Aromatic polyethers with oxadiazole units – synthesis and application in organic light emitting diodes

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SUMMARY:

Detailed synthetic aspects of new aromatic polyethers containing oxadiazole units are described. They are obtained by the nucleophilic displacement reaction of 2,2-bis(4-hydroxyphenyl)hexafluoropropane with 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole. The purity of the polyethers strongly depends on the reaction solvent. Best results were achieved with Ph_2SO_2 as compared to *N*-methyl-2-pyrrolidone (NMP) and 1,3-dimethyltetrahydro-2(1H)-pyrimidinone (DMPU) in the temperature range from 190–200 °C. All polyethers are fully soluble in common organic solvents and excellent films are obtained by spin-coating. High molecular weight polyethers without oligomers were only achieved, when Ph_2SO_2 was used as solvent. All polyethers are characterized by high thermal stability and high glass transition temperatures. The substitution of bisphenyloxadiazole by bisnaphthyloxadiazole units in the polyethers leads to a bathochromic shift of the absorption from 299 nm to 345 nm. Polyethers with bisnaphthyloxadiazole units show a blue fluorescence with a maximum at 427 nm. The application of these novel polyethers as efficient electron transport and injection layer in bilayer light emitting diodes based on poly(1,4-phenylenevinylene) is shown. The best results were obtained with oxadiazole polyethers containing bisnaphthyloxadiazole units.

Introduction

Polymers with 1,3,4-oxadiazole units in the polymer backbone are known for many years[1–3]. They are characterized by an excellent thermal and chemical stability[4], which makes them good candidates for a variety of applications as films and fibres.

One of the main disadvantages of these polymers is their poor solubility. It has been demonstrated that the incorporation of flexible linkages in the backbone improves both solubility and processability[4]. So aromatic ether and hexafluoroisopropylidene groups are often used as linkages, because the resulting polymers are still soluble and retain their thermal stability[5,6]. The first poly(arylethers) containing 2,5-diphenyloxadiazole were prepared by Johnson[7–9] in the 60es. Recently, Hedrick reported the synthesis of some oxadiazole polyethers from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazoles and various *para*-substituted bisphenols[10,11].

A big advantage is the synthesis of the oxadiazole containing polyethers via nucleophilic aromatic substitution polymerization[10–15]. The heterocyclic ring is formed throughout the monomer synthesis and purified prior to polymerization. In the subsequent polycondensation the ether linkage is generated. This route yields polymers with higher purity compared to the most popular route to polyoxadiazoles, which involves the preparation of polyhydrazides and subsequent cyclodehydration by thermal treatment in the presence of dehydrating agents[13], which leads to incomplete cyclization. The drastic conditions often cause chemical defects in the polyoxadiazoles[10, 14].

With the discovery of electroluminescence in organic light emitting diodes (LEDs)[16, 17] oxadiazole compounds have achieved considerable interest. The electron-deficient oxadiazole ring facilitates the reduction to the corresponding radical anion and thus polymers can act as electron injection and transport material.

A number of low molecular weight aromatic oxadiazole compounds such as 2-(*tert*-butylphenyl)-5-biphenyl-1,3,4-oxadiazole (PBD)[18] and blends of PBD with poly(methyl methacrylate) (PMMA)[19] increase the quantum efficiency in two-layer LEDs with an appropriate hole transport layer like poly(1,4-phenylenevinylene) (PPV). In recent years polymers with oxadiazole units used in LEDs have been reported by several groups[20–26]. Such polymers have the advantage that the concentration of the active groups is higher compared to guest-host systems and the crystallization tendency is decreased.

Recently, we have reported the application of a novel oxadiazole polyether with bisnaphthyloxadiazole units in bilayer LEDs based on PPV[26]. In these devices a considerable increase of the external quantum efficiency to 0.1% has been measured. Compared to PPV monolayer LEDs the improved bilayer devices show a higher brightness of a few hundred cd/m^2 (with Ca as electron injecting electrode), while the threshold voltage for electroluminescence is only slightly increased from 2 V to 4 V.

These diodes show a significantly improved performance compared to the LEDs from oxadiazole polyethers recently reported by Strukelj et al.[21] They report high turn-on voltages in the range from 20 to 30 V with PPV as hole transporting and emission layer. Kido et al.[23] used a poly(arylene ether) containing a hole transporting tetraphenylbenzidine unit and an electron transporting 1,3,4-oxadiazole unit in a single layer device and obtained a maximum luminance of 26 cd/m^2 at 12 V. Low turn-on voltages and enhanced external quantum efficiencies are also obtained by Pei et al. using polymers with the oxadiazole ring fixed in the main chain[22]. But their polymers have the disadvantage that their synthetic route causes defects in the polymer backbone by incomplete cyclodehydration of the polyhydrazide, which can be detected in the infrared spectra. Such defects might lead to a decrease in the long time stability of the devices.

This paper is a detailed report of the synthesis of the new aromatic oxadiazole polyethers involving the nucleophilic displacement reaction of 2,2-bis(4-hydroxyphenyl)hexafluoropropane (hexafluorobisphenol A)[a] with 2,5-bis(4-fluorophenyl)-

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[a] Bisphenol A: systematic name: 4,4′-isopropylidenediphenol.

1,3,4-oxadiazole and 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole. The bisnaphthyl substituted oxadiazoles posess a larger conjugated system compared to the phenyl substituted oxadiazoles. Therefore radical anions, which are responsible for carrier transport during device operation, should be stabilized more effective in the bisnaphthyloxadiazoles. To test this hypothesis both homopolymers and a series of copolymers were prepared. The results of the chemical characterization of all oxadiazole polyethers and their application in organic light emitting diodes (LEDs) is reported.

