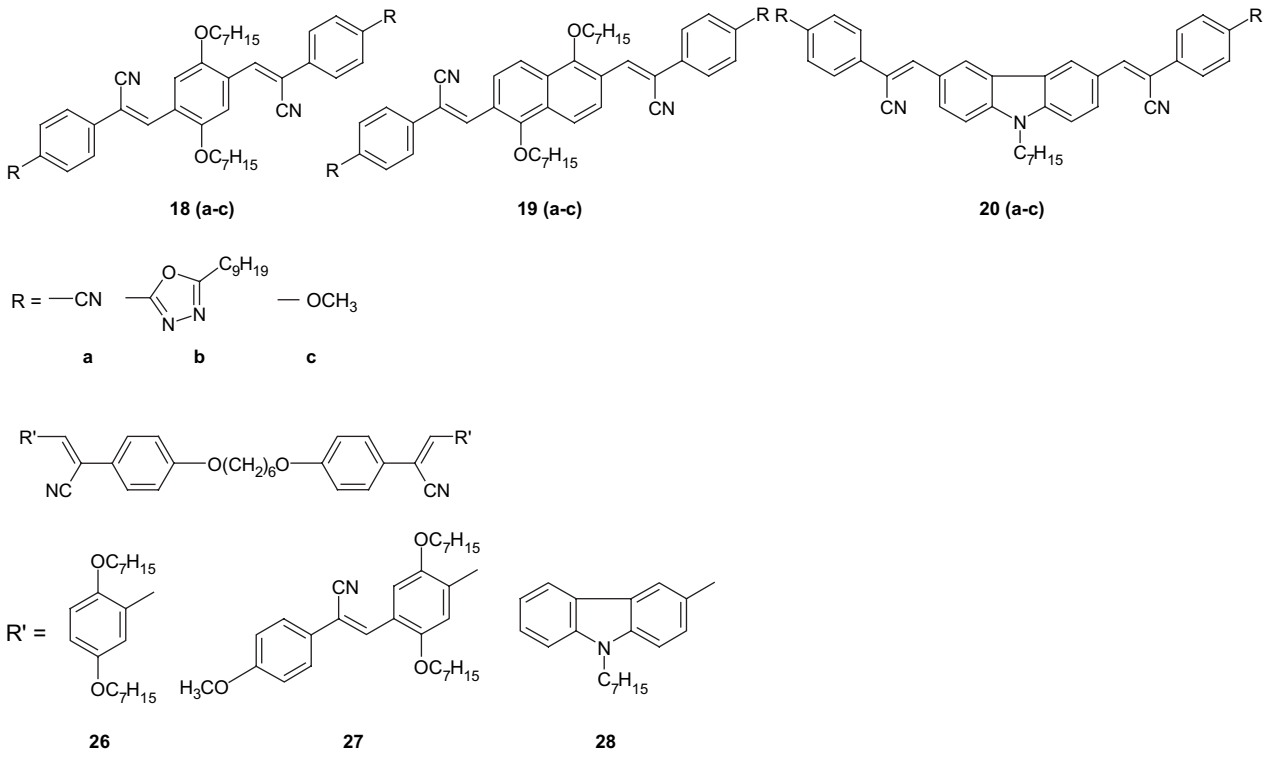
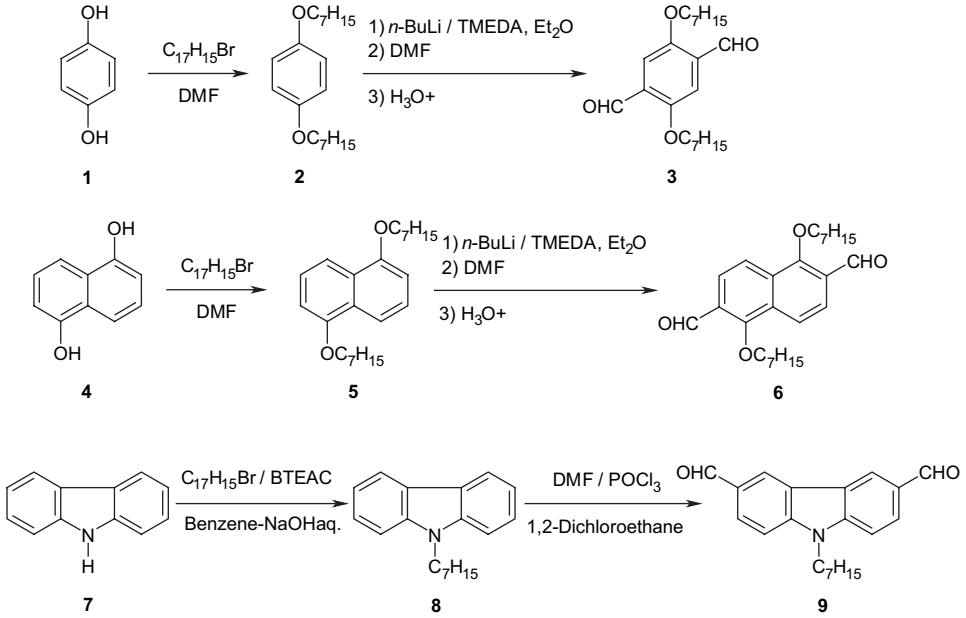


Figure 1. General structures of model compounds **18**–**20** and **26**–**28**.

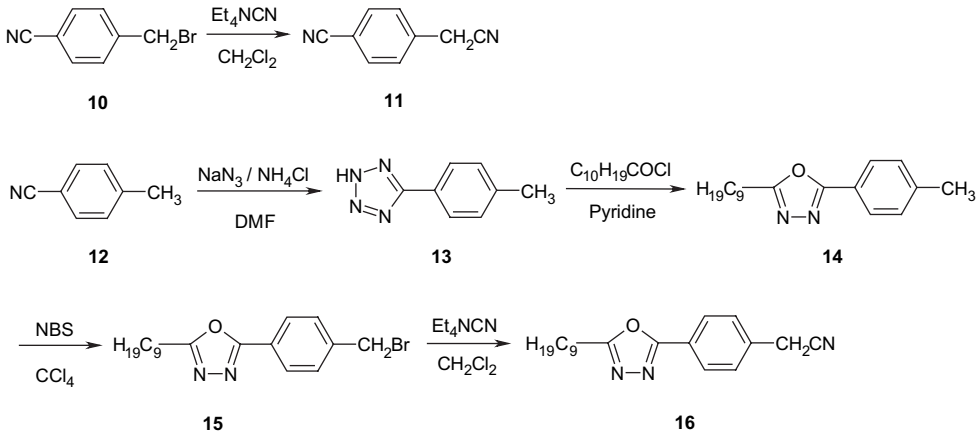
2. Results and discussion

The synthetic pathways for the precursors of the central units of the model compounds **18**–**20** are shown in Scheme 1. Dialdehydes **3** and **6** were prepared via dilithiation of aromatic ethers **2** and **5**, which were obtained by alkylation of commercially available hydroquinone and 1,5-dihydroxynaphthalene with *n*-bromoheptane in the presence of potassium carbonate in dimethyl formamide (DMF).[10] The dilithiated intermediate of **2** and **5** was allowed to react with DMF employing an excess of *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) complex in diethyl ether to give the dialdehydes **3** and **6**.[11]

Compound **9** was obtained from **8** by Vilsmeier reaction with an excess of phosphorus oxychloride and DMF.[12] Alkylation of commercially available carbazole **7** was accomplished with *n*-bromoheptane in the presence of benzyltriethylammonium chloride (BTEAC) and aqueous sodium hydroxide in benzene to obtain **8**.[13]



Scheme 1. Syntheses of dialdehyde precursors **3**, **6**, and **9**.

