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Z/E isomerization of poly-*para*-phenylenevinylene model compounds[†]

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ABSTRACT: The poly-*para*-phenylenevinylene (PPV) model compound **1** with cyano groups on the vinylene moieties and 2-ethylhexyloxy chains on the central phenylene unit has been synthesized by Knoevenagel condensation of 1,4-bis(cyanomethyl)-2,5-bis(2-ethylhexyloxy)benzene and benzaldehyde. The only isomer that was obtained has been identified to have the *Z,Z* configuration. UV irradiation of the *Z,Z* isomer **1a** in solution with a medium-pressure mercury lamp gave a mixture of all three possible isomers (*Z,Z, Z,E* and *E,E*; **1a**, **1b** and **1c** respectively). The isomers were separated by column chromatography and identified spectroscopically. Electrochemical studies and fluorescence emission spectra of **1a** and **1c** are reported. The substituted PPVs **2, 3** and **4** have been synthesized and their absorption and emission spectra before and after UV irradiation are compared. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: cyano-substituted distyrylbenzenes; PPV model compounds; *Z/E* isomerization; organic light-emitting diodes; electrochemistry

INTRODUCTION

Conjugated polymers for the construction of light-emitting diodes (LEDs) are of wide research interest. Since the discovery of light emission of poly-*para*-phenylenevinylene (PPV),[1] many derivatives of this conjugated polymer have been synthesized.[2–6] Substitution with alkyl or alkoxy groups increases the solubility and changes their electronic properties.[2–6] Short-chain model compounds of defined structure help one to understand the influence of substituents on the behaviour of polymers;[7–9] they are also suitable as emissive layers in organic LEDs (OLEDs).[10,11] In our systematic investigations of cyano-substituted distyrylbenzenes,[7,8,12–18] we observed the *Z/E*-isomerization of the vinylene moiety under the influence of visible and UV light. Ohsumi *et al.*[19] used UV radiation to obtain the *E*-configuration of stilbenes with a cyano group on the vinyl double bond.

The configuration of the PPV backbone is of great importance for the electronic and optical properties of these compounds, as shown in the example of 1,4-bis(3,5-di-*tert*-butylstyryl)benzene.[20] The absorption and emission spectra of the three isomers of this compound show significant differences. Thus, effects of configuration on the efficiency of OLEDs can be expected.

In the following we report on a systematic study on the *Z/E* isomerization of the model compound 1,4-bis-(1-cyano-2-phenylethenyl)-2,5-bis(2-ethylhexyloxy)benzene (**1**) under the influence of daylight and UV-light of a medium-pressure mercury lamp around 380 nm. The effect of this radiation on the polymers **2, 3** and **4** was also investigated. The different isomers that were formed during the irradiation of **1** were additionally investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

RESULTS AND DISCUSSION

Compound **1** was synthesized by Knoevenagel condensation of 1,4-bis(cyanomethyl)-2,5-bis(2-ethylhexyloxy)-benzene and benzaldehyde according to Scheme **1**.[21] Under these conditions, only one isomer is obtained in a yield of about 60%, which, according to the general experience with Knoevenagel reactions and based on an X-ray structure[9] of a similar compound, has been assigned the *Z,Z* configuration **1a** (see Scheme **3**). Crystals of **1a** are light yellow and soluble in many common organic solvents. On the other hand, the crystals

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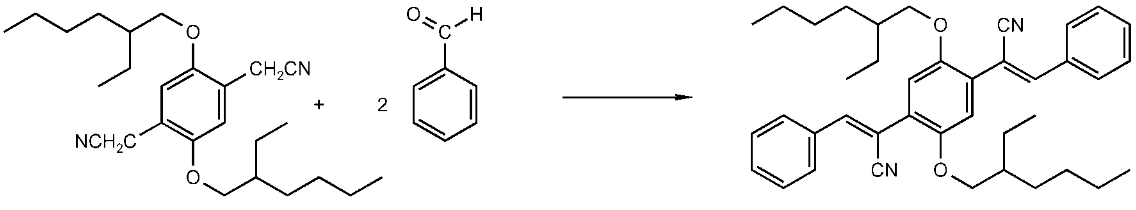
[†] Dedicated to Professor Dr Hans-Jörg Schneider on the occasion of his 65th birthday.