Experimental part

Materials

Diphenyl sulfone (Ph_2SO_2) (Lanchaster 99%) was recrystallized from ethanol. *N*-Methyl-2-pyrrolidone (NMP) (Merck 99%) was stirred over P_2O_5 and distilled under reduced pressure. 1,3-Dimethyltetrahydro-2(1H)pyrimidinone (DMPU) (Merck 99%) was stirred over molecular sieve for several days and distilled under reduced pressure. 4-Fluorobenzoic acid (Fluka 98%), 4-fluoro-1-naphthoic acid (Aldrich 98%), thionyl chloride (Merck-Schuchardt 99%) and phosphorus trichloride oxide (Merck 99%), potassium carbonate (Merck extra pure) and toluene p.a. (Merck) were used without further purification. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (Aldrich 97%) was purified by recrystallization from hexane/toluene/ethyl acetate (75/21/4) and subsequent sublimation under reduced pressure.

All other solvents were technical grade and distilled before use.

Synthesis of the monomers

4-Fluorobenzoyl chloride (**2**): 30.8 g (220 mmol) of 4-fluorobenzoic acid were refluxed with 200 mL thionyl chloride in an argon atmosphere for 4 h. 4-Fluorobenzoyl chloride (**2**) was concentrated and purified by distillation under reduced pressure.

Yield:	33.1 g (95%)
IR (film):	1780, 1751 (—COCl) 1599, 1504, 1413, 1297, 1242, 1201, 1158, 886, 848, 803, 641, 612 cm^{-1}.

4-Fluoronaphthoyl chloride (**6**) was prepared according to 4-fluorobenzoyl chloride (**2**). To remove $SOCl_2$ completely 4-naphthoyl chloride was dried for 20 h under reduced pressure. The white solid was used without further purification.

Yield:	95%
IR (film):	1755 (—COCl), 1600, 1571, 1509, 1428, 1216, 1171, 1148, 1047, 1018, 835, 806, 765 cm^{-1}.

Bis(4-fluorobenzo)hydrazide (**3**): A solution of 32.58 g (205 mmol) 4-fluorobenzoyl chloride (**2**) in 150 mL NMP was cooled to 0 °C in an argon atmosphere and 4.88 g (97 mmol) of hydrazine hydrate dissolved in 30 mL NMP were added within 40 min. After stirring for 18 h at room temperature the reaction mixture was poured into 1800 mL water. The colourless precipitate was isolated by filtration, washed with water and dried over P_2O_5.

Yield:	20.4 g (76%)
IR (KBr):	3210 (—NH), 1609 (—C=O), 1581 (—N—C=O), 1512, 1461, 1267, 1240, 1226, 1155, 1096, 749 cm^{-1}.

^{1}H NMR (DMSO): $\delta = 7.35$ (m, ar), 8.0 (m, ar), 10.5 (m, NH).
Intensity ratio: 4:4:2.

Bis(4-fluoronaphtho)hydrazide (**7**) was prepared from a solution of 13.75 g (65.9 mmol) 4-fluoronaphthoyl chloride in 160 mL of NMP and 1.752 g (35 mmol) hydrazine hydrate in 25 mL of NMP according to bis(4-fluorobenzo)hydrazide (**3**).

Yield:	16.3 g (81%).
IR (KBr):	3180 (—NH), 1606 (—C═O), 1592, 1571, 1511, 1478, 1458, 1256, 1234, 1053, 767 cm^{-1}.
^{1}H NMR (DMSO):	$\delta = 7.45$ (m, ar), 7.77 (m, ar), 8.17 (m, ar), 8.57 (m, ar), 10.65 (d, NH). Intensity ratio: 2:2:2:4:2.

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (**4**): 20.3 g (73 mmol) bis(4-fluorobenzo)hydrazide (**3**) were suspended in 150 mL $POCl_3$. The reaction mixture was refluxed for 5 h in an argon atmosphere, whereby a clear light brown solution was obtained. Upon cooling of the reaction mixture a white solid precipitated. The suspension was poured into 1500 mL of ice-water. The precipitate was filtered off, washed with water and further purified by recrystallization from hexane/ethyl acetate (vol. ratio 1:1).

Yield:	13.8 g (73%)
IR (KBr):	1607 (—C═N), 1494, 1471, 1410, 1239, 1226, 1159, 1095, 1067, 845, 745 cm^{-1}.
^{1}H NMR ($CDCl_3$):	$\delta = 7.18$ (m, ar), 8.10 (m, ar). Intensity ratio: 4:4.

2,5-Bis(4-fluoronaphthyl)-1,3,4-oxadiazole (**8**) was prepared like 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**4**). For purification the crude product was sublimed under reduced pressure and afterwards recrystallized from THF.

Yield:	59%
IR (KBr):	1600 (—C═N), 1579, 1531, 1512, 1465, 1394, 1372, 1238, 1053, 832, 759 cm^{-1}.
^{1}H NMR ($CDCl_3$):	$\delta = 7.3$ (m, ar), 7.75 (m, ar), 8.25 (d, ar), 8.32 (d, ar), 9.4 (d, ar). Intensity ratio: 2:4:2:2:2.

Polycondensation

The synthesis of the oxadiazole polyether **10a** is described as a typical example.

