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Short communication:

(9,9-Dialkylfluorene-*co*-fluorenone) copolymers containing low fluorenone fractions as model systems for degradation-induced changes in polyfluorene-type semiconducting materials

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Abstract: This short communication describes synthesis, optical and electronic properties of novel 9,9-dialkylfluorene-*co*-fluorenone copolymers which function as model systems for degradation-induced changes in polyfluorene-type semiconducting materials. Only very small fractions of incorporated fluorenone building blocks lead to a dramatic change of the solid state properties (photo- and electroluminescence). The results are discussed in terms of intra- vs. intermolecular excitation energy transfer.

Introduction

Over the last years poly(9,9-dialkylfluorene)s (PF) [1] have emerged as a very promising class of conjugated polymers, which can be utilized as blue emission layers in polymer light emitting diodes (PLEDs) [2-4], also for linearly polarized light emission [5] due to the liquid crystallinity of PF derivatives with long alkyl substituents.

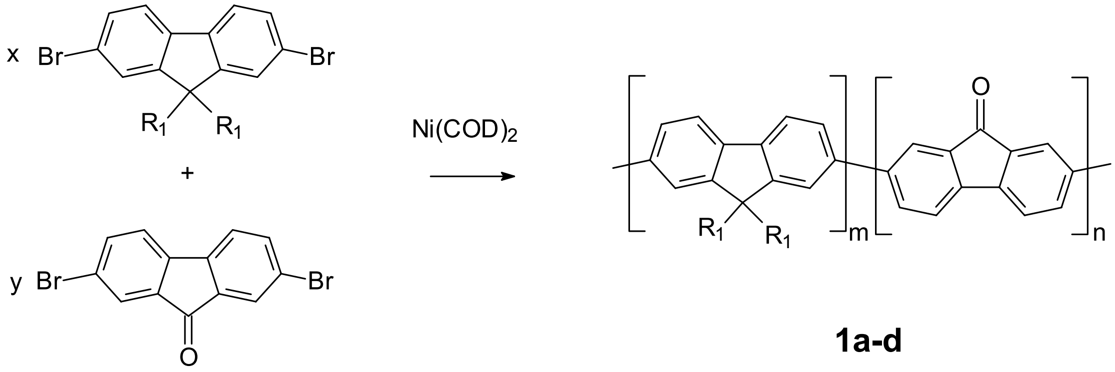
Unfortunately, most of the PF-based PLEDs suffer from spectral changes of the emission under long-term operation which is documented in the formation of a low energy emission band at *c.* 2.3 eV turning the desired blue into a greenish emission. This band, which can be also detected in photoluminescence (PL), especially after photo-oxidation of the polymer, has been attributed to excimer formation [6].

As presented by us in a previously published paper [7] we have identified this low energy emission band as originating from fluorenone defect sites. We could show that such keto defects can be formed already during polymer synthesis (especially for 9-monoalkylated polyfluorenes), or by a photo- (or electro-)oxidative degradation process. Our results suggest that the photo- (or electro-)oxidative degradation of 9,9-dialkylated PFs is probably coupled to the presence of a small (sub-percent) amount of monoalkylated fluorene building blocks. This would also explain often observed batch-to-batch differences in the optical properties of structurally identical PF derivatives.

This assignment of the 2.3 eV-emission band to fluorenone defect sites is fully in line with investigations on novel fluorene-based copolymers containing a well defined fraction of fluorenone units. This results will be described and discussed in the following short communication.

Synthesis

The (9,9-dialkylfluorene-*co*-fluorenone) copolymers **1a-d** with fluorenone fractions *n* below 1 mol-% have been synthesized following the well-known aryl-aryl coupling protocol after Yamamoto. For this, mixtures of the dialkylated 2,7-dibromofluorene monomer and 2,7-dibromofluorenone are reductively coupled with $Ni(COD)_2$ as transition metal coupling agent. We used long, branched 3,7,11-trimethyldodecyl-sidegroups to guarantee a sufficient solubility of the coupling products. The synthesis is outlined in Scheme 1. The yellow-orange colored products **1a-d** possess number average molecular weights M_n (GPC, polystyrene calibration) between 8 000 and 18 000 (see Tab. 1). The molecular weights are significantly lowered when compared to the corresponding PF homopolymers (M_n of up to 250 000 [8], in our example 93 000). This may be caused by a somewhat reduced reactivity of the dibromo-fluorenone monomer in the reductive coupling reaction. Please note that the GPC analysis (polystyrene calibration) provides somewhat overestimated M_n and M_w values for the semi-rigid PF-type polymers; for a detailed light scattering study see ref. [9].



