Pseudoisocyanine J-Aggregate to Optical Waveguiding Crystallite Transition: Microscopic and Microspectroscopic Exploration

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Using fluorescent microscopy and microspectroscopy, optical properties and morphology transformations in individual pseudoisocyanine (PIC) J-aggregates in aqueous electrolyte solutions have been explored. A stringlike structure of J-aggregates with a string diameter much less than 1 μm has been observed. Photodestruction of the strings under short-wavelength excitation has been revealed. Rodlike PIC crystallites, about 1 μm in diameter, have been observed with time. The fluorescence spectrum of rodlike crystallites has been found to differ from that of stringlike J-aggregate and from PIC crystal powder spectra. The crystallites are very stable, and their photodestruction has not been observed under any excitation conditions. It has been found that rodlike crystallites in contrast to stringlike J-aggregates possess optical waveguide properties. The luminescence of crystallites can be observed only at the excitation spot and at butt ends located up to hundreds of micrometers from the excitation spot.

Introduction

More than 70 years ago Jelley and Scheibe discovered independently that cyanine and merocyanine dyes can form ordered aggregates, which were named J-aggregates or S-polymers in honor of their discoverers. J-aggregates are assemblies of noncovalently coupled luminophores in the form of linear or circular chains, which, in turn, can form complex cylindrical patterns.[1–3] J-aggregates are characterized by a narrow absorption band red-shifted with respect to the relevant monomer band. The main optical properties of J-aggregates such as superradiance and coherent exciton transport are well-described on the basis of a one-dimensional exciton model.[1,2,4] However, J-aggregate structure and morphology have been poorly understood for a long time due to the impossibility of observing J-aggregates in solution in situ. Recently a series of experiments on J-aggregate structure exploration have been carried out using such advanced techniques as near-field scanning optical spectroscopy (NSOM), atomic force microscopy (AFM), cryotransmission electron microscopy (cryo-TEM), fluorescent microscopy, and microspectroscopy.[3,5–16]

1,1′-Diethyl-2,2′-cyanine (pseudoisocyanine, PIC) is one of the most studied organic dyes and forms J-aggregates both in aqueous solution and at the solid/liquid interface. Higgins and Barbara were among the first to investigate PIC J-aggregate structure in a poly(vinyl sulfate) (PVS) film using NSOM.[5,6] PIC J-aggregates were found to form a supramolecular network from fibers with lengths of up to hundreds of micrometers and widths of about 50 nm. The localized photodestruction of the J-aggregates was used as a measure of the physical extent of exciton migration along the J-aggregate. The excitons were found to migrate less than about 50 nm from the NSOM tip. It should be noted that these data contradict results cited in ref 1, where strong quenching of PIC J-aggregate luminescence by energy traps was observed at the ratio PIC molecules:trap = 2600:1.

Using AFM, Yao et al. observed PIC J-aggregate formation at a mica/solution interface in solution.[7] J-aggregates were shown to possess a three-dimensional island structure. The size of the islands ranges about 400–600 nm long, 80–100 nm wide, and 3–6 nm high.

Von Berlepsch and co-workers studied PIC J-aggregate structure in aqueous solutions by cryotransmission electron microscopy (cryo-TEM) and polarized-light optical microscopy.[9] They observed a homogeneous and closely packed network of long J-aggregate fibers, with fiber diameter of 2.3 nm and length on the order of 350 nm. It was revealed that J-aggregate structure strongly depends on dye concentration and at high concentration the transition to the more concentrated hexagonal phase was observed. They also found a formation of complex fiber bundles from isolated fibers for PIC J-aggregates in aqueous sodium chloride solution.[10]

It is clear now that the supramolecular structure of J-aggregates depends strongly on the type of dye, substitutes, and preparation conditions and can change in time (hours, days, and months). Moreover, despite a relatively long history of J-aggregate investigation, some questions concerning J-aggregate structure (i.e., aggregation number, geometric shape, and size) and the effect of structure on exciton properties and exciton energy migration still remain even for the most investigated PIC J-aggregates.