Polyether (**10a**)*:* A 250 mL three-necked flask fitted with a Dean-Stark trap, a reflux condenser, an argon inlet and a thermometer was charged with 1.174 g (3.493 mmol) of 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 1.250 g (3.493 mmol) 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole (**8**) and 728 mg (5.28 mmol) powdered potassium carbonate and degassed. In an argon atmosphere 33 g diphenyl sulfone and 30 mL toluene were added. The suspension was heated to 160 °C within 90 min, whereby the monomers dissolve completely. Besides, the toluene begins to reflux. The reaction mixture was maintained at 160 °C for another 90 min and the water was gradually removed by azeotropic distillation with toluene through the Dean-Stark trap. Thereby the temperature rised to 200 °C within 60 min and was maintained at this temperature for 18.5 h. The suspension was cooled to 180 °C and diluted with 50 mL DMPU. After cooling down to room temperature the reaction mixture was acidified with acetic acid to neutralize the phenoxide groups. The polymer was isolated by precipitation into 650 mL acetone. The precipitate is filtered off and stirred in water to remove the inorganic salts. After extraction with methanol for 20 h the crude product was further purified by two reprecipitations from chloroform resp. DMPU solution into acetone.

Yield: 1.3 g (59%)

IR (film): 1610 (—C=N), 1579, 1530, 1507, 1461, 1394, 1243 (—CF_3), 1206 (—CF_3), 1175 (—CF_3), 1053 (—C—O—C), 968, 928, 830, 767 cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.01$ (d, ar), 7.09 (d, ar), 7.43 (d, ar), 7.59 (t, ar), 7.72 (t, ar), 8.17 (d, ar), 8.32 (d, ar), 9.37 (d, ar). Intensity ratio: 2:4:4:2:2:4:2:2.

^{13}C NMR ($CDCl_3$): $\delta = 63.7$, 111.9, 116.1, 118.8, 122.4, 124.0, 126.4, 126.9, 127.0, 128.8, 129.0, 132.0, 155.9, 157.1, 163.7.

$(C_{37}H_{20}F_6N_2O_3)_n$ $(654)_n$	Calc.	C 67.89	H 3.08	F 17.41	N 4.2	O 7.33
	Found	C 67.97	H 2.89	F 17.40	N 4.28	O 7.39

The polycondensation of all other oxadiazole polyethers was carried out by a similar procedure except the solvent and the reaction time (cf. Tab. 1). When NMP or DMPU were used as solvent, the polymers were precipitated into methanol instead of acetone.

Polyether (**14c**):

IR (film): 1603 (—C=N), 1510, 1488, 1415, 1240 (—CF_3), 1207 (—CF_3), 1175 (—CF_3), 1137, 1067 (—C—O—C), 968, 929, 836, 745 cm^{-1}.

^1H NMR ($CDCl_3$): $\delta = 7.05$ (d, ar), 7.14 (d, ar), 7.40 (d, ar), 8.13 (d, ar). Intensity ratio: 4:4:4:4.

^{13}C NMR ($CDCl_3$): $\delta = 63.8$, 116.6, 119.4, 124.0, 128.7, 128.9, 131.5, 132.0, 156.7, 159.3, 164.9.

LED fabrication

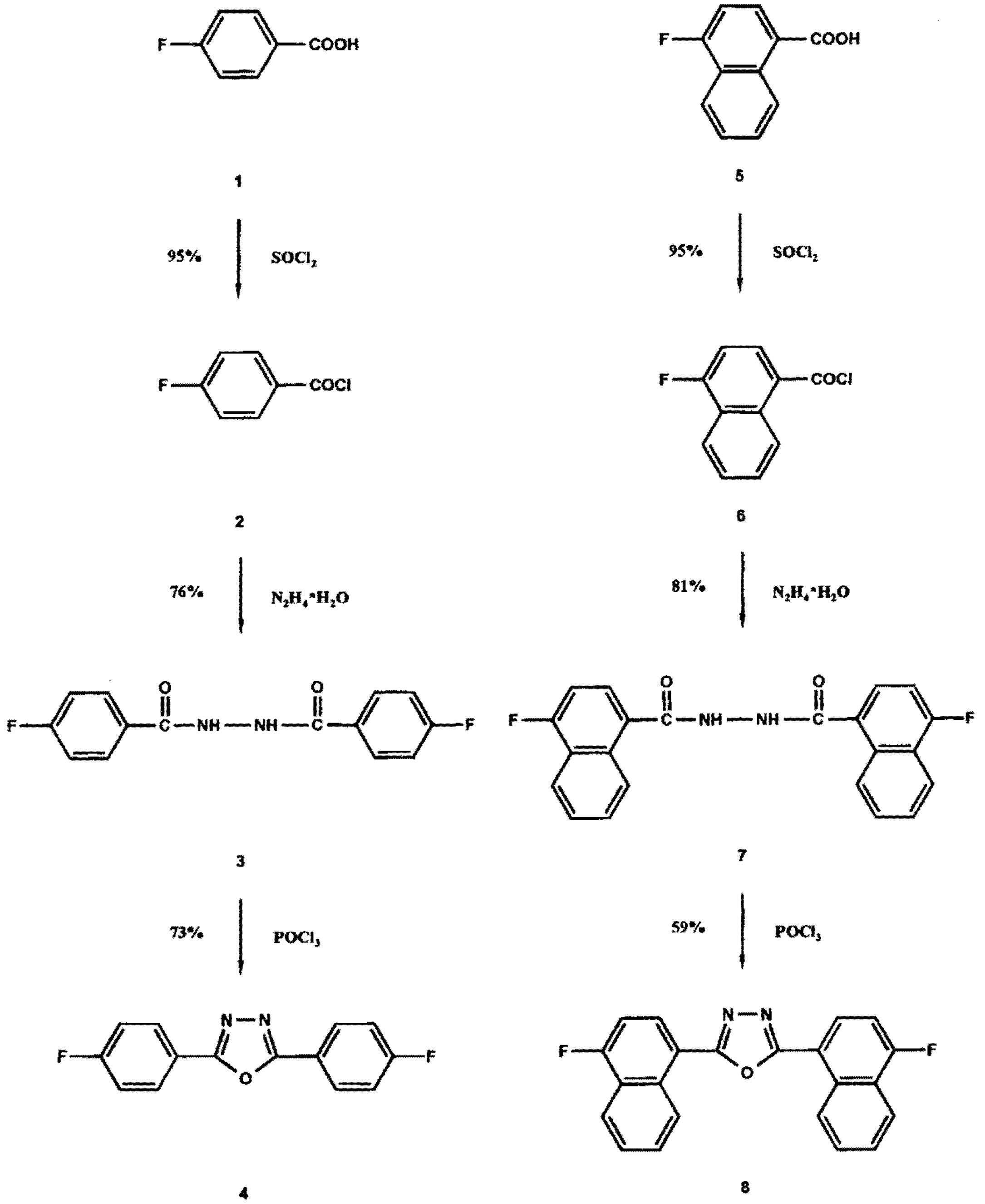
The fabrication of light emitting diodes was performed in three steps: First the PPV precursor polymer was cast on an indium-tin oxide (ITO) coated glass substrate with the doctor blade technique and thermally converted into PPV as previously described[27,28)]. In the second step the oxadiazole layer was prepared by spin-coating a solution of the polymers in $CHCl_3$ onto the PPV layer. Finally, the electron injecting electrode of the LED was deposited by evaporation of low work function metals like Ca or Al on top. For comparison all devices with different oxadiazole polyethers (and also a PPV single layer device as reference) were fabricated from the same PPV batch with the same thickness of the organic layers (PPV: 200 nm; oxadiazole polyether: 30 nm) and in one and the same evaporation run. The current-voltage characteristics and light intensity were simultaneously measured with a Keithley 236 Source Measure Unit and a Bentham silicon photodiode (DH-SI) in a calibrated integrating sphere.