Scheme 1: Synthesis of poly(9,9-dialkylfluorene-*co*-fluorenone)s, **1** (R_1: 3,7,11-trimethyldodecyl)

The incorporation of the fluorenone building blocks is documented in the IR spectra of the copolymers **1a-d** (>C=O stretching mode at 1721 cm^{-1} of increasing intensity with increasing mole fraction of fluorenone building blocks). The ^1H and ^{13}C NMR spectra of **1a-d** display only the well-described signals of the 9,9-dialkylfluorene-2,7-diyl building blocks [8]. The fluorenone moieties cannot be detected due to their low mole fraction in the copolymer.

Tab. 1. Molecular weight and color of poly(9,9-dialkylfluorene-*co*-fluorenone)s, **1**

Polymer	Mole fraction of 2,7-dibromofluorenone (y)	M_n(GPC)/ M_w(GPC)	Color
PF	0	93000/190000	slightly yellow
1a	0.1	18000/36000	yellow
1b	0.2	15000/34000	yellow
1c	0.5	17000/34000	yellow
1d	1.0	8300/13000	dark yellow

Characterization of the optical and electronic properties

The absorption spectra of **1a-d** both in dilute solution and in the solid state do not display any significant changes in relation to the corresponding homopolymer PF. They show a broad, unstructured absorption band which peaks at *c.* 384 nm (3.23 eV; in toluene solution), and *c.* 392 nm (3.16 eV; solid state, film). The mole fraction of fluorenone building blocks is below the visualization limit in the UV/Vis spectra of **1a-d**.

Photoluminescence (PL) spectra in dilute solution are depicted in Fig. 1. Again, there are no significant differences between the homopolymer PF and two representative copolymers **1c** and **1d**. The solution PL spectra display two emission bands at *c.* 418 (0-0 transition; 2.97 eV) and 438 nm (0-1 transition; 2.83 eV). This behavior reflects a neglectable amount of excitation energy transfer to the fluorenone moieties in dilute solution. In dilute solution only an *intra*chain energy transfer can occur. A simple calculation gives that both for **1c** and **1d** approximately every 7th chain contains a fluorenone building block. However, the complete absence of fluorenone-related emission peaks (in the spectral region between 2.2 and 2.4 eV) documents a very inefficient *intra*chain energy transfer in spite of the π-conjugated character of the polyarylene main chain.

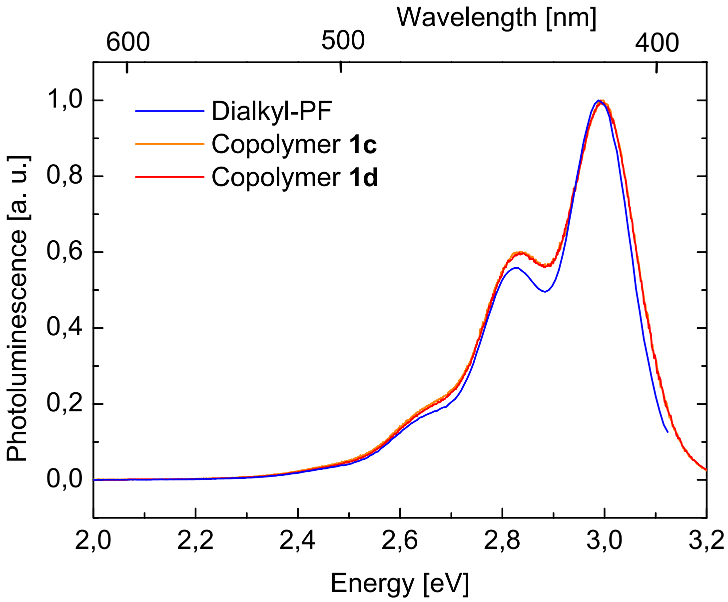


Fig. 1. Photoluminescence spectra of PF, and copolymers **1c** and **1d**, in dilute toluene solution

The solid state photoluminescence spectrum of these copolymers **1c** and **1d** (starting from 0.5 and 1.0 mol-%, respectively, of the fluorenone monomer, Fig. 2) now displays an extra emission band corresponding to the fluorenone building blocks at *c.* 2.38 eV (521 nm). This yellow-orange emission component exhibits an increasing intensity with increasing fluorenone content. **1c** shows blue and yellow-orange PL components of similar intensity, but already in **1d** the 2.38 eV-band becomes the dominating emission component. This turns the initially blue PL into a greenish (**1c**) or whitish (**1d**) emission. The effective *inter*chain Förster-type excitation energy transfer in the solid state leads to the situation that already for **1d** the 2.38 eV-band is more intense in relation to the “native” blue emission band of PF-type homopolymers.

