AROMATIC POLYETHERS WITH 1,3,5-TRIAZINE UNITS AS HOLE BLOCKING/ELECTRON TRANSPORT MATERIALS IN LEDs

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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)diphenol. The polymers have excellent thermal stability and are amorphous with glass transition temperatures in the range of 190-250°C. In order to examine the potential to apply these polymers in organic electroluminescent devices, the redox properties were studied by cyclic voltammetry. It was found that the monomers have high electron affinity 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. First LED results are in accordance to these high electron affinities.

INTRODUCTION

LEDs based on polymers have compared to inorganic LEDs primarly the advantage of an easy fabrication of large area devices utilizing well estabilshed solvent casting techniques. Polymeric materials for such devices have to fullfill various chemical and physical requirements. These are for example thermal and light stability, high glass transition temperatures, good film forming properties, easy injection of charges and sufficient charge mobility. In multilayer LED-devices the chemical and physical properties of a hole transport layer (HTL), an emission layer (EML) and an electron transport layer (ETL) have to be optimized and adjusted.

We report on the synthesis of polymeric 1,3,5-triazines (s-triazines) as hole blocking/electron transport layer for application in multilayer LEDs. Various aromatic

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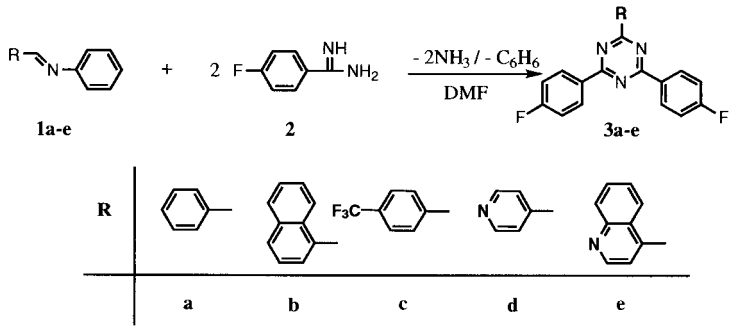
polyethers containing 1,3,5-triazine-units have been prepared. Due to the high electron affinity and structural symmetry of the s-triazine unit electron injection and transport should be favoured. In order to determine the electrochemical properties cyclovoltammetry was used.

RESULTS AND DISCUSSION

The synthesis of asymmetrically substituted bifunctional triazine monomers was carried out by the reaction of anilidene derivatives (**1a-e**) and 4-fluoro-benzamidine (**2**) according to Scheme 1. In order to influence the electron affinities five different substituents (phenyl-, naphthyl-, trifluoromethylphenyl-, pyridyl- and quinolyl-substituent) were attached to the 1,3,5-triazine core (**3a-e**).

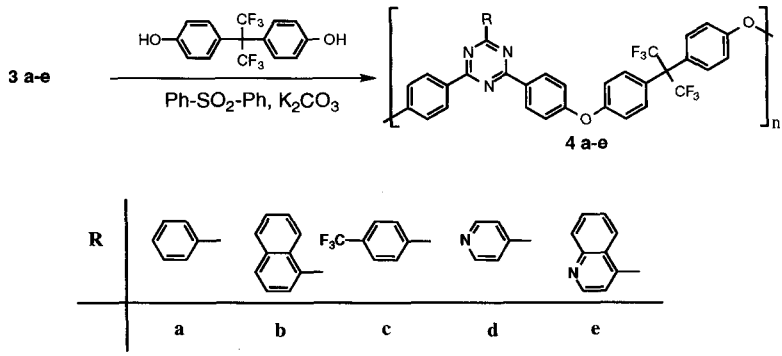
The polyethers **4a-e** were synthesized by a nucleophilic displacement reaction (Scheme 2) using difluoro-1,3,5-triazine derivatives (**3a-e**) and hexafluoro-bisphenol A in diphenylsulfone in presence of potassium carbonate at 190 °C (1). Table 1 summarizes the chemical and physical properties of the prepared polyethers **4a-e**.



Scheme 1: Synthesis of Difluorotriazine monomers 3a-3e

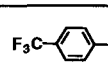
All polymers with exception of **4c** and **4d** have molecular weights ($\overline{M}_n$) between 18000-26000 g/mol and show molecular weight distributions ($\overline{M}_w/\overline{M}_n$) between 2 and 4. Glass transition temperatures determined by DSC (heating/cooling rate: 10 K/min) are in the range of 193-247 °C. Thermal stability of these polyethers were measured by thermogravimetric analysis under nitrogen atmosphere with a heating rate of 10 K/min. All polymers have similar thermostability and show no weight loss up to 430 °C. The highest thermostabilities exhibit polymer **4b** and **4e** with 486 °C and 469 °C which is in

correspondence to a higher molecular weight and consequently a smaller number of endgroups.