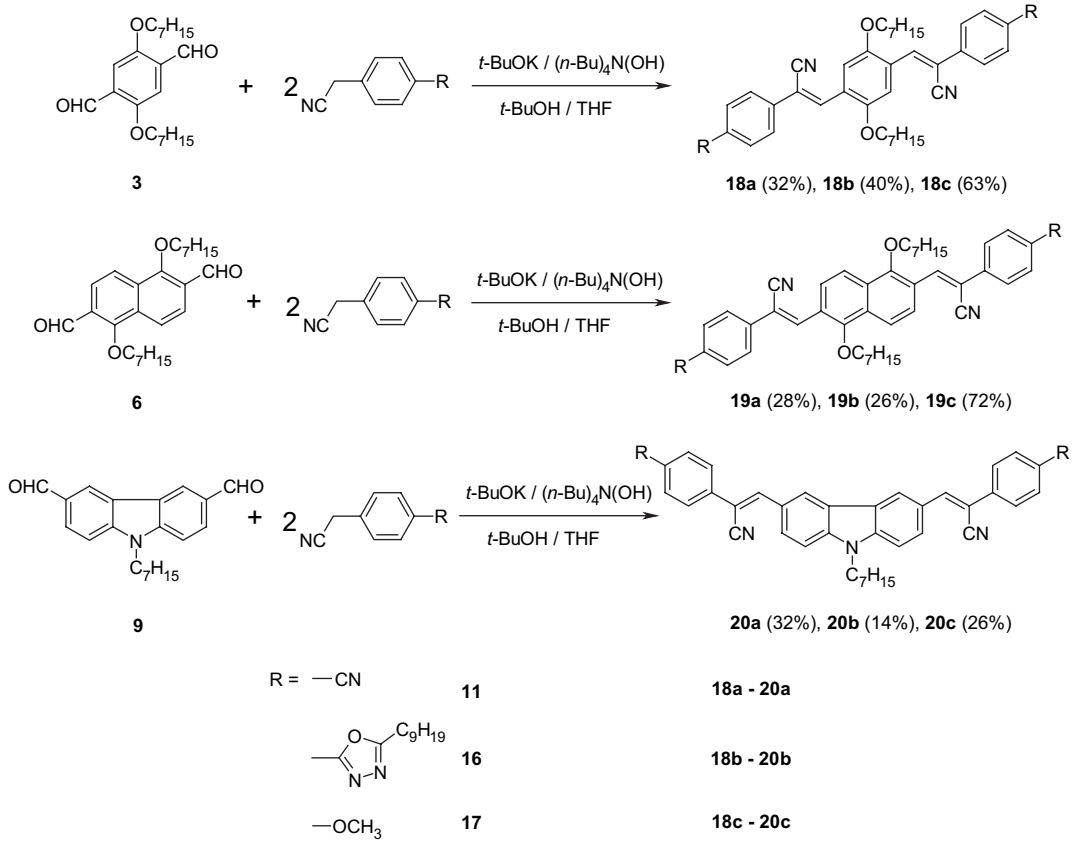


Scheme 2. Syntheses of acetonitrile precursors **11** and **16**.

The acetonitriles **11** and **16**, which contain various substituents were prepared as shown in Scheme 2. *p*-Bromomethylbenzonitrile readily reacted with tetraethylammonium cyanide (Et_4NCN) in dichloromethane to give acetonitrile **11** under mild conditions.[14]

Two synthetic routes to oxadiazoles are ring closure of bishydrazides with dehydrating agents[15] and intramolecular ring transformation of tetrazoles with acid chlorides.[16] In this work the oxadiazole **14** was obtained via tetrazole **13** as an intermediate. This synthetic route has some advantages, such as short reaction time and facile work-up procedure, in comparison to ring closure of bishydrazides with dehydrating agent. The tetrazole **13** was prepared by reacting 4-tolunitrile **12** with sodium azide in DMF.[17] Compound **13** reacted with decanecarboxylic acid chloride in pyridine under reflux to afford oxadiazole **14**, which was then converted to bromide **15** with *N*-bromosuccinimide (NBS) in CCl_4. Treatment of **15** with Et_4NCN in dichloromethane gave oxadiazole **16** using the same method as mentioned above.

The syntheses of model compounds **18**–**20** were accomplished using Knoevenagel condensation[18] between alkoxy- or alkyl-substituted dialdehydes **3**, **6**, **9** and acetonitriles **11**, **16**, the commercially available 4-methoxyphenylacetonitrile **17**, respectively, in *tert*-butyl alcohol and tetrahydrofuran (THF) at 50 °C (see Scheme 3). Potassium *tert*-butoxide and tetra-*n*-butylammonium hydroxide were used as bases.



Scheme 3. Synthesis of model compounds **18**–**20**.

The Knoevenagel reaction is stereoselective, resulting in the *E*,*E*-product. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, IR, and UV–vis spectroscopy (see Section 4).

The monoformylation[19] of **2** was accomplished by Friedel–Crafts reaction with titanium tetrachloride as a Lewis acid catalyst and dichloromethyl methyl ether to result in the formation of **21**. Compound **22** was prepared by Knoevenagel condensation between excess of **3** and 4-methoxyphenylacetonitrile **17** using potassium *tert*-butoxide as base in *tert*-butyl alcohol and THF. The monoformylation of **8** was carried out by using Vilsmeier reagent to afford compound **23** (Scheme 4).

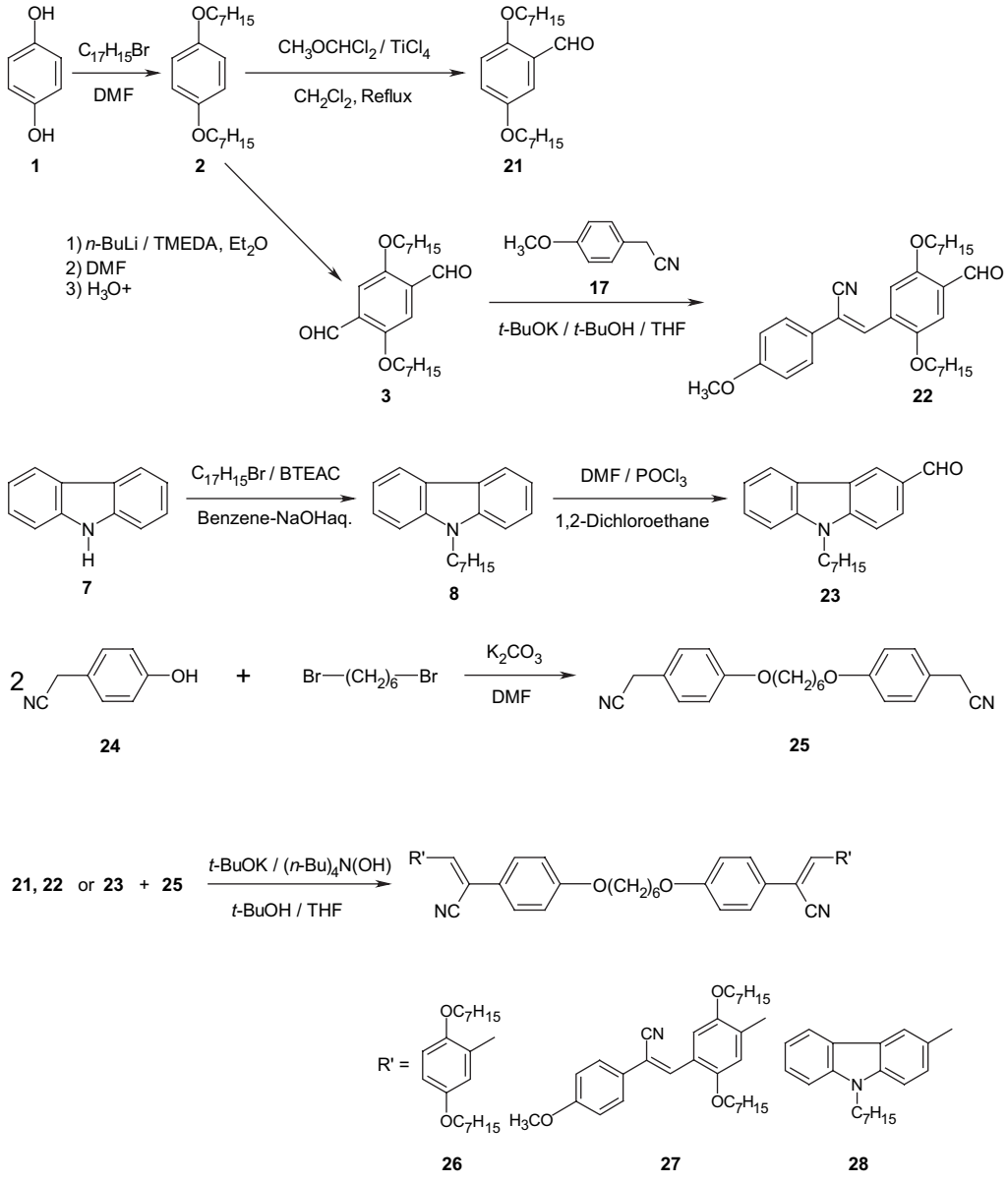
The reaction between 4-hydroxyphenylacetonitrile **24** and 1,6-dibromohexane was carried out in DMF with potassium carbonate as base leading to **25**, in which the two phenylacetonitriles are separated by the alkoxy spacer –O(CH$_2$)$_6$O–.

Compounds **26**–**28** were synthesized by Knoevenagel condensation between the monoaldehydes **21**–**23** and 1,6-bis(4-cyanomethylphenoxy)hexane **25**, respectively, in *tert*-butyl alcohol and THF at 50 °C with potassium *tert*-butoxide and tetra-*n*-butylammonium hydroxide as bases to result in the *E*,*E*-products. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS, IR, and UV–vis-spectroscopy (see Section 4).

2.1. Optical properties

Figures 2 and 3 show the UV–vis absorption and photoluminescence (PL) spectra of **18**–**20** and **26**–**28**, respectively. The PL spectra were measured as thin films.

Optical and electrical properties of conjugated materials are dependent on the length of the conjugated π-system, interchain distance of the conjugated segment, and the influence of substituents (electron-donating or electron-withdrawing)



Scheme 4. Synthetic pathways for model compounds **26**–**28**.