Scheme 1. Synthesis of model compound **1**

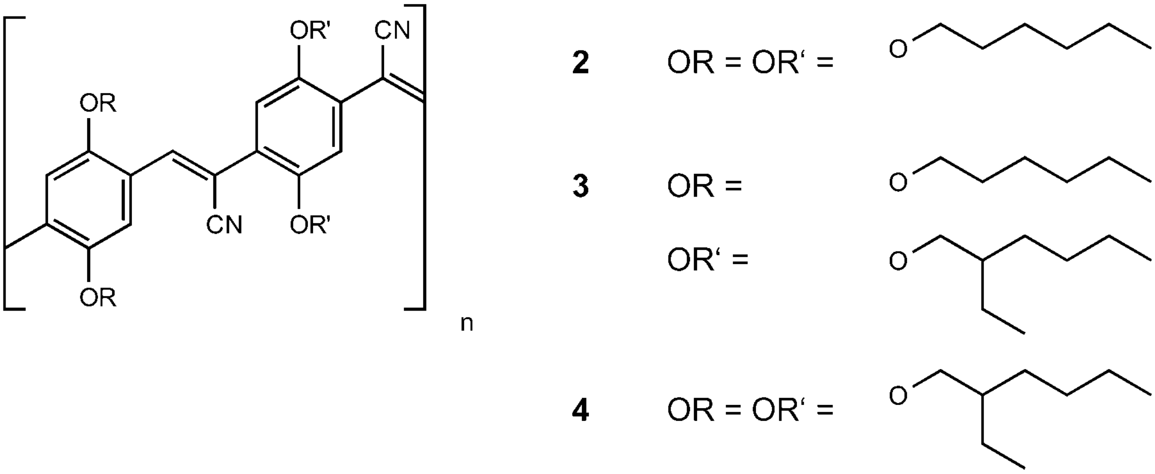


Figure 1. The polymers **2, 3** and **4**

turned out to be not stable enough under the conditions used to obtain an X-ray structure.

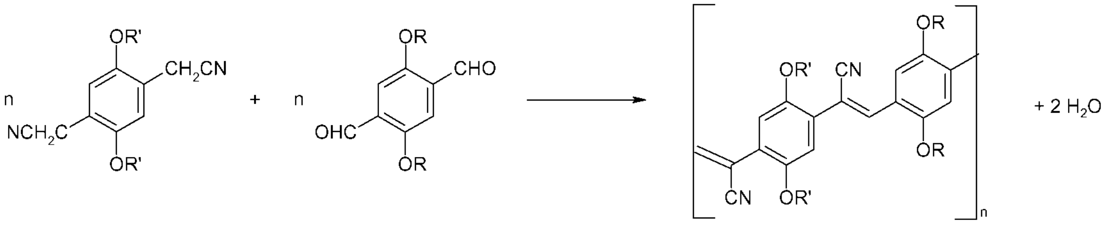
Polymer **2** was prepared by the reported procedure[21] and polymers **3** and **4** (see Fig. 1) were prepared by Knoevenagel-condensation of 2,5-dialkoxy-substituted terephthalaldehydes and 2,5-dialkoxy-substituted dicyanomethylbenzenes as shown in Scheme 2.[4] They were characterized by elemental analyses and spectroscopic methods (see Experimental Section).

Though the crystals of **1a** are stable in daylight and remain in the *Z,Z* configuration, a solution of **1a** in dichloromethane, chloroform or acetonitrile shows isomerization under daylight or the radiation of a medium-pressure mercury lamp. A mixture of the three possible isomers **1a, 1b** and **1c** (*Z,Z, Z,E* and *E,E* respectively) is obtained under both conditions (Scheme 3).

