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Liquid Crystalline Polyfluorenes for Blue Polarized Electroluminescence

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SUMMARY: A series of 9,9-dialkyl-poly(fluorene-2,7-diyl)s containing linear and branched alkyl substituents with a M_n of up to 200000 g/mol has been synthesized. Moreover, some of the polymers were end capped with a suitable hole transport functionality, such as a triphenylamine derivative, to improve their charge transport properties and to control the molecular weight. The thermal alignment of these novel polymers on a rubbed polyimide layer led to highly anisotropic film formation with dichroic ratios (absorption parallel and perpendicular to the rubbing direction) of up to 26 in absorption and 21 in emission.

Introduction

Among the various types of conjugated polymers, polyfluorenes (PFs) **1** have recently attracted much interest as blue-light emitters in organic light-emitting devices (OLEDs). A characteristic feature of polyfluorenes is their thermotropic liquid crystallinity (formation of nematic LC-phases) offering the opportunity of thermal alignment on appropriate substrates1). Active (light-emitting) devices capable of polarized emission are well-suited for information processing and storage or display applications. In principle, optical or electronic excitation of

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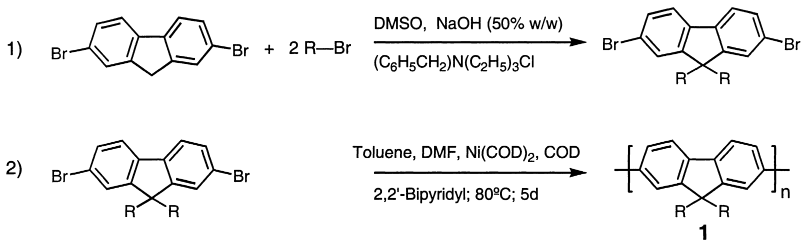
materials containing uniaxially aligned polyfluorenes should produce linearly polarized emission[2,3].

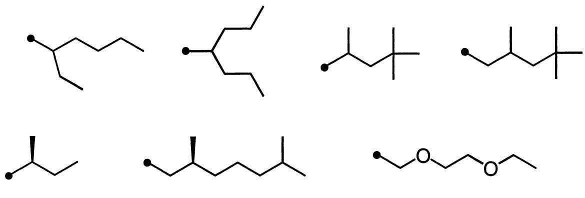
Synthesis and Characterization

The synthesis of high molecular weight, soluble polyfluorenes **1** by transition metal catalyzed aryl-aryl coupling was firstly described by Pei and Yang from UNIAX Corp.[4].The materials investigated in our study were synthesized *via* Yamamoto-type polycondensation with Ni(COD)$_2$ as an effective aryl-aryl coupling agent[5]. The 9,9-dialkyl-substituted monomers were prepared in close analogy to literature methods[6]. Where required, a primary alcohol was converted into the corresponding alkylbromide prior to the alkylation of 2,7-dibromofluorene (Scheme 1).



Scheme 1: General synthetic route to poly(9,9-dialkylfluorene-2,7-diyl)s **1**.

R = n-C_4H_9 ; n-C_6H_{13} ; n-C_8H_{17} ; n-C_8D_{17} ; n-$C_{10}H_{21}$; n-$C_{12}H_{25}$;

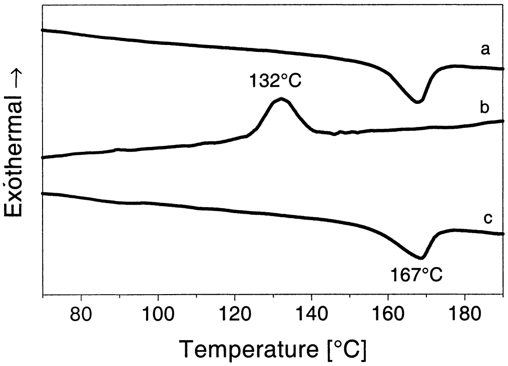


• = point of attachment

Scheme 2: Substitution patterns employed for the synthesis of polyfluorenes **1**.

The molecular weights M_n of the resulting polymers range between 30000 g/mol and 200000 g/mol (PS standard) depending upon the length of the alkyl-substituents which have a strong impact on the solubility of the product. Alkyl-chains containing 6-10 carbon atoms are favorable. Scheme 2 summarizes the different substitution patterns employed so far. Aside from the corresponding homopolymers a variety of statistical copolymers consisting of two different monomer units have been prepared. The chiral derivatives shown in Scheme 2 have been thoroughly investigated with respect to their chiroptical properties, which will be not discussed in the framework of this paper7).

Thermotropic LC-phases of such alkyl-substituted polyfluorenes can be observed in a temperature range between 100 and 250°C depending upon the molecular weight and the substitution pattern. As an example Fig. 1 depicts the calorimetric characterization of a sample of poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF2/6) **2** (M_n = 127000, M_W = 210000).



