

Stabilization of Individual Tubular *J*-Aggregates by Poly(vinyl alcohol)

Hans von Berlepsch,^{*,†} Stefan Kirstein,[‡] Ralph Hania,[§] Cătălin Didraga,[§]
Audrius Pugžlys,[§] and Christoph Böttcher[†]

Forschungszentrum für Elektronenmikroskopie der Freien Universität Berlin, Fabockstrasse 36 a,
D-14195 Berlin, Germany, Institut für Physik, Humboldt Universität zu Berlin, Newtonstrasse 15,
D-12489 Berlin, Germany, and Materials Science Center, University of Groningen, Nijenborgh 4,
9747AG Groningen, The Netherlands

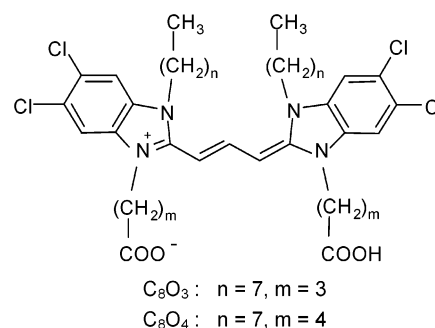
Received: April 28, 2003; In Final Form: September 9, 2003

The changes in the optical properties and morphology of *J*-aggregates formed by the 3,3'-bis(3-carboxypropyl)-5,5',6,6'-tetrachloro-1,1'-dioctylbenzimidacarbocyanine dye (C_8O_3) in aqueous solution that are induced by the addition of poly(vinyl alcohol) (PVA) were investigated by optical spectroscopy and cryo-transmission electron microscopy (cryo-TEM). Upon increase of PVA concentration, aggregates evolve that show a similar tubular morphology as those in pure aqueous solution but with new spectroscopic features. The absorption spectrum of the modified *J*-aggregates differs from that of the unmodified aggregates by a shift of one of the four transitions that constitute the excitonic spectrum. Additionally, fluorescence emission is observed not only from the exciton band with lowest energy but also from a second band at higher energy. Measurements of the linear dichroism (LD) on oriented samples reveal that three of the transitions are polarized parallel to the long axis of the aggregates, while the fourth transition is polarized perpendicular. Cryo-TEM revealed a majority of individual tubular strands for PVA-containing solutions, which is different compared to pure C_8O_3 solutions showing bundles of tubular strands. The individual strands are assumed to be PVA-coated tubular aggregates being stabilized against bundling by repulsive forces induced by the adsorbed polymer chains. The spectroscopic changes are ascribed to slight rearrangements in the molecular packing of dye molecules upon binding of PVA to the aggregates.

I. Introduction

Exciton dynamics in molecular assemblies has attracted much interest due to its role in light-harvesting antenna complexes of photosynthetic organisms.¹ Besides the investigation of biological light-harvesting complexes, it has become a challenging task in supramolecular chemistry to mimic the optical properties of such systems by assembly of synthetic dyes.^{2,3} Within the group of suitable dyes that spontaneously form supramolecular assemblies in solution, the cyanine dyes are of special interest.⁴ Many of them form so-called Jelly (*J*-) or Scheibe aggregates, which are characterized by at least one new excitonic transition shifted toward lower energy with respect to the monomeric absorption energy and resonance fluorescence emission from the lowest energy transition.^{5–8} The cyanine dyes are characterized by extended delocalized π -electron systems along the polymethine backbone, which cause extraordinarily high optical polarizability. The high polarizability leads to dispersion forces between neighboring molecules and gives rise to substantial attractive forces for aggregation.⁹ On the other hand, the high polarizability causes strong excitonic coupling and hence delocalization of the excited state over several molecules. These extended excitons determine the optical properties of the aggregates, namely, the appearance of new electronic transitions accompanied by efficient energy migration.¹⁰

CHART 1: Chemical Structure of the 5,5',6,6'-Tetrachlorobenzimidacarbocyanine Dyes with Different Substituents and the Abbreviations Used throughout the Text.