In this paper we report on the structural transformation of pseudoisocyanine iodide (PIC) J-aggregates in aqueous electrolyte solution using fluorescent microscopy and microspectroscopic techniques, as it was found that adding electrolyte in aqueous solution can significantly affect J-aggregate morphology.[8,10]

Experimental Section

1,1′-Diethyl-2,2′-cyanine iodide (Sigma Aldrich) was used without further purification. Sample solutions were prepared by

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dissolving PIC (0.5 mM) in an aqueous NaCl (0.2 M) solution under moderate heating (<80 °C).[17] Then the solutions were cooled to room temperature. Fluorescent microscope images were taken at different aging periods t_a. For microscopic investigations a drop of the sample solution was placed between a glass slide and a coverslip.

Fluorescence microscope images were obtained by using a CCD camera (Canon 300D, Japan) set on a handmade confocal luminescent microscope equipped with objectives 40× and 100× (LOMO, Russia). For scaling, 1 μm luminescent polystyrene microspheres (Molecular Probes) were used. Fluorescent spectroscopic measurements under the microscope were carried out using a grating monochromator (MDR-23, LOMO, Russia). A YAG:Nd^{3+} laser beam ($\lambda = 532$ nm, second harmonic) and a superbright light-emitting diode (LED) ($\lambda_{max} = 476$ nm) were used as excitation sources for fluorescence imaging and spectroscopy. LED was also used for the wide-field illumination of the samples. The excitation beam was directed to the sample via a dichroic mirror (580, LOMO, Russia), which separated emitted fluorescence from scattered excitation light. A short-cut filter was mounted in front of the CCD camera to block unwanted spectral components of the emitted fluorescence.

Results and Discussion

PIC J-aggregate formation was controlled by the appearance of the J-band ($\lambda_{max} = 573$ nm) in the absorption spectrum of PIC solution. The fluorescent image of a fresh solution represents a continuous luminescent "cloud" where it is impossible to distinguish individual objects. This observation agrees with the data of PIC cryo-TEM microscopy[10] that revealed the formation of a network superstructure consisting of isolated fibers of 2.3 nm diameter and fiber bundles in aqueous electrolyte solutions, which we could not resolve by the optical microscope. In 6 h separate strings begin to form from the luminescent "cloud", and 24 h after the sample preparation a network of individual well-distinguishable strings with diameters of less than 1 μm and lengths of several hundred micrometers was observed (Figure 1a). Similar strings were observed for PIC in PVS films by NSOM.[5,6] We suppose strings to be fiber bundles that extended in length and diameter by an adjunction of individual fibers due to low solubility of PIC in water and screening of electrostatic repulsion forces between separate fibers by high amount of counterions. During such a transformation of PIC J-aggregate morphology, the absorption spectrum of the initial solution also changed. The J-band became about 2 times narrower ($\Delta\nu_{fwhm}$(fresh solution) $\sim$ 270 cm^{-1}, $\Delta\nu_{fwhm}$(24 h) $\sim$ 150 cm^{-1}); that indicates a more ordered structure of stringlike J-aggregates.

The luminescence spectra of individual strings represent a typical narrow J-aggregate band with the maximum located within the 573−580 nm range and $\Delta\nu_{fwhm}$ changed in the 200−350 cm^{-1} range for different strings. Luminescence bands of different strings have been revealed to be 1.5−2 times narrower than those of PIC J-aggregates in a PVS film,[5,6] suggesting a more ordered structure of molecular chains that form stringlike PIC J-aggregates in a solution (Figure 1b). Such a deviation of luminescence band parameters for different PIC J-aggregate strings leads to broadening the luminescence band of a solution and a small shift ($\sim$3 nm) of the band maximum (Figure 1b). Moreover, such a feature can be observed even for a pack containing several tens of strings only (Figure 1b).