The incorporation of the fluorenone building blocks also leads to a dramatic reduction of the PL quantum efficiency (e.g., of more than one order of magnitude for **1c** in relation to the corresponding PF homopolymer).

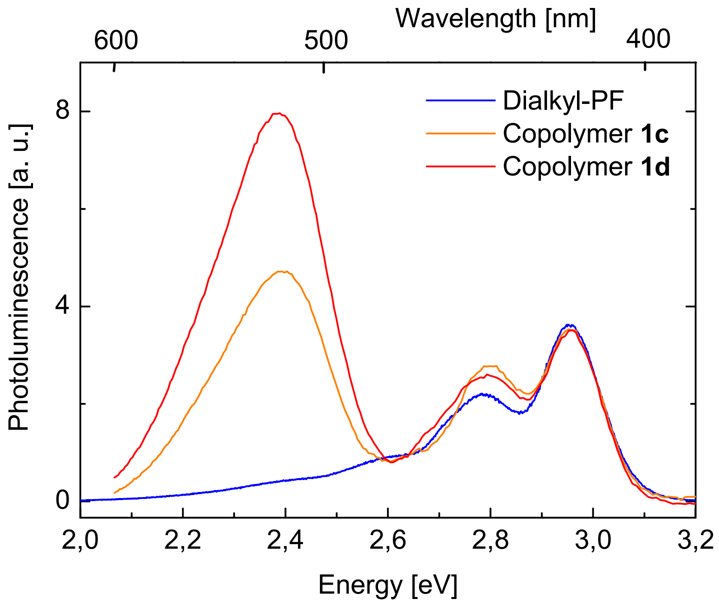


Fig. 2. Photoluminescence spectra of PF, and copolymers **1c** and **1d**, in the solid state (thin films)

These effects can be also observed in electroluminescence (EL). Fig. 3 gives EL spectra of PF, and the fluorene/fluorenone copolymers **1c** and **1d**. Especially for copolymer **1d**, the yellow-orange emission component in EL is more pronounced in relation to the PL results.

This may be caused by the pinning of charge carriers (preferably electrons) at the lower energy fluorenone sites (charge carrier trapping) which opens a second channel of generation and emissive deactivation of excited states which are localized at the fluorenone building blocks (Förster-type energy transfer to, plus charge carrier trapping at the fluorenone sites).

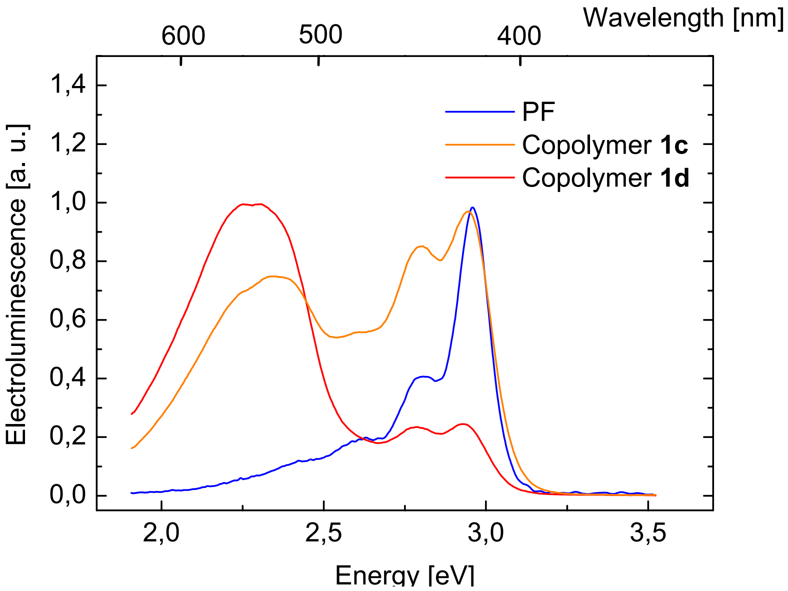
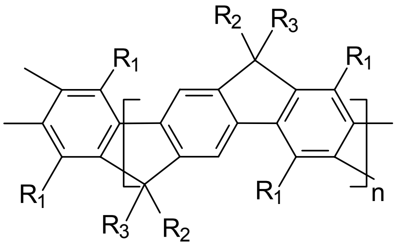