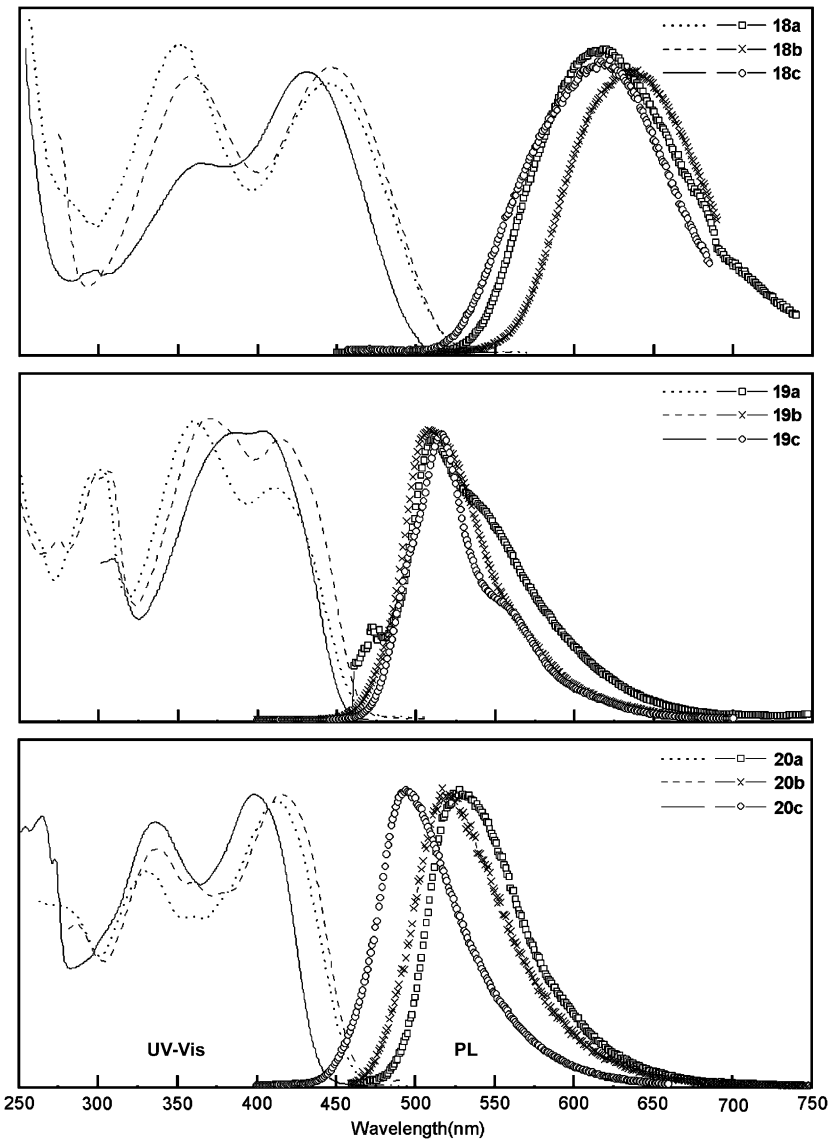


Figure 2. UV–vis absorption (CH_2Cl_2) and PL spectra (thin film) of **18**–**20**.

of the conjugated system. The influence of donor and acceptor substituents on the electronic structure of PPV derivatives has been studied.[20] Electron-donating substituents lead to an overall destabilization of the HOMO and LUMO levels. In contrast, electron-withdrawing substituents give a stabilization of the frontier levels. These substituents influence the location of HOMO and LUMO levels, respectively, to result in a decrease of the band gap.

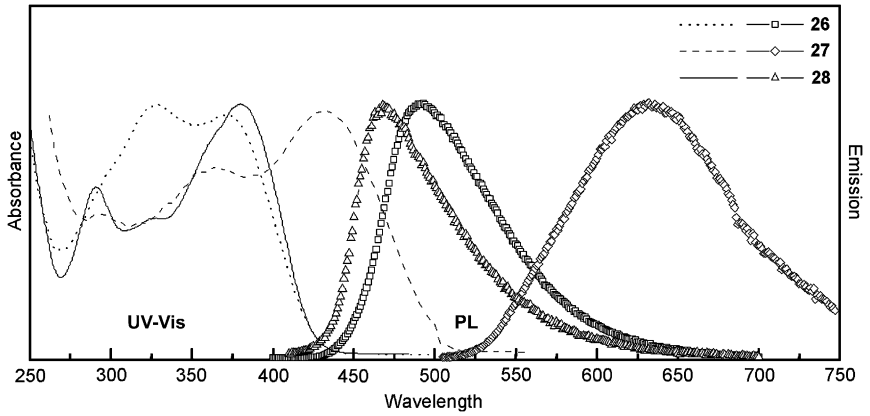


Figure 3. UV–vis and PL spectra of **26**–**28**.

Table 1. UV–vis absorption maxima, the calculated band gap energy, and PL maxima of **18–20** and **26–28**

Compound	UV–vis (nm)[a]	E_g (eV)[b]	PL (nm)[c]
18a	353, 442	2.36	618
18b	360, 446	2.35	636
18c	366, 432	2.45	615
19a	361, 412	2.65	511
19b	370, 416	2.63	508
19c	386, 404	2.71	515
20a	332, 412	2.65	528
20b	339, 417	2.65	522
20c	336, 399	2.79	495
26	330, 374	2.85	493
27	364, 433	2.45	632
28	291, 381	2.85	468

[a] UV–vis absorption in dichloromethane.
[b] Band gaps were calculated from the absorption spectra of the given model compound solutions.
[c] PL emission in solid state (thin film on glass).

In this work the band gap energy of compounds **18–20** were estimated from their UV–vis absorption spectra in solution as shown in Table 1.

Compounds **18a** and **18b** containing electron-withdrawing groups have smaller band gaps (π–π^* transition energy) than **18c** possessing electron-donating substituent (Table 1). This result can be explained by the effect of π-electron delocalization along the entire conjugated system. The introduction of the electron-withdrawing groups at the end phenyl rings in **18a** and **18b** increases the electron density of the chromophoric block due to the induction of strong permanent dipoles affecting the donor/acceptor strengths of the donating and withdrawing groups to result in a decrease of the energy in the excited state. This increasing electron density causes an enhanced delocalization of conjugated system. Although compound **18a** has smaller band gap than **18c**, both of them exhibit almost identical PL maximum in the solid state. It is assumed that the interchain distance of conjugated segment of **18a** and **18c** is similar in the solid state. Compound **18b** shows a red-shift in its PL spectrum compared to **18a** and **18c** due to the interchain interaction of oxadiazole moieties in the solid state.[21]

Earlier studies have shown that partial replacement of the phenylene unit in PPV by a naphthalene system linked through 1,4-position shows a significant effect in photoluminescence and electroluminescence emission maxima.[22] However, in the case of conjugated materials based on naphthalene unit linked through 2,6-positions, their optical properties are more dependent on the steric effects than their band structure.[23] The geometry optimization has been carried out by the Austin model 1 (AM 1) semiempirical technique to study the torsion and its effect on their structural and electronic properties. The bulky 1,5-dialkoxynaphthalene ring induces torsion of the main chain and, consequently, reduces the planarity of the backbone. The lack of planarity in conjugated materials based on 1,5-dialkoxynaphthalene unit linked through the 2,6-positions leads to a loss of conjugation and results in a blue-shift in their UV–vis spectra.[23] The band gaps were increased by replacing the central phenyl ring in cyano-substituted PPV derivatives with a bulky 1,5-diheptyloxynaphthalene ring (compounds **19**) compared to compounds **18** as shown in Table 1. Therefore, the PL emission maxima of compounds **19** show a significant blue-shift due to the loss of conjugation. The substituents at the *para*-position of end phenyl ring (electron-donating or -withdrawing) in compounds **19** do not affect the optical properties in PL emission spectra. It is assumed that the influence of substituents is compensated by an opposite effect due to predominant steric effects, therefore, compounds **19** exhibit similar PL maxima.

The carbazole unit is very well known as a hole transporting, electroluminescent material, and a wide band gap component.[24] Due to its wide band gap property conjugated systems based on carbazole units in compounds **20** exhibit a blue-shift in comparison to the system based on phenyl rings (compounds **18**). Compounds **20** exhibit PL emission maxima in the green or greenish yellow region (495–528 nm). The optical properties of these compounds show the same tendency as a result of their calculated band gap. The electron-withdrawing (cyano or alkyl oxadiazolyl) substituted **20a** and **20b** exhibit a red-shift compared to electron-donating (methoxy) substituted **20c**. The results show that the electron-withdrawing group affects more to reduce the band gap in conjugated system unit than the donating group on account of the effect of π-electron delocalization along the entire conjugated system as described above.

In general, OLEDs based on short chain PPV derivatives exhibit no detectable electroluminescence (EL) due to their electron conductive qualities. Therefore, an additional hole transporting layer, thermally stable copper phthalocyanine (PcCu) was used. The vacuum deposition of PcCu and model compounds **18–20** onto ITO covered glass substrates was accomplished, and the patterning of the devices were structured as described earlier.[25] The configuration of bilayer device is ITO/PcCu/model compound/Al as shown in Figure 4a.