In order to investigate this isomerization in more detail, the short-chain model compound **1a** was irradiated in acetonitrile with a medium-pressure mercury lamp. After about 1 min of irradiation the ^1H NMR spectrum shows additional peaks compared with the spectrum of unirradiated **1a** (see Scheme 3). After about 15 min the equilibrium is reached.

The separation of the isomers was carried out by column chromatography on silica gel with a mixture of *n*-hexane and dichloromethane (4:3). Compound **1c** is crystalline and pale yellow in colour and melts at 108–109 °C, whereas **1a** melts at 126–129 °C. Compound **1b** is an oil.

The ^1H NMR spectrum of the *Z,Z* isomer **1a** shows a doublet at 3.95 ppm, due to the OCH_2 groups of the alkoxy chains. Because of the lower symmetry of the *Z,E* configuration in **1b**, two doublets at 3.85 and 3.74 ppm are observed. The *E,E* isomer **1c** is characterized by one doublet at 3.62 ppm. Thus ^1H NMR spectroscopy provides easy criteria to distinguish between the isomers.



Scheme 2. Synthesis of the polymers **2, 3** and **4**

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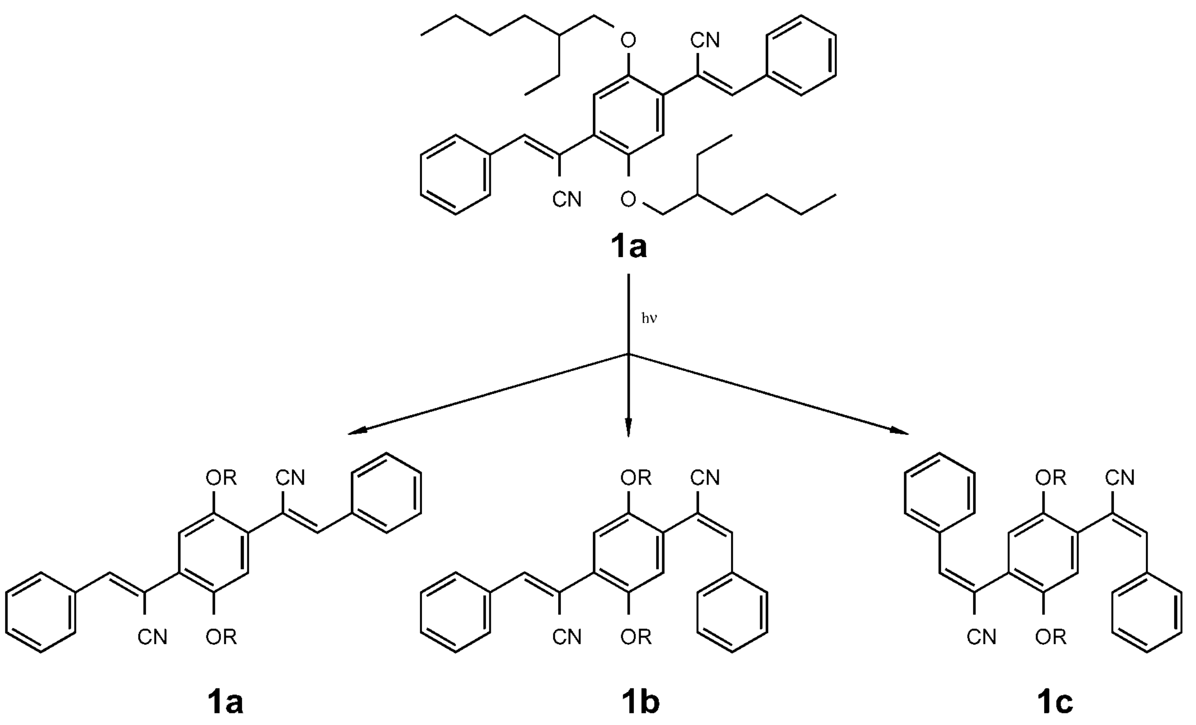

Scheme 3. Isomerization of compound **1**

PPV and related compounds are of special interest for the construction of OLEDs and hence the luminescence properties of **1a–1c** are of great importance. In order to investigate the influence of *Z,E* isomerization, the UV–Vis spectra of the isomers **1a–1c** and the photoluminescence (PL) spectra of the solid isomers **1a** and **1c** were measured (see Fig. 2). The maxima are given in Table 1.