Results and discussion

Synthesis of the oxadiazole monomers **4** *and* **8**

The synthesis of the main chain oxadiazole polyethers **10**–**14** requires the symmetric bifunctional oxadiazole monomers 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole (**8**) and 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**4**). The difluorides were chosen for the polycondensation reaction, since it is known that they are much more reactive than the corresponding dichlorides[7)]. The synthetic route is outlined in *Scheme 1*:

Scheme 1: Synthesis of the bifunctional oxadiazole monomers **4** and **8**



The first step involves the preparation of 4-fluorobenzoyl chloride (**2**) and 4-fluoronaphthoyl chloride (**6**) from 4-fluorobenzoic acid (**1**) or 4-fluoronaphthoic acid (**5**), respectively, and thionyl chloride. The reaction of 4-fluorobenzoyl chloride (**2**) and 4-fluoronaphthoyl chloride (**6**) with hydrazine hydrate in NMP yields the corresponding bisacylhydrazides. To achieve 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**4**), and 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole (**8**) cyclodehydration of the bishydrazides **3** and **7** was carried out in refluxing phosphorus trichloride oxide. After recrystallization 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**4**) was obtained as a white crystalline solid. The purification of 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole (**8**) involves sublimation and subsequent recrystallization in tetrahydrofuran (THF). The identity of the compounds was confirmed by NMR and FTIR spectroscopy.

Synthesis of the oxadiazole polyethers **10–14**

The oxadiazole polyethers **10–14** were synthesized from the bisfluorooxadiazoles **4** and **8** with 2,2-bis(4-hydroxyphenyl)hexafluoropropane (**9**) in a solution polycondensation (*Scheme 2*). In this reaction the fluorine atoms undergo nucleophilic displacement and an aryl ether linkage is generated forming the polyether. The ease of the nucleophilic displacement of the fluorine atoms is a result of the activation by the electron-withdrawing oxadiazole unit[7)].

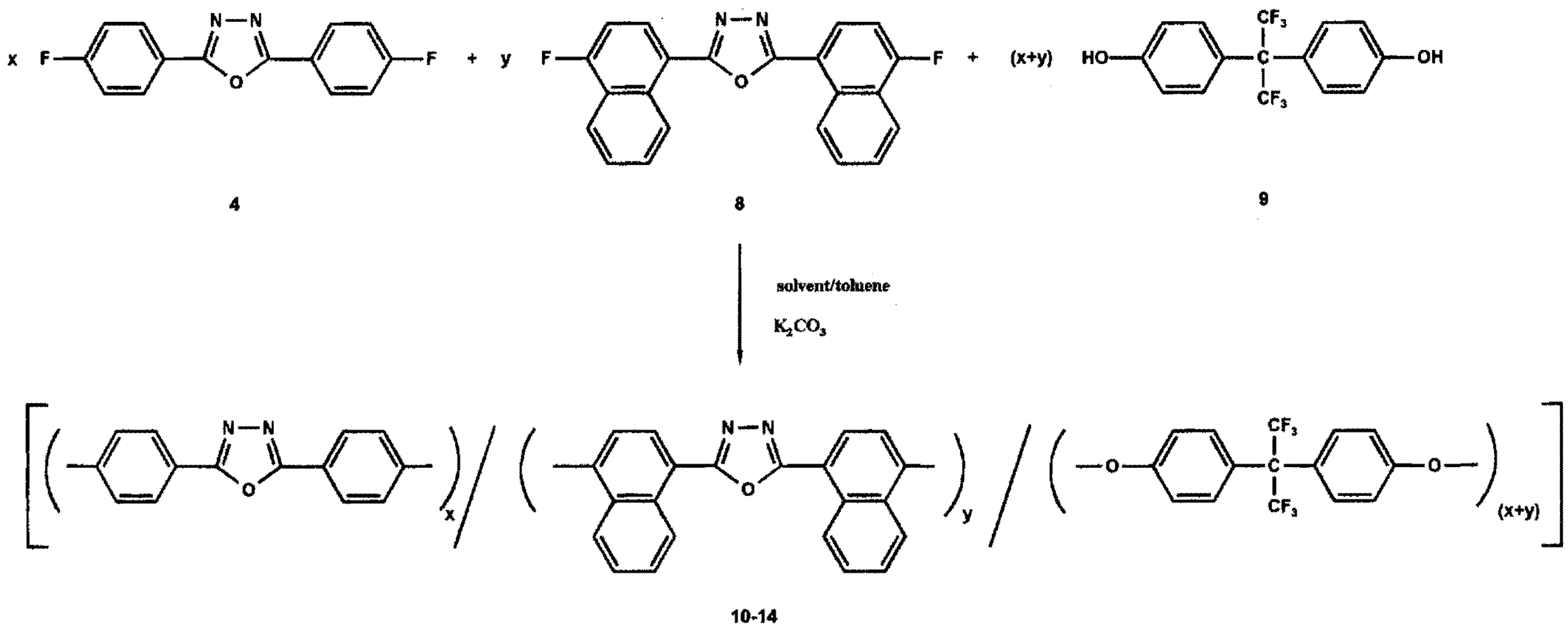
In order to create the nucleophilic phenoxide from 2,2-bis(4-hydroxyphenyl)hexafluoropropane a suitable base has to be added to the reaction mixture. The synthesis of poly(aryl ethers) is in most cases performed in the presence of K_2CO_3, because the weaker base reduces the number of side reactions and higher molecular weight reaction products are obtained with K_2CO_3 in contrast to alkali hydroxides.