*Scheme 2: Synthesis of triazine containing polyethers **4a-4e***

*Table 1: Chemical and physical properties of the s-triazine polyethers (**4a-e**)*

R:					
	4a	4b	4c	4d	4e
$\overline{M}_n$ [a] [g/mol]	2,6x10^4	2,1x10^4	5,0x10^3	6,0x10^3	2,3x10^4
$\overline{M}_w$ [a] [g/mol]	3,2x10^4	6,0x10^4	1,6x10^4	7,3x10^3	9,4x10^4
$\overline{M}_w/\overline{M}_n$	1,2	2,9	3,2	1,2	4,1
T_g [b] [°C]	241	247	193	186	232
T_{Onset} [c] [°C]	466	486	432	431	469
$\lambda_{abs;max}$ [d] [nm]	293	304	301	305	309
$\lambda_{Fl;max}$ [d] [nm]	--	411	--	--	486

a) GPC (eluent THF; polystyrene standards)
b) second heating, heating rate 10 K/min
c) onset of weight loss, N_2-athmosphere, 10 K/min
d) film on quartz substrate

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

Cyclic Voltammetry

In order to study the redox behaviour of the triazines cyclic voltammetry was utilized. The measurements were carried out at a Pt-electrode in acetonitrile solutions containing 0.1 m tetrabutylamoniumhexafluorophosphate (TBAPF6) as conducting salt using a three electrode cell and potentiostat assembly. The potentials were measured versus Ag/AgCl as reference electrode. Each measurement was done with an internal standard Ferrocene/Ferrocenium (2).

It was found that the monomers have high electron affinity and reach LUMO values in the range of -2.7 to -3.1 eV. The comparison to 3,5-diphenyl-1,2,4-oxadiazole as an example for a different heteroaromatic electron deficient structure which shows a LUMO value of -2.26 eV the triazines **3a-e** have lower LUMO values. Additionally the oxidation potentials of **3a-e** are very high, corresponding to a HOMO lower than -6.4 eV. This leads to an "hole blocking" capability of the triazines. This opens the possibility to utilize 1,3,5-triazine containing materials as electron injecting and hole blocking layer in LEDs.

LED Devices

In a two layer device consisting of poly-p-phenylene vinylene (PPV) as a hole conducting and emitting layer on an ITO (indium-tin-oxide; 30 Ω/cm^2 sheet resistance) subtrate and polymer **4e** as an electron injecting/transporting layer, the performance is improved compared to a single layer PPV device (Fig. 1). The thickness of the hole transporting and emitting material PPV was 100 nm, the thickness of the electron transporting/hole blocking polymer **4e** is 40 nm. The cathodic metal contact was Aluminium with a thickness of 300 nm. 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/m^2. Furthermore the current density at 1 cd/m^2 decreases from $5x10^{-2}$ A/cm^2 (18V) to

$2x10^{-4}$ A/cm^2 (≈ 11 V). Both increased light intensity and decreased current density leads to an improved efficiency.

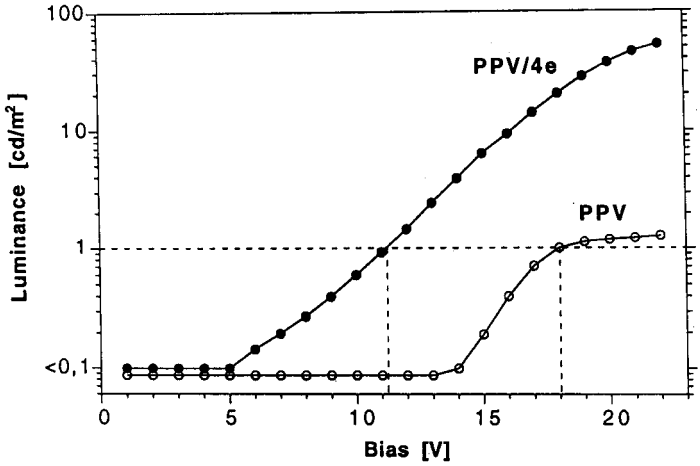


Fig. 1: *Luminance /Voltage characteristics of*
o: ITO/PPV (100nm)/Al
•: ITO/PPV (100nm)/4e (40nm)/Al

ACKNOWLEDGEMENT

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REFERENCES

(1) H.R. Kricheldorf, "Handbook of Polymer Synthesis", Chap. 9, New York 1992; D.H. Solomon, M. Dekker, "Step-Growth Polymerizations", Chap. 5, New York 1972

(2) J. Pommerehne, H. Vestweber, W. Guss, R.F. Mahrt, H. Bässler, M. Porsch, J. Daub, *Adv. Mater.* **7** (6), 551 (1995)