Synthesis and Characterization of Aromatic Poly(1,3,5-triazine−ether)s for Electroluminescent Devices

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ABSTRACT: Various difluoro functionalized aromatic 1,3,5-triazine monomers were prepared. A series of poly(1,3,5-triazine−ether)s was synthesized by polycondensation with 4,4′-hexafluoroisopropylidene-bis[phenol]. The polymers have excellent thermal stability and are amorphous with glass transition temperatures in the range 190−250 °C. In order to examine the potential application these polymers may possess for use in organic electroluminescent devices, the redox properties were studied by cyclic voltammetry. It was found that the monomers have high electron affinities and reach LUMO values in the range of −2.7 to −3.1 eV. This opens the possibility to utilize 1,3,5-triazine-containing materials as electron injecting/hole blocking layer in LEDs. Initial LED results are in accordance with these high electron affinities.

Introduction

In the past, significant synthetic effort has been devoted to the development of light emitting devices (LEDs) based on low molar mass[1−4] and polymeric organic materials.[5−11] For example, semiconducting conjugated polymers such as poly(*p*-phenylenevinylene) (PPV) or triphenylamine derivatives in combination with suitable emitters such as tris(8-quinolinolato)aluminum (Alq3) were utilized. A balanced charge injection, transport of both holes and electrons, and the confinement of the recombination zone away from the electrodes are needed for high durability and efficiency of the device. Both PPV and triphenylamine derivatives favor hole injection and transport. Consequently in two-layer devices a hole blocking/electron transporting layer (ETL) on top of a hole transport layer (HTL) has improved the efficiency to a large extent.[8,12] The materials employed in most applications are low molar mass or polymeric oxadiazoles,[6−8,13] triazoles,[4,6,7] and, recently, quinoxalines.[14]

In this paper we report the synthesis of polymeric 1,3,5-triazines (s-triazines) as hole blocking/electron transport layers for application in multilayer LEDs. Various aromatic polyethers containing 1,3,5-triazine units have been prepared. Because of the high electron affinity and structural symmetry of the s-triazine units, electron injection and transport should be favored. In order to determine the electrochemical behavior, cyclovoltammetry was used. The CV measurements of the monomers were carried out in acetonitrile in the presence of 0.1 M tetrabutylammonium hexafluorophospate (TBAPF) as conducting salt with ferrocene as internal standard.[18,19] The monomers have high electron affinities and reach LUMO values up to −3.1 eV. The poly(1,3,5-triazine−ether)s were synthesized via a nucleophilic substitution reaction. In all cases 4,4′-hexafluoroisopropylidenebis[phenol] (hexafluoro−Bisphenol A) was used in order to enhance the polymer solubility. The chemical structure of the synthesized polyethers is shown in Chart 1.

Chart 1. Chemical Structures of the Synthesized Aromatic Poly(1,3,5-triazine−ether)s
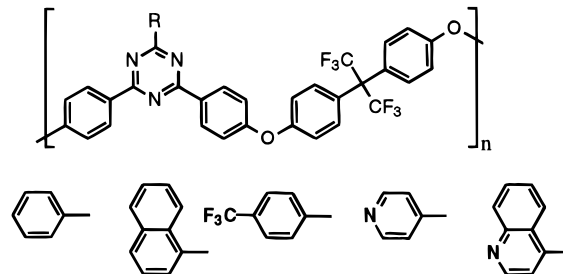
Initial results of two-layer devices reveal that the high electron affinities of the poly(triazines) improve the efficiency of the LED.

Materials and Methods

Materials. The reagents (Aldrich and Lancaster) for the monomer synthesis were used as received. The solvents (ethanol, benzene, DMF) were freshly distilled and dried using common methods.[17] *N*-Benzylideneaniline (**1a**) was purchased (Aldrich) as was diphenyl sulfone 99+% (Lancaster). 4,4′-Hexafluoroisopropylidenebis[phenol] (hexafluoro−Bisphenol A) (Aldrich) was sublimed under reduced pressure (160−190 °C, 10^{-6} mbar).

