Micro-spectroscopy of individual nanostructures of molecular aggregates: relationship between morphology and optical properties

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Abstract

Results on microscopic reflection imaging and spectroscopy of J-aggregates of pseudoisocyanine dyes in thin film matrices of polyvinyl sulfate, polyvinyl alcohol and polystyrene are reported. Despite different aggregation mechanisms in the three polymers, reflection images show formation of similar, highly reflecting fiber-like nanostructures in all samples. Local reflectance spectra reveal large inhomogeneities of local optical properties that are determined by an onset of exciton–polariton character.

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1. Introduction

Aggregates of organic molecules are ordered molecular assemblies different from molecular crystals that have specific optical properties. Because of them, aggregates play crucial roles in many biological processes, such as photosynthesis, and have great potential in technological applications as linear and non-linear nano-optical materials. Among organic dyes, cyanines readily form large aggregated structures that consist of hundreds of molecular units. This phenomenon has been observed as early as in the 1930s [1,2] and the corresponding type of molecular aggregates is referred to as J-aggregates. Their characteristic narrow red-shifted spectral band (J-band) has been explained due to delocalized Frenkel exciton states in one-dimensional aggregates of large coherent length [3–5]. This model has been later confirmed by numerous experiments performed on bulk samples of the original pseudoisocyanine (PIC) dye and related compounds. Only recently, however, have PIC aggregates in a polymer film been studied with an optical microscopic technique, the near-field scanning optical microscope (NSOM) [6]. The images have shown self-assembled structures of higher dimensionality that resemble flexible fibers. The similarity of a local fluorescence
spectrum obtained with NSOM at individual fibers with the bulk fluorescence suggested that the excitonic structure within the fibers can be identified with the one-dimensional aggregate chain concept. Later, reflection micro-spectroscopic study of a closely related system [7] revealed large inhomogeneity of local optical properties of the fiber-like aggregate nanostructures. High reflectivity values, broadening of local reflectance spectra and evolution of polariton modes are signs of an onset of exciton–polariton interaction in some aggregate nanostructures as a result of increasing exciton–photon coupling. The polariton-like character of local reflectance spectra has also been correlated with the aggregate morphology by a simultaneous reflection and atomic force microscopic study [8]. Finally, polarization microscopic experiments have shown [9] that the transition dipole moment of the exciton responsible for the main J-band can be oriented at a wide range of angles, from parallel to perpendicular, with respect to the long axis of the fiber nanostructures. All these results have posed questions on the nature of the nanostructures observed, on the role of the polymer in their assembly, and on the character of the PIC J-aggregates themselves.

Here, we attempt to address some of these questions. We perform reflection micro-spectroscopic and polarization study of PIC–Cl and PIC–Br aggregates in three different polymer matrices: polyvinyl sulfate (PVS), polyvinyl alcohol (PVA) and polystyrene (PS). The mechanisms of J-aggregate formation in each of these three matrices are different. In case of PVS, aggregates are formed by electrostatic interactions of the PIC cationic sites with the PVS anionic groups of $\text{SO}_3^-$ [10,11]. In PVA, aggregates self-assemble by cooling in concentrated aqueous solution [1], while in PS they are formed by precipitation from concentrated polar solution in a non-polar solvent [1]. Despite these differences in the formation mechanisms and the differences in physical properties of individual polymers, such as dipole moments and refractive indices, the results show growth of highly reflecting self-assembled nanostructures with similar local spectroscopic and polarization properties in all samples studied.