EL spectra of **18a**, **18c**, and **20c** are almost identical to their PL spectra, indicating that the same excited state is involved in both EL and PL emission processes.[26] However, EL spectra of **19a** and **20a** exhibit a red-shift compared to their PL spectra (Fig. 4). It is assumed that interchain interactions are maximum in vapor deposited thin film of model compounds and interchain excitation is accelerated to result in the red-shift.[27]

In the case of **19c**, the EL spectrum shows a blue-shift compared to its PL spectrum due to the re-absorption effect of PcCu. Figure 4 shows the PL and EL spectra of **18–20**.

In compounds **26–28** the photoluminescent cyano-substituted PPV derivatives are separated by the nonconjugated segment, $-O(CH_2)_6O-$, as spacer group (Fig. 1). The UV–vis absorption and PL emission spectra were measured in dichloromethane and in solid state, respectively. The results are shown in Table 1.

The π-conjugated systems in **26–28** are isolated from each other through a flexible nonconjugated spacer. The introduction of the spacer improves the solubility in common organic solvents and decreases crystallinity, enhancing the properties of the film formation in OLED application. Furthermore, it is a convenient way to obtain a blue-shifted emission due

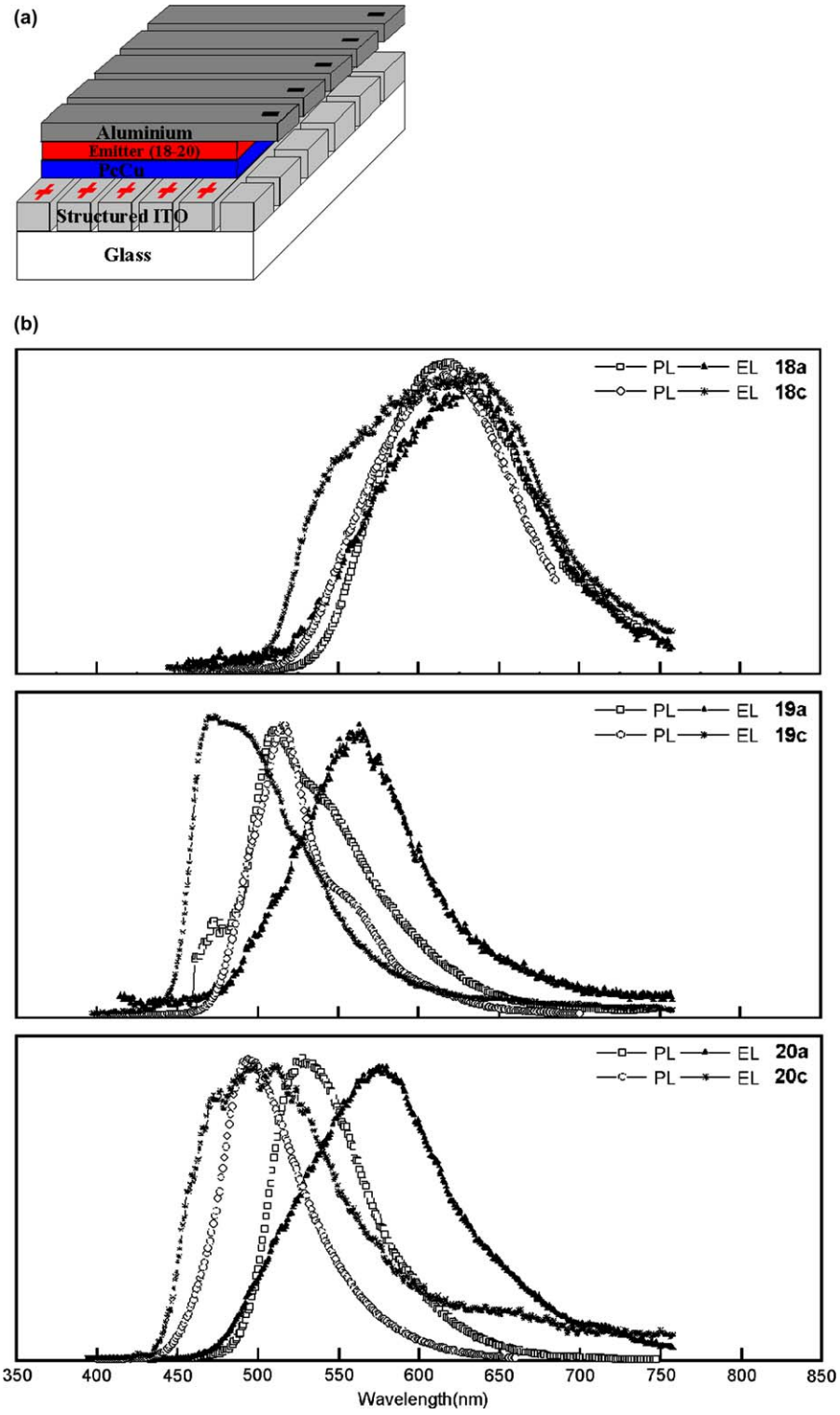


Figure 4. (a) Schematic setup of OLED, (b) PL and EL spectra of **18**–**20**.

to an increase in the band gap by interrupting conjugation in comparison with its fully conjugated system.

Concerning the end-groups of **26**–**28**, the band gap of **27** was decreased significantly compared to **26** to result in a red-shift in the UV–vis and PL spectra due to the extension of π-conjugated system. Compound **28** in which the carbazole ring is combined to cyano-substituted stilbene moiety exhibits a small blue-shift in its PL spectrum compared to **26** and **27** due to the influence of wide band gap component, carbazole.

3. Conclusions

The influence of different substituents on the α-cyanostyryl compounds **18**–**20** (phenyl, naphthalene or carbazole) was investigated by studying their UV–vis, PL, and EL spectra.

The introduction of electron-donating or electron-withdrawing groups into the conjugated system results in a red-shift in their PL spectra on account of the decrease in the band gap, and the effect is stronger in compounds containing electron-withdrawing substituent due to the effect of π-electron delocalization along the entire conjugated system. In the case of conjugated systems based on bulky 1,5-dialkoxynaphthalene ring linked through 2,6-positions, a similar PL maxima were observed. This is explained by predominant steric effect on their optical properties. The steric hindrance of the bulky 1,5-diheptyloxynaphthalene ring reduces the planarity of the backbone and results in a loss of conjugation, thus the influence of substituents are similar between electron-donating and electron-withdrawing substituents. The replacement of the central phenyl ring with a wide band gap carbazole results in a blue-shift in their UV–vis and PL spectra compared to α-cyanostyryl compound based on phenyl ring. The electron-withdrawing substituents affect more to reduce the band gap in the conjugated system based on carbazole unit than the electron-donating substituents due to the effect of π-electron delocalization along the entire conjugated system.

The electroluminescent properties of the model compounds **18**–**20** were studied in bilayer OLEDs with additional hole transporting layer (PcCu). In general, the PL and EL spectra are expected to be identical. However, the observed red- and blue-shift in the EL spectra compared to PL spectra are due to the film morphology of compounds and re-absorption effect of PcCu as hole transporting material, respectively.

The optical properties of model compounds **26**–**28** containing spacer group were studied by extending the cyano-substituted styryl moiety and replacing the phenyl ring with a carbazole ring (i.e., wide band gap component) resulting in a red- and blue-shift, respectively. The introduction of spacer moiety, $-O(CH_2)_6O-$, improves the solubility in common organic solvents and decreases crystallinity, enhancing the properties of the film formation with physical vapor deposition technique in OLED application. Furthermore, it is a convenient way to obtain a blue-shifted emission due to an increase in the band gap by interrupting conjugation, i.e., shortening of chromophore unit.

4. Experimental

4.1. General

Chemicals received from commercial sources (Aldrich, Merck, and Fluka) were used without further purification. All reactions were performed under a dry argon atmosphere. Solvents were dried according to standard procedures. The melting points are uncorrected.

Infrared spectra were taken as KBr pellets or with NaCl plate using a Bruker IFS 48 spectrometer. UV–vis spectra were recorded in CH_2Cl_2 solution with a Shimadzu UV-2102 PC. PL of evaporated films was measured with a SPEX fluorolog 112 in the 45° configuration. For EL measurements an HP 6030A voltage source was used together with a Keithley 171 DMM. The EL spectra were taken from devices with ITO/copper phthalocyanine (PcCu)/trimer **18**–**20**/Al configuration with a waveguide diode array setup in air at room temperature. NMR spectra were recorded on a Bruker AC 250 spectrometer at 250 MHz (^{1}H) and 62.9 MHz (^{13}C) in $CDCl_3$ and internally referenced to $CHCl_3$ (^{1}H: δ=7.24 ppm, ^{13}C: δ=77.00 ppm). 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 Carlo Erba Elemental Analyzer 1106.