Monomer Synthesis. *N*-(4-Trifluoromethyl)benzylidene)aniline (1b), *N*-(4-Pyridylidene)aniline (1c), *N*-(1-Naphthylidene)aniline (1d) and *N*-(6-Quinolylidene)-aniline (1e). Aniline and the corresponding aldehyde were added in stochiometric amounts to chloroform and refluxed for 4 h in a Dean−Stark apparatus. From the resulting yellow solutions the solvent was removed using a rotary evaporator. In all cases the purity was already sufficient for the following synthesis step. The yields for these reactions were in all cases almost quantitative.

^{1}H-NMR (CDCl₃): (**1b**) δ = 8.75 (1H, s), 8.75 (2H, d), 7.80 (2H, d), 7.30 (5H, m); (**1c**) δ = 8.75 (2H, d), 8.45 (1H, s), 7.70 (2H, d), 7.30 (5H, m); (**1d**) δ = 9.10 (1H, s), 9.05 (1H, d), 8.10 (1H, d), 7.95 (1H, d), 7.90 (1H, d), 7.55 (3H, m), 7.35 (5H, m); (**1e**) δ =9.10 (1H, s), 9.00 (1H, d), 8.85 (1H, d), 8.15 (1H, d), 7.90 (1H, d), 7.75 (1H, t), 7.60 (1H, t), 7.40 (5H, m)

4-Fluorobenzamidine−Hydrochloride (2). 4-Fluorobenzonitrile (200 mmol) and ethanol (205 mmol) were dissolved in 100 mL of benzene. Through this solution dry hydrochloric acid was purged for 40 min. After an additional 3 h of stirring at room temperature the solution was added dropwise to

diethyl ether (1:100 by volume) to precipitate the product. The solid 4-fluorobenzimidoethyl ether hydrochloride was filtered and dried at reduced pressure. Yield: 52%.

This 4-fluorobenzimidoethyl ether hydrochloride (100 mmol) was dissolved in 250 mL of ethanol. Dry ammonia was bubbled through the solution for 20 min. The mixture was heated to 50 °C until a clear solution was obtained. Finally, the solvent was completely removed at reduced pressure. Yield: 98%.

^{1}H-NMR (DMSO): δ = 9.35 (4H, s), 7.95 (2H, m), 7.50 (2H, m).

Mp: 104°C.

4,4′-Difluoro-2,4,6-triphenyl-1,3,5-triazine (3a), 4,4′-Difluoro-2,4-diphenyl-6-(1-naphthyl)-1,3,5-triazine (3b), 4,4′-Difluoro-4″-(trifluoromethyl)-2,4,6-triphenyl-1,3,5-triazine (3c), 4,4′-Difluoro-2,4-diphenyl-6-(6-pyridyl)-1,3,5-triazine (3d), and 4,4′-Difluoro-2,4-diphenyl-6-(6-quinolyl)-1,3,5-triazine (3e). A 50 mmol sample of 4-fluorobenzamidine and 23 mmol of the corresponding anilidene were dissolved in 40 mL of DMF and heated for 24 h at 80 °C. After the reaction mixture was cooled to room temperature, the product was precipitated by dropwise addition to a 100-fold excess of methanol. The product was filtered and dried at reduced pressure. For further purification the products were sublimed (220−290 °C; 10^{-6} mbar). Yields after sublimation: (**3a**) 23%; (**3b**) 34%; (**3c**) 49%; (**3d**) 21%; (**3e**) 44%.

^{1}H-NMR (C$_2$D$_2$Cl$_4$ or CDCl$_3$): (**3a**) δ = 8.65 (6H, m), 7.55 (3H, m.), 7.20 (4H, m); (**3b**) δ = 9.15 (1H, d), 8.75 (4H, d), 8.50 (1H, d), 8.05 (2H, 2d), 7.65 (3H, m) 7.20 (4H, m); (**3c**) δ = 8.75 (6H, m), 8.00 (2H, d), 7.45 (4H, m); (**3d**) δ = 8.85 (2H, d), 8.70 (4H, d), 8.50 (2H, d),7.20 (4H, m); (**3e**) δ = 9.15 (1H, d), 9.00 (1H, d), 8.65 (4H, m), 8.21 (2H, d), 7.65 (2H, m), 7.15 (4H, m).