Recently, a series of 5,5',6,6'-tetrachlorobenzimidacarbocyanines having different 1,1'- and 3,3'-substituents at their nitrogen atoms were synthesized by Dähne and co-workers.^{11,12} In these dyes, the peculiar properties of the polymethine backbone causing the strong dispersion forces between neighboring molecules are combined with structural elements typical for amphiphilic molecules by introducing long hydrophobic side chains and hydrophilic side groups to the chromophore. Solvophobic interactions gain significant influence here resulting in the formation of a variety of complex molecular and supramolecular structures,¹³ which all show the typical spectroscopic features of *J*-aggregates. Because of these features, the dyes have been termed¹⁴ amphi-PIPEs (amphiphiles with pigment interaction performing energy migration).

* To whom correspondence should be addressed. E-mail: berlepse@chemie.fu-berlin.de.

[†] Freie Universität Berlin.

[‡] Humboldt Universität zu Berlin.

[§] University of Groningen.

In the spectroscopic studies by Dähne and co-workers,^{14–18} the 3,3'-bis(3-carboxypropyl)-5,5',6,6'-tetrachloro-1,1'-dioctylbenzimidacarbocyanine derivative (C_8O_3) appeared to be the most interesting one, because its *J*-aggregates show a complex excitonic spectrum composed of several optical transitions and in addition a strong circular dichroism.^{15,16,19} A theoretical description of the optical properties by using a simplified model of cylindrical molecular aggregates was later provided by Knoester and co-workers.^{14,18,20,21}

The morphologies of the *J*-aggregates of different amphiphiles have been thoroughly investigated by von Berlepsch et al.¹³ using cryo-transmission electron microscopy (cryo-TEM). It is now well established that the C_8O_3 derivative self-aggregates in sodium hydroxide solution into ropelike assemblies composed of several helically twisted tubular strands of ~10 nm cross-sectional diameter and a wall thickness of ~4 nm. The wall thickness value indicates a packing of the dye in a molecular bilayer arrangement. The chromophores are stacked within each layer in a plane-to-plane orientation, whereas the attached octyl chains are intercalated between the layers to avoid contact with the surrounding aqueous medium due to the hydrophobic effect.

Fixation of anisotropically shaped aggregates in polymer films serves as a method to induce preferential orientation along certain directions. The resulting macroscopic anisotropy enables angle-dependent spectroscopy, such as polarized absorption or fluorescence polarization. Although this could also be accomplished for solutions by simple shear flow as first done by Scheibe²² and repeated recently using a rotating cell²³ or by magnetic field induced alignment,²⁴ the polymeric route has the advantage that the orientation remains fixed after alignment. Because of its good water solubility, simple handling, and the absence of measurable spectral effects, poly(vinyl alcohol) has been most commonly used as a polymer matrix.^{25–28} Thin films may be cast from a dilute polymer solution of *J*-aggregates, dried and uniaxially stretched to orient the dispersed aggregates or alternatively prepared by the “vertical spin coating” technique.²⁵

Spitz et al.¹⁷ succeeded in preparing PVA films that contain *J*-aggregates of C_8O_3 . The films have been stretched to induce a preferential orientation of the aggregates, which was used to prove the circular dichroism and to distinguish it unambiguously from linear dichroism. In their studies, the authors reported that the absorption spectra of aggregates did not change after they were immersed into the PVA matrix. From these observations, it is suggested that PVA might be suitable as an embedding material that does not change the molecular structure of the aggregates. On the other hand, it was found in later studies that low molecular weight surface-active additives such as typical ionic surfactants^{29–31} or low-valent alcohols^{31–33} can have a strong effect on the spectra, as well as on the morphology, of *J*-aggregates of the tetrachlorobenzimidacarbocyanines, in particular, the C_8O_3 derivative.

These different observations taken together, it appears interesting to see whether the alcoholic nature of PVA might alter the spectral and morphological behavior of the C_8O_3 dye aggregates or whether the polymeric matrix promotes a stabilization effect leaving the molecular or supramolecular structure or both unchanged. In this paper, it will be shown that PVA indeed serves as a stabilizing agent and causes separation of the ropelike aggregates of C_8O_3 into single tubular strands. The influence of the PVA on the molecular packing and hence the optical spectra of the aggregates, which appear to be different from those of the pure dye aggregates, is investigated for various

molar PVA concentrations and also in the presence of additional low molecular weight alcohols.

