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Micro-Scale Spectroscopy in Organic Solids

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Low temperature excitation spectra of pseudoisocyanine J-aggregates in poly(vinyl sulfate) thin films on sub-micron scales are presented. Individual J-aggregates are located by scanning microscopy using a gradient index SELFOC lens. The excitation spectra show large inhomogeneous broadening with super-imposed statistical fine structure.

Keywords: single molecule spectroscopy; scanning microscopy; pseudoisocyanine J-aggregates

INTRODUCTION

In the past decade the spectroscopy of organic dyes in low temperature solids has been successfully reduced to microscopic scales. As a result, detection and characterization of single dye molecules in different matrices have become reality[1]. The extreme sensitivity of individual molecular lines to the changes in the local environment has made single molecule spectroscopy an ultimate tool in the study of solid state matter on a microscopic (nm) level.

We have recently introduced a gradient index SELFOC micro-lens as a sample substrate and fluorescence focusing element for single molecule spectroscopy[2]. Especially, in the back-illumination configuration[3] the SELFOC lens offers an enormous potential for scanning microscopy and spectroscopy in the temperature range between 1.5 K and room temperature.

In this paper we present preliminary results on low temperature sub-micron scale spectroscopy and microscopy of J-aggregates of pseudoisocyanine (PIC) dyes in thin polymer films. Optical spectra of J-aggregates are characterized by a narrow intense line, called J-band, shifted to the blue from the monomer transitions. The J-band originates from the aggregate excitonic transitions and its narrow width is a result of motional narrowing process.

EXPERIMENTAL

The principal of micro-scale spectroscopy and scanning microscopy using a SELFOC lens is shown in Fig. 1. One side of the SELFOC lens (Nippon Sheet Glass) is covered with the sample. The opposite side is illuminated with a near-parallel laser beam. By passing the lens the beam is focused to a sub-micron diameter (approx. 0.8 μm for the W-type lens) and excites the sample. Luminescence from the sample is focused into a parallel beam and is detected by a photomultiplier together with a photon counter. With the laser spot in a fixed position the classical single molecule spectroscopy can be performed[3]. By changing the incident angle ß the laser spot can be scanned across the sample. Relative position r of the beam is related to ß (in rad) as $r = ß/(n_0.A^{-1/2})$, where n_0 is the axial refractive index of the lens and $A^{-1/2}$ is a SELFOC lens parameter (its values range between 0.304 and 0.430 mm^{-1} for lens types used). By this, scanning microscopy with a sub-micron resolution is achieved. The scanning range is principally limited only by the size of the lens surface; in practice, we obtain ranges of more than 400 microns. Excitation spectra were obtained by scanning a single mode dye laser (Coherent 699-29).

The samples were prepared according to the method of ref. [4]. PIC-Cl was dissolved in aqueous solution of poly(vinyl sulfate) (PVS) at 80-90° C and spin-coated at 3000 rpm on the top of the SELFOC lens. Reference bulk samples were prepared in the same way by spin-coating on a cover glass. The structure of the reference samples was checked with an optical fluorescence

microscope at 1000x magnification. The microscope resolves stretched fibers of J-aggregates that are tens of microns long and have a sub-micron diameter.

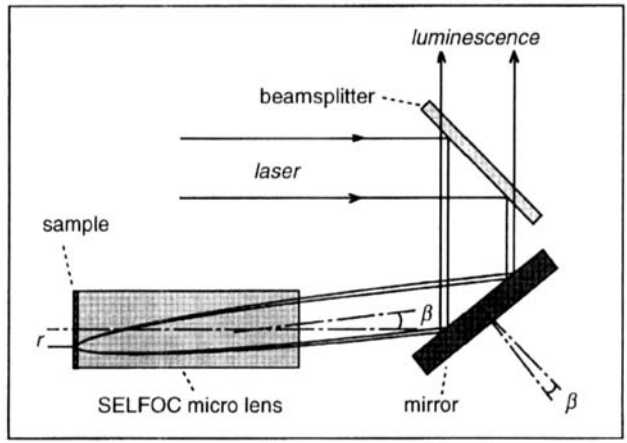

FIGURE 1 The principle of single molecule spectroscopy and scanning microscopy using a gradient index SELFOC lens.

RESULTS AND DISCUSSION

Low temperature excitation and fluorescence spectra of the bulk samples are shown in Fig. 2. The absorption J-band has a maximum at 567.4 nm at 4.2 K. The fluorescence spectrum exhibits a broad band shifted to the red from the J-band. This broad band is observable at cryogenic temperatures only and originates from emission from traps that are populated by energy transfer from the lowest level of the J-aggregate excitonic band[5]. The traps are located near the aggregate fibers. Their transition dipoles are oriented parallel with the J-band transitions dipole moments. The trapping states are photochemically unstable under strong laser illumination of the J-band. The photoproducts exhibit PIC monomer-like absorption spectra. In the excitation spectra of the microscopic samples and in the scanning microscopy we use the emission from the traps to monitor the J-band transitions.

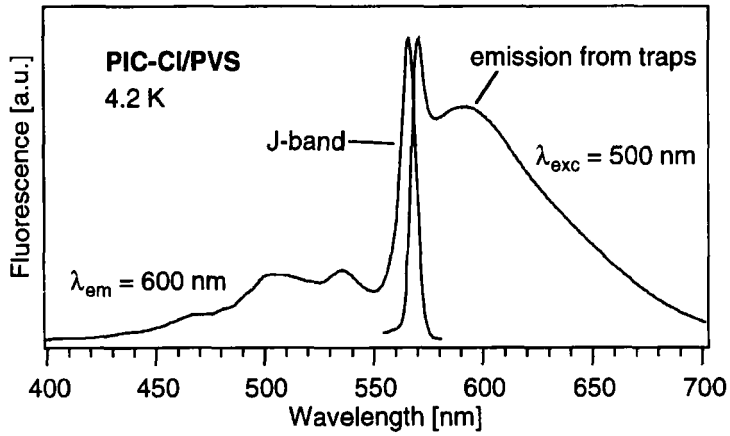

FIGURE 2 Excitation (left) and fluorescence (right) spectra of the bulk samples.