FT-IR (KBr): (**3a**) 3065 (arom), 1604 (C=N, C=C), 1522 cm^{-1} (C=N, C=C); (**3b**) 3065 (arom), 1602 (C=N, C=C), 1524 cm^{-1} (C=N, C=C); (**3c**) 3065 (arom), 1590 (C=N, C=C), 1526 cm^{-1} (C=N, C=C); (**3d**) 3064 (arom), 1601 (C=N, C=C), 1521 cm^{-1} (C=N, C=C); (**3e**) 3067 (arom), 1603 (C=N, C=C), 1518 cm^{-1} (C=N, C=C).

MS (70 eV), m/z: (**3a**) 345 (M$^+$), 121 (C$_6$H$_4$(CN)F), 103 (C$_6$H$_4$CN); (**3b**) 395 (M$^+$), 300 (M$^+$ − C$_6$H$_4$), 273 (M$^+$ − C$_6$H$_4$(CN)F); (**3c**) 413 (M$^+$), 121 (C$_6$H$_4$(CN)F); (**3d**) 346 (M$^+$), 251 (M$^+$ − C$_6$H$_4$F), 224 (M$^+$ − C$_6$H$_4$(CN)F) ; (**3e**) 396 (M$^+$), 301 (M$^+$ − C$_6$H$_4$F), 274 (M$^+$ − C$_6$H$_4$(CN)F).

Mp: (**3a**) 254 °C; (**3b**) 224 °C; (**3c**) 189 °C; (**3d**) 267 °C; (**3e**) 219 °C.

Polymer Synthesis. Equivalent amounts of difluoro-s-triazine (3 mmol), **3a−e**, and hexafluoro−Bisphenol A (3 mmol) and 0.6 g of potassium carbonate were dissolved in 30 g of diphenyl sulfone and 60 mL toluene. The water formed during the reaction was removed using a Dean−Stark trap with toluene. Finally, toluene was distilled off and the reaction mixture was heated for additional 12 h at 190 °C. After the reaction cooled to room temperature, 100 mL of NMP and 3 mL of 2 N HCl were added, and the mixture was heated to reflux and cooled to room temperature. The polyethers were purified by reprecipitation in methanol and extracted with acetone (**4a−e**). The yields ranged from 85 to 95%.

^{1}H-NMR: (**4a**) δ = 8.65 (6H; m), 7.55 (3H, m), 7.35 (4H, d), 7.15 (4H, d), 7.05 (4H, d); (**4b**) δ = 9.05 (1H, d), 8.70 (4H, d), 8.45 (1H, d), 8.00 (1H, d), 7.90 (1H, d), 7.55 (1H, m), 7.40 (4H, d), 7.15 (4H, d), 7.05 (4H, d); (**4c**) δ = 8.70 (6H, m), 7.70 (2H, d), 7.30 (4H, d), 7.15 (4H, d), 7.05 (4H, d); (**4d**) δ = 8.80 (2H, d), 8.70 (4H, m), 8.50 (2H, d), 7.40 (4H, m), 7.15 (4H, d), 7.05 (4H, d); (**4e**) δ = 9.05 (1H, d), 9.00 (1H, d), 8.70 (4H, d), 8.20 (2H, d), 7.75 (1H, t), 7.65 (1H, t), 7.40 (4H, d), 7.15 (4H, d), 7.05 (4H, d).

FT-IR (KBr): (**4a**) 3065 (arom), 1601 (C=N, C=C), 1523 (C=N, C=C), 1366, 1242, 1163, 823 cm^{-1}; (**4b**) 2992 (arom), 1596 (C=N, C=C), 1520 (C=N, C=C), 1369, 1247, 1173, 828 cm^{-1}; (**4c**) 3064 (arom), 1597 (C=N, C=C), 1519 (C=N, C=C), 1370, 1251, 1171, 821 cm^{-1}; (**4d**) 2940 (arom), 1604 (C=N, C=C), 1451 (C=N, C=C), 1208, 1174, 815 cm^{-1}; (**4e**) 3060 (arom), 1600 (C=N, C=C), 1501 (C=N, C=C), 1366, 1246, 1172, 823 cm^{-1}.

