Directional energy transfer in partly ordered polymer films

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Application Note

Here, we present data recorded from stretched thin PVA films for several systems based on carbocyanines and rhodamines. Energy transfer is studied with different donor and acceptor transition moments orientation relative to the axis of stretching. The data demonstrate that donor - acceptor emission anisotropy spectra differ for these systems in uniaxially stretched films, whereas they are the same in unstretched films. We measured acceptor fluorescence and it can be either strongly polarized after nonradiative energy transfer in stretched films or depolarized depending on the angular distribution of acceptor transition moments in the film. For such disordered systems sensibilized fluorescence emitted by acceptors excited exclusively through energy transfer from donors is almost totally depolarized [1–3]. Quite different observations have been reported for uniaxially oriented polymer films, where emission anisotropy remains high [3,4].

Fluorescence spectra and quantum yields were measured upon front face excitation and observation of sample fluorescence using spectrofluorometer constructed in our laboratory (see Fig. 1). The polarization plane of the exciting light was set vertical and was parallel to the direction of polymer stretching. Fluorescence light was recorded by the H10721P-01 photomultiplier (Hamamatsu Photonics K.K., Japan) mounted at exit slit of a Czerny-Turner spectrograph (SR-303i-B, Andor Technology, UK). This configuration gives many opportunities for full control measurements condition using LabVIEW environment. Emission spectra were collected using a CCD camera (iVac DR-324B-FI, Andor Technology, UK) mounted at the second exit port of the same spectrograph. Time-resolved emission anisotropy measurements upon the excitation λ_{exc} = 378 nm were performed with the use of a laser head LDH-D-C-375 with controller PDL 800-D, PCI-board for TCSPC TimeHarp 200

Figure 1 Experimental set up

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(PicoQuant, Germany). Emission anisotropy decays for two carbocyanines at R_S=3 and RS=5 were measured within donor (λ_{obs}=510 nm) and acceptor (λ_{obs}=600 nm) fluorescence bands at UV excitation λ_{exc}=378 nm.

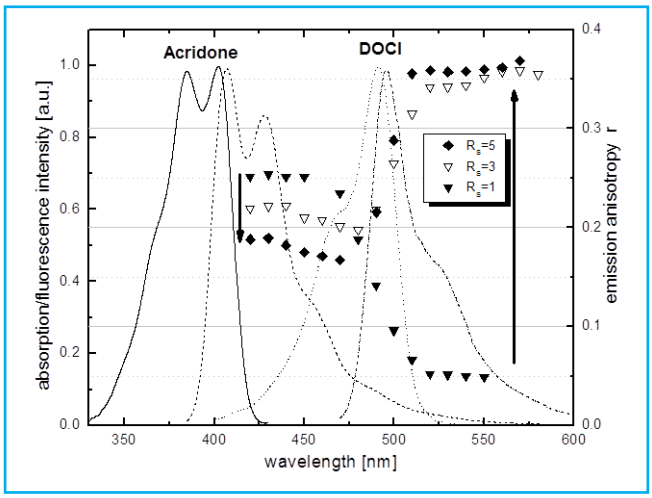

Figure 2

Fig. 2 shows fluorescence repolarization in the band of acceptor emission for R_S=3 and R_S=5 in the donor-acceptor system. Energy transfer takes place from donor molecules with transition moments localized perpendicular to long molecular axis to acceptors, transition moments of which are localized parallel to long molecular axis. Long molecular axes of acridone and DOCI tend to orientate towards the axis of matrix stretching, however, transition moments of both species orientate a little differently upon matrix stretching. Emission anisotropy in the donor emission band decreases with the increase of matrix stretching in view of more and more effective orientation of acridone transition moment in the direction perpendicular to the direction of stretching. The repolarization effect in the time domain can be also illustrated by a somewhat different presentation visible in Fig. 3. For the acridone-DOCI system, where relative emission anisotropy decays in the donor and acceptor band are shown. Sensitized acceptor emission anisotropy (λ_{obs}=540 nm) decays much slower than that of the donor (λ_{obs}=440 nm) due to the preferential orientation of acceptor transition moments towards the direction of stretching.

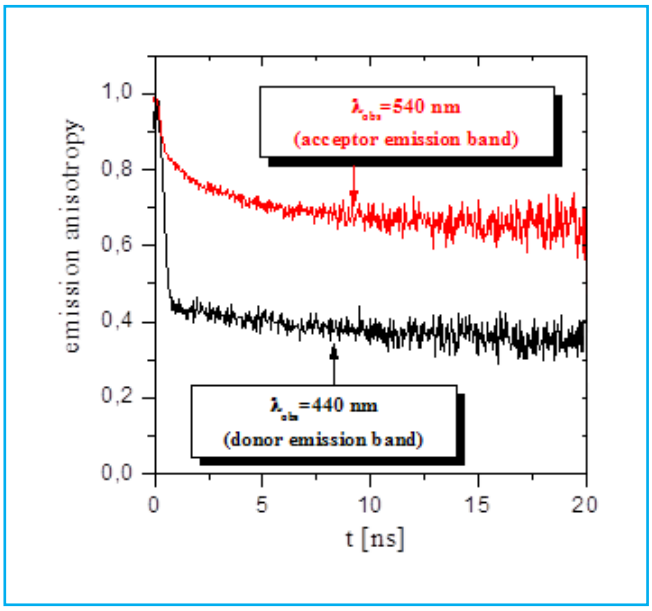

Figure 3

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