When the excitation beam was focused on a fragment of the string, the luminescence was observed only within the excited spot. Our observation agrees with the data[5,6] for PIC J-aggregates
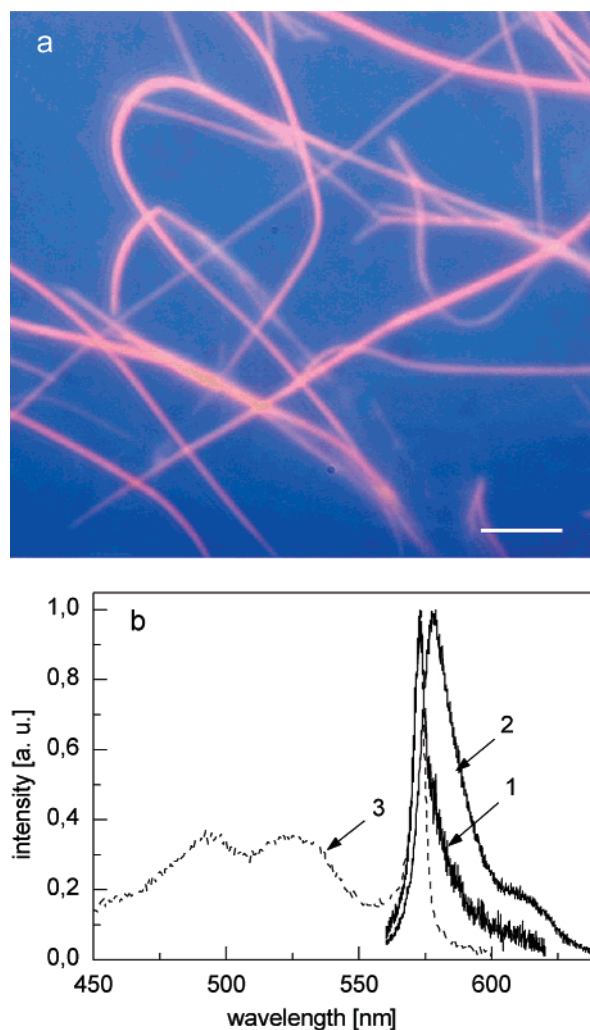

Figure 1. (a) Fluorescent image of stringlike PIC J-aggregates (bar = 5 μm). (b) Luminescence spectrum of individual string (1) and pack of about 30 strings (2); (3) absorption spectrum of the solution.

in a PVS film and contradict the data in ref 1. An intense background emission has also been observed. The luminescence spectrum recorded in this area corresponds to the luminescence spectrum of a fresh solution. By analogy with ref 11 we can suppose that there are a lot of small J-aggregates in the solution that do not participate in the formation of strings.