II. Experimental Section

Materials and Sample Preparation. The dyes C_8O_3 and C_8O_4 were supplied by FEW Chemicals (Wolfen, Germany). C_8O_4 has been used as received. It consists of the pure dye betain. The molecular mass is 836.8 g/mol. The molar extinction coefficient in dimethyl sulfoxide (DMSO) is $\epsilon = 1.85 \times 10^5$ L/(mol·cm).³¹ The C_8O_3 dye has been recrystallized at least one time from DMSO giving the pure betain with the same molar extinction coefficient in DMSO (1.85×10^5 L/(mol·cm)). The molecular mass was taken to be 848 g/mol, considering the result of X-ray structure analysis,¹⁹ which showed that the single crystals obtained by crystallization from DMSO contain $1/2$ mol of DMSO. The sample has been thoroughly characterized³¹ showing no impurities (HPLC) and was the same as that used in former studies.^{14,32}

PVA with an average molar mass of $M_w = 72\,000$ g/mol (saponification value, 15–25; degree of hydrolysis, 97.5–99.5 mol %) was purchased from Fluka and has been used as received. Unless otherwise specified, this PVA with mean molecular mass was used for sample preparation. Additional absorption and LD spectra were measured for samples containing PVA of $M_w = 190\,000$ g/mol (MOWIOL 50–98; degree of hydrolysis, 98–98.8%) and $M_w = 205\,000$ g/mol (degree of hydrolysis, 86.7–88.7%, Fluka), respectively.

Methanol and ethanol (pa) were obtained from Merck; 1-decanol of 99% chemical purity was obtained from Fluka. The 1-decanol was first dissolved in ethanol (220 mM) and then added to the dye solution up to the desired concentration using a microliter syringe (Hamilton). Double-distilled deionized water was used for preparing the solutions.

To get homogeneous dye solutions with maximum formation of *J*-aggregates, 10 mM NaOH was used as solvent. Stock solutions of 4.0×10^{-4} M dye were prepared through stirring at room temperature for at least 24 h. To prepare a 3 wt % PVA stock solution, the polymer was dissolved under stirring at ~80° C. Different routes of sample preparation were used: (i) for low [polymer]/[dye] mixing ratios, dye solutions were titrated by a (concentrated) PVA solution; (ii) at high [polymer]/[dye] mixing ratios, the polymer solution containing 10 mM NaOH was titrated by a dye solution; (iii) aggregation in the presence of the polymer was accomplished by adding methanolic dye solutions to PVA solutions in the presence of 10 mM NaOH; (iv) thin films of PVA-embedded aggregates were prepared by casting of dye-containing polymer solutions on glass slides and subsequent drying at room temperature; (v) for the LD measurement, concentrated dye solutions in 10 mM NaOH were prepared, to which PVA solutions in 10 mM NaOH were added up to the desired concentration.

Methods. The isotropic absorption spectra were measured with a Lambda 9 spectrophotometer (Perkin-Elmer), the fluorescence spectra with a luminescence spectrometer LS 50B (Perkin-Elmer), and the circular dichroism spectra with a J-715 spectropolarimeter (Jasco Corporation). The measurements were carried out at 21 ± 1 °C after the solutions had been stored for at least 1 day in the dark.

The LD spectra were measured by aligning the aggregates in a streaming flow of the liquid and monitoring the absorption for light polarized parallel and perpendicular to the flow direction. The flow was created by a peristaltic pump (Cole-Parmer's Masterflex), which pumped the aggregated dye solutions through a 0.1 mm cell. As a polarized light source, a white

light continuum was used. The white light was generated in a 2 mm sapphire plate by pumping with 800 nm pulses originating from a titanium–sapphire laser system (120 fs, 1 kHz; Hurricane, Spectra Physics). The energy of the incident light and of the light transmitted through the sample was monitored via a polychromator by an OMA system (Princeton Instruments).

The samples for cryo-TEM were prepared at room temperature by placing a droplet (10 μL) of the solution on a hydrophilized perforated carbon filmed grid (60s plasma treatment at 8 W using a BALTEC MED 020 device). The excess fluid was blotted off to create an ultrathin layer (typical thickness of 100 nm) of the solution spanning the holes of the carbon film. The grids were immediately vitrified in liquid ethane at its freezing point ($-184\text{ }^\circ\text{C}$) using a standard plunging device. Ultrafast cooling is necessary for an artifact-free thermal fixation (vitrification) of the aqueous solution avoiding crystallization of the solvent or rearrangement of the assemblies. The vitrified samples were transferred under liquid nitrogen into a Philips CM12 transmission electron microscope using the Gatan cryo-holder and stage (model 626). Microscopy was carried out at $-175\text{ }^\circ\text{C}$ sample temperature using the low dose protocol of the microscope at a primary magnification of 58 300 \times . The defocus was chosen in all cases to be 0.9 μm corresponding to a first zero of the phase contrast transfer function at 1.8 nm.

