Threshold Reduction in Polymer Lasers Based on Poly(9,9-dioctylfluorene) with Statistical Binaphthyl Units


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Introduction:
Poly(9,9-dialkylfluorene)s (PF)s have attracted widespread attention and have been shown to be efficient blue-light emitters in organic light emitting diodes (OLEDs) and in organic solid state lasers.[1] However, PFs often display an unfavorable solid-state aggregation, the so called β-phase formation which is evidenced by a red-shifted emission with respect to that of the glassy state. It has been found that films containing even low fractions of the “agglomerated” PF β-phase suffer from a serious deterioration of the PL efficiency.[2] This quenching effect is expected to have a dramatic effect on organic solid state lasers. Therefore, the elimination of such packing behaviour seems a worthwhile endeavour and promises particular improvements for organic thin-film lasers.

Synthesis:
- Interchain interactions should be suppressed by incorporating non-planar fragments. We use binaphthyl (BN) as a pseudo-orthogonal moiety
- Polymers were prepared via a Ni(0) mediated Yamamoto coupling with varying amounts of BN co-monomer
- The % BN incorporated was calculated from the 1H NMR
- Samples 3c and 3d form a stable amorphous glass (T_g~83°C), while the 3b shows a clear T_g at 78°C and a T_L at 147°C in DSC measurements

Optical Properties:
- The β-phase shows a distinct red-shifted emission with a well resolved vibronic progression
- The PL characteristics are due to high intra-chain order and are comparable with the fully planar ladder-like structure (Fig. 2)
- Even low concentration levels of β-phase (3b-c) results in low-energy emission peak at 442 nm
- 3d with BN > 12% does not show emission from β-phase
- The α-phase maximum shifts only slightly upon incorporating the BN-units which reflects only a very moderate shortening of the conjugation length

Polymers Laser:
- Laser emission could be tuned from 435 to 465 nm by varying the grating period (Fig. 3)
- The threshold energy is reduced with increasing BN incorporation from 12 – 3 μJ/cm² (Fig. 4)
- Lowest threshold energies (3 μJ/cm²) have been observed close to the ASE maximum (Fig. 5)

Conclusions & Outlook:
- A new class of binaphthyl- containing fluorene based copolymers has been introduced
- β-phase formation is efficiently suppressed for copolymers with a BN content > 12%
- Simultaneously the lasing threshold in a 2nd order DFB laser is distinctly lowered from 12 – 3 μJ/cm² upon increased %BN
- Lasing experiments utilizing 3d as the host-polymer for different laser dyes are in progress

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