

APPROACHES TOWARDS AMORPHOUS POLY-2,7-FLUORENE NETWORKS

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Introduction

While electroluminescent small molecule based full-color devices are beginning to appear¹, 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 *para*-phenylene (PPP) derivatives - arise from their intrinsic structural features: the rigid backbone of these materials leads via π - π -interaction to the formation of aggregates and/or excimers upon thermal treatment or passage of current quenching the highly efficient emission of the single polymer chains as observed in solutions². The ideal high band-gap material for light-emitting diodes (LED)s, however, would be a highly amorphous polymer exhibiting good solubility and having almost no tendency to aggregate in the solid state. Two main concepts have been applied to control and stabilize the amorphous state in solid thin films of conjugated polymers: the first approach involves lowering the crystallisation tendency of the rod-like macromolecules by introducing bulky solubilizing groups in the side chain or at the end of the polymer chains^{3,4}, synthesizing copolymers⁵ or introducing saturated spacers in the polymer main chain^{6,7}. A second approach to maintain the amorphous state at elevated temperatures is the spiro-concept introduced by Salbeck and co-workers⁸. They synthesized a spiro-bifluorene containing a tetrahedral bonding atom at the center of two biphenylene units maintaining a 90° angle between the connected conjugated units via a σ -bonded network. This structural feature minimizes the crystallization tendency, increases the T_g and enhances at the same time the solubility. All these features resulted in the successful incorporation of this glass-forming fluorescent molecule as emissive layer in organic LED structures. Recently Heeger et al. showed that by incorporating spiro-bifluorenes in alternating copolymers the T_g and color stability of 2,7-PFs can be improved⁹. Here we present a novel approach towards amorphous 2,7-PF emitters suitable for incorporation in multilayer LED devices.

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.

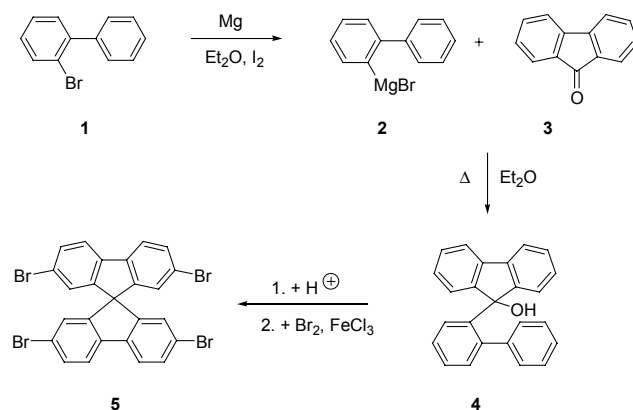
Synthesis of 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (5)⁸. 4.58 g (25.4 mmol) of 9-fluorenone were dissolved in 70 ml of dry diethylether and were added to a Grignard solution prepared from 625 mg (25.7 mmol) of magnesium turnings, 6 g (25.7 mmol) 2-bromobiphenyl and 30 ml diethylether. After the addition was complete the mixture was boiled for a further 2 hours. After cooling, the yellow precipitate formed was being isolated by filtration, hydrolyzed in 100 ml of ice water containing 4 g of ammonium hydroxide. After stirring for 1 hour, the 9-(2-biphenyl)-9-fluorenol formed was filtered off, washed with water and dried under vacuum. The 9-(2-biphenyl)-9-fluorenol was then dissolved in 55 ml of hot glacial acetic acid and 0.05 ml of concentrated hydrochloric acid were added. The solution was allowed to boil for 15 minutes. Then water was added until the solution becomes turbid. After cooling, the product was separated by filtration, washed with water and recrystallized from ethanol to give 1.5 g (4.7 mmol, yield: 19 %) of 9,9'-spirobifluorene. The fourfold bromination was conducted by slowly adding a solution of 1.66 g (10.37 mmol) bromine in 2

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 precipitate formed 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 equivolume mixture of methanol and acetone and dried at 60°C under vacuum.