During a short-wavelength excitation of stringlike PIC J-aggregates with LED ($\lambda_{max} = 476$ nm), even at low excitation intensity the photodestruction of the J-aggregate has been detected (Figure 2). In several minutes after the beginning of J-aggregate illumination, we observed luminescence disappearing for some string fragments. Moreover, these fragments reveal a good reflection feature (Figure 2) in contrast to PIC J-aggregate photobleaching observed in a PVS film.[5,6] The number of such fragments increases in time, while neither the shape nor the luminescence spectrum characteristics (maximum location, $\Delta\nu_{fwhm}$) of the string changes. During similar long-wavelength laser excitation ($\lambda = 532$ nm), such features were not observed despite a more intense excitation. Recently, for amphi-PIC J-aggregates photoinduced reorganization of molecular packing at short-wavelength excitation has been reported.[13] This reorganization was accompanied by the appearance of a new band in the luminescence spectrum that was attributed to new thermodynamically stable chromophore packing of amphi-PIC J-aggregates.[13] We suppose that in the case
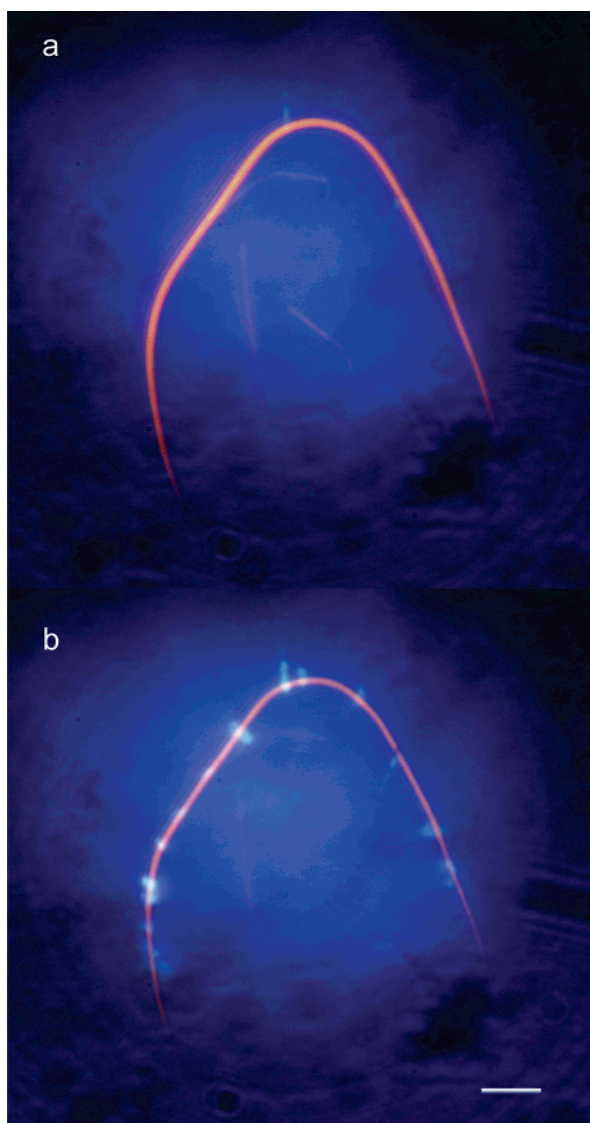
Figure 2. Photodestruction of the PIC J-aggregate string during short-wavelength excitation (bar = 5 μm): (a) at the beginning of the illumination; (b) in 5 min.

Figure 3. (a) Fluorescence image of the rodlike PIC crystallite (bar = 5 μm). (b) Luminescence spectra of the crystallite (1) and PIC crystal powder (2).

of PIC J-aggregates some kind of photoreorganization of molecular chains forming the string can also take place.