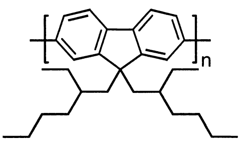


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Fig. 1: Calorimetric characterization of PF2/6. (a) heating scan (10°C/min) of a solution cast sample (toluene) (b) cooling scan of the sample (10°C/min) (c) heating scan for a sample which was quickly quenched from 200°C.

A solution cast sample of **2** shows no crystallization on heating, but a phase transition at 167°C (Fig. 1a). Also, PF2/6 was observed to soften considerably at approximately 155°C. On cooling (Fig. 1b), the reverse transition is observed at 132°C. Even for a sample quenched from 200°C to room temperature, we find an identical transition (Fig 1c). Above its transition point, PF2/6 showed a birefringent, fluid phase, i.e. liquid crystallinity.

Figure 2 shows the UV/Vis absorption and photoluminescence spectra of PF2/6 **2** in solution and in solid state. Since the substitution pattern does not affect the main chain conformation, all presented polyfluorenes exhibit similar absorption and photoluminescence spectra in solution, with an absorption maximum at about 383-389 nm and emission maxima at about 415 nm and 440 nm.

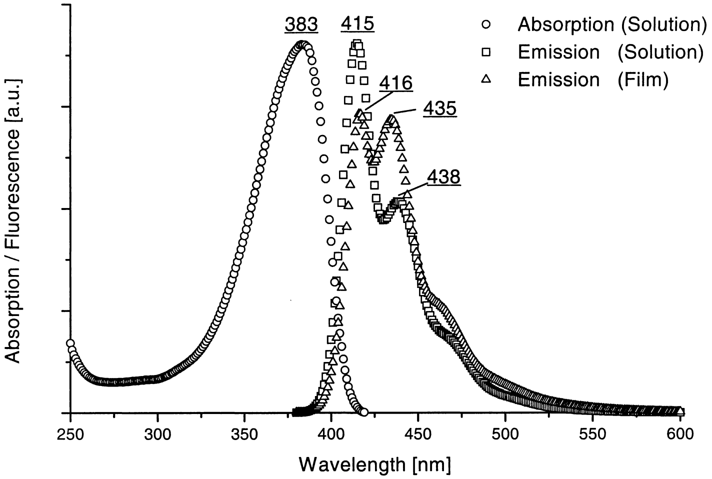


Fig. 2: UV/Vis and photoluminescence spectra of PF2/6 **2** in solution ($CHCl_3$) and in solid state.

However, in the solid state, ordering effects become important. It has been demonstrated for a PF **1**, with linear n-octyl sidechains, that a strong correlation exists between the optical properties in absorption and the mainchain order8).

A particular feature of the ordered state was the appearance of an additional sharp absorption peak at 437nm8). This additional absorption peak can also be easily induced in solution just by adding a non-solvent such as methanol and forcing the polymer chains to form aggregates in which the PF chains are flattened.

Moreover, this aggregation in the solid state causes an additional long-wavelength emission at 440 – 500 nm (Figure 2). This contribution can significantly affect the emission color, especially in electroluminescence (EL). However, according to our studies, such additional red-shifted emission bands are much less pronounced

PF2/6 **2**.

Thermal Alignment of Polyfluorene Films

To achieve a high degree of uniaxial orientation of the polyfluorene chains the polymers were aligned thermally on rubbed polyimide layers. Details on thermal alignment conditions for PF2/6 **2**, in addition to the more device related part of the work, can be found in Grell et al.[1].