III. Results and Discussion

Isotropic Spectra. In Figure 1a, the changes of the C_8O_3 absorption spectra upon titration with PVA are shown. The *J*-band absorption of the pure C_8O_3 dye is composed of three components¹³ peaked at 561, 582, and 600 nm, which are all due to the band structure of the extended molecular excitons. The most striking feature of the spectral changes upon addition of PVA is the reduction of the band around 582 nm accompanied by the appearance of a new strong band with a maximum at 591 nm and a weak band around 577 nm. A closer inspection of the spectrum of the pure dye reveals that the component around 582 nm is obviously composed of two bands, one with a maximum at 577 nm and the other with a maximum at 582 nm. The third subband of the original spectrum peaked at 561 nm remains nearly unaffected, except for slightly decreased absorbance. First spectral changes become visible for mixing ratios *R* (molar concentration of polymer repeat units per molar dye concentration, $R = [\text{polymer}]_{\text{mono}}/[\text{dye}]$) on the order of 0.5, while the new spectral pattern is fully resolved and does not show further changes when a characteristic ratio of $R \approx 8$ is reached.

An isosbestic point is observed at 587 nm, which indicates an equilibrium state between two types of aggregates during the addition of PVA. The two coexisting species are the pure aggregates and the PVA-modified aggregates when PVA is present in large excess (i.e., “PVA-saturated” aggregates). The main spectroscopic difference between the two types of aggregates is the position of an absorption band at either 582 or 591 nm. The intensity of the spectrum of the unmodified aggregates (arrows downward) decreases at the expense of the intensity of the spectrum that is characteristic for the PVA-modified aggregates (arrow upward). We would like to emphasize, however, that the spectra result from excitonic coupling within the aggregate which extends over a few molecules only. This is much less than the physical size of the aggregates, which extends over micrometers (see below). Therefore, the two types of aggregates identified by spectroscopy could also be represented by two different areas within one physical aggregate,