The presence of water causes side reactions and a reduction of the molecular weight[9)]. Therefore toluene was added to the reaction mixture to remove the water generated by phenoxide formation by azeotropic distillation.

The choice of the solvent is decisive for the formation of the poly(aryl ethers). Both monomers and polymers must be soluble. Besides the stabilization of the Meisenheimer complex, formed as an intermediate, the halide elimination must be assisted by the solvent[10,11)]. Dipolar aprotic solvents are the best choice for polyether synthesis. Dimethyl sulfoxide (DMSO) is generally useful for temperatures up to 150 °C[7)]. Due to the moderate solubility of our oxadiazole monomers higher polymerization temperatures are required. When temperatures above 150 °C are necessary, the polycondensation is generally carried out either in amide solvents like NMP or DMPU[11,14)] or in Ph_2SO_2[29)]. We have synthesized several polyethers **10a–14c** with different ratios of bisphenyloxadiazole and bisnaphthyloxadiazole groups using NMP, DMPU and Ph_2SO_2 (Tab. 1). During polymerization the reaction mixture was slowly heated to 160 °C. After removing the water with a Dean-Stark trap the temperature was raised to 190–200 °C and maintained at this temperature for a certain time. When the polymerization is carried out in NMP or DMPU, the reaction mixture darkens within one hour and the reaction has to be terminated in order to avoid the formation of large amounts of by-products. After isolation and purification these polymers are still light brown. On the other hand the reaction mixture of the polymers obtained in Ph_2SO_2 is only slightly yellow even after a reaction time of 18 h and colourless polymers are achieved after purification.

A comparison of our aromatic polyethers shows that in the temperature range from 190–200 °C Ph_2SO_2 is a superior solvent compared to NMP and DMPU. This result is in contrast to Hedrick[11)], who observed no significant advantage preparing polymer **14** either in Ph_2SO_2 or in a *N*-cyclohexyl-2-pyrrolidone/NMP solvent mixture. The colour change during polymerization points out that side reactions occur in

Scheme 2: Synthesis of the oxadiazole containing polyethers **10–14**



Tab. 1. Reaction conditions for the synthesis of the oxadiazole polyethers **10–14**

Polyether	Content of bisnaphthyl monomer **8** in mol-%	Content of bisphenyl monomer **4** in mol-%	Solvent	Reaction temp. in °C	Reaction time in h
10a	100	0	Ph_2SO_2	190–200	18.5
10b	100	0	DMPU	190–200	0.5
10c	100	0	NMP	200	0.5
11a	80	20	Ph_2SO_2	190–200	18.5
11b	80	20	DMPU	190–200	2.5
12a	50	50	Ph_2SO_2	190–200	18.5
12b	51	49	DMPU	180	18
13a	20	80	Ph_2SO_2	190–200	18.5
13c	17	83	NMP	180	18
14a	0	100	Ph_2SO_2	190–200	18.5
14c	0	100	NMP	210	1

NMP and DMPU. So polyether **13c**, which was allowed to react in NMP for 18 h, is only partially soluble and has an extremely broad molecular weight distribution ($\overline{M}_w/\overline{M}_n = 26.8$). One explanation might be that the lactam rings are opened by the base. This leads to an incorporation of amines into the main chain of the polyethers. Such groups are missing in Ph_2SO_2, which is inert under the reaction conditions. As a consequence polymers with higher purity are obtained, which is confirmed by the chemical characterization.

The good agreements of the structure of polyethers **10a**, **11a**, **12a**, **13a** and **14a**, which were synthesized in Ph_2SO_2, with the desired structure could not only be shown by NMR- and FTIR spectroscopy but also in the elemental analysis. The calculated and experimentally found content of each element agree very well. The differences are less than 0.2%.

The intensity ratios in the NMR spectra of copolymers **11–13** showed that the bisphenyloxadiazole and bisnaphthyloxadizole content in the polyethers is the same as in the monomer mixture.