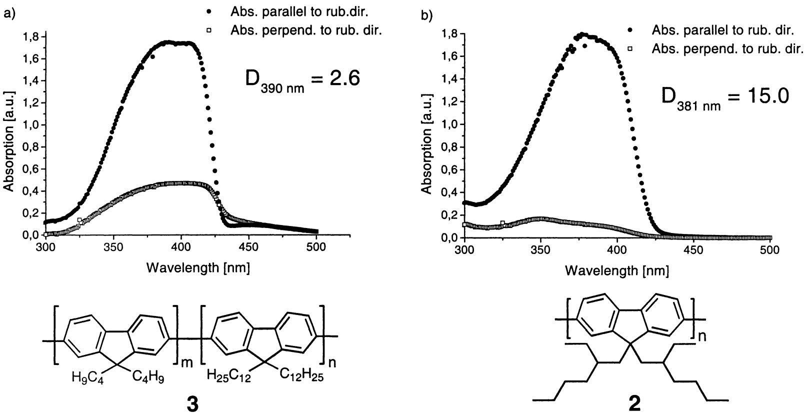


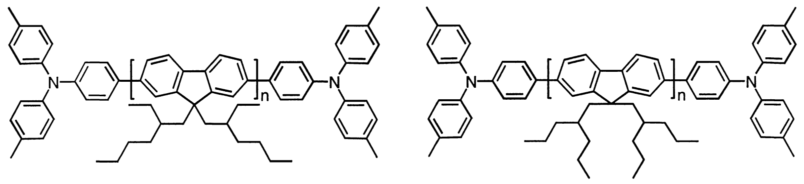
Fig. 3: UV/Vis absorption spectra of thermally aligned PFs taken parallel and perpendicular to the rubbing direction
(a) Poly((9,9-dibutyl-*co*-9,9-didodecyl)fluorene-2,7-diyl) **3** on rubbed polyimide
(b) Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF2/6) **2** on rubbed polyimide

Figure 3 reveals evidently the strong influence of the chain length of the alkyl substituents on the alignment properties. The highest dichroic ratios were obtained with branched sidechain derivatives such as PF2/6 **2** so far. We expect that a branched sidechain will lead to a lower effective diameter and therefore increase the order paramater (S) well in excess of 0.9 determined for thermally aligned poly(9,9-dioctylfluorene-2,7-diyl)[3] and according to our own results. In contrast to the homopolymer PF2/6 **2** aggregation is much more favored with the copolymer **3** containing only linear alkyl-sidechains. The absorption spectrum of an aligned sample of **3** is characterized by an additional broad absorption shoulder in the region between 400 and 430 nm indicating a significant contribution of supramolecular ordering8) (Figure 3a). Therefore, the EL spectrum of such a polymer (not depicted) shows a broad and unstructured emission band in the region between 450 and 600 nm resulting in a significant red-shift of the emission color compared to the blue emission of PF2/6 **2**.

In general, it has been found that polyfluorene derivatives containing branched C_8-sidechains are best suited for thermally induced alignment with respect to both comfortable transition temperatures and high order parameters. Future work will be devoted to the influence of molecular weight and the molecular weight distribution on the alignment properties.

End capped Polyfluorenes

Since polyfluorenes are known for their hole current limited electroluminescence9), our efforts to overcome this problem are based on a straightforward approach. An incorporation of hole transport moieties into the polymer backbone9) would lead to a significant deviation of the almost linear structure of the polymer chain required for polarized luminescence. To surmount such difficulties we used bis(4-methylphenyl)(4-bromophenyl)amine11) as a suitable monofunctional end capping reagent. The triphenylamine derivative is added at a concentration of 2-6 mol % and present in the reaction mixture from the beginning. Furthermore, this strategy gives us the opportunity to gain control over the molecular weight of the polymer. Scheme 3 depicts the structure of two of such end capped derivatives.



4 **5**

Scheme 3: Chemical structures of end capped PFs
Poly(2,7-(9,9-bis(2-ethylhexyl))fluorene)-2,7-bis(4-methylphenyl)phenylamine **4** (M_n = 48000 g/mol, 4 mol% endc. added)
Poly(2,7-(9,9-bis(2-propylpentyl))fluorene)-2,7-bis(4-methylphenyl)phenylamine) **5** (M_n = 29000 g/mol, 6 mol% endc. added).

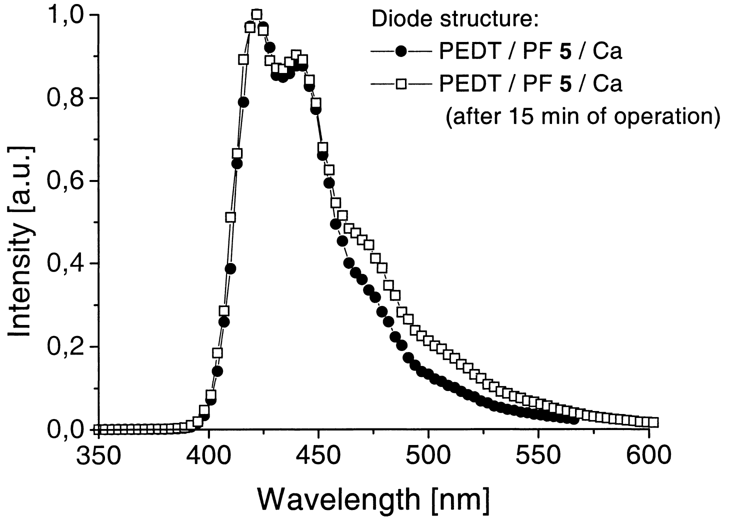


Fig. 4: Electroluminescence spectrum of PF **5** with poly(3,4-ethylenedioxythiophene) (PEDT) as hole injection layer

The isotropic EL spectrum of polymer **5** (Figure 4) exhibits a fairly narrow emission band. There is no change of emission color within 15 min operation. Generally, onset voltages between 3-4 V are observed in monolayer isotropic light-emitting devices (PEDT injection layer) and, therefore, significantly lower compared to similar devices with PF2/6 **2** as emissive layer[10)].