The *Z,Z* isomer **1a** shows a distinct UV–Vis maximum at 374 nm (see Fig. 2). This maximum is shifted to shorter wavelength in *Z,E* isomer **1b** with a decrease in the intensity. This tendency continues in the *E,E* isomer **1c**. The highest maximum shifts from 311 nm in compound **1a** to 281 nm in **1c**. In general, the UV–Vis maxima shift to shorter wavelength if *Z*-bonds are changed to *E*-bonds. Similar observations have been made with distyrylbenzenes without cyano groups at the double bonds.^{20,22} In these compounds, the *trans* isomers have absorption maxima at longer wavelength than the *cis* isomers. The PL maximum of the *E,E* isomer **1c**, on the other hand, is shifted 13 nm bathochromic compared with the *Z,Z* isomer **1a**.

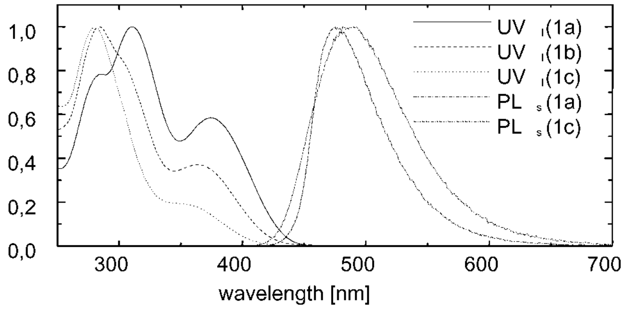

Figure 2. UV–Vis spectra of **1a, 1b** and **1c**

Table 1. PL- and UV–Vis-maxima of the isomers **1a, 1b** and **1c**

	λ_{max} (nm)	
	PL (solid)	UV–Vis (CH_2Cl_2)
1a (*Z,Z*)	475	286, 311, 374
1b (*Z,E*)	–	284, 363
1c (*E,E*)	488	281, 355

To obtain more information about the band gaps of the

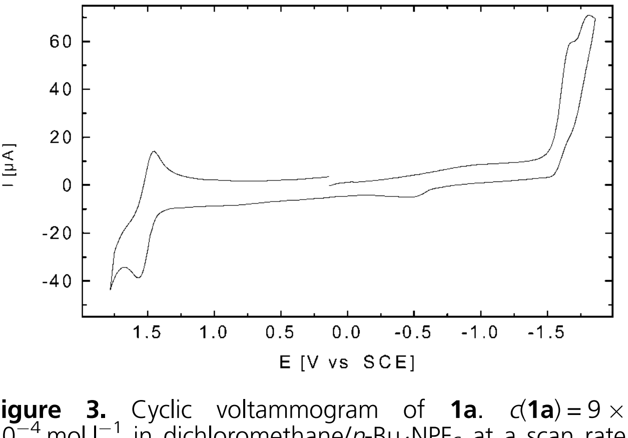

Figure 3. Cyclic voltammogram of **1a**. $c(\mathbf{1a}) = 9 \times 10^{-4}$ mol l^{-1} in dichloromethane/*n*-Bu_4NPF_6 at a scan rate of 500 mV s^{-1}

Table 2. Redox potentials obtained by CV and DPV measurements in dichloromethane/n-Bu_4NPF_6 (0.1 mol l^{-1}) at room temperature, scan rates $\upsilon_{CV} = 500/100/20$ mV s^{-1} and $\upsilon_{DPV} = 181.8/100/20$ mV s^{-1}, $c(Z,Z) = 9 \times 10^{-4}$ mol l^{-1} and $c(E,E) = 7.5 \times 10^{-4}$ mol l^{-1}

