Fluorescence quenching of 2,5-disubstituted 1,4-divinylbenzene monomers by chloroform

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Metathetically synthesized all-trans 2,5-disubstituted *p*-divinylbenzene oligomers [1,2,3] and their monomers have been investigated by time-resolved fluorescence measurements. These conjugated oligomers show like the polymer (PPV) valuable photo- and electrooptical properties and as a consequence, the preparation of highly regular products is in the focus of interest. The fluorescence of the diheptyloxy as well as the diheptyl substituted oligomers has been investigated in dilute solutions (c ≈ 10^{-5}; oxygen equilibrated). Measurements have been performed in the solvents cyclohexane, chloroform and ethanol. The results obtained show a decrease of the fluorescence lifetimes with increasing conjugation length. Additionally, the solvent used has an influence on the fluorescence lifetimes as well; especially in case of the monomers.
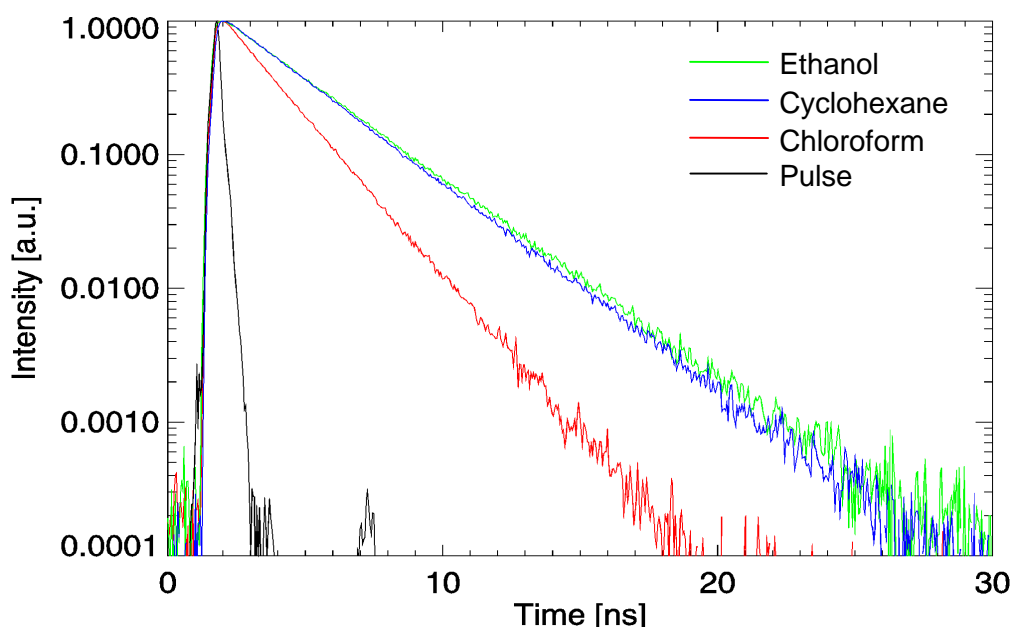

Figure 1: Fluorescence decay curves of 2,5-diheptyloxy-*p*-divinylbenzene in ethanol, cyclohexane and chloroform

Exemplarily, the fluorescence decay curves of the diheptyloxy substituted monomer are illustrated in Fig. 1. All decay curves are monoexponential. The fluorescence lifetime of the monomer is significantly shorter in chloroform compared to the two other solvents. The same observation was made for the diheptyl substituted monomer. A decrease of the fluorescence lifetime could originate in a quenching process. In order to examine the capability of chloroform as a quencher experiments in cyclohexane with different amounts of chloroform were carried out. With increasing chloroform concentration a decrease of the fluorescence lifetimes were observed. A decreasing lifetime indicates a dynamic quenching process. In this case an exciplex formation between the excited monomer and the solvent chloroform is suggested.

Over the entire emitting range the decay behavior remains unchanged. This requires that the exciplex decomposes non radiatively only. Furthermore, the monoexponentiality indicates that a backreaction from the exciplex to an excited monomer is negligible. In order to obtain more information a Stern-Volmer plot was analyzed.

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]$$
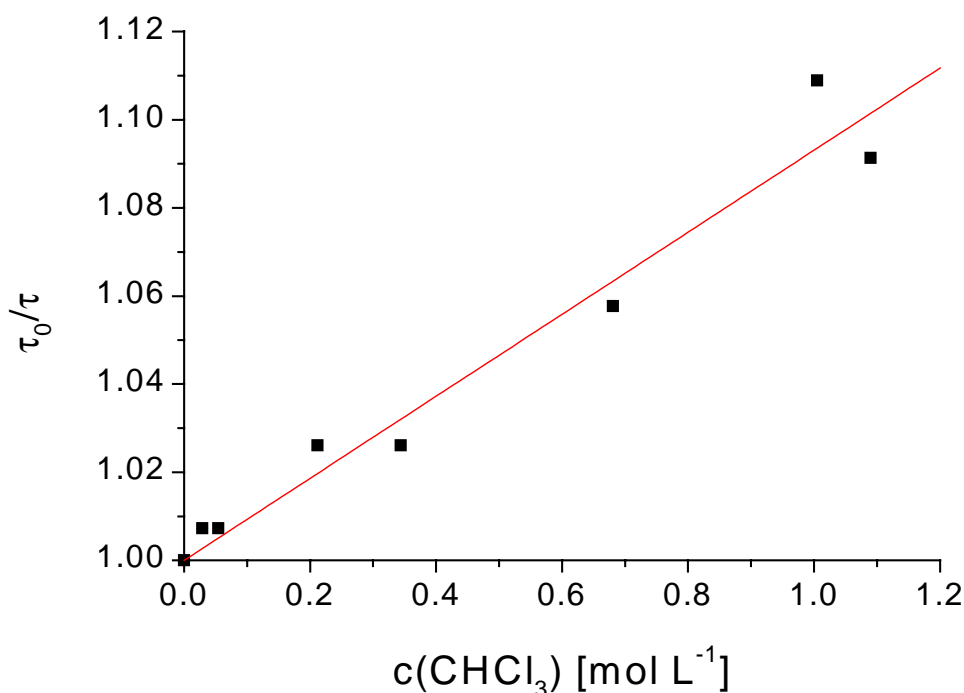(Eq. 1)

Figure 2: Stern-Volmer plot of the fluorescence quenching of 2,5-diheptyloxy-*p*-divinylbenzene by chloroform at 296 K.

Fig. 2 shows the plot τ_0/τ versus the chloroform concentration [Q], where τ_0 represents the fluorescence lifetime of the monomer in the absence of the quencher in pure cyclohexane solution and τ is the measured lifetime in the presence of chloroform. The quenching rate constant k_q was calculated to be $3.2 \cdot 10^7 \, M^{-1} \, s^{-1}$. Since k_q is about three orders of magnitude less than the diffusion rate constant k_{diff} [4] the rate determined process seems to be the formation of the exciplex between the excited monomer and the solvent chloroform. Moreover, the quantum yields of the diheptyloxy substituted monomer were determined in chloroform and cyclohexane to be 11% and 38%, respectively [5]. These results support the evidence of the quenching by chloroform

References

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