In 6−7 days after the sample preparation, new rodlike objects with diameters of about 1 μm and lengths of several hundred micrometers have been observed (Figure 3). The rods were mainly straight or slightly bent and rigid. Such a transformation of the J-aggregate morphology was observed for 5,5′-dichloro-3,3′-disulfopropyl thiacyanine (TC) J-aggregates in an aqueous sodium chloride solution[8,14] and for J-aggregates of 3,3′-bis(4-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine dye (C_8O_4) in aqueous solution with the cationic surfactant trimethyltetradecylammonium bromide (TTAB),[15] but for PIC J-aggregates it has been observed for the first time. The luminescence spectrum of the rod differs strongly from the luminescence spectrum of stringlike J-aggregates. It consists of two bands with maxima at 595 and 640 nm, respectively (Figure 3b). The band that corresponds to the J-aggregate luminescence is not observed in the spectrum. The absorption spectrum of the rods solution also does not reveal the J-band and is similar to the spectrum of PIC monomer solution (with a maximum at 525 nm and a shoulder at 495 nm). Unlike strings, rods are characterized by nonuniform light emission. In the rod there
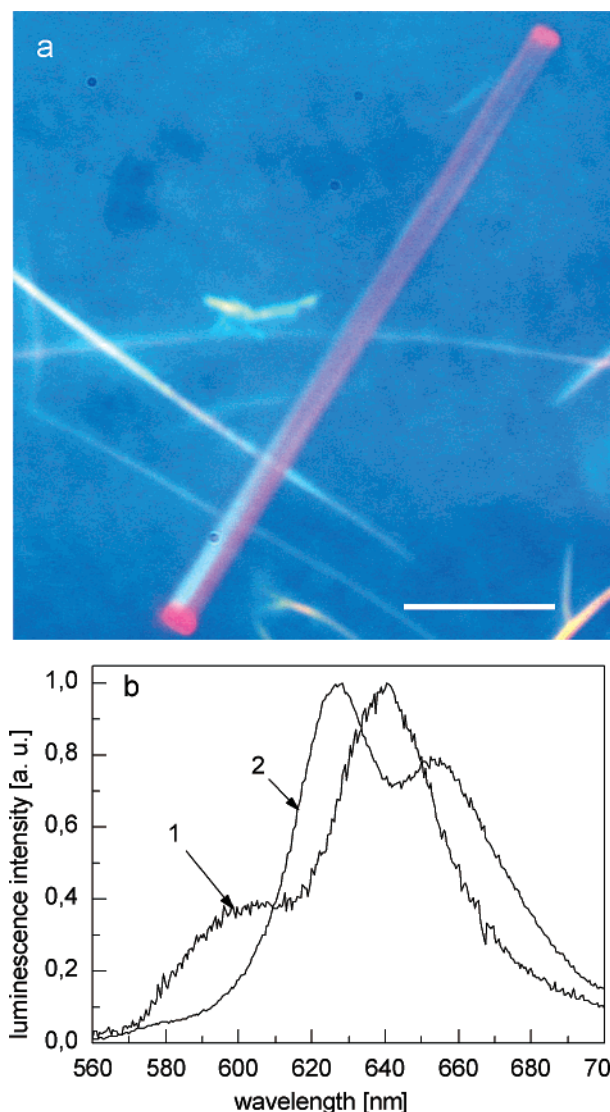
are areas with a strong light reflection (Figure 3a). Emitting and reflecting areas seem to be swirled along the rod axis. The photodestruction of such rods has not been observed at any excitation conditions (LED or laser beam) and exposure time.

The number of rods increases in time, and in 15−20 days the strings are not observed at all. These rodlike objects are supposed to be crystallites. It should be noted that the molecular packing in such crystallites differs from that for both PIC J-aggregates and PIC monomer crystal powder,[6,16] as the luminescence spectrum of rods differs also from the spectrum of the PIC crystal powder (Figure 3b). This is the feature of PIC crystallites that distinguishes them from similar structures described for TC[14] and C_8O_4[15] dyes. When the solution containing only rodlike crystallites was evaporated, the precipitate represented a pile of rods that differed from the initial PIC crystal powder. A luminescence band corresponding to J-aggregates was not observed in the luminescence spectrum of the precipitate even in background emission.