Characterization of the oxadiazole polyethers **10–14**

All polyethers are characterized by a good solubility. Polyethers **10a**, **11a**, **12a**, **13a**, **14a**, **13c** and **14c** are fully soluble in organic solvents like $CHCl_3$, THF, *N,N*-dimethylacetamide (DMAc), diglyme, cyclohexanone, chlorobenzene, NMP or DMPU. They are not soluble in 1,2,3-trichloropropane, acetone, methanol or hexane. On the other hand, polyethers **10b**, **10c**, **11b** and **12b**, prepared in amide solvents, are only partially soluble in THF and $CHCl_3$. A possible explanation of the different solubility might be the presence of oligomers in the polyethers synthesized in NMP and DMPU. We expect that the oligomers have a lower solubility than the polymer. With the exception of DMAc all solutions show excellent film forming properties. Homogeneous transparent films could be easily fabricated by spin-coating.

Tab. 2. Number- and weight-average molecular weights of the oxadiazole polyethers **10–14** determined by GPC[a] ($\overline{M}_n$, $\overline{M}_w$)

Polyether	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
10a	30000	83000	2.8
10b	3500	12500	3.6
10c	8100[b]	35000[b]	4.4[b]
11a	27000	94000	3.5
11b	2700	7500	2.8
12a	29000	130000	4.5
12b	5200[b]	14000[b]	2.7[b]
13a	37000	135000	3.6
13c	7900[b]	212000[b]	26.8[b]
14a	23000	50000	2.2
14c	16000[b]	63000[b]	3.9[b]

[a] $CHCl_3$ as eluent, polystyrene calibration, UV-detection at 254 nm.
[b] Eluent: THF.

The molecular weights were determined by gel permeation chromatography (GPC) using a polystyrene calibration and $CHCl_3$ or THF as eluent. Tab. 2 gives a survey of the molecular weights. The molecular weight of the polyethers strongly depends on the solvent in which the polymerisation is performed. Polyethers **10c**, **13c**, **14c** prepared in NMP have $\overline{M}_n$ in the range from 8000 to 16000, whereas $\overline{M}_n$ of the DMPU polyethers **10b**, **11b**, **12b** is in the range from 3000 to 5000. In contrast to this, polyethers from Ph_2SO_2 **10a**, **11a**, **12a**, **13a**, **14a** show a higher molecular weight. They have $\overline{M}_n$ between 23000 and 37000. Thus the use of Ph_2SO_2 instead of NMP or DMPU generally leads to polyethers with higher molecular weights. A comparison of the elution chromatograms of **10a** and **10b** (Fig. 1) shows another difference between the two solvent systems. Polymers derived from NMP respectively DMPU contain a large amount of oligomers, whereas oligomers are absent in the polyethers prepared in Ph_2SO_2.

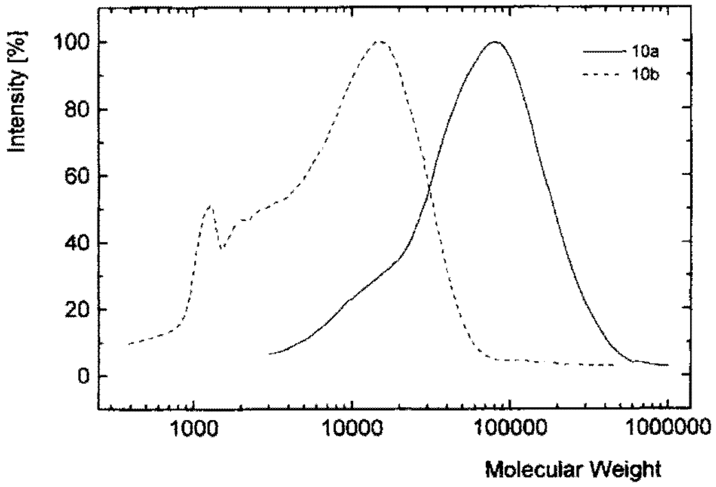


Fig. 1. GPC diagram of the oxadiazole polyethers **10a** (from Ph_2SO_2) and **10b** (from DMPU)

Tab. 3. Thermal and optical properties of the oxadiazole polyethers **10–14**

Polyether	T_{dec}/°C[a]	$T_{10\%}$/°C[b]	T_g/°C[c]	ABS[d] λ_{max}/nm	FL[e] λ_{max}/nm
10a	436	468	229	345	427
10b	412	460	213	348	429
10c	415	462	220	347	434
11a	431	473	225	347 (316)	425
11b	413	455	207	347 (318)	461
12a	434	477	219	303 (350)	423
12b	412	469	207	305 (350)	467
13a	438	489	214	299 (349)	419
13c	377	470	200	300 (350)	462
14a	446	499	202	299	360
14c	446	494	204	297	378

[a] Thermogravimetric analysis, onset of decomposition in N_2, 10 °C/min.
[b] Thermogravimetric analysis, 10% weight loss in N_2, 10 °C/min.
[c] Glass transition temperature determined by DSC, second heating, 10 °C/min.
[d] Absorption (ABS), films on quartz substrates, layer thickness: ≈70 nm.
[e] Fluorescence (FL), films on quartz substrates, layer thickness: ≈70 nm. Excition wavelength corresponds to the absorption maximum.

All oxadiazole polyethers are characterized by high thermal stability, which is important for an application in organic LEDs. Thermogravimetric analysis (TGA) shows that the stability is in the range for other oxadiazole polyethers described in the literature[8,11,14]. In most cases the onset of decomposition is in the range from 410 to 450 °C (Tab. 3). The onset of decomposition and the 10% weight loss temperatures are generally higher for polyethers **10a**, **11a**, **12a**, **13a**, **14a** derived from Ph_2SO_2 compared to polyethers **10b**, **10c**, **11b**, **12b**, **13c**, **14c** synthesized in NMP and DMPU.

