APPRAOHS TOWARDS AMORPHOUS POLY-2,7-FLUORENE NETWORKS

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Introduction

While electroluminescent small molecule based full-color devices are beginning to appear,1 conjugated polymer based displays – highly desirable because of their ease of fabrication and possibility of building flexible displays - still suffer from the lack of a long-term stable blue emitting material. The shortcomings of these high band-gap polymers - typical polydisplays - still suffer from the lack of a long-term stable blue emitting material because of their ease of fabrication and possibility of building flexible displays.

Results and Discussion

Our approach is based on utilizing a small amount of a tetrafunctional spiro-bifluorene 5 as a three-dimensional unit and comonomer in the nickel(0)-mediated polymerization of 2,7-dibromo-9,9-diarylfluorene derivatives in combination with 4-bromostyrene as endcapping reagent. The spiro-bifluorene leads to a 9° branch of the growing 2,7-PF chain after a via the feed ratio determined number of repeat units resulting in a three-dimensional network of 2,7-PF. The termination of the growing network with 4-vinylphenyl endgroups plays a key role in obtaining a processable material.

Experimental

Materials. All reagents were purchased from Aldrich or Strem and used as received. All reactions were carried out under an argon atmosphere.

Instrumentation. The 1H- and 13C-NMR-spectra were recorded on a Bruker AF 250 MHz spectrometer. TGA measurements of the dendron-functionalized 2,7-PFs were performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a Perkin-Elmer TGS-2 instrument. The polymer molecular weights were determined using a Waters 150-C gel permeation chromatography instrument calibrated with polystyrene standards. The optical properties of the polymers 8a-d were investigated with a Hewlett-Packard 8452A diode array spectrophotometer and an SA Instruments FL3-11 fluorimeter.

Synthesis of 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (5)8. 4.58 g (25.4 mmol) of 9-fluorenone were dissolved in 70 ml of dry diethylether and 0.183 mmol of 4-bromostyrene and 0.02 g (0.127 mmol) anhydrous ferric chloride in 10 ml methylene chloride to a solution of 0.8 g (2.53 mmol) 9,9-spirobifluorene and 0.02 g (0.127 mmol) anhydrous ferric chloride in 10 ml methylene chloride. The resulting mixture was refluxed for 6 hours. After cooling the precipitated was isolated by filtration to give after drying 0.77 g (1.62 mmol, yield: 64 %) of 2,2',7,7'-tetrabromo-9,9-spirobifluorene (5).

General Procedure for the synthesis of the 2,7-PF networks 8a-d. A Schlenk tube containing 14 ml degassed toluene, 10 ml degassed DMF, bis(1,5-cyclooctadiene)nickel(0) (704 mg, 2.56 mmol), 2,2'-bipyridine (400 mg, 2.56 mmol) and 1,5-cyclooctadiene (0.31 ml, 2.56 mmol) was heated under argon to 80°C for 20 minutes. The respective comonomers (1.22 mmol of 2,7-dibromo-9,9-dihexylfluorene, 0.183 mmol of 4-bromostyrene and various amounts of 2,2',7,7'-tetrabromo-9,9-spirobifluorene) dissolved in 20 ml of degassed toluene were added to the above solution via a syringe, and the polymerization was maintained at 80°C for 24 h. After reaction 50 ml toluene was added and the solution was filtered over silica. The polymer was precipitated from an equivalent mixture of methanol and acetone and dried at 60°C under vacuum.

Scheme 1. Synthesis of the tetrafunctional spiro-bifluorene 5.

since without the addition of the endcapping reagent an insoluble material would result. A second function of the styrene termini is to render the 2,7-PF material insoluble after thermal treatment and to spin-coat an electron transport layer on top of the emissive layer. The synthesis of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene 2 is outlined in scheme 1. The nickel(0)-mediated Yamamoto polymerization10 has been used for the polymerization of the monomers 5, 6 and the endcapper 7. The amount of 4-bromostyrene (7) was kept constant in all the polymerization reactions (15 mol-% based on 2,7-dibromo-9,9-dihexyl-fluorene). This amount of terminating reagent would afford a linear 2,7-PF with a molecular weight of approximately 7000 g/mol in the polymerization of 2,7-dibromo-fluorenes.11 Different amounts of the spiro-crosslinker 5 ranging from 2-20 % were added to check the influence of the monomer/spiro compound ratio on the materials properties (see table 1). The polymerizations with up to 4 % of 5 proceeded smoothly in contrast to the reaction with 10% and 20 % of 5, where partial precipitation visible by eye occurred during the polymerization. The resulting polyfluorene networks were isolated and purified by filtration of the reaction mixtures over silica and repeated precipitation steps. The molecular weights were determined using gel permeation chromatography (GPC) and are shown in table 1. It is well-known, however, that GPC using coil-like polystyrene standards seems to over-estimate the real molecular weight of rigid rod type PPP derivatives. The polydispersities of the materials are as expected high and display the
bifluorene could be analyzed by comparison of the 1H-NMR signal intensities. Polymodal growth is probably due to partial precipitation (2,7-PF network).