2. Experimental

Preparation of the PIC/PVS system is based on the method of [6]. The method involves addition of 10 mM methanol solution of 1,1'-diethyl-2,2'-cyanine chloride (PIC–Cl, Nippon Kankoh Shikiso Kenkyusho) or PIC–Br to hot stirring aqueous solution of 7.5 mg/ml of potassium polyvinyl sulfate and immediate spin-coating of the mixture at 3000 rpm on a cover glass. The PIC/PVA system was prepared according to the method of [12]. 40–60 mg of polyvinyl alcohol were mixed with 2 ml of water and heated up to 90 °C. After complete dissolution of the polymer, 5 mg of PIC–Cl were added to the stirring solution and the mixture was spin-coated at 3000 rpm on a cover glass. PIC/PS system was prepared by dissolving 40 mg of polystyrene in 3.5 ml of benzene at 40 °C. Concentrated solution of PIC–Cl was prepared by mixing 3.2 mg of PIC with 1 ml of pyridin, followed by 30 min sonification and centrifuge separation of the clear solution. 0.4 ml of the PIC/pyridine solution was added to the stirring polymer solution and the mixture was immediately spin-coated at 3000 rpm on a cover glass.

The method of reflection micro-spectroscopy has been described in detail elsewhere [7,9]. Briefly, light from a tungsten lamp and a 1.5 m monochromator is introduced into a large core optical fiber and brought to an inverted reflection mode microscope (Union Tokyo, 100× oil immersion lens, NA 1.25). Typical light intensity at the sample is 1.2 mW cm$^{-2}$ at the J-band maximum. Reflection images at specified wavelengths are detected with a cooled CCD camera (Princeton Instruments PentaMAX) and local reflectance spectra are reconstructed from a series of images by plotting the reflected light intensity at certain location against the wavelength. The polarization of the incident light is modified by rotating a sheet polarizer placed behind the microscope collimator. The extinction ratio at the sample position is typically 70:1. Polarized reflectance data at specified wavelengths are obtained by rotating the polarizer in increments of 5° and recording a reflection image with the CCD camera at each step. Local polarization dependence is reconstructed by plotting the reflected light intensity at
certain location against the polarizer angle. The data have been corrected for the spectral and polarization characteristics of the light source, optical fiber, microscope and CCD camera. All experiments are done at room temperature.

3. Results

3.1. PIC in polyvinyl sulfate

Typical reflection image of the PIC–Br J-aggregates in a thin film PVS is shown in Fig. 1(a). The image consists of highly reflecting fiber-like structures on a dark background, similar to those observed by NSOM [6]. The structures can be up to tens of microns long, their width at half-height above the polymer film is typically 80–300 nm and their thickness above the film varies between a few and more than 100 nm as observed by atomic force microscope [8]. The line bars in the image indicate absolute orientations of the exciton transition dipole moments at 572 nm. The orientations were obtained by fitting the polarization dependence data at each location with an $a + b \cos^2 (c \gamma + \delta)$ function. The resulting phase $\delta$ has been taken as the exciton dipole angle projection in the image plane. It can be seen that for this particular sample the dipole orientations with respect to the fiber long axis can range from almost parallel (location 4 and its vicinity) to perpendicular (location 1). This is a typical observation for most of the PIC/PVS samples studied so far; while the fraction of locations that show large deviations from the parallel direction varies from sample to sample, it has never been observed that the dipole moment would be aligned solely parallel with the fiber direction throughout any of the samples studied. This is in contradiction to most of the results of polarization absorption experiments on oriented aggregates reported on bulk samples [12,13] as well as by microscopic studies [14,15], where the dipole has been found or assumed oriented parallel with the one-dimensional J-aggregate chains. Fig. 1(b) showing local reflectance spectra at selected locations of Fig. 1(a), demonstrates the variety of local optical properties observed even on the scales of a few microns. The spectra range in shape from a dominant peak (locations 1 and 5) to broadened bands with mode structure (locations 2–4). The evolution of the mode structure, typically observed in reflectance spectra of thin organic crystals [16], has been ascribed to an onset of exciton–polariton character due to increased exciton–photon coupling [7]. This interpretation is based on the fact