Characterization Methods and Measurements. IR: BioRad Digilab FTS-40 (FT-IR). NMR: Bruker AC 250 (250

Table 1. Molecular Weight and Thermal and Optical Properties of Poly(1,3,5-triazine−ether)s 4a−e

R:					
	8a	**8b**	**8c**	**8d**	**8e**
M_n [g/mol] (PS-standard)	26*10^3	18*10^3	5*10^3	6*10^3	23*10^3
T_g [°C]	241	247	193	186	232
TGA [°C] (N$_2$)	466	486	432	431	469
$\lambda_{abs;max}$ [nm]	293	304	301	305	309
$\lambda_{Fl;max}$ [nm]	--	411	--	--	486
Solubilty*	**8a**	**8b**	**8c**	**8d**	**8e**
CHCl$_3$	--	+/-	+/-	+/-	+/-
THF	+	+	+	--	+
NMP	+	+	+	+	+
Cyclohexanon	+	+	+	+/-	+

*: 5mg/1ml; + soluble, +/- partially soluble, --, insoluble

MHz). GPC: Waters 510 (UV- and RI-detector; PS-standard, eluent THF). DSC: Perkin-Elmer DSC 7 (heating rate: 10K/min), N$_2$ purged. UV/vis: Hitachi U-3000 (films on quartz substrate). Fluorescence: Shimatsu RF 5301 PC (films on quartz substrate). TGA: Netsch STA 409C (heating rate: 10 K/min, nitrogen atmosphere). Cyclic voltammetry: EG&G Princeton Applied Research (Acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate, Ag/AgCl (reference electrode), ferrocene/ferrocenium (internal standard). Electroluminescence: Keithley 2000 multimeter (current), SMT ME 305F (photo multiplier), luminescence values in cd/m^2 were calculated from calibrated photo multiplier data using a Luminometer Minolta LS 100. Film thickness: Dektak 3030 ST.

LED Preparation. The soluble polymeric PPV precursor tetrahydrothiopheneum chloride was synthesized according to a known synthetic route.[20] This PPV precursor was solution cast (draw bar coating) on an ITO/glass substrate (30 Ω/cm^2 sheet resistance) as anodic contact and eliminated at 180 °C under exposure to air for 2 h resulting in a 100 nm thick film. The poly(1,3,5-triazine−ether) **4e** was cast (draw bar coating) from a 0.3% by weight solution in cyclohexanone forming a 100 nm film. Aluminum contacts were vapor deposited at 10^{-6} mbar, giving approximately a 300 nm cathodic contact.

Results and Discussion

Aromatic triazine-containing polymers are known as thermostable polymers.[15] The synthesis of asymmetrically substituted bifunctional triazine monomers was carried out by the reaction of anilidene derivatives (**1a−e**) and 4-fluorobenzamidine (**2**) according to Scheme 1.[16] In order to influence the electron affinities, five different substituents (phenyl, naphthyl, (trifluoromethyl)phenyl, pyridyl, and quinolyl substituents) were attached to the 1,3,5-triazine core.

The polyethers **4a−e** were synthesized by a nucleophilic displacement reaction (Scheme 2) using difluoro-1,3,5-triazine derivatives (**3a−e**) and hexafluoro−Bisphenol A in diphenyl sulfone in presence of potassium carbonate at 190 °C. All polymers were obtained in good yields and characterized by spectroscopical methods (^{1}H-NMR, FT-IR, UV/vis, and fluorescence spectroscopy), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). Table 1 summarizes the chemical and physical properties of the obtained polyethers **4a−e**.