Isomer	$E_{1/2,CV}$(Ox1) [V] ($\Delta E_p = E_{pa} - E_{pk}$ [mV])	E_{DPV}(Ox1) [V]	$E_{1/2,CV}$(Red1) [V] (ΔE_p [mV])	E_{DPV}(Red1) [V]	$E_{1/2,CV}$(Red2) [V] (ΔE_p [mV])	E_{DPV}(Red2) [V]	$E_{1/2,CV}$(Red3) [V] (ΔE_p [mV])	E_{DPV}(Red3) [V]	
1c (*E,E*)	–/1.56(165)/–		−1.74(130)/ −1.74(110)/ −1.73(105)		−1.90(155)/ −1.90(160)/–				
Isomeric mixture[a]	1.58(140)/1.60(150)/ 1.59(145)	1.59/1.60/1.60	−1.64(150)/ −1.61(140)/ −1.60(150)	−1.61/−1.59/ −1.60	−1.79(170)/ −1.79(175)/ −1.78(170)	−1.75/−1.73/ −1.74			
1a (*Z,Z*)	1.51(110)/ 1.50(100)/–(–)	1.48/1.49/1.49	−1.60(150)/ −1.59(150)/ −1.58(60)	−1.58/−1.56/ −1.58	−1.75(140)/ −1.76(180)/ −1.76(150)	−1.72/−1.72/ −1.73		−2.08/−2.08/ −2.08	
1a[b] (*Z,Z*)			−1.54(130)[b] −1.53(130)[b] −1.54(150)[b]	−1.53/−1.53/ −1.53[c]	−1.77(130)[b] −1.75(120)[b] −1.77(100)[b]	−1.76/−1.76/ −1.76[c]	−2.09(200)[b]/ −2.08(170)[b]/ −2.08(140)[b]	−1.93/−1.93/ −1.93[c]	−2.08/−2.06/ −2.06[c]
Isomeric mixture[d]	1.57(110)/ 1.58(155)/–(–)	1.54/–/1.53	−1.62(170)/ −1.59(130)/–(–)	−1.55/–/−1.55	−1.77(125)/ −1.78(175)/–(–)	−1.70/–/−1.69			

[a] Caused by electrochemical oxidation and reduction.

[b] In THF.

[c] DPV measurements in THF.

[d] After UV irradiation of the *Z,Z* isomer.

different isomers we also investigated their electrochemical behaviour. For this reason CV and DPV measurements were carried out for the *Z,Z* and *E,E* isomers, **1a** and **1c** respectively, in dichloromethane and, because of the larger reductive potential range, likewise in tetrahydrofuran (THF). The electrochemically determined redox potentials are shown in Table 2. All potentials given refer to the saturated calomel electrode (SCE) if not otherwise indicated.

The cyclic voltammogram of the pure *Z,Z* isomer **1a** performed in dichloromethane shows three redox steps, of which two appear in the reductive and one in the oxidative potential range (see Fig. 3). The reduction waves are at −1.60 and −1.75 V (see Table 2). The first reductive electron transfer is negligibly reversible at slow scan rates υ, but the peak current for the oxidation of the reduced species increases with faster scan rates. In addition, at scan rates $\upsilon > 20$ mV s^{-1} a new anodic wave at −0.51 V appears, which originates from the oxidation of a sequential product. The oxidation at $E_{1/2}$,CV(Ox1) = + 1.51 V is quasi-reversible.

On the other hand, cyclic voltammograms of **1a** measured in THF show three reduction waves but no oxidation wave. The first reduction at −1.50 V is not entirely reversible, but the anodic peak current increases with the increasing scan rates. Thus at a scan rate $\upsilon = 500$ mV s^{-1} the cathodic and anodic peak currents are almost in the same range of magnitude. This points to the formation of a sequential product, which is relatively slow (compared with the scan rate), i.e. the rate constant of sequential product formation is small compared with that of the electrochemical oxidation of the first radical anion formed. Another hint to the resulting product is the appearance of a new anodic wave at −0.62 V. The second and third reductions at −1.74 and −2.07 V are likewise not entirely reversible. Moreover, the radical dianion forms a sequential product, which is characterized by a new anodic wave at −0.52 V. The differential pulse voltammogram shows for the third reduction at E_{DPV}(Red3) = −2.06 V a peak with a distinct shoulder at −1.93 V. The information gained by the electrochemical measurements points to a complicated mechanism for the reduction.