The differential scanning calorimetry (DSC) investigation of the polyethers shows only glass transitions for all polyethers. No melting or crystallization is detected. The polyethers have glass transition temperatures in the range from 200 to 230 °C. The comparison of the polyethers shows that the glass transition temperature increases with increasing content of the bisnaphthyloxadiazole units. This is a consequence of the increased chain stiffness resulting from the bulky chain segments. Polyethers **10a**, **11a**, **12a**, **13a** polymerized in Ph_2SO_2, have higher glass transition temperatures as the polyethers derived from NMP and DMPU. The glass transition temperature for polyether **10c** prepared in NMP is 220 °C, whereas polyether **10b** prepared in DMPU has a glass transition temperature of 213 °C. Polyether **10a** derived from Ph_2SO_2 shows the highest glass transition (229 °C).

The absorbance maxima of bisnaphthyloxadiazole polyethers **10a**, **10b**, **10c** are between 345–348 nm, whereas polyethers with bisphenyloxadiazole units like **14a** have their absorbance maximum at 299 nm. The bisnaphthyloxadiazole group leads to a bathochromic shift as a consequence of an increase in π-conjugation. The copolymers show a superposition of both spectra, in which a maximum and a shoulder

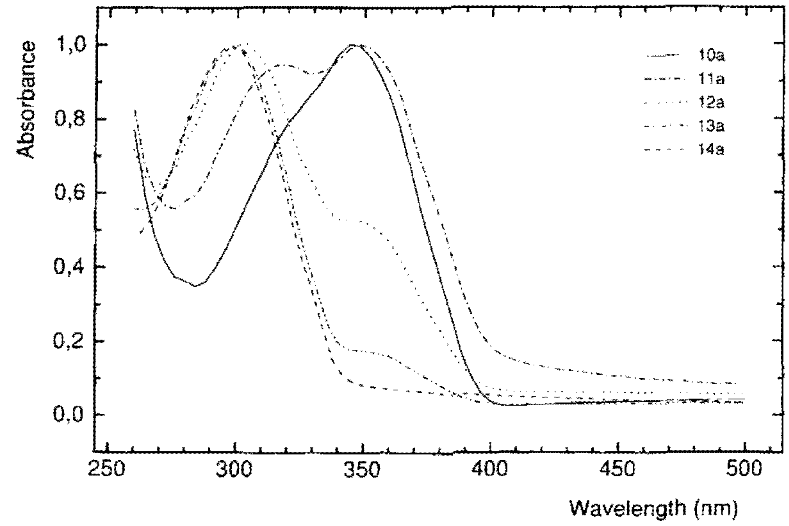


Fig. 2. UV spectra of the oxadiazole polyethers **10a**, **11a**, **12a**, **13a**, **14a** (all spectra recorded from films on quartz substrates, layer thickness: 70 nm)

can be detected depending on the content of the bisphenyloxadiazole and bisnaphthyloxadiazole groups (Fig. 2). The fluorescence spectra show the same trend. In the spectrum of **14a**, only the fluorescence of the bisphenyloxadiazole chromophores at 360 nm is detectable. In comparison, polyether **10a** exhibits a bright blue fluorescence with a maximum at 427 nm. The fluorescence maxima of the copolymers **11a**, **12a**, **13a** from Ph_2SO_2 are, even at low bisnaphthyloxadiazole content, similar to the bisnaphthyloxadiazole homopolymer **10a** (Fig. 3). An increasing bisphenyloxadiazole content effects only a small hypochromic shift of the emission

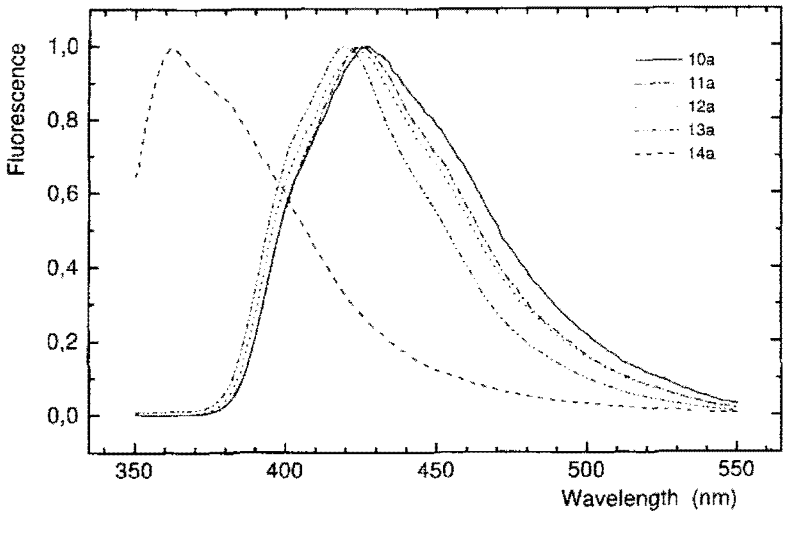


Fig. 3. Fluorescence spectra of the oxadiazole polyethers **10a**, **11a**, **12a**, **13a**, **14a** (all spectra recorded from films on quartz substrates, layer thickness: 70 nm)

maximum. Polyether **11a** with 20% bisphenyloxadiazole units has a fluorescence maximum at 425 nm. An increase of the bisphenyloxadiazole content to 80% in polyether **13a** shifts the fluorescence maximum only to 419 nm.

Properties of light emitting diodes containing oxadiazole polyethers

In order to test the applicability of these materials as electron injection and transport material for polymeric LEDs, we have investigated current-voltage (I-V) characteristics and electroluminescence (EL) intensity of heterolayer devices with PPV as the hole transport and emission layer.