Scheme 1. Synthesis of Difluoro-1,3,5-triazine Monomers 3a−e

R

R			F$_3$C—		
	a	**b**	**c**	**d**	**e**
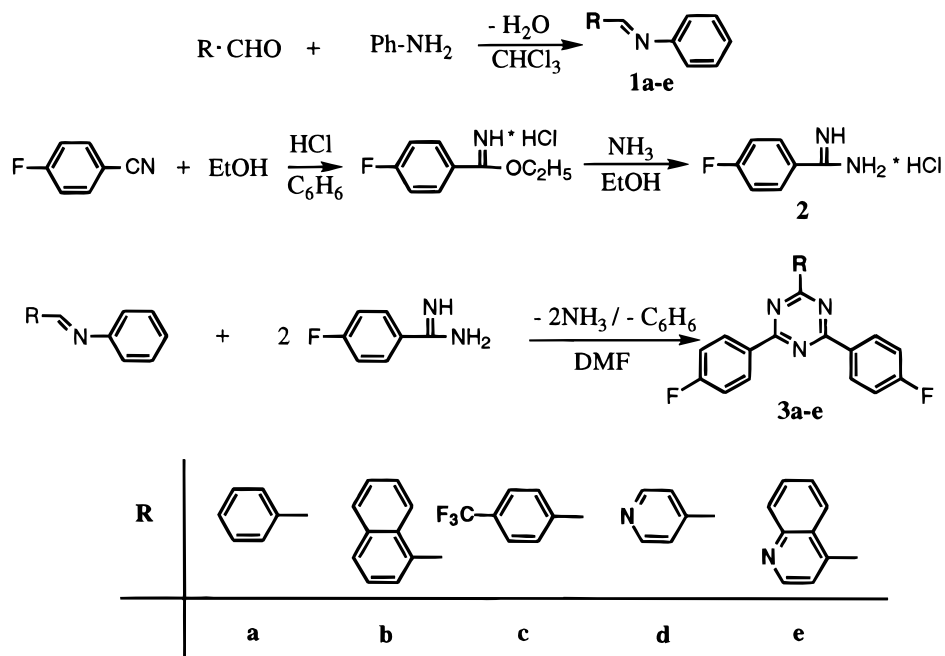
Scheme 2. Synthesis of Poly(1,3,5-triazine−ether)s

R			F$_3$C—		
	a	**b**	**c**	**d**	**e**
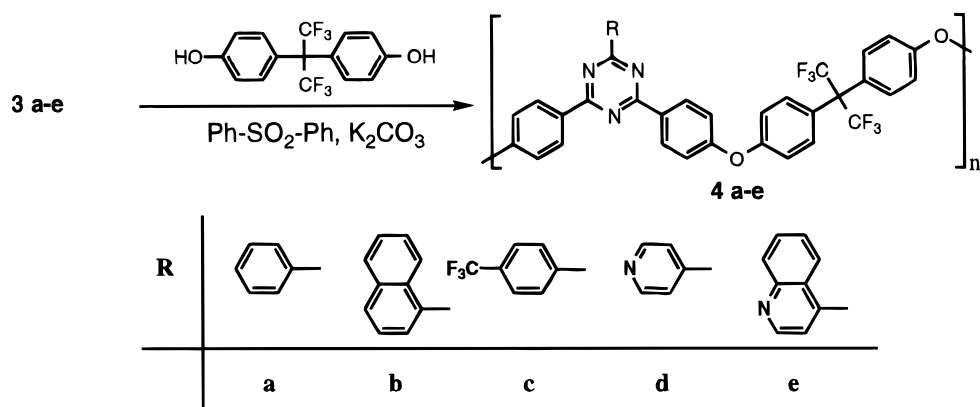
All polymers with the exception of **4c** and **4d** have molecular weights between 18 000 and 26 000 and show molecular weight distributions (M_w/M_n) between 2 and 4. The lower molecular weights of polymer **4c** and **4d** is because of precipitation during the polymerization reaction (Table 1).

Glass transition temperatures determined by DSC (heating/cooling rate: 10 K/min) are in the range of 193−247 °C. As shown in Figure 1, no additional melting transition is observed. The highest glass transition temperature was found for the polymer with the 1-naphthyl substituent. Thermal stabilities of these polyethers were measured by thermogravimetric analysis (Figure 2) under nitrogen atmosphere with a heating rate of 10 K/min. All polymers have similar thermal stability and show no weight loss up to 430 °C. The highest thermostabilities were exhibited by polymers **4b** and **4e** at 486 and 469 °C, which is in correspondence to a higher molecular weight and consequently a smaller number of end groups. The lower degree of polymerization of polymers **4c** and **4d** results in lower thermostabilities (432 and 431 °C) and thus lower glass transition temperatures (193 and 186 °C). The polymers do not show absorption in the visible region. Their absorption maximum is in the range of 293−309 nm. In case of the polymers **4b** and **4e**, an additionally weak
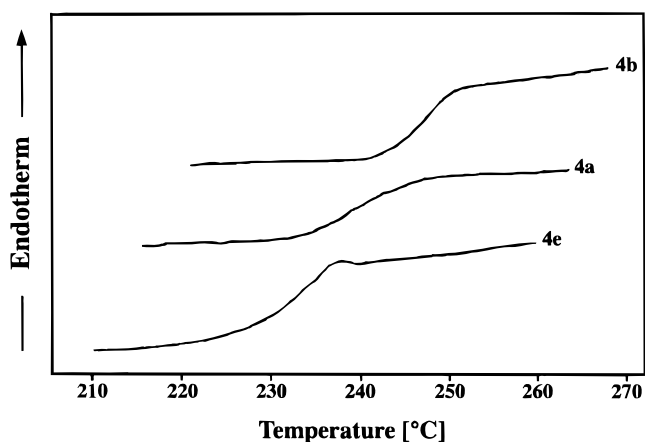