Fig. 3. Electroluminescence spectra of PF, and copolymers **1c** and **1d** (LED devices of configuration: ITO/PF or copolymer **1**/Al)

Conclusion

Our findings on novel (9,9-dialkylfluorene-*co*-fluorenone) copolymers further document the key role of fluorenone (keto) sites as source of the low energy emission bands in polyfluorenes and other $-CR_2-$ bridged polyphenylene and polyarylene derivatives (e.g., ladder-type poly(*p*-phenylene)s LPPP [10]). Such localized fluorenone moieties give rise to an unwanted color change of the initially blue photo- and electroluminescence and lead to dramatic reduction of the overall PL and EL quantum yield. The absence of such defect sites is, therefore, of primary importance for designing highly efficient blue, PF-based PLEDs.

In this light, the often favored interpretation of the low energy emission bands in PF (and also in ladder-type LPPP, in which such low energy emission bands also occur at a similar spectral position of *c.* 2,2 eV !) with an ongoing aggregate or excimer formation is at the very least questionable [6,11,12]. Hereby, the strong influence of di- and triarylamine-type dopants and building blocks (in copolymers) on the intensity of the low energy emission bands in PFs [13,14] may be related to PL (and EL) quenching processes.



LPPP

As demonstrated previously, also the decoration of the PF backbone with bulky arylene-type dendronic side-chains leads to an increased chemical stability and reduced *inter*chain energy transfer [15]. The first finding may be, thereby, related to an increased photooxidative stability of 9,9-diarylated PF derivatives.

Carbonyl defect sites have been also identified in so-called precursor-PPV after oxidative degradation which cause a dramatic reduction of the PL (and EL) efficiencies [16].

Experimental part

The 9,9-dialkyl-2,7-dibromofluorene monomer was synthesized according to literature procedures [8]. All other chemicals and solvents were used in commercial p.a. quality.

^{1}H and ^{13}C NMR spectra were obtained on a Brucker AMX 300. Absorption spectra were recorded on a Jasco V-550, PL spectra on a FluoroMax-3 (Jobin Yvon). The molecular weights were determined by gel permeation chromatography (GPC) using three columns (5 µm gel, pore widths $10^3/10^5/10^6$ Å) with UV and RI detection (solutions in tetrahydrofuran at 30°C, polystyrene calibration).

Poly[9,9-bis(3,7,11-trimethyldodecyl)fluorene-2,7-diyl-co-9-fluorenone-2,7-diyl]

1a-d were synthesized in a Yamamoto-type polycondensation [17] of 2,7-dibromo-9,9-bis(3,7,11-trimethyldodecyl)fluorene and 2,7-dibromo-9-fluorenone as condensation monomers (the detailed mole ratios are given in Tab. 1). The reaction was carried out under argon atmosphere, $Ni(COD)_2$ was used as a reductive coupling agent.

General polymerization procedure. A thoroughly dried Schlenk tube (100 ml) was flushed with argon and filled with the 2,7-dibromo-9,9-dialkylfluorene (1.58 mmol), the required amount of 2,7-dibromo-9-fluorenone, and 5 ml of dry toluene. A second Schlenk tube (100 ml) containing $Ni(COD)_2$ (1.0 g, 3.64 mmol), 2,2'-bipyridyl (0.567 g, 3.64 mmol), 4 ml of dry *N*,*N*-dimethylformamide , and 10 ml of dry toluene was degassed under argon at 80°C for 30 min. COD (0.246 g, 2.28 mmol) and the solution of the monomers were added to the mixture. The reaction was maintained at 80°C under exclusion of light for 3-5 days. Next the solution was diluted with chloroform and the polymers were precipitated in a 1/1/1-mixture (100 ml each) of methanol/acetone/conc. hydrochloric acid. Following a Soxhlet-extraction with ethyl acetate for 5 days the polymers were finally re-dissolved in toluene, the solvent partially evaporated and the polymer re-precipitated into a mixture of methanol/ acetone, and dried in vacuum at room temperature.

PF: yield 64 %; M_n 93000; M_w 190000; M_w/M_n 2.04

1a: yield 93 %; M_n 18000; M_w 36000; M_w/M_n 2.0

1b: yield 92 %; M_n 15000; M_w 34000; M_w/M_n 2.27

1c: yield 93 %; M_n 17000; M_w 34000; M_w/M_n 2.0

1d: yield 86 %; M_n 8300; M_w 13000; M_w/M_n 1.57

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