4.2. Synthesis

The following compounds were prepared according to literature procedures: 1,4-di-*n*-heptyloxybenzene (**2**),[10] 1,5-di-*n*-heptyloxynaphthalene (**5**),[10] 9-*n*-heptylcarbazole (**8**),[13] 3,6-diformyl-9-*n*-heptylcarbazole (**9**),[12] *p*-cyanomethylbenzonitrile (**11**),[14] 5-(*p*-tolyl)tetrazole (**13**),[17] and 2,5-di-*n*-heptyloxybenzaldehyde (**21**).[19] *p*-Bromomethylbenzonitrile (**10**), 4-methoxyphenylacetonitrile (**17**), and 4-hydroxyphenylacetonitrile (**24**) are commercially available.

4.2.1. 2,5-Di-*n*-heptyloxyterephthaldialdehyde (3). A 2.5 M hexane solution of *n*-BuLi (24.6 ml, 61.5 mmol) was added dropwise to a solution of 1,4-di-*n*-heptyloxybenzene (**2**) (3.78 g, 12.3 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (7.38 g, 63.5 mmol) in diethyl ether (190 ml) at −78 °C. The mixture was stirred at 0 °C for 1 h and DMF (7.3 g, 100 mmol) was added, which caused a yellow color to darken progressively. After refluxing for 16 h, the resulting pale brown suspension was placed in an ice bath. The mixture was stirred for 90 min at 0 °C and then 4 N HCl solution (37 ml) was added slowly under vigorous stirring. The resulting two-phase system was stirred for 30 min at room temperature. The organic layer was separated, washed with 0.5 N HCl solution (62 ml), saturated $NaHCO_3$ solution (62 ml), and brine (62 ml), and then dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to give a yellow solid. The crude product was purified on a silica gel column (dichloromethane/*n*-hexane). Yield: 1.1 g (25%). Yellow solid. Mp 72–74 °C. ^{1}H NMR ($CDCl_3$): 10.49 (s, 2H), 7.40 (s, 2H), 4.05 (t, *J*=6.4 Hz, 4H), 1.81 (m, 4H), 1.47 (m, 4H), 1.29 (m, 12H), 0.87 (t, *J*=7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): 189.34, 155.21, 129.28, 111.60, 69.24, 31.71, 29.21, 29.02, 25.95, 22.55, 14.01. IR (KBr): 2918, 2879, 1682, 1491, 1470, 1427, 1388, 1283, 1215, 1130, 1007, 696. MS: 362 (M^+), 264, 166, 57. Anal. Calcd: C, 72.89; H, 9.45. Found: C, 73.21; H, 9.52.

4.2.2. 1,5-Di-*n*-heptyloxynaphthalene-2,6-dicarbaldehyde (6). Compound **6** was prepared by the same method as **3** except for the starting material and the amount of reagents: 1,5-di-*n*-heptyloxynaphthalene (**5**) (5.3 g, 15 mmol), 2.5 M *n*-BuLi (75 mmol), TMEDA (75 mmol), DMF (8.8 g, 121 mmol), and diethyl ether (200 ml). The purification of the product was accomplished by chromatography on a silica gel column (dichloromethane/*n*-hexane). Yield: 1.0 g (16%). Yellowish white solid. Mp 88–90 °C. ^{1}H NMR ($CDCl_3$): 10.57 (s, 2H), 7.99 (d, *J*=8.8 Hz, 2H), 7.93 (*J*=8.8 Hz, 2H), 4.15 (t, *J*=6.4 Hz, 4H), 1.95 (m, 4H), 1.33 (m, 16H), 0.89 (t, *J*=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): 189.48, 161.53, 133.13, 127.45, 123.63, 119.50, 79.47, 31.72, 30.24, 29.07, 25.90, 22.56, 14.03. IR (KBr): 2949, 2948, 2854, 1682, 1499, 1466, 1377, 1366, 1227,

1015, 822, 762. MS: 412 (M^+), 314, 216, 131, 57. Anal. Calcd: C, 75.69; H, 8.80, Found: C, 75.71; H, 8.55.

4.2.3. 5-(*p*-Tolyl)-2-*n*-nonyl-1,3,4-oxadiazole (14). To a solution of 5-(*p*-tolyl)tetrazole (**13**) (9.6 g, 60 mmol) in pyridine (95 ml) was added decanecarboxylic acid chloride (11.5 g, 60 mmol). After refluxing for 2 h under argon, the reaction mixture was cooled and poured into water containing crushed ice. The precipitate was collected in a sintered glass filter and then washed with water several times. The crude product was dried under vacuum for overnight. The purification was accomplished by chromatography on a silica gel column using chloroform as eluent. Yield: 14.1 g (82%). White solid. Mp 55–57 °C. ^{1}H NMR ($CDCl_3$): 7.88 (d, J=7.9 Hz, 2H), 7.29 (d, J=7.9 Hz, 2H), 2.88 (t, J=7.3 Hz, 2H), 2.40 (s, 3H), 1.81 (m, 2H), 1.24 (m, 12H), 0.85 (t, J=6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): 166.75, 164.78, 141.91, 129.66, 126.69, 121.37, 31.81, 29.34, 29.21, 29.10, 29.01, 26.60, 25.43, 23.63, 21.58, 14.06. IR (KBr): 2920, 2851, 1616, 1569, 1556, 1501, 1475, 1180, 1088, 1011, 959, 824, 727. MS: 286 (M^+), 257, 243, 229, 216, 201, 187, 174, 119, 117, 91, 55, 43, 41. Anal. Calcd: C, 75.48; H, 9.15; N, 9.78. Found: C, 75.15; H, 8.83; N, 9.11.

4.2.4. 5-(*p*-Bromomethylphenyl)-2-*n*-nonyl-1,3,4-oxadiazole (15). A mixture of 5-(*p*-tolyl)-2-*n*-nonyl-1,3,4-oxadiazole (**14**) (13.0 g, 45.4 mmol), *N*-bromosuccinimide (8.3 g, 46.6 mmol), dry carbon tetrachloride (250 ml), and catalytic amount of azobisisobutyronitrile was stirred at reflux under nitrogen for 10 h. The warm solution was filtered, and the filtrate was concentrated to give a light yellow solid. The crude product was purified by recrystallization from carbon tetrachloride. Yield: 8.4 g (51%). White solid. Mp 87–89 °C. ^{1}H NMR ($CDCl_3$): 8.00 (d, J=8.2 Hz, 2H), 7.51 (d, J=8.5 Hz, 2H), 4.49 (s, 2H), 2.90 (t, J=7.3 Hz, 2H), 1.82 (m, 2H), 1.24 (m, 12H), 0.85 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): 167.17, 141.15, 129.63, 127.14, 124.02, 32.25, 31.80, 29.33, 29.18, 29.09, 28.99, 26.55, 25.43, 22.61, 14.06. IR (KBr): 2918, 2851, 1587, 1566, 1501, 1472, 1418, 1229, 1204, 1086, 1015, 854, 704. MS: 364 (M^+), 335, 321, 308, 294, 285, 265, 252, 228, 197, 186, 173, 131, 118, 116, 90, 43. Anal. Calcd: C, 59.18; H, 6.90; Br, 21.87; N, 7.67. Found: C, 58.98; H, 6.11; Br, 21.86; N, 7.60.

4.2.5. 5-(*p*-Cyanomethylphenyl)-2-*n*-nonyl-1,3,4-oxadiazole (16). A portion of tetraethylammonium cyanide (2.0 g, 12.8 mmol) was added to a stirred solution of 5-(*p*-bromomethylphenyl)-2-*n*-nonyl-1,3,4-oxadiazole (**15**) (3.0 g, 8.2 mmol) and dichloromethane (150 ml). The reaction mixture was stirred for 5 h at room temperature and then washed with water. After evaporation of the solvent, the product was purified by chromatography on a silica gel column using dichloromethane/ethyl acetate as eluent. Yield: 2.1 g (82%). White solid. Mp 93–95 °C. ^{1}H NMR ($CDCl_3$): 8.02 (d, J=8.2 Hz, 2H), 7.48 (d, J=8.5 Hz, 2H), 3.82 (s, 2H), 2.90 (t, J=7.3 Hz, 2H), 1.82 (m, 2H), 1.24 (m, 12H), 0.85 (t, J=6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): 167.28, 163.99, 133.33, 128.60, 127.49, 124.13, 117.01, 31.81, 29.34, 29.19, 29.09, 29.01, 26.57, 25.45, 23.64, 22.61, 14.06. IR (KBr): 2953, 2916, 2849, 2245, 1697, 1589, 1570, 1504, 1472, 1421, 1090, 918, 825, 723. MS: 311 (M^+), 282, 268, 241, 212, 199, 157, 144, 116, 89, 55, 41. Anal. Calcd: C, 73.28; H, 8.09; N, 13.49. Found: C, 72.40; H, 7.80; N, 13.06.