Figure 1. DSC heating curves of polymers **4a**, **4b** and **4e** (10 K/min; N$_2$ purged).

solid state fluorescence in the blue region is observable. This is due to naphthyl (**4b**) and quinolyl (**4e**) substituents, increasing the aromaticity of the system. All polymers are soluble in NMP with exception of **4d**, which is soluble in cyclohexanone. The solubilities are sufficiently high to prepare uniform films by spin coating or other solution casting techniques.

Table 2. Cyclic Voltammetry Results for 1,3,5-Triazine Monomers 3a−e

	OXD[a]	TRZ[b]	3a	3b	3c	3d	3e
E_{RED} (V) (vs Ag/AgCl)	−2.09	−1.65	−1.63	−1.59	−1.44	−1.44	−1.31/−1.59[c]
E_{RED} (V) (vs FOC)	−2.54	−2.09	−2.09	−2.00	−1.90	−1.84	−1.70/−1.98[c]
LUMO (eV)	−2.26	−2.71	−2.71	−2.80	−2.90	−2.96	−3.10/−2.82[c]

[a] 2,5-Diphenyl-1,2,4-oxadiazole. [b] 2,4,6-Triphenyl-1,3,5-triazine. [c] Second reversible reduction.
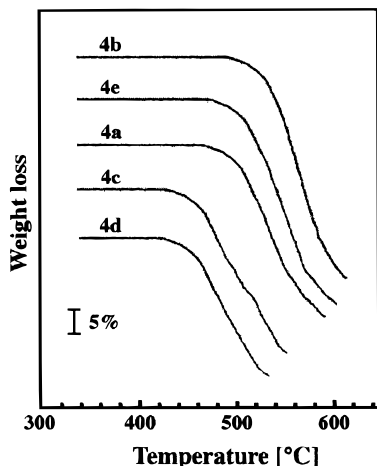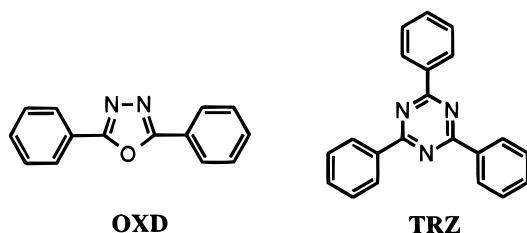

Figure 2. Thermogravimetric analysis (TGA; N₂, 10 K/min) of polyethers **4a−e**.

Chart 2. Chemical Structures of the Model Compounds: 3,5-Diphenyl-1,2,4-oxadiazole (OXD) and 2,4,6-Triphenyl-1,3,5-triazine (TRZ)

Cyclic Voltammetry. In order to study the redox behavior of the triazines, cyclic voltammetry was utilized. The measurements were carried out on a Pt electrode in acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as the conducting salt using a three-electrode cell and potentiostat assembly. The potentials were measured using Ag/AgCl as reference electrode. Each measurement was done with an internal standard ferrocene/ferrocenium (FOC) as described in the literature.[18] The LUMO energy values were calculated using the FOC value of −4.8 eV and are given as negative values with respect to the vaccum level which is defined as zero. The reduction potentials and the LUMO values are listed in Table 2.[19] For example the model compound 2,4,6-triphenyl-1,3,5-triazine (**TRZ**; Chart 2) has a reversible reduction potential at −1.65 eV vs Ag/AgCl. FOC shows an oxidation potential at 0.44 V vs Ag/AgCl which gives rise to a reduction potential of **TRZ** vs FOC of −2.09 V. Assuming the value of −4.8 eV for FOC, **TRZ** has a LUMO of −2.71 eV [= −4.8 + 2.09].[19] The cyclic voltammograms of compounds **3a** and **3e** are shown in Figure 3.