Fig. 1. Reflection micro-spectroscopy and polarization dependence of PIC–Br in thin film of polyvinyl sulfate. (a) Reflection image taken with unpolarized light at 572 nm; the lines indicate orientations of exciton transition dipole moments at this wavelength; (b) local reflectance spectra taken at locations 1–5 of (a); (c) dependence of the angle $\alpha$ between the 572 nm transition dipole moment and the fiber long axis on the reflectivity of J-band; the line is drawn as a guide for the eye.
that the modes (more specifically, the minima of
the spectral dips) are shifted exclusively to the red
with respect to the resonant J-band transition [17].
The magnitude of the shift may vary from a few to
more than 100 cm$^{-1}$. Frequency of the resonant
transition is determined in each sample individually
according to the average position of the sharp
J-band reflectance peak of the low-reflectivity loca-
tions. An alternative explanation of the mode structure, most often used in interpretation of re-
flexance bands in organic crystals, is in terms of
exciton–vibronic coupling. Thus, e.g., a series of
reflectivity minima in reflection bands of PIC
crystals, shifted to higher energies from resonance
[18], has been explained due to coupling to an
intramolecular vibration mode. A different
phenomenon may appear in low temperature reflec-
tion spectra of high-purity organic crystals
where a sharp dip or a series of dips is a result of
the interaction of light with crystal surface excit-
tons. Due to the lack of interaction with neigh-
boring crystal layers surface excitons have higher
energy compared to bulk excitons and their mode
structure is again shifted to higher energies com-
pared to the bulk resonance. In our data, the ref-
lecance dips (virtual polariton modes [17]) are
due to standing waves inside the fiber nanostruc-
tures that start coupling above certain thickness of
the fiber [8]. Similar observation has been made
recently in bulk reflectance spectra of glassy PIC
thin films [18]. Results obtained on a statistical
ensemble of 42 locations of three different samples
revealed that there is an obvious correlation be-
tween the magnitude of the angle $\alpha$ between the
exciton dipole direction and the long axis of the
fiber structures, and the local spectral properties.
The correlation is evident from Fig. 1(c), where the
angle $\alpha$ is plotted against reflectivity values of the
J-band. With increasing reflectivity the 572 nm
exciton dipole moment gradually changes from
direction parallel to the fiber structure to direction
perpendicular to it.

3.2. PIC in polyvinyl alcohol

As in the case of the PIC/PVS samples, the
morphology of the PIC aggregates in thin film
polyvinyl alcohol strongly depends on the sample
preparation procedure. Figs. 2(a) and 3(a) show
reflection images of samples prepared with different
PVA concentrations. In the case of 2 wt%

![Reflection micro-spectroscopy of PIC–Cl in thin film of 2 wt% polyvinyl alcohol](image_url)
sample (Fig. 2(a)) the image consists of nearly homogeneous distribution of structureless PIC aggregate “film” forming a strongly reflecting background, on top of which appears a flow-oriented network of fiber-like structures. The strong background is the main difference between the PIC/PVA and the PIC/PVS samples. In case of PVS the reflectivity between the fiber structures is close to zero, while for PIC/PVA the reflectivity ratio between, e.g., the strongly reflecting location 1 and the background location 4 of Fig. 2(a) is only 1.3. The fiber structures themselves resemble those of the PIC/PVS samples. Fig. 2(b) shows local reflectance spectra taken at different locations of the image. All four spectra have almost identical lineshapes consisting of a single narrow peak with a maximum at 571.5 nm and half-width of 9–10 nm. The only difference between the spectra of the fiber structures and those of the background is the total reflectivity. The lineshapes resemble the exciton-like reflectance peaks observed in low reflectivity structures of the PIC/PVS samples [7] and are close to the lineshape of the bulk J-band absorption spectrum (Fig. 2(c)). Polarization experiments show that the exciton dipole moments within the background film are oriented isotropically, resulting in zero polarization dependence of the background reflectivity. The dipole moments of the fiber structures show definite orientation but their extinction ratio (ratio of the maximum to minimum polarized reflectivity) is rather low due to the overlap with the strong isotropic background.