4.3. General procedure for the preparation of α-cyanostyryl compounds (18–20)

To a *tert*-butyl alcohol/THF solution of an aldehydes (**3**, **6** or **9**) and acetonitrile derivatives (**11**, **16** or **17**), respectively, at 50 °C under inert gas, a stoichiometric amount of potassium *tert*-butoxide and a methanolic solution of tetra-*n*-butylammonium hydroxide (catalytic amount) were added quickly (Scheme 3). The mixture was stirred vigorously for 20 min at 50 °C. After cooling, the mixture was poured into methanol. The precipitate (**18**–**20**) was collected using a sintered glass filter, washed with methanol, and dried under vacuum. The purification of **18**–**20** was accomplished by chromatography on a silica gel column using dichloromethane or chloroform as eluent.

4.3.1. 1,4-Bis(4-cyano-α-cyanostyryl)-2,5-di-*n*-heptyloxybenzene (18a). Yield: 32%. Orange solid. Mp 244–246 °C. ^{1}H NMR ($CDCl_3$): 8.12 (s, 2H), 7.89 (s, 2H), 7.77 (d, J=8.9 Hz, 4H), 7.75 (d, J=8.9 Hz, 4H), 4.11 (t, J=6.4 Hz, 4H), 1.84 (m, 4H), 1.29 (m, 16H), 0.86 (t, J=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): 151.84, 138.83, 126.60, 125.85, 118.18, 117.47, 112.81, 111.37, 110.48, 69.56, 31.77, 29.09, 28.96, 26.10, 22.54, 14.06. IR (KBr): 2951, 2930, 2856, 2226, 2212, 1585, 1510, 1499, 1431, 1366, 1294, 1252, 1219, 1024, 835. MS: 610 (M^+). UV–vis (CH_2Cl_2): 353, 442. PL: 618. EL: 632. Anal. Calcd: C, 78.66; H, 6.93; N, 9.17. Found: C, 78.11; H, 6.89; N, 9.23.

4.3.2. 1,4-Bis[4-(2-*n*-nonyl-1,3,4-oxadiazolyl)-α-cyanostyryl]-2,5-di-*n*-heptyloxybenzene (18b). Yield: 40%. Pale red solid. Mp 165–167 °C. ^{1}H NMR ($CDCl_3$): 8.13 (s, 2H), 8.09 (d, J=8.9 Hz, 4H), 7.91 (s, 2H), 7.83 (d, J=8.6 Hz, 4H), 4.13 (t, J=6.4 Hz, 4H), 2.93 (t, J=7.3 Hz, 4H), 1.85 (m, 8H), 1.26 (m, 40H), 0.86 (t, J=6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$): 167.37, 163.99, 151.77, 137.45, 137.19, 127.42, 126.58, 125.92, 124.66, 117.86, 111.42, 110.95, 69.54, 31.83, 31.78, 29.36, 29.21, 29.16, 29.12, 29.04, 29.01, 26.60, 26.14, 25.49, 22.64, 22.55, 14.06. IR (KBr): 2955, 2922, 2851, 2214, 1583, 1497, 1466, 1416, 1366, 1294, 1217, 1007, 847. MS: 949 (M^+). UV–vis (CH_2Cl_2): 360, 446. PL: 636. EL: 655. Anal. Calcd: C, 75.91; H, 8.49; N, 8.85. Found: C, 75.63; H, 8.15; N, 8.89.

4.3.3. 1,4-Bis(4-methoxy-α-cyanostyryl)-2,5-di-*n*-heptyloxybenzene (18c). Yield: 63%. Orange solid. Mp 158–160 °C. ^{1}H NMR ($CDCl_3$): 7.89 (s, 2H), 7.85 (s, 2H), 7.60 (d, J=8.9 Hz, 4H), 6.97 (d, J=8.9 Hz, 4H), 4.10 (t, J=6.4 Hz, 4H), 3.85 (s, 6H), 1.83 (m, 4H), 1.31 (m, 16H), 0.87 (t, J=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): 160.50, 151.42, 134.03, 127.42, 125.76, 118.52, 114.48, 111.19, 69.46, 55.42, 31.80, 29.24, 29.02, 26.16, 22.53, 14.04. IR (KBr): 2955, 2930, 2854, 2208, 1607, 1514, 1466, 1431, 1367, 1300, 1250, 1217, 1180, 1036, 822. MS: 620 (M^+). UV–vis (CH_2Cl_2): 366, 432. PL: 615. EL: 633. Anal. Calcd: C, 77.39; H, 7.79; N, 4.51. Found: C, 77.36; H, 8.03; N, 4.47.

4.3.4. 2,6-Bis(4-cyano-α-cyanostyryl)-1,5-di-*n*-heptyloxynaphthalene (19a). Yield: 28%. Yellow solid. Mp

221–223 °C. ^{1}H NMR ($CDCl_3$): 8.37 (d, J=8.9 Hz, 2H), 8.20 (s, 2H), 8.02 (d, J=8.9 Hz, 2H), 7.83 (d, J=8.9 Hz, 4H), 7.78 (d, J=8.9 Hz, 4H), 4.02 (t, J=6.4 Hz, 4H), 1.91 (m, 4H), 1.32 (m, 16H), 0.88 (t, J=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): 157.01, 139.02, 138.74, 132.94, 130.77, 126.51, 124.76, 119.15, 118.11, 117.15, 112.94, 111.10, 77.80, 31.78, 30.42, 29.13, 26.28, 22.57, 14.06. IR (KBr): 2961, 2928, 2854, 2228, 2214, 1591, 1506, 1467, 1412, 1371, 1250, 1186, 1063, 991, 841, 824. MS: 660 (M^+). UV–vis (CH_2Cl_2): 361, 412. PL: 511. EL: 563. Anal. Calcd: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.54; H, 6.76; N, 8.44.

4.3.5. 2,6-Bis[4-(2-*n*-nonyl-1,3,4-oxadiazolyl)-α-cyanostyryl]-1,5-di-*n*-heptyloxynaphthalene (19b). Yield: 26%. Greenish yellow solid. Mp 165–167 °C. ^{1}H NMR ($CDCl_3$): 8.38 (d, J=9.2 Hz, 2H), 8.21 (s, 2H), 8.12 (d, J=8.9 Hz, 4H), 8.02 (d, J=9.2 Hz, 2H), 7.89 (d, J=8.9 Hz, 4H), 4.03 (t, J=6.7 Hz, 4H), 2.94 (t, J=7.6 Hz, 4H), 1.89 (m, 4H), 1.26 (m, 40H), 0.86 (t, J=7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$): 167.40, 163.96, 156.71, 137.80, 137.32, 130.63, 127.48, 126.49, 124.88, 119.52, 117.56, 111.66, 31.83, 30.45, 29.36, 29.22, 29.18, 29.12, 29.04, 26.60, 26.31, 25.49, 22.64, 22.58, 14.06. IR (KBr): 2920, 2851, 2218, 1601, 1585, 1568, 1499, 1470, 1416, 1371, 1242, 1180, 1034, 1011, 851, 841. MS: 999 (M^+). UV–vis (CH_2Cl_2): 370, 416. PL: 508. EL: 500. Anal. Calcd: C, 76.92; H, 8.27; N, 8.41. Found: C, 76.61; H, 8.23; N, 8.32.

4.3.6. 2,6-Bis(4-methoxy-α-cyanostyryl)-1,5-di-*n*-heptyloxynaphthalene (19c). Yield: 72%. Greenish yellow solid. Mp 162–164 °C. ^{1}H NMR ($CDCl_3$): 8.31 (d, J=9.2 Hz, 2H), 7.98 (d, J=8.9 Hz, 2H), 7.97 (s, 2H), 7.65 (d, J=8.9 Hz, 4H), 7.00 (d, J=8.9 Hz, 4H), 4.00 (t, J=6.4 Hz, 4H), 3.86 (s, 6H), 1.90 (m, 4H), 1.31 (m, 16H), 0.88 (t, J=6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): 160.64, 155.88, 134.45, 130.25, 127.34, 125.02, 124.91, 119.15, 118.20, 114.57, 112.19, 77.08, 55.45, 31.81, 30.45, 29.19, 26.31, 22.58, 14.04. IR (KBr): 2955, 2928, 2854, 2218, 1609, 1510, 1458, 1408, 1369, 1288, 1261, 1182, 1072, 1034, 835. MS: 670 (M^+). UV–vis (CH_2Cl_2): 386, 404. PL: 515. EL: 473. Anal. Calcd: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.72; H, 7.55; N, 4.25.