When an excited beam was focused on a small spot on the rod crystallite surface, the fluorescence of crystallite butt ends could be observed, although the excited spot could be focused at a distance of about several hundred micrometers from the butt ends (Figure 4). Besides the excitation spot and butt ends,
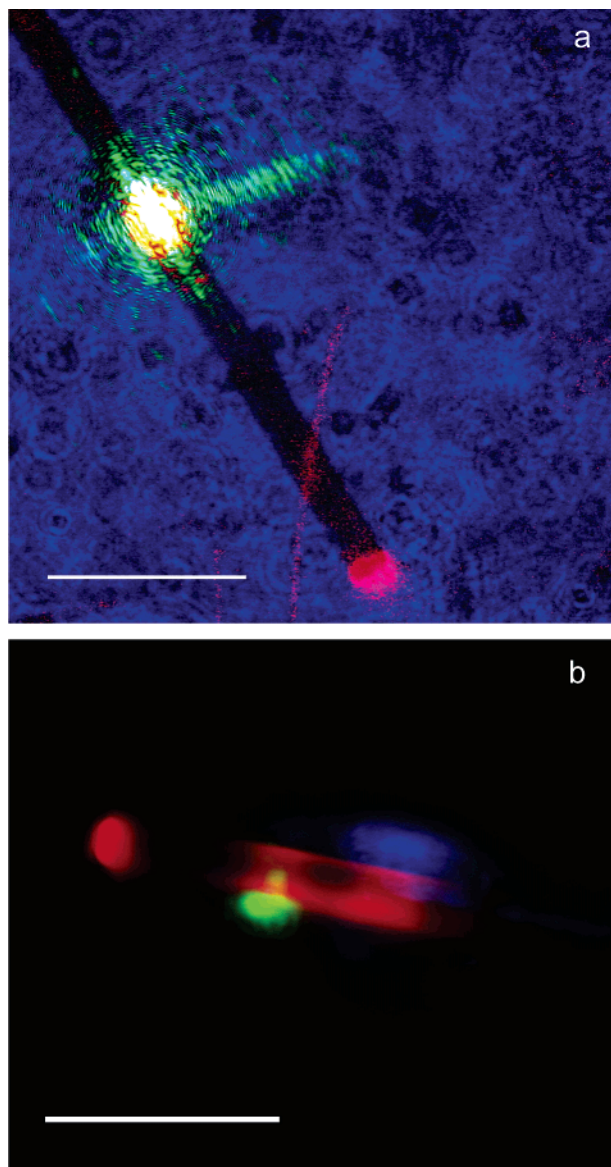
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Figure 4. Fluorescence images of the rodlike PIC crystallite (bar = 5 μm): (a) with focused YAG:Nd^{3+} laser beam (λ = 532 nm) on its surface and background illumination and (b) excited by LED (λ_{max} = 476 nm) (the green ball on the backside is a 1 μm luminescent polystyrene microsphere).

luminescence from other areas of the crystalline rod was not observed (Figure 4b). Figure 4b shows a sport of glowing LED focused on a rod. The sport is characterized by complex geometric shape and nonuniform emission. One can see that there is no emission from the area which is not excited, but is located between two excited parts of the rod. That indicates that the excitation energy migration along the rod is absent. Figure 4b shows also a luminescent image of a polymeric sphere of 1 μm diameter that is located behind the rod, but its luminescence can be observed. By analogy with rodlike structures of TC,[14] we suppose a quill cylinder structure of the rod. Taking into account high light reflection of the rod surface, we assume that crystalline rods act as an optical waveguide. Recently, similar optical waveguiding properties have been reported for nanometer-scale organic fibers of *p*-hexaphenyl (*p*-6P)[18,19] and TC H-aggregates.[20] It can be supposed that due to a large enough diameter of the crystallite (which is larger than excitation and luminescence wavelength) luminescence excited on the rod fragment spreads out inside the rod by means of

total internal reflection. Really, using the theory describing the propagating of light mode in rectangular optically uniaxial nanofibers, placed on a dielectric substrate,[19] we can estimate the possibility for optical waveguiding in PIC rodlike crystallites. For simplification, let us assume the rodlike crystallite to be optically isotropic ($\epsilon_{\parallel} = \epsilon_{\perp}$) and possess a rectangular cross section. Thus, the minimum rod width required for light propagation at 640 nm is given by $a_{min} = (\lambda/2)/\sqrt{\epsilon_{rod}-\epsilon_s}$,[19,20] where ϵ_{rod} is the dielectric constant of PIC crystallite (for PIC crystals[16] $\epsilon = 2.75$) and ϵ_s is the dielectric constant of substrate (for glass $\epsilon_s = 2.34$). Hence, $a_{min} = 205$ nm, which is much less than the rod width. Taking into account the significant Stokes shift between the absorption (525 nm) and luminescence (640 nm) maxima, which excludes readsorption, we can consider PIC rodlike crystallites to be efficient optical waveguides. Owing to this effect, PIC crystallites are attractive as optical fibers for optical microdevices.