Based on the resulting electrochemical measurements, the solution of pure isomer **1a** in dichloromethane was irradiated for about 20 min. Subsequently, further cyclic voltammetric measurements were carried out. It can be shown that the isomeric mixture exhibits slightly different redox potentials than the pure *Z,Z* isomer **1a**. The first reductive electron transfer is shifted to $E_{1/2,\mathrm{CV}}$(Red1) = −1.62 V, the second one to $E_{1/2,\mathrm{CV}}$ (Red2) = −1.77 V, and the first oxidation wave is shifted to $E_{1/2,\mathrm{CV}}$(Ox1) = 1.57 V. Therefore, the band gap (the distance between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), or between the first oxidation and the first reduction potential, respectively) increases. The band gap of pure **1a** is 3.11 eV and that of the isomeric mixture 3.19 eV. In the differential pulse voltammogram the first oxidation wave is clearly broadened compared with **1a** and even shows a small shoulder at +1.6 V.

Likewise, the pure *E,E* isomer (**1c**) was investigated with regard to its redox behaviour in dichloromethane. The shapes of the cyclovoltammetric peaks correspond to those of **1a**. Again, the cyclic voltammograms show one oxidative electron transfer with the oxidation potential $E_{1/2,\mathrm{CV}}$(Ox1) = 1.58 V and two reduction waves. The first oxidation again is quasi-reversible. The reductions take place at −1.74 and −1.90 V. During the electrochemical measurements these reductive electron transfers shift to higher potentials. After about 40 scans the reduction potentials shifted to $E_{1/2,\mathrm{CV}}$(Red1) = −1.64 V and $E_{1/2,\mathrm{CV}}$(Red2) = −1.79 V. In the ground state no rotation of the double bond is possible. After reduction or oxidation the bond order is reduced, resulting in rotation and isomerization. The redox potentials approach the values of the isomeric mixture, caused by UV radiation. The first oxidation of the isomeric mixture is again quasi-reversible. The first reduction is negligibly reversible and forms a sequential product, which is oxidized at −0.65 V, where a new wave appears. Likewise, the second reduction forms a sequential product. A hint to this is the appearance of a new anodic wave at −0.54 V, which shows the oxidation of the sequential product. The HOMO–LUMO distance is 3.31 eV (see Table 2). The increase of the band gap caused by changing *Z*-bonds to *E*-bonds can be explained by a stronger torsion within the molecule in the case of *E*-configuration compared with the *Z*-configuration. Because of this steric hindrance the outer phenyl rings are distorted against the central phenylene unit, which leads to a shorter conjugation length and a larger HOMO–LUMO distance. The electrochemically and optically determined HOMO–LUMO distances of the different isomers are given in Table 3.

The PL, UV and CV data show, that the configuration of the double bond is of great importance for the HOMO–LUMO distance of the model compound. In order to investigate the influence of *Z,E*-isomerization of the polymers **2, 3**, and **4** (see Fig. 1), the PL spectra of the unirradiated and irradiated (30 min, medium-pressure mercury lamp) polymers were measured (see Table 4).

Owing to the observations made on the model compound **1**, an increase of the number of *E* bonds in

Table 3. Electrochemically and optically determined HOMO–LUMO distances (measured in dichloromethane) for **1a–c**

Compound	ΔE_{CV} (eV)	$\Delta E_{\mathrm{UV-Vis}}$ (eV)
1a (*Z,Z*)	3.11	3.30
1c (*E,E*)	3.31	3.49
1b (*E,Z*)	3.22[a]	3.41

[a] Isomeric mixture after UV irradiation of the (*Z,Z*) isomer.