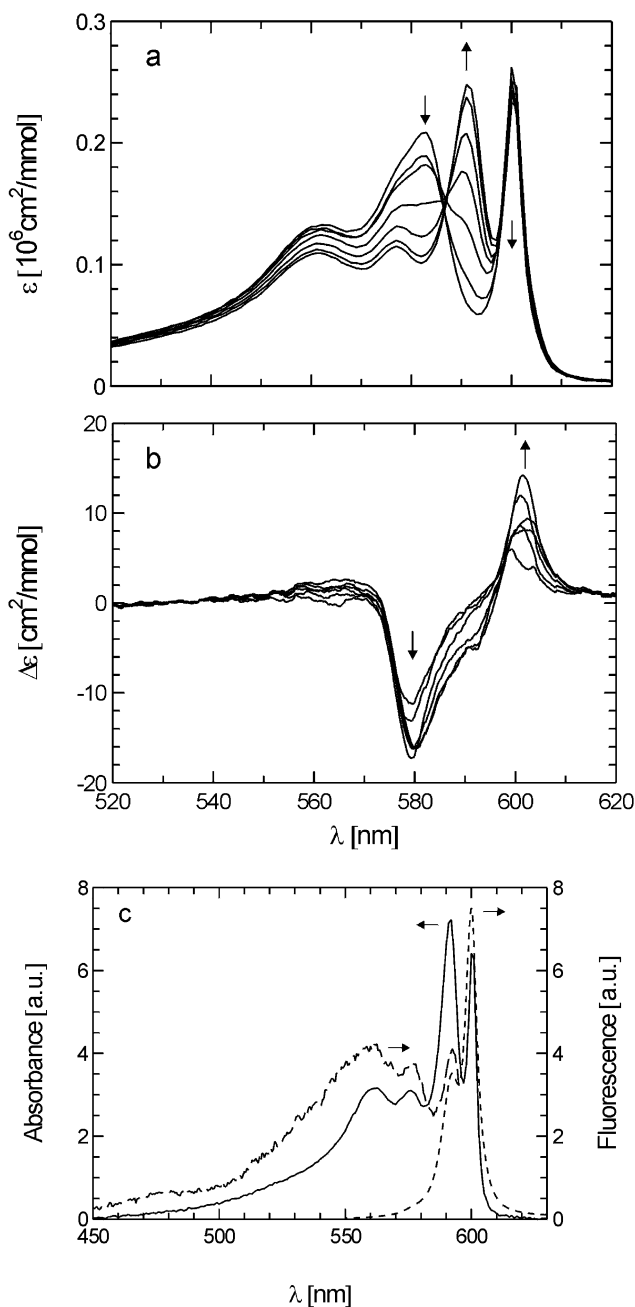


Figure 1. Panel a shows the change of absorption spectra of a 4.0×10^{-4} M C_8O_3 solution (containing 10 mM NaOH) as a function of added PVA. [Polymer]/[dye] mixing ratios $R = 0, 0.5, 1.2, 2.1, 3.3, 5.3$, and 7.8 . Arrows indicate the effect of increasing PVA concentration. Panel b shows the change of circular dichroism spectra of an 8.0×10^{-5} M C_8O_3 solution (containing 10 mM NaOH) as a function of added PVA: $R = 0, 0.5, 1, 2, 4$, and 8 . Arrows indicate the effect of increasing PVA concentration. Panel c shows absorption (left ordinate, solid line), fluorescence excitation (right ordinate, long dashes), and emission spectra (right ordinate, short dashes) of a PVA/ C_8O_3 solution ($[\text{C}_8\text{O}_3] = 4.0 \times 10^{-4}$ mol/L) 1 day after mixing ($R = 5$). For the fluorescence measurements, the solution was strongly diluted ($[\text{C}_8\text{O}_3] = 4.0 \times 10^{-7}$ mol/L, optical density, $\text{OD}(591\text{ nm}) = 0.11$). The excitation spectrum was collected at 600 nm; the emission spectrum was collected by exciting at 540 nm. The emission spectrum was corrected for reabsorption. The slit width of excitation and emission monochromators was set to 2.5 nm.

that is, parts that are covered by PVA and others that are not. It is important to notice that the modification of the molecular arrangement due to the PVA leads to a marked shift of the absorption band from 582 to 591 nm.

The CD spectra represented in Figure 1b also indicate chirality of the PVA-modified aggregates.^{32,33} The effect of the added PVA on the CD signal is less pronounced than it is in the case of absorption spectra. Only a slight enhancement of the signal without qualitative changes in the shape of spectra is observed upon titration with PVA for *R*-values ranging between 0 and 8. A similarly strong enhancement of the CD effect as it was induced by the addition of low-valent alcohols³² is not observed for the PVA.

The absorption spectrum is complemented by fluorescence emission as shown in Figure 1c. The emission spectrum reveals peaks at 591 and 600 nm, respectively. The position of these peaks is identical with the position of the corresponding absorption bands, which indicates resonant emission from these optical transitions. The excitation spectrum, recorded at the emission of the band at 600 nm, shows peaks at the same position as the absorption spectrum but with different intensity ratios. Especially, the relative intensity of the third band at 591 nm is significantly lower in the excitation than in the absorption spectrum.

This fluorescence behavior is unexpected. It is generally accepted that the whole absorption spectrum of such aggregates belongs to their excitonic band structure. Because of the high density of states within the exciton spectrum, an optical excitation into higher energy levels should relax to the bottom edge of the exciton band before it undergoes a transition to the ground state under emission of radiation. Emission is therefore expected to come solely from states at the lower-energy side of the spectrum, which is represented by the band at 600 nm in this case. In contrast to this expectation, additional fluorescence at the band at 591 nm is observed. It is excluded that this emission originates from different coexisting aggregate structures because the intensity ratio of these two bands is always the same. Therefore, the relaxation of excitation energy from the band at 591 nm into the lowest-energy band must be hindered, which enables emission from the band with higher energy. This indicates that these optical transitions are loosely coupled. On the other hand, the excitation spectrum indicates that exciton relaxation into the lowest-energy state is more efficient from states within the spectrum that are at even higher energies than the band at 591 nm. Therefore, additional pathways must exist for the relaxation of the exciton from the higher-energy states into the lowest-energy state, bypassing the levels at the 591 nm band. The details of this complex exciton dynamic within the aggregates are far from being understood at present and are the subject of current investigations.³⁴