Conclusions

It has been revealed that in aqueous electrolyte solution of PIC the formation of individual stringlike J-aggregates from a uniform network of J-aggregate fibers occurs in time. The strings possess a more ordered molecular packing. During short-wavelength excitation the photodestruction of the strings has been detected. We suppose that it is accompanied by photo-induced reorganization of molecular packing in a J-aggregate. At long aging period, new rodlike crystallites have been observed in the solution, whose luminescence spectrum differs from those for both PIC J-aggregates and monomer crystal powder. Intense luminescence of crystallite butt ends has been observed at a distance of hundreds of micrometers from the excitation spot. At the same time, luminescence of other parts of the crystallite has not been detected, pointing to the waveguide nature of excitation energy transfer.

References and Notes

(1) Mobius, D. *Adv. Mater.* **1995**, *7*, 437.
(2) *J-aggregates*; Kobayashi, T., Ed.; World Scientific: Singapore, 1996.
(3) von Berlepsch, H.; Bottcher, C.; Ouart, A.; Burger, C.; Dähne, S.; Kirstein, S. *J. Phys. Chem. B* **2000**, *104*, 5255.
(4) Spano, F. C.; Kuklinski, J. R.; Mukamel, S. *Phys. Rev. Lett.* **1990**, *65*, 211.
(5) Higgins, D. A.; Barbara, P. F. *J. Phys. Chem.* **1995**, *99*, 3.
(6) Higgins, D. A.; Kerimo, J.; Vanden Bout, D. A.; Barbara, P. F. *J. Am. Chem. Soc.* **1996**, *118*, 4049.
(7) Yao, H.; Sugiyama, S.; Kawabata, R.; Ikeda, H.; Matsuoka, O.; Yamamoto, S.; Kitamura, N. *J. Phys. Chem. B* **1999**, *103*, 4452.
(8) Yao, H.; Kitamura, S.; Kimura, K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4560.
(9) von Berlepsch, H.; Bottcher, C.; Dähne, L. *J. Phys. Chem. B* **2000**, *104*, 8792.
(10) von Berlepsch, H.; Bottcher, C. *J. Phys. Chem. B* **2002**, *106*, 3146.
(11) Tani, T.; Yamaguchi, Y.; Saeki, M.; Oda, M.; Vacha, M. *J. Lumin.* **2003**, *102−103*, 27.
(12) Tani, T.; Saeki, M.; Yamaguchi, Y.; Hayashi, T.; Oda, M. *J. Lumin.* **2004**, *107*, 339.
(13) Malyukin, Yu. V.; Sorokin, A. V.; Efimova, S. L.; Lebedenko, A. N. *J. Lumin.* **2005**, *112*, 429.
(14) Yao, H.; Michaels, C. A.; Stranick, S. J.; Isohashia, T.; Kimura, K. *Lett. Org. Chem.* **2004**, *1*, 280.
(15) von Berlepsch, H.; Regenbrecht, M.; Dähne, S.; Kirstein, S.; Böttcher, C. *Langmuir* **2002**, *18*, 2901.
(16) von Berlepsch, H.; Möller, S.; Dähne, L. *J. Phys. Chem. B* **2001**, *105*, 5689.
(17) Struganova, I. *J. Phys. Chem. A* **2000**, *104*, 9670.
(18) Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H.-G. *Appl. Phys. Lett.* **2003**, *82*, 10.
(19) Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H.-G. *Phys. Rev. B* **2003**, *67*, 115408.
(20) Takazawa, K.; Kitahama, Y.; Kimura, Y.; Kido, G. *Nano Lett.* **2005**, *5*, 1293.