4.3.7. 2,6-Bis(4-cyano-α-cyanostyryl)-9-*n*-heptylcarbazole (20a). Yield: 32%. Yellow solid. Mp 225–227 °C. ^{1}H NMR ($CDCl_3$): 8.67 (d, J_1=1.5 Hz, 2H), 8.16 (dd, J_1=1.8 Hz, J_2=8.9 Hz, 2H), 7.79 (s, 2H), 7.77 (d, J=8.5 Hz, 4H), 7.72 (d, J=8.5 Hz, 4H), 7.51 (d, J=8.6 Hz, 2H), 4.32 (t, J=7.0 Hz, 2H), 1.89 (m, 2H), 1.24 (m, 8H), 0.85 (t, J=6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): 145.25, 142.66, 139.29, 132.75, 128.28, 126.13, 125.22, 123.31, 123.19, 118.33, 118.09, 112.00, 109.95, 106.40, 43.73, 31.65, 28.95, 27.18, 22.50, 13.98. IR (KBr): 2953, 2928, 2226, 2212, 1580, 1487, 1391, 1259, 1238, 1196, 1138, 839. MS: 569 (M^+). UV–vis (CH_2Cl_2): 332, 412. PL: 528. EL: 580. Anal. Calcd: C, 82.22; H, 5.48; N, 12.29. Found: C, 82.53; H, 4.43; N, 12.29.

4.3.8. 3,6-Bis[4-(2-*n*-nonyl-1,3,4-oxadiazolyl)-α-cyanostyryl]-9-*n*-heptylcarbazole (20b). Yield: 14%. Dark yellow solid. Mp 154–156 °C. ^{1}H NMR ($CDCl_3$): 8.64 (s, 2H), 8.16 (d, J=8.5 Hz, 2H), 8.06 (d, J=8.6 Hz, 4H), 7.79 (d, J=8.5 Hz, 4H), 7.78 (s, 2H), 7.48 (d, J=8.6 Hz, 2H), 4.30 (t, J=6.7 Hz, 2H), 2.92 (t, J=7.3 Hz, 4H), 1.85 (m, 6H), 1.26 (m, 32H), 0.87 (m, 9H). ^{13}C NMR ($CDCl_3$): 167.25, 164.06, 144.00, 142.37, 137.80, 127.89, 127.31, 126.11, 125.45, 123.94, 123.14, 118.47, 109.77, 107.02, 43.66, 31.36, 29.36, 29.21, 29.12, 29.04, 28.96, 27.18, 26.58, 25.48, 22.62, 22.52, 14.06. IR (KBr): 2955, 2926, 2854, 2210, 1585, 1566, 1499, 1420, 1308, 1236, 1204, 1138, 843. MS: 908 (M^+). UV–vis (CH_2Cl_2): 339, 417. PL: 522. Anal. Calcd: C, 78.02; H, 7.66; N, 10.80. Found: C, 77.14; H, 7.86; N, 10.56.

4.3.9. 3,6-Bis(4-methoxy-α-cyanostyryl)-9-*n*-heptylcarbazole (20c). Yield: 26%. Greenish yellow solid. Mp 119–121 °C. ^{1}H NMR ($CDCl_3$): 8.54 (s, 2H), 8.12 (d, J=8.5 Hz, 2H), 7.60 (d, J=8.9 Hz, 4H), 7.57 (s, 2H), 7.43 (d, J=8.9 Hz, 2H), 6.97 (d, J=8.9 Hz, 4H), 4.27 (t, J=7.0 Hz, 2H), 3.84 (s, 6H), 1.86 (m, 2H), 1.25 (m, 8H), 0.85 (t, J=6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): 160.05, 141.79, 141.02, 127.58, 127.04, 125.88, 123.06, 122.50, 119.06, 114.39, 109.46, 107.87, 55.41, 43.52, 31.65, 28.98, 27.18, 22.52, 14.00. IR (KBr): 2953, 2930, 2208, 1605, 1585, 1512, 1485, 1389, 1356, 1286, 1250, 1182, 1036, 829. MS: 579 (M^+). UV–vis (CH_2Cl_2): 336, 399. PL: 495. EL: 495. Anal. Calcd: C, 80.80; H, 6.43; N, 7.25. Found: C, 80.36; H, 5.76; N, 7.29.

4.3.10. 4-(4-Methoxy-α-cyanostyryl)-2,5-di-*n*-heptyloxybenzaldehyde (22). To a solution of 2,5-di-*n*-heptyloxyterephthaldialdehyde (**3**) (0.69 g, 1.90 mmol) and 4-methoxyphenylacetonitrile (**17**) (0.16 g, 1.09 mmol) in a mixture of *tert*-butyl alcohol (4 ml) and THF (7 ml) under inert gas was added potassium *tert*-butoxide (0.02 g, 0.18 mmol) in one portion at 40 °C. The mixture was stirred for 15 min at 40 °C, cooled, and poured into methanol. The precipitate was filtered off and dichloromethane (100 ml) was added to the filtrate. The solution was washed with water several times, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude product. The purification was accomplished by column chromatography on silica gel using dichloromethane/*n*-hexane as eluent. Yield: 0.14 g (26%). Yellow solid. Mp 60–62 °C. ^{1}H NMR ($CDCl_3$): 10.47 (s, 1H), 7.84–7.83 (ss, 2H), 7.63 (d, J=8.9 Hz, 2H), 7.32 (s, 1H), 6.97 (d, J=8.9 Hz, 2H), 4.13 (t, J=6.1 Hz, 2H), 4.01 (t, J=6.4 Hz, 2H), 3.84 (s, 3H), 1.81 (m, 4H), 1.29 (m, 16H), 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$): 188.98, 160.78, 155.60, 151.31, 133.71, 130.13, 127.57, 126.84, 125.98, 118.05, 114.39, 113.42, 112.77, 109.69, 69.37, 69.21, 55.44, 31.75, 29.16, 29.09, 28.99, 28.96, 26.04, 22.57, 22.54, 14.04. IR (KBr): 2957, 2935, 2856, 2212, 1684, 1607, 1516, 1487, 1427, 1393, 1285, 1244, 1207, 1186, 1132, 1036, 831. MS: 491 (M^+). UV–vis (CH_2Cl_2): 355, 408. Anal. Calcd: C, 75.73; H, 8.41; N, 2.85. Found: C, 75.68; H, 8.52; N, 2.85.

4.3.11. 3-Formyl-9-*n*-heptylcarbazole (23). Phosphorus oxychloride (3.7 g, 24 mmol) was added dropwise to DMF (1.7 g, 23 mmol) at 0 °C. 9-*n*-Heptylcarbazole (**8**) (6.0 g, 22.6 mmol) in 1,2-dichloroethane (30 ml) was added to the reaction mixture at room temperature. The mixture was refluxed for 6 h. After cooling, the mixture was poured into water and extracted with dichloromethane. The solution was washed with water, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude product.

The purification was accomplished by chromatography on a silica gel column using ethyl acetate/*n*-hexane as eluent. The viscous pale yellow liquid was solidified on standing at room temperature. Yield: 2.7 g (41%). Pale yellow solid. Mp 60–62 °C. ^{1}H NMR ($CDCl_3$): 10.07 (s, 1H), 8.58 (d, J_1=1.2 Hz, 1H), 8.12 (d, J=7.6 Hz, 1H), 7.96 (dd, J_1=1.8 Hz, J_2=8.5 Hz, 1H), 7.46–7.30 (m, 4H), 4.30 (t, J=7.3 Hz, 2H), 1.86 (m, 2H), 1.22 (m, 8H), 0.84 (t, J=6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): 191.69, 144.03, 141.14, 128.48, 127.10, 126.66, 123.93, 123.03, 122.97, 120.69, 120.24, 109.36, 108.89, 43.40, 31.63, 28.98, 28.90, 27.19, 22.52, 13.98. IR (KBr): 2951, 2916, 2852, 1690, 1626, 1591, 1497, 1470, 1381, 1339, 1234, 1180, 1134, 810, 752. MS: 293 (M^+), 208, 180, 152, 84, 49. Anal. Calcd: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.53; H, 7.80; N, 4.76.

4.3.12. 1,6-Bis(4-cyanomethylphenoxy)hexane (25). A solution of 4-hydroxyphenylacetonitrile (**24**) (1.9 g, 14.3 mmol), 1,6-dibromohexane (1.6 g, 6.6 mmol), and potassium carbonate (4.0 g, 29.0 mmol) in DMF (50 ml) was stirred at 70 °C overnight. The resulting mixture was poured into cold water. The precipitate was collected and dried under vacuum. The crude product was purified by chromatography on a silica gel column using dichloromethane as eluent. Yield: 1.8 g (79%). White solid. Mp 119–121 °C. ^{1}H NMR ($CDCl_3$): 7.18 (d, J=8.9 Hz, 4H), 6.88 (d, J=8.9 Hz, 4H), 3.94 (t, J=6.4 Hz, 4H), 3.66 (s, 4H), 1.80 (m, 4H), 1.52 (m, 4H). ^{13}C NMR ($CDCl_3$): 158.80, 129.01, 121.59, 118.18, 115.03, 67.89, 29.07, 25.76, 22.76. IR (KBr): 2937, 2872, 2245, 1614, 1585, 1514, 1475, 1408, 1254, 1180, 1111, 1028, 820, 804. MS: 348 (M^+), 216, 172, 146, 133, 116, 83, 67, 55. Anal. Calcd: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.53; H, 6.20; N, 7.98.

4.4. General procedure for the preparation of α-cyanostyryl compounds with spacer group (26–28)

The model compounds **26–28** were prepared by reacting the aldehydes (**21**, **22** or **23**) with acetonitrile **25**, respectively, by the same method as model compounds **18–20**.