Table 4. PL spectra of the polymers **2, 3** and **4**

	2		**3**		**4**	
	UV–Vis (nm)	PL (nm)	UV–Vis (nm)	PL (nm)	UV–Vis (nm)	PL (nm)
Unirradiated	453	618	459	577	453	567
Irradiated	443	640	450	570	449	566

the polymers caused by the radiation can be assumed. The spectral differences between irradiated and unirradiated polymers depend on the number of branched alkyl chains on the polymers. Polymer **2**, which only carries unbranched hexyl chains, shows the largest effect caused by the irradiation; the spectra of polymer **4** show the smallest differences between the irradiated and unirradiated states. Polymer **4** also shows strong torsion of the polymer chain in the unirradiated state, caused by steric hindrance between the bulky 2-ethylhexyloxy chains and the cyano groups.[9] Hence the additional torsion caused by the shorter distances between the phenylene units in the *E*-configuration is relatively low.

CONCLUSION

In conclusion, the observed *Z/E* isomerization of **1** affects the luminescence properties of cyano-substituted distyrylbenzenes, which are considered as model compounds for corresponding polymers. Although the isomerization was only observed in solution, a similar effect in the solid state cannot be excluded, for example in compounds used for the construction of OLEDs, due to the long duration of their use in devices. Because of the need for high purity of the luminescent layer, this could reduce the efficiency and lifetime of OLEDs.

EXPERIMENTAL

General

Melting points (uncorrected): Gallenkamp melting point apparatus. UV–Vis: Shimadzu UV-2102 PC. MS: Finnigan MAT 711A. NMR: Bruker AC 250 spectrometer (250 MHz). $CHCl_3$ and $CHDCl_2$ were used as references. Emission spectra: Spex Fluorolog 112. CV: a standard one-compartment, three-electrode arrangement was used with a platinum disc as the working electrode, a platinum wire as the counter electrode and a silver wire as the pseudo reference electrode. The reversible oxidation signal of ferrocene/ferrocenium (Fc) was used as the internal standard. The dichloromethane and THF used as solvents were dried over calcium hydride and distilled twice in an inert gas atmosphere. The supporting electrolyte (tetrabutylammonium hexafluorophosphate) was purified by recrystallization from ethanol. All measurements were carried out under argon at room temperature and exclusion of moisture.

Synthesis

Solvents and reagents were used as purchased without further purification unless stated otherwise. THF and *tert*-butanol were dried over sodium. All reactions were carried out under nitrogen. Polymer **2** was prepared as reported in the literature.[21]

(*Z,Z*)-1,4-Bis-(1-cyano-2-phenylethenyl)-2,5-bis-(2-ethyloxyhexyl)benzene (1a). 1,4-Bis(cyanomethyl)-2,5-bis(2-ethylhexyloxy)benzene (1.0 mmol) and benzaldehyde (2.5 mmol) were dissolved in dry THF (2 ml) and dry *tert*-butanol (2 ml). At a temperature of 35 °C potassium *tert*-butoxide and tetrabutylammonium hydroxide were added. The mixture was stirred for 30 min. After reaction the mixture was diluted with water (50 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic fractions were washed three times with water. The solvent was evaporated, and the residue was washed with methanol several times and reprecipitated from dichloromethane and methanol.

Under these conditions, only the *Z,Z* isomer **1a** was obtained in a yield of about 60%. M.p. 125–127 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.86 (m, 4H), 7.70 (s, 2H), 7.44 (m, 6H), 7.10 (s, 2H), 3.95 (d, $J = 5.3$ Hz, 4H), 1.75 (m, 2H), 1.45 (m, 8H), 1.26 (m, 8H), 0.90 (m, 12H); MS (FD) *m/z* 588.7 (M^+); UV (dichloromethane) $\lambda_{max1} = 310$ nm, $\lambda_{max2} = 375$ nm.

Isomerization of 1a to a mixture of 1a–c. 589 mg (*Z,Z*)-1,4-bis(1-cyan-2-phenylethenyl)-2,5-bis(2-ethylhexyloxy)benzene (**1a**) (1 mmol) dissolved in 350 mL of acetonitrile was irradiated for 20 min under stirring in a photoreactor (Heraeus UV-RS-1, UV-Tauchstrahler TQ 150). After removal of the solvent by distillation, the yellow oil was separated by column chromatography (*n*-hexane/dichloromethane 4:3) to give **1b** and **1c**.