The monomers **3a−d** and 2,4,6-triphenyl-1,3,5-triazine (**TRZ**) as a model compound undergo at least one reversible reduction. The monomer **3e** exhibits two reversible reductions due to the additional quinoline ring. Compared with 3,5-diphenyl-1,2,4-oxadiazole (**OXD**), which shows a reversible reduction at −2.09 V vs Ag/AgCl (corresponding to a LUMO value of −2.26
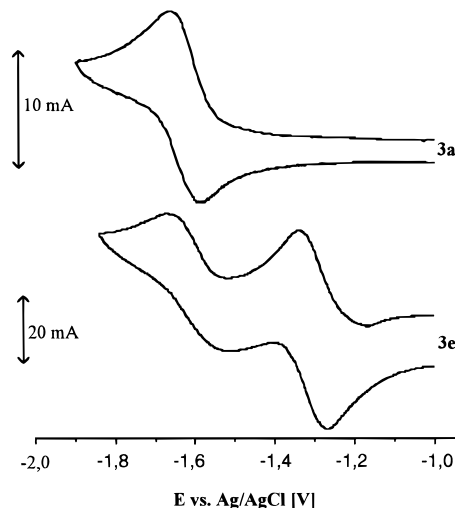

Figure 3. Cyclic Voltammograms of **3a−e**, measured at a Pt electrode in acetonitrile/0.1 M TBAPF at 100 mV/s.

eV), the triazines **3a−e** have lower LUMO values (−2.7 to −3.1 eV). The gradual decrease in LUMO values from **3a−e** implies that triazines are favorable for electron injection. A corresponding increase in electron affinity of the triazine ring with an increasing electron-withdrawing effect of the substituent is detectable in the series **3a−d**. A very low LUMO value of −3.1 eV is achieved in **3e** with a quinoline substituent. Comparing the reduction potentials of **TRZ** and **3a**, the influence of *p*-fluoro substitution can be neglected. The oxidation potentials of **3a−e** are higher than +2.0 V (vs Ag/AgCl) which corresponds to a HOMO higher than −6.4 eV. This leads to an additional "hole blocking" capability of the triazines.

LED Devices. Strukelj and co-workers have examined the applicability of various hole-blocking/electron-transporting materials such as polyoxadiazoles and polytriazoles in two-layer devices. A considerable improvement in device-performance was obtained using these materials.[6,7] As specific example, polymer **4e** having the lowest LUMO energy value was tested as a hole-blocking/electron-transporting material in a LED based on PPV. In a two-layer device consisting of poly(*p*-phenylene-vinylene) (PPV) as both a hole-conducting and emitting layer on an ITO (indium−tin oxide; 30 Ω/cm² sheet resistance) substrate and polymer **4e** as an electron-injecting/-transporting layer the performance is improved compared to a single layer PPV device (Figure 4a,b). The thickness of the hole-transporting and emitting material PPV is 100 nm, the thickness of the electron-transporting/hole-blocking polymer **4e** is 40 nm. It should be mentioned that these thicknesses are not optimized. The cathodic metal contact is aluminum with a thickness of 300 nm. This first result shows the hole blocking/electron injecting properties of poly(s-triazine) ethers in two aspects. In comparison the maximum light intensity of a PPV single layer to a two-layer LED with an additional triazine polymer is increased from 1 to 50 cd/m². Furthermore the current density at 1 cd/m² decreases from 5×10^{-2}
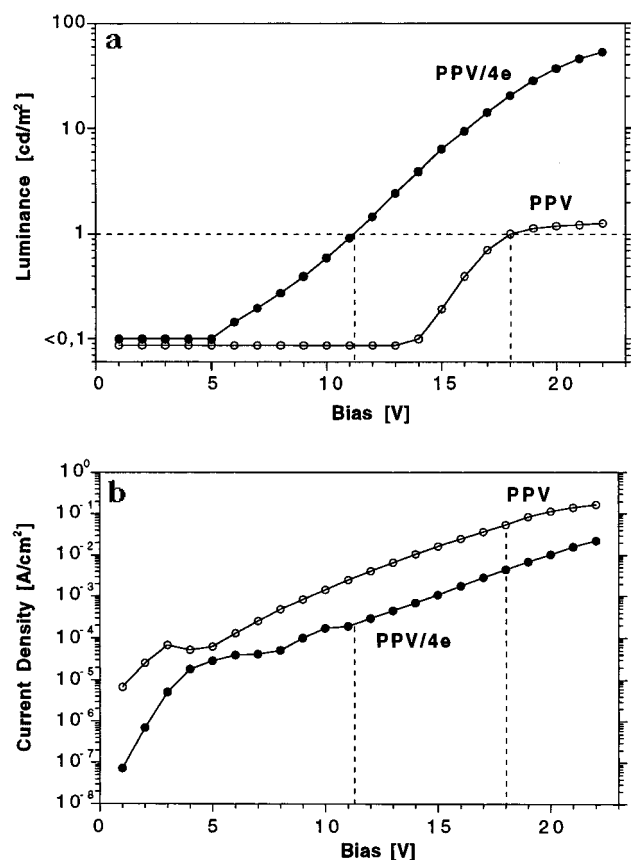
Figure 4. (a) Luminescence/voltage characteristics: (○) ITO/PPV (100 nm)/Al; (●) ITO/PPV (100 nm)/**4e** (40 nm)/Al. A Luminometer Minolta LS 100 was used; note that a luminescence values <0.1 cd/m^2 were not evaluated. (b) Current density/voltage characteristics: (○) ITO/PPV (100 nm)/Al; (●) ITO/PPV (100 nm)/**4e** (40 nm)/Al.

