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Notes

Excimers or Emissive On-Chain Defects?

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The origin of the low-energy PL and EL peaks occurring after thermal treatment of polyfluorenes and related ladder-type poly(*p*-phenylene)s has been intensively investigated and discussed during the past years. The low-energy emission bands have been mostly attributed to aggregate or excimer formation in the bulk material.[1,2] However, more recent studies show (for a review see ref 3) that this interpretation of the low-energy emission bands is questionable.

Despite several new insights, not all observations in the field are fully understood. But there are a couple of key aspects that have to be considered in each interpretation:

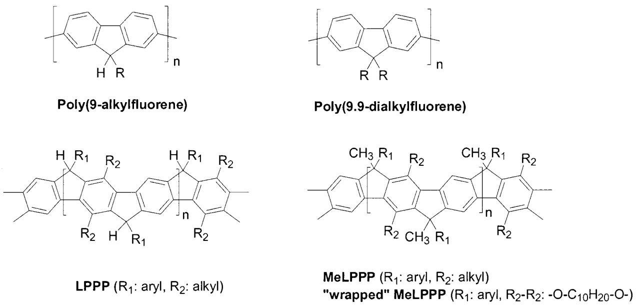
1. Any hydrogen substituents at the bridge positions (9-position) dramatically decrease the photo- and thermostability. This was shown for example for fluorene end-capped poly(9,9-dialkylfluorene)s as well as for poly(9-alkylfluorene)s[1−4] (see Chart 1). Moreover, the same observation was made for structurally related, fully planarized polyphenylene ladder polymers (LPPP vs MeLPPP).[5] This observation is not related to steric effects (suppression of intermolecular stacking), since also a simple replacement of −H by $-CH_3$ (LPPP/MeLPPP) in the presence of other much more bulky substituents results in a distinctly improved thermo- and photostability of dialkylated polyfluorenes and *p*-phenylene ladder polymers.

2. Blending of poly(9,9-dialkylfluorene)s with low amounts of polar dopands (e.g., triarylamines)[6] or end-capping with such polar moieties[7,8] can efficiently suppress the green emission components.

3. Structurally related ladder-type polyphenylene derivatives have been completely "wrapped" with substituents which should prevent any aggregation ($-O-C_{10}H_{20}-O-$ loops on both sides of the molecular ladder). However, the green emission component at ca. 550 nm cannot be suppressed in such "wrapped" LPPPs.[9]

4. Monodisperse oligo(9,9-dialkylfluorene)s (penta- and hexamers) did not show any green PL components.[10] Such molecular materials can be carefully purified by repeated chromatographic steps, recrystallization, or sublimation. However, other structurally related fluorene oligomers displayed weak low-energy PL components which have been attributed to defects.[14] This may be due to differences in purity between the oligofluorenes.

Chart 1



Poly(9-alkylfluorene)

Poly(9.9-dialkylfluorene)

LPPP (R_1: aryl, R_2: alkyl)

MeLPPP (R_1: aryl, R_2: alkyl)
"wrapped" MeLPPP (R_1: aryl, R_2-R_2: $-O-C_{10}H_{20}-O-$)

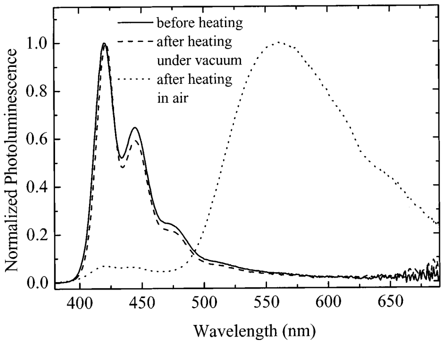


Figure 1. Photoluminescence of a spin-coated poly(9,9-dialkylfluorene) film before annealing (solid line), after annealing at 200 °C (3 h) under dynamic vacuum, and after annealing at 200 °C (2 h) in air; R (alkyl) = 3,7,11-trimethyldodecyl (for polyfluorene synthesis see ref 4).

Some of these findings described above cannot be simply explained with the existence and formation of aggregates or excimers. Now, the paper of Huang et al.[15] presents a couple of findings with the conclusion that they count as a clear proof for the excimer hypothesis:

1. The occurrence of green PL components after thermal treatment of poly(9,9-dialkylfluorene)s under nitrogen at a hot stage is presented as an argument against oxidative degeneration processes. For this, however, oxygen must be completely excluded (glovebox conditions). We have reexamined these experiments using real inert conditions. Figure 1 shows the PL spectra of heat-treated films of a highest quality poly(9,9-dialkylfluorene) under dynamic vacuum (pressure $< 1 \times 10^{-4}$ mbar) as well as at ambient conditions. Essentially no low-energy PL peaks can be observed after annealing in a vacuum. Note that simultaneous illumination with light did not alter the results. As depicted in the same figure, the control experiment

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under ambient conditions displays the expected development of a strong low-energy PL contribution. Therefore, the low-energy emission component has to be related to oxidative processes (degeneration).

2. The reduction of the low-energy PL band after "quenching" in liquid methanol/carbon dioxide is an interesting observation. However, an explanation for this effect is not given. The "quenching" should conserve the more ordered molecular arrangement formed during thermal treatment when following the logics of the paper by Huang et al.[15] We have repeated this experiments and could not observe any quenching of the low-energy emission component after shock cooling to liquid nitrogen temperature.

3. The thermal stability seems to be not clearly related to T_g (or T_m) values. The poly(9,9-dialkylfluorene) used in our reexamination is a low-T_g derivative (T_g < 50 °C).[3] However, no "aging" effects could be observed after annealing under inert conditions. In addition, the fully planarized MeLPPP as similar phenylene-type ladder polymer possesses a high T_g of >300 °C but shows distinct spectral changes (formation of low-energy PL bands) after annealing at ambient conditions to 200 °C, a temperature much below T_g.[5]

In summary, the paper of Huang et al.,[15] in our opinion, cannot count as a proof for the excimer hypothesis. Moreover, there are several strong indications for the existence of emissive on-chain keto defects as source of the low-energy PL components. That are, especially, (i) the occurrence of (weak) low-energy emission bands in both polyfluorene and ladder-type polyphenylenes also in dilute solution,[14,16] (ii) the absence of any concentration dependence for this bands in solution, and (iii) experimental and theoretical results derived from polyfluorenes containing small amounts of emissive on-chain fluorenone units.[11−13] They show that the incorporation of 0.1−2% of fluorenone units into the conjugated PF main chain leads to strong low-energy emission components at 2.2−2.3 eV of high oscillator strength. (For other arguments supporting the presence of emissive on-chain defects in polyfluorenes, see refs 14 and 16.) Please note that also (electro)phosphorescence can produce low-energy (electro)luminescence contributions in phenylene-type semiconducting polymers.[17]

Experimental Section

For the annealing experiments, the PF films were first stored under dynamic vacuum at room temperature for 30 min until a pressure of less than 10^{-4} mbar was reached. Then, using an integrated heater, the PF films were heated to 200 °C under exclusion of any light. The films were cooled to room temperature under vacuum. For the measurements under ambient conditions the PF films were simply heated in air.

Please note that a highly sensitive Shimadzu PL spectrometer has to be used for the PL measurements after annealing in air since the overall PL quantum yield is strongly reduced.

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