(*Z,E*)-1,4-Bis-(1-cyano-2-phenylethenyl)-2,5-bis-(2-ethyloxyhexyl)benzene (1b). ^1H NMR (250 MHz, CD_2Cl_2) δ 7.89 (s, 1H), 7.69 (s, 1H), 7.49 (d, 2H), 7.41 (s, 1H), 7.24 (m, 4H), 7.10 (s, 1H), 6.84 (s, 1H), 3.86 (d, $J = 5.4$ Hz, 2H), 3.75 (d, $J = 5.4$ Hz, 2H), 1.23–1.68 (m, 18H), 0.85 (m, 12H); UV (dichloromethane) $\lambda_{max1} = 284$ nm, $\lambda_{max2} = 363$ nm.

(*E,E*)-1,4-Bis-(1-cyano-2-phenylethenyl)-2,5-bis-(2-ethyloxyhexyl)benzene (1c). M.p. 108–109 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.41 (s, 2H), 7.26 (m, 6H), 7.18 (m, 4H), 6.80 (s, 2H), 3.62 (d, $J = 5.5$ Hz, 4H), 1.45 (m, 2H), 1.19 (m, 16H), 0.82 (m, 12H); MS (FD) *m/z* 588.5 (M^+); UV (dichloromethane) $\lambda_{max1} = 281$ nm, $\lambda_{max2} = 355$ nm.

Polymers 2, 3 and 4. The polymers **2, 3** and **4** were prepared by Knoevenagel-condensation of 2,5-dialkoxy - substituted terephthalaldehydes (1.0 mmol) with 2,5-dialkoxy - substituted dicyanomethylbenzenes (1.0 mmol), which were dissolved in dry THF (2 ml) and dry *tert*-butanol (2 ml).[4] At a temperature of 35 °C, potassium *tert*-butoxide and tetrabutylammonium hydroxide were added. The mixture was stirred for 0.5 h. After the reaction was completed, the mixture was diluted with water (50 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic fractions were washed three times with water. Then the solvent was evaporated. The residue was washed with methanol several times and reprecipitated from dichloromethane and methanol.

Polymer 3. Yield 93%, orange fluffy solid, m.p. 232–238 °C. IR (KBr) ν 2959 s, 2928 s, 2871 m, 2212 w, 1593 w, 1504 s, 1468 m, 1416 s, 1381 m, 1275 w, 1213 s, 1030 m, 930 w cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.03 (s, 2H), 7.92 (s, 2H), 7.12 (s, 2H), 4.13 (t, 4H), 4.13 (t, 4H), 3.99 (d, $J = 4.7$ Hz, 4H), 1.82 (m, 6H), 1.52–1.32 (m, 28H), 0.97–0.86 (m, 18H); UV–Vis (CH_2Cl_2) $\lambda_{max} = 461$, 333 nm; PL (solid state) $\lambda_{max} = 577$ nm. Anal. $(C_{46}H_{66}N_2O_4)_n$ calc.: C, 77.70; H, 9.36; N, 3.94; found: C, 76.99; H, 8.84; N, 3.86%.

Polymer 4. IR (KBr) ν 2959 s, 2928 s, 2874 m, 2214 w, 1740 w, 1607 w, 1504 s, 1466 m, 1428 m, 1381 w, 1275 w, 1211 s, 1032 s, 912 w cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.95, 7.93(2 s, 2 × 2 H), 4.03–3.72 (m, 8H), 1.82 (m, 36H), 0.95–0.86 (m, 24H); UV–Vis $\lambda_{max} = 453$, 330 nm; PL (solid state) $\lambda = 567$ nm. Anal. $(C_{50}H_{74}N_2O_4)_n$ calc. C, 78.27; H, 9.73; N, 3.65; found: C, 77.43; H, 9.90; N, 3.66%.

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