A/cm^2 (18 V) to 2×10^{-4} A/cm^2 ($\approx$11 V). Both increased light intensity and decreased current density leads to an improved efficiency. The further optimization and application of the polymers **4a**−**e** as electron materials in various LED configurations are under investigation and may be published elsewhere.

Conclusion

Various aromatic poly(s-triazine) ethers were synthesized and characterized. The polymers have high glass transition temperatures, are amorphous, and exhibit lower reduction potentials because of higher electron affinities compared to other hole-blocking/electron-transporting materials such as oxadiazoles. The lower reduction potentials and the higher oxidation potentials results in a decreased barrier for electron injection and an increased barrier for holes. These properties were revealed in a two-layer device using a s-triazine polyether as ETL and PPV as HTL and EML.

References and Notes

(1) Tang, C. W.; vanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
(2) Shirota, Y.; Kuwahara, Y.; Inada, H.; Wakimoto, T.; Wakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807.
(3) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *57*, 531.
(4) Kido, J.; Ohtaki, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L917.
(5) 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 (London)* **1990**, *347*, 539.
(6) Strukelj, M. J. *Science* **1995**, 267.
(7) Strukelj, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 11976.
(8) Buchwald, E.; Meier, M.; Karg, S.; Pösch, P.; Schmidt, H.-W.; Strohriegel, P.; Riess, W.; Schwoerer, M. *Adv. Mater. 7* **1995**, *7*, 839.
(9) Moratti, S. C.; Cerini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.; Grüner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117.
(10) von Seggern, H.; Schmidt-Winkel, P.; Zhang, C.; Schmidt, H.-W. *Macromol. Chem. Phys.* **1994**, 2023.
(11) Yang, Y.; Westerweele, E.; Zhang, C.; Smith, P.; Heeger, A.; *J. Appl. Phys.* **1995**, *77*, 694.
(12) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.
(13) Bettenhausen, J.; Strohriegel, P. *Adv. Mater.* **1996**, *8*, 507.
(14) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inone, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3939.
(15) Rossbach, V.; Oberlein, G.; In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Dekker Inc.: New York, 1992; Chapter 19. Solomon, D. H.; *Step-Growth Polymerizations*; M. Dekker: New York, 1972; Chapter 5.
(16) Borovik, V. P.; Mamaev, V. P. *Sib. Khim. Zh.* **1991**, *4*, 96.
(17) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed.; Pergamon Press: Oxford, England, 1988.
(18) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.
(19) The HOMO energy value of −4.8 eV for FOC was obtained from the calculated value of −4.6 eV for standard electrode potential for normal hydrogen electrode (NHE) (Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; p 634) on the zero vacuum level and the value of 0.2 V for FOC vs NHE (Koepp, H.-M.; Wendt, H.; Strehlow, H. *Z. Electrochem.* **1960**, *64*, 483.
(20) Gmeiner, J.; Karg, S.; Meier, M.; Riess, W.; Strohriegel, P.; Schwoerer, M. *Acta Polym.* **1993**, *44*, 201.

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