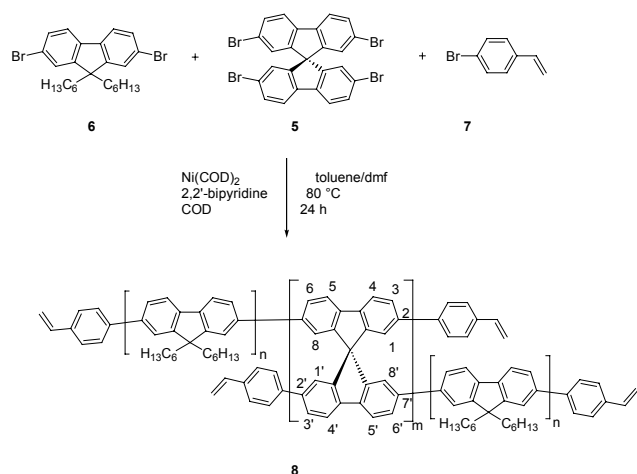
Results and Discussion

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-dialkylfluorene derivatives in combination with 4-bromostyrene as endcapping reagent. The spiro-bifluorene leads to a 90° 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



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-dibromofluorenes¹¹. 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 derivatives¹². The polydispersities of the materials are as expected high and display the



Scheme 2. Synthesis of the 2,7-PF networks **8a-d**

random growth of the 2,7-PF networks. The elution diagrams of **8c** and **8d** are polymodal which is probably due to partial precipitation of the 2,7-PF network during the polymerization. The incorporation ratio of the spiro-bifluorene could be analyzed by comparison of the $^1\text{H-NMR}$ signal intensities of protons H-3, H-6, H-3' and H-6' ($\delta = 7.33\text{-}7.40$) of the spiro-bifluorene (see **scheme 2**) with that of the fluorene repeat unit ($\delta = 7.46\text{-}7.76$). The considerably lower incorporation than feed-ratio of **8c** and **8d** is probably due to partial precipitation (visible by eye for **8d**) during the polymerization. The thermal properties of **8a-d** were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and are summarized in table 1. The 2,7-PF network **8a** already has a higher glass transition temperature ($T_g = 105^\circ\text{C}$) than poly-2,7-(9,9-bis-hexylfluorene) (DHF) ($T_g = 75^\circ\text{C}$)⁸. It is evident, that an increasing incorporation ratio of the spiro-bifluorene **5** leads to a higher T_g of the resulting 2,7-PF network. All materials 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 oligomers¹³ 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 spiro-bifluorene **5** 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 $c =$

Table 2

	λ_{max} [nm] (THF)	λ_{em} [nm] (THF)	λ_{max} [nm] (Film)	λ_{em} [nm] (Film)
8a	374	413, 436	375	440
8b	376	414, 438	381	429, 444
8c	375	415, 439	378	427, 440
8d	377	414, 436	381	435

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

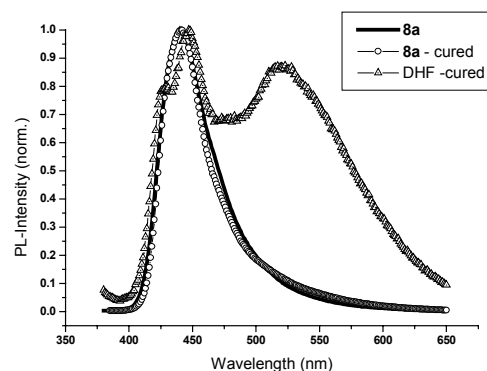


Figure 1. Thin-film PL-spectra of **8a** (before and after curing) and DHF after curing at 120°C for 30 minutes.

polymer backbone in combination with the concept of cross-linkable endgroups. An incorporation ratio of up to 4 % of **5** leads to amorphous

Table 1

	M_n^*	D	n:m (feed ratio)	n:m (NMR)	T_g	T_D	c_M
8a	3.8	3.04	98 : 2	97.7 : 2.3	105	435	14
8b	12.8	7.67	96 : 4	95.7 : 4.3	144	440	10
8c	4.6	5.25	90 : 10	98 : 2	93	430	12
8d	6.4	9.27	80 : 20	98.1 : 1.9	90	445	8

* M_n in $\cdot 10^3$ [g/mol]

materials with high glass transition temperatures, excellent thermal stability and the capability of being incorporated into multilayer LED devices.

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