The dichroic ratios found for the thermally aligned polymers **4** and **5** are very promising with 26 and 13, respectively (Figure 5). The next step will be the fabrication of aligned devices using the end capped polyfluorenes for polarized electroluminescence.

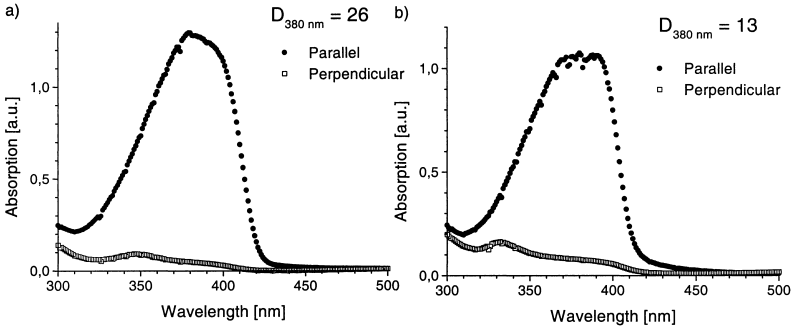


Fig. 5: Polarized UV/Vis absorption spectra of thermally aligned PFs
(a) Absorption parallel and perp. to the rubbing direction for polymer **4**
(b) Absorption parallel and perp. to the rubbing direction for polymer **5**.

Polarized Electroluminescence

Since the rubbed polyimide [poly(phenoxyphenylimide)] (PI) alignment layer used in our study is itself an insulator, it was doped with appropriate starburst-type hole conductors such as ST638 or ST16/7[11]. Further studies will be focused now on improvement of the hole injection/transport layer in polarized LEDs. Hitherto, the employed hole conductor filled polyimide layer meets solely the requirements as a conductive and transparent substrate suitable for alignment. Figure 6 shows the polarized EL spectrum of such an aligned ITO : ST638 : (PI+ST16/7) : PF2/6 : Ca device measured parallel and orthogonal to the rubbing direction. The polarized electroluminescence of such a fabricated device is blue with emission maxima in parallel detection at 425, 450 and 475 nm with respect to the rubbing direction and a shoulder at approximately 505 nm. The polarization ratio of 21 was determined at 450 nm (Figure 6). Further studies will also be focused on narrowing the emission band.

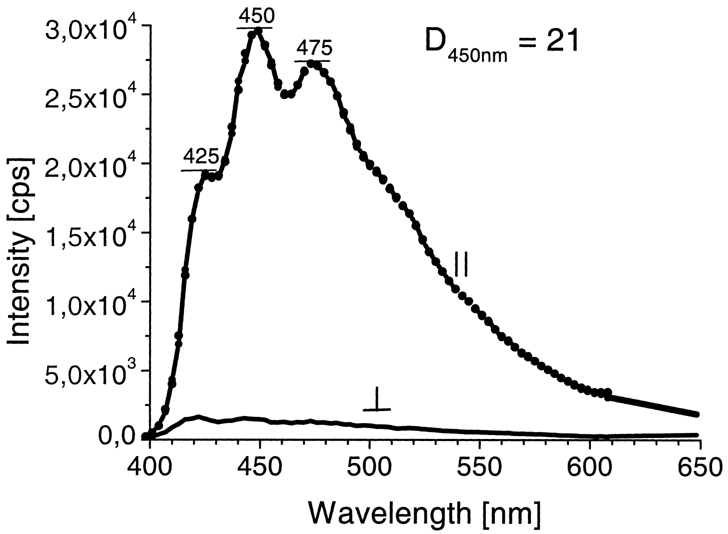


Fig. 6: Polarized electroluminescence spectra of thermally aligned PF2/6 **2**
Device structure ITO : ST638 : (PI+ST16/7) : PF2/6 : Ca

Conclusion

Polarized LEDs, with a state of the art dichroic ratio in emission of more than 20 and a brightness in excess of 100 Cd/m^2, have been fabricated. The maximum alignment in thin solid films of a series of polyfluorene derivatives **1** depends on the nature of the sidechains. While the dichroic ratio in absorption barely exceeds 10 for **1** with linear n-octyl sidechains, values larger than 25 are achievable in the case of an ethylhexyl substitution (**2** and **4**). Tuning both molecular weight and conductive properties of alkyl-substituted polyfluorenes, *via* suitable monofunctional end cappers, offers a promising strategy for highly polarized LEDs.

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