The elution diagrams of the 2,7-PF network exhibit considerable lower incorporation than feed-ratio of spiro-bifluorene (see scheme 2) during the polymerization. The incorporation ratio of up to 4% of spiro-bifluorene into the polymer backbone in combination with the concept of cross-linkable endgroups leads to amorphous materials with high glass transition temperatures, excellent thermal stability and the capability of being incorporated into multilayer LED devices.

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References
(1) see for example www.kodak.com/go/oled

Figure 1. Thin-film PL-spectra of 8a (before and after curing) and DHF after curing at 120 °C for 30 minutes.

Table 1

<table>
<thead>
<tr>
<th>M_n (g/mol)</th>
<th>D</th>
<th>m:n (feed ratio)</th>
<th>m:n (NMR)</th>
<th>T_g (°C)</th>
<th>T_d (°C)</th>
<th>cm</th>
</tr>
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<tr>
<td>8a</td>
<td>3.8</td>
<td>3.04</td>
<td>98:2</td>
<td>97.7:2.3</td>
<td>105</td>
<td>435</td>
</tr>
<tr>
<td>8b</td>
<td>12.8</td>
<td>7.67</td>
<td>96:4</td>
<td>95.7:4.3</td>
<td>144</td>
<td>440</td>
</tr>
<tr>
<td>8c</td>
<td>4.6</td>
<td>5.25</td>
<td>90:10</td>
<td>98:2</td>
<td>93</td>
<td>430</td>
</tr>
<tr>
<td>8d</td>
<td>6.4</td>
<td>5.29</td>
<td>80:20</td>
<td>98.1:1.9</td>
<td>90</td>
<td>445</td>
</tr>
</tbody>
</table>

* M_n in *10^3 [g/mol]

<table>
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<tr>
<th>Scheme 2. Synthesis of the 2,7-PF networks 8a-d</th>
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random growth of the 2,7-PF networks. The elution diagrams of 8c and 8d are polyemodal which is probably due to partial precipitation of the 2,7-PF network during the polymerization. The incorporation ratio of the spirobifluorene could be analyzed by comparison of the 1H-NMR signal intensities of protons H-3, H-6, H-3' and H-6' (δ = 7.33-7.40) of the spiro-bifluorene (see scheme 2) with that of the fluorene repeat unit (δ = 7.46-7.76). The elution diagrams of thermal properties of (TGA) and differential scanning calorimetry (DSC) and are summarized in table 1. The 2,7-PF network exhibit similar to their rigid rod analogues, excellent thermal stability (5% weight-loss well above 400 °C).

The 2,7-PF derivatives 8a-d are soluble in common organic solvents like toluene, THF, p-xylene and exhibit deep blue fluorescence. Maximum concentrations in THF range from 8 mg/ml – 14 mg/ml. The UV- and fluorescence data of 8a-d in solution (THF) show, that according to the UV- and PL-data on 2,7-PF oligomers the emissive properties of these networks derive from ~5–6 conjugated fluorene units (see table 2). The results indicate, that the statistical incorporation of the spirobifluorene into the polymer main chain does not change the electronic nature of the polymer backbone.

Thin films of the amorphous 2,7-PFs 8a-d were prepared by spin-coating on quartz substrates from p-xylene solution (c = 10 mg/ml except for 8d with c = 8 mg/ml) for 1 minute at 2500 rpm. The absorption and fluorescence maxima of 8a-d in solid state are slightly bathochromically shifted compared to the solution values. All networks 8a-d exhibit deep blue fluorescence with narrow bandwidths. To investigate the optical properties after thermal treatment, the films were kept at 120 °C for 30 minutes; a process which leads to cross-linking of the 4-vinylphenyl endgroups and rendering the films insoluble. In figure 1 films of poly-2,7-(9,9-dihexylfluorene) and 8a before and after thermal treatment are shown. It is evident, that the curing did not cause any spectral change in the emission spectra of 8a while in the PL-spectrum of the poly-2,7-(9,9-dihexylfluorene) the broad excimer band at ~540 nm leading to blue-green emission appears.

Conclusions
We have presented a novel design for color-stable emission from 2,7-PF derivatives by incorporation of a tetrafunctional spiro-bifluorene into the polymer backbone in combination with the concept of cross-linkable endgroups. An incorporation ratio of up to 4 % of 5 leads to amorphous...