Scan of the laser beam across the sample on the surface of the SELFOC lens at 77 K is shown in Fig. 3 as the top line. The intensity of the scanning light is attenuated to avoid photodamage. The scan exhibits a series of sharp lines of varying intensity and width that are distributed randomly over the scan range of 380 μm. The widths of the narrowest lines are determined by the optical resolution. The width of the broader lines is probably a result of the orientation of the fibers partly in the direction of the scan. Some of the lines have a complex shape indicating that they are composed of several fibers unresolved with the 0.8 μm resolution. The varying intensity results from several factors: size of the fiber, its orientation with respect to the polarization of the laser beam, and the number of the traps associated with the fiber. The bottom lines in Fig. 3 represents an identical scan performed after a "burning" scan. During the burning the intensity of the laser light is 3 orders of magnitude larger and scanning speed 10 times larger. The burning causes photo-degradation of most of the traps and leaves only a flat background in the following scan. This is a proof that all the signal in the original scan comes from the J-aggregate excitonic transitions.

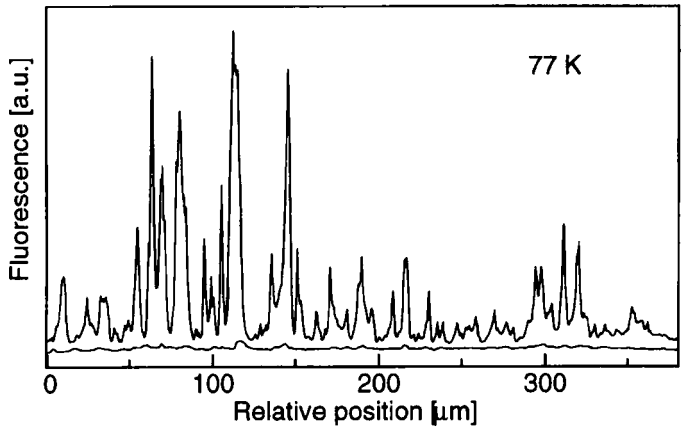

FIGURE 3 Spatial scan across the sample before (top) and after (bottom) intensive laser irradiation.

After locating an aggregate fiber by the scanning microscope we measured fluorescence excitation spectra of the J-band at 1.5 K. Some of the characteristic results are presented in Fig. 4. The top spectrum in Fig. 4a represents a scan of more than 2 nm (accomplished with a single mode dye laser) on the red side from the J-band maximum. The spectrum shows monotonously decreasing signal with a weak structure at the arrow position. The bottom spectrum was taken after several minutes of burning at 568 nm with a full laser power. The burning kinetics is seen as the inset. The conclusions from Fig. 4a are: 1. On the scale of ~ 1 μm the aggregate fibers are comprised of a large ensembles of coherently coupled J-aggregates. Their corresponding homogeneous excitonic transitions are inhomogeneously distributed over the whole range of the macroscopic the J-band. 2. Narrow-band laser irradiation does not produce a narrow hole but causes a broadband decrease of luminescence - that is, the trap(s) being burned out by the laser are common to the whole inhomogeneous distribution of the excitonic transitions.

Fig. 4b shows excitation spectrum at a different location in the sample - a peak arising probably from one or a few homogeneous excitonic transitions can

be recognized. The appearance of the peak on the broad background resembles the statistical fine structure in single molecule spectroscopy[1]. For comparison, a resonant hole in absorption spectra of the bulk samples[5] is shown in Fig. 4c.

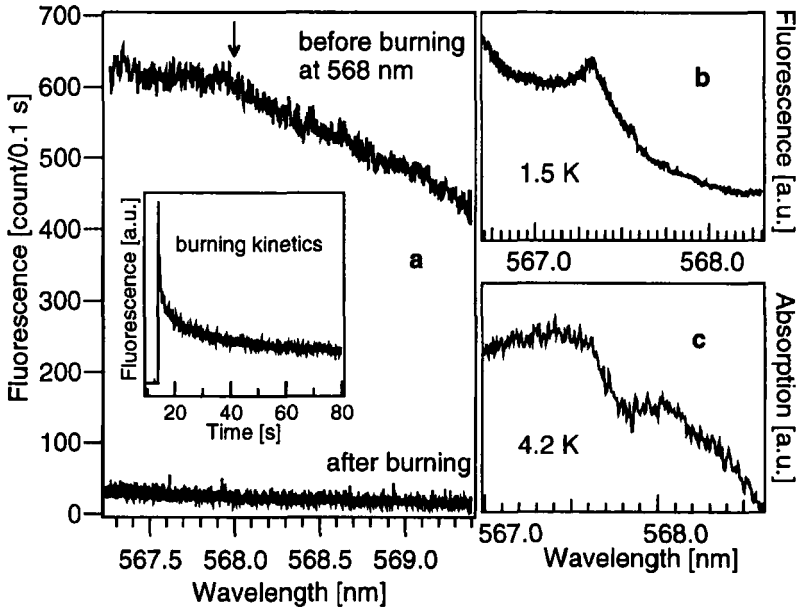

FIGURE 4 a,b - Excitation spectra of the microscopic samples at 1.5 K c - Resonant hole in absorption spectrum of the bulk sample.

Acknowledgments

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