4.4.1. 1,6-Bis[(1,4-di-*n*-heptyloxyphenyl)-4-β-cyanostyryloxy]hexane (26). Yield: 76%. Greenish yellow solid. Mp 88–90 °C. ^{1}H NMR ($CDCl_3$): 7.84 (s, 2H), 7.72 (d, J=2.8 Hz, 2H), 7.57 (d, J=8.9 Hz, 4H), 6.95 (d, J=9.2 Hz, 4H), 6.90 (d, J=2.8 Hz, 2H), 6.84 (d, J=9.15 Hz, 2H), 3.97 (m, 12H), 1.77 (m, 12H), 1.29 (m, 36H), 0.87 (m, 12H). ^{13}C NMR ($CDCl_3$): 159.74, 152.92, 151.72, 135.16, 127.28, 123.81, 118.71, 118.42, 114.86, 113.42, 112.95, 110.69, 69.37, 68.77, 67.98, 31.77, 29.30, 29.13, 29.07, 28.99, 26.10, 26.01, 25.86, 22.60, 22.53, 14.06. IR (KBr): 2930, 2856, 2208, 1607, 1512, 1497, 1470, 1433, 1394, 1296, 1244, 1225, 1186, 1038, 824, 814. MS: 981 (M^+). UV–vis: 330, 374. PL: 493. Anal. Calcd: C, 79.36; H, 9.13; N, 2.99. Found: C, 78.25; H, 9.88; N, 2.81.

4.4.2. Oligomer (27). Yield: 21%. Orange solid. Mp 175–177 °C. ^{1}H NMR ($CDCl_3$): 7.89 (s, 4H), 7.83 (s, 4H), 7.59 (dd, J_1=2.4 Hz, J_2=8.9 Hz, 8H), 6.96 (dd, J_1=2.1 Hz, J_2=8.9 Hz, 8H), 4.09 (m, 12H), 3.85 (s, 6H), 1.79 (m, 12H), 1.30 (m, 36H), 0.86 (t, J=7 Hz, 12H). ^{13}C NMR ($CDCl_3$): 160.46, 159.99, 151.37, 134.01, 133.91, 127.40, 127.33, 127.16, 125.75, 125.69, 118.56, 114.97, 114.45, 111.19, 111.12, 69.42, 68.01, 31.80, 29.24, 29.13, 29.04, 26.16, 25.83, 22.57, 14.09. IR (KBr): 2932, 2854, 2208, 1607, 1514, 1431, 1300, 1248, 1217, 1182, 1034, 824. MS: 1295 (M^+). UV–vis: 364, 433. PL: 632. EL: 545, 641. Anal. Calcd: C, 77.86; H, 7.93; N, 4.32. Found: C, 77.64; H, 7.80; N, 4.21.

4.4.3. 1,6-Bis[(3-(9-*n*-heptylcarbazyl))-4-β-cyanostyryloxy]hexane (28). Yield: 39%. Pale yellow solid. Mp 126–128 °C. ^{1}H NMR ($CDCl_3$): 8.57 (d, J=1.2 Hz, 2H), 8.11 (d, J=7.9 Hz, 2H), 8.06 (dd, J_1=1.5 Hz, J_2=8.9 Hz, 2H), 7.60 (d, J=8.9 Hz, 4H), 7.58 (s, 2H), 7.42–7.26 (m, 8H), 6.97 (d, J=8.9 Hz, 4H), 4.27 (t, J=7.3 Hz, 4H), 4.02 (t, J=6.4 Hz, 4H), 1.85 (m, 8H), 1.56 (m, 4H), 1.25 (m, 16H), 0.85 (t, J=7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): 159.44, 141.47, 141.35, 140.96, 127.67, 126.98, 126.83, 126.26, 125.02, 123.16, 122.79, 122.14, 120.67, 119.62, 119.26, 114.91, 109.07, 108.98, 107.14, 67.96, 43.26, 31.66, 29.13, 29.01, 28.96, 27.22, 25.80, 22.54, 14.00. IR (KBr): 2928, 2860, 2208, 1605, 1589, 1512, 1493, 1475, 1389, 1348, 1288, 1248, 1182, 1028, 833, 748. MS: 898 (M^+). UV–vis: 291, 381. PL: 468. Anal. Calcd: C, 82.81; H, 7.40; N, 6.23. Found: C, 81.69; H, 6.99; N, 6.08.

References and notes

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
2. Salaneck, W. P.; Lundström, I.; Rånby, B. *Conjugated Polymers and Related Materials*; Oxford University Press: Oxford, 1993; pp 65–169.
3. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
4. Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
5. Anderson, S.; Taylor, P. N.; Verschoor, G. L. B. *Chem.—Eur. J.* **2004**, *10*, 518.
6. Cho, N. S.; Hwang, D.-H.; Jung, B.-J.; Oh, J.; Chu, H. Y.; Shim, H.-K. *Synth. Met.* **2004**, *143*, 277.
7. (a) Oelkrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H.-J.; Hanack, M.; Hohloch, M.; Steinhuber, E. *J. Phys. Chem. B* **1998**, *102*, 1902; (b) Lange, F.; Hohnholz, D.; Leuze, M.; Ryu, H.; Hohloch, M.; Freudenmann, R.; Hanack, M. *Synth. Met.* **1999**, *101*, 652; (c) Behnisch, B.; Martinez-Ruiz, P.; Schweikart, K.-H.; Hanack, M. *Eur. J. Org. Chem.* **2000**, 2541.
8. Li, J. Y.; Liu, D.; Ma, C. W.; Lengyel, O.; Lee, C.-S.; Tung, C.-H.; Lee, S. T. *Adv. Mater.* **2004**, *16*, 1538.
9. (a) Zheng, M.; Sarker, A. M.; Gürel, E. E.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **2000**, *33*, 7426; (b) Wu, S.-H.; Chen, J.-H.; Shen, C.-H.; Tsiang, R. C.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6061.
10. Haisch, P. A. Ph.D. Dissertation, Universität Tübingen, 1995.
11. Stock, H. T.; Kellogg, R. M. *J. Org. Chem.* **1996**, *61*, 3093.
12. Zhang, Y.; Wang, L.; Wada, T.; Sasabe, H. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1359.
13. Lowen, S. V.; Buschek, J.; Mastantuono, R.; Holden, D. A.; Kovacs, G. J.; Loutfy, R. O. *Macromolecules* **1990**, *23*, 3242.

14. Kobler, H.; Schuster, K.-H.; Simchen, G. *Liebigs Ann. Chem.* **1978**, 1946.
15. Klingsberg, E. *J. Am. Chem. Soc.* **1958**, *80*, 5786.
16. Huisgen, R.; Sauer, J.; Sturm, H. J.; Markgraf, J. H. *Chem. Ber.* **1960**, *93*, 2106.
17. Finnegan, W. G.; Henry, R. A.; Lofquist, R. *J. Am. Chem. Soc.* **1958**, *80*, 3908.
18. Moratti, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.; Grüner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117.
19. Rieche, A.; Gross, H.; Höft, E. *Org. Synth., Coll. Vol. 5* **1967**, 49.
20. Cornil, J.; dos Santos, D. A.; Beljonne, D.; Brédas, J. L. *J. Phys. Chem.* **1995**, *99*, 5604.
21. Peng, Z.; Bao, Z.; Galvin, M. E. *CHEMTECH* **1999**, 41.
22. Faraggi, E. Z.; Chayet, H.; Cohen, G.; Neuman, R.; Avny, Y.; Davidov, D. *Adv. Mater.* **1995**, *7*, 742.
23. (a) Hanack, M.; Segura, J. L.; Spreitzer, H. *Adv. Mater.* **1996**, *8*, 663; (b) Hohloch, M.; Segura, J. L.; Döttinger, S. E.; Hohnholz, D.; Steinhuber, E.; Spreitzer, H.; Hanack, M. *Synth. Met.* **1997**, *84*, 319; (c) Segura, J. L.; Martin, N.; Hanack, M. *Eur. J. Org. Chem.* **1999**, 643.
24. (a) Romero, D. B.; Schaer, M.; Leclere, M.; Adès, D.; Siove, A.; Zuppiroli, L. *Synth. Met.* **1996**, *80*, 271; (b) Zang, C.; von Seggern, H.; Pakbaz, K.; Kraabel, B.; Schmidt, H.-W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35; (c) Gebler, D. D.; Wang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Fu, D.-K.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Appl. Phys. Lett.* **1997**, *7*, 1644.
25. Hohnholz, D.; Schweikart, K.-H.; Hanack, M. *Adv. Mater.* **1999**, *11*, 646.
26. Onoda, M.; Ohmori, Y.; Kawai, T.; Yoshino, K. *Synth. Met.* **1995**, *71*, 2181.
27. (a) Samuel, I. D. W.; Rumbles, G.; Collison, C. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1997**, *84*, 497; (b) Klärner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markievicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.