Fig. 4 shows I-V characteristics and light intensity of the PPV single layer LEDs compared to the heterolayer devices with the oxadiazole polyethers **10a**, **12a** and **14a** containing 100, 50 and 0% bisnaphthyloxadiazole units, respectively. The PPV single layer devices show a Schottky diode behaviour with an exponential current rise for voltages above 2 V and the onset for electroluminescence at about 3 V. However, since PPV Schottky diodes are majority carrier devices (with holes as the majority carriers), there is a strong imbalance in the number of injected holes and electrons resulting in very low electroluminescence quantum efficiencies of less than 10^{-3}% (for Al as the electron injecting contact)[30]. In the PPV/oxadiazole heterolayer devices the large hole current in forward direction is reduced due to an offset in the HOMO levels of PPV and the oxadiazole polyethers, which acts as a hole barrier[31]. The onset for electroluminescence is shifted to higher voltages, but, as can be seen from Fig. 5, light emission is detected already at much lower currents and the maximum achievable brightness before degradation is almost two orders of magnitude higher than in the single layer device. With the best heterolayer devices we have achieved external quantum efficiencies of about 0.1% and a luminance of

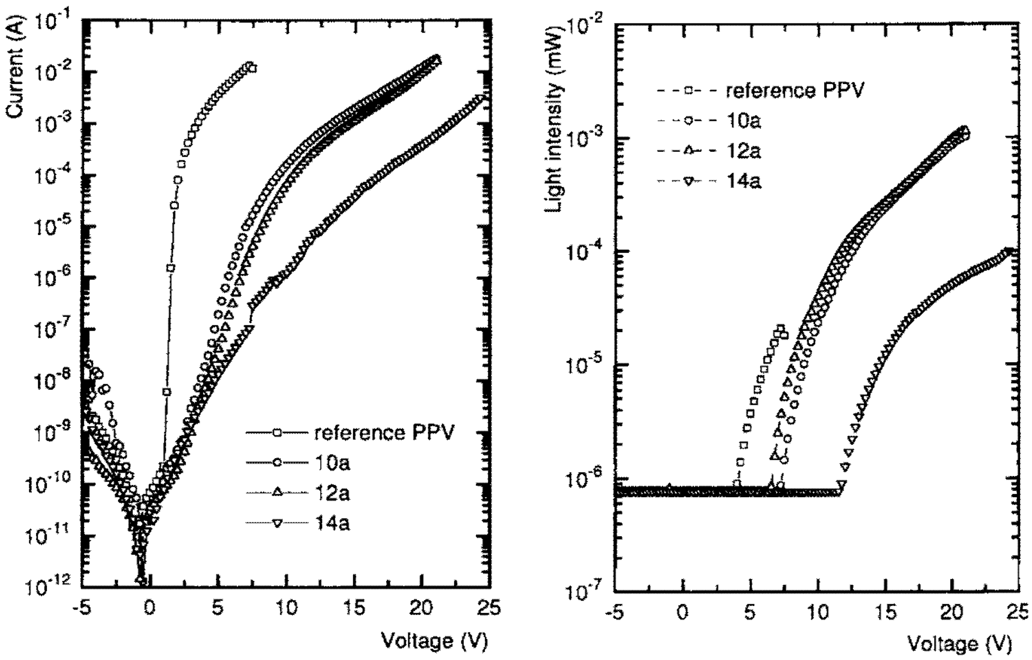


Fig. 4. I-V characteristics and light intensity of ITO/PPV/Al single layer and ITO/PPV/oxadiazole polyether/Al heterolayer LEDs (layer thickness: PPV 200 nm, oxadiazole polyether 30 nm; device area: 0.25 cm^2)

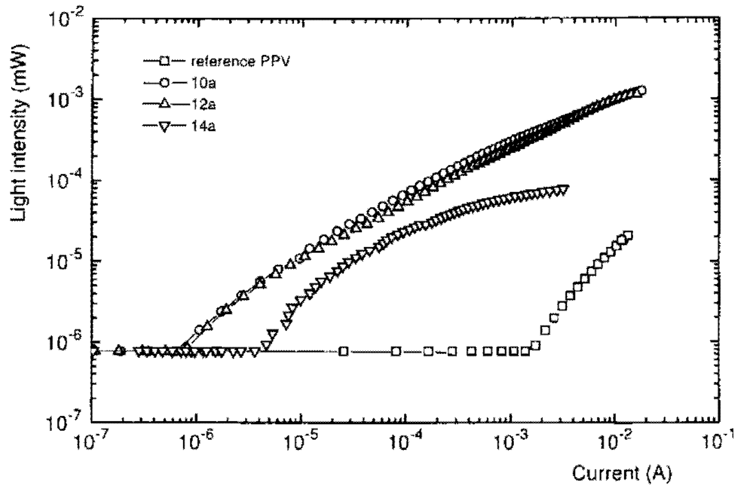


Fig. 5. Light intensity versus current calculated from the curves of Fig. 4; the light intensity divided by the current is proportional to the external quantum efficiency

several hundred cd/m^2. This clearly shows the improved electron injection and transport properties in PPV/oxadiazole polyether devices.

The comparison of the oxadiazole polyethers **10a**, **12a** and **14a** with different content of bisnaphthyloxadiazole and bisphenyloxadiazole units in Figs. 4 and 5 yields comparable onset voltage (about 6 V) and brightness for polyethers **10a** and **12a** containing bisnaphthyloxadiazole units. The curves for polyether **11a** and **13a** containing 80 and 20% bisnaphthyloxadiazole units have been omitted for reasons of lucidity. Polymer **14a** containing only bisphenyloxadiazole units however has a significantly higher turn-on voltage (11.5 V) and a lower brightness. The same result was also obtained using Ca as cathode material.

Thus we conclude that for good electron injection and transport properties in PPV heterolayer LEDs oxadiazole polyethers with bisnaphthyloxadiazole units are necessary. The content of the bisnaphthyloxadiazole units (from 20 to 100%) has no significant influence on the LED performance.

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