With increasing PVA concentration there appears to be an increasing fraction of locations where the reflectance of the background film drops and the sample morphology as a whole resembles that of the PIC/PVS films. An example of a 3 wt% sample is shown in Fig. 3. The fibers generally appear more rigid and randomly oriented than those of the 2 wt% sample. Local reflectance spectra in Fig. 3(b), especially those at locations 1 and 2 along the straight part of the strong fiber, are very similar to those observed in many PVS samples. They feature a broadened main J-band, a shoulder around 540 nm and pronounced mode structure. Interestingly, signs of mode structure appear also in the narrower bands of the spectra at locations 3 and 4. The exciton dipole at all four locations is oriented far from parallel with the fiber directions, and at locations 1–3 it is close to
perpendicular to it. Fig. 3(c) shows an example of the corrected polarization reflectance data at two locations fitted with the cosine function mentioned above. As can be seen, the extinction ratio varies strongly, between 1.6:1 and 9:1 for the data shown.

3.3. PIC in polystyrene

Preliminary data obtained on the PIC/PS system are summarized in Fig. 4. Macroscopically, the film appears less homogeneous compared with the PVA samples. On the microscopic level, the reflection image of Fig. 4(a) shows again the formation of highly reflecting structures on a dark background. Compared to, e.g., Fig. 3, the morphology of these structures is more complex: the fibers are shorter and their branching ratio is much higher. Reflectance spectra in Fig. 4(b) reveal high degree of inhomogeneity of the local optical properties, similar to what has been observed for the other two systems. Between locations 4 and 1 the J-band gradually broadens, its reflectivity increases and its position changes. In spectrum 1 an onset of the mode structure is apparent near the band maximum. The relative intensity of the 540 nm shoulder also increases and the band is more pronounced compared to PVS or PVA. Further work on this system is now in progress.

4. Discussion

The role of specific polyanions in the formation of dye aggregates has been noticed before [19]. For example, it has been found that the spacing of the negative groups on the polymer chain is important as J-aggregates are formed with polyvinyl alcohol sulfate ester but not with sulfonated polystyrene [20]. Our results reconfirm the function of the ionic polymer of PVS in the J-aggregate formation, as good quality J-aggregates start forming at the PIC concentrations of as low as 0.45 mM. On the other hand, to obtain samples with qualitatively same bulk absorption spectra the PIC concentration in the PVA solution must be at least 6.1 mM. In the PS system, the PIC concentration was on the order of 1 mM. In the light of the different J-aggregate formation mechanisms, the observation of similar fiber-like nanostructures with comparable optical properties comes as a surprise. It indicates that the polymer itself might not be structurally involved in the growth of the nanostructures and that the model [21] according to which individual one-dimensional (1D) PIC/PVS complexes bind together by a novel non-covalent mechanism to form alternating PIC/PVS layers that comprise the observed aggregate fibers might not be universally valid. The results obtained on the PIC/PVA samples also pose questions on the validity of the meso-macro aggregate hierarchical structural model used to explain the results in [12]. The polarization reflection experiments provide evidence that the fiber structures are not simple aligned one-dimensional threads or blocks of J-aggregates. The correlation between the exciton transition dipole angle and the spectral properties of individual fi-
bers indicates that together with the growth of the fibers there is a qualitative structural change that demonstrates itself, apart from the dipole angle change, by an increase of polariton character of the light–matter interaction. While at this stage there is no evidence for concrete molecular arrangement of the PIC and polymer molecules inside the fiber structures, this arrangement is definitely different from one-dimensional aggregate chain as well as from bulk crystal state. One speculation might be for a growth of PIC nanocrystals upon a framework of aligned one-dimensional chains serving as nucleation cores, where the relative fraction of the nanocrystalline states would determine the polarization and spectral properties. In this picture, large oscillator strength of the crystal exciton would explain the polariton-like character of the spectra; the 540 nm transition could be a crystal Davydov component. Another possible model would be one in which individual linear one-dimensional aggregates are woven into a complex rope-like structure. The degree into which an originally loosely bound rope is compressed axially would determine the density and angle of individual chain packing and consequently the spectral and polarization properties. We note that recently reported results on glassy PIC films show similar morphological and optical properties [18] and might be structurally close to the fiber nanostructures observed here.

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