Next, we tried to find out whether the absorption spectrum is modified in the presence of a large excess of the polymer. Samples were prepared by titrating a concentrated PVA solution (3.0 wt % PVA in 10 mM NaOH) with an aggregated $C_{8}O_3$ solution. The final dye concentration ranged between 1.84×10^{-7} and 2.0×10^{-4} M, which corresponds to mixing ratios *R* between 3.6×10^6 and 1.7×10^3 . The corresponding absorption spectra are presented in Figure 2. Aside from a noticeable amount of residual dye monomers and an enlarged level of noise in the case of the 1.84×10^{-7} M dye solution, all samples gave spectra that are similar to those of PVA/dye aggregates at a mixing ratio of $R \approx 8$. This means that the spectral features are independent of polymer concentration if the mixing ratio exceeds a characteristic value of $R \approx 8$ (estimated from the set of spectra given in Figure 1a). Obviously, the interface of the aggregate to the surrounding solvent becomes saturated with PVA at this ratio. However, because of the unknown partitioning of PVA

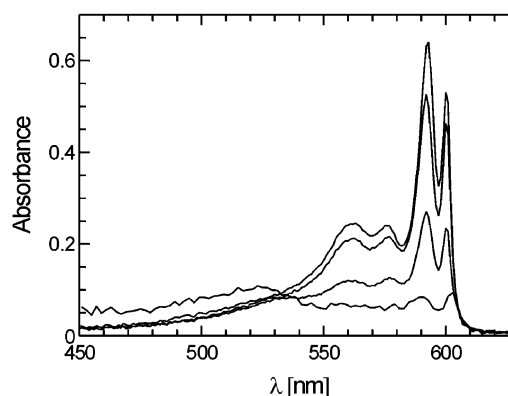


Figure 2. Absorption spectra of solutions prepared by titration of concentrated PVA solutions (containing 10 mM NaOH) with C_8O_3 . [PVA] = 3 wt % (except the top curve with 1.5 wt %). $[C_8O_3] = 1.84 \times 10^{-7}$, 2.2×10^{-6} , 1.92×10^{-5} , and 2.0×10^{-4} mol/L (from bottom to top). Sample path length = 10, 10, 1, and 0.1 mm (from bottom to top). Note that the bottom curve is multiplied by a factor of 5.

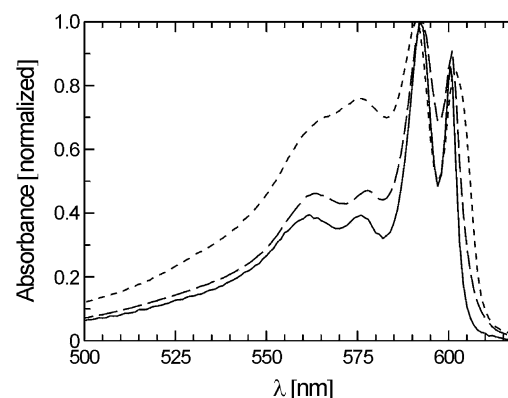


Figure 3. Comparison of the absorbance of differently prepared PVA/ C_8O_3 samples: (i) solution obtained by the "alcoholic route" from dye monomers (dissolved in methanol) after 1 day of aggregation in 3 wt % PVA solution containing 10 mM NaOH (short dashes) at $[C_8O_3] = 1.8 \times 10^{-4}$ mol/L; (ii) solution prepared by mixing aggregated dye and PVA solutions in 10 mM NaOH (solid line) at $[C_8O_3] = 2.0 \times 10^{-4}$ mol/L; (iii) film obtained by casting solution from sample ii on a glass slide and drying for 1 day at room temperature (long dashes).

molecules between the solvent and the interface, this numerical value does not allow estimation of a geometrical "degree of coverage".

In solid films of polymer-dispersed aggregates, the PVA/dye ratio is also well above the saturation limit of $R \approx 8$. In Figure 3, the typical absorption spectra are plotted for a cast polymer film (long dashes), together with the spectrum of the corresponding casting solution (solid line). Despite a slightly increased half-width of the longest wavelength subbands for the film, both spectra are quite similar. Additionally, the spectrum of a solution that was prepared by the "alcoholic route"^{31,32} is added to the figure (short dashes) as an example of a further preparation method. Here, dye monomers were dissolved in methanol and added to a 3 wt % PVA solution (containing 10 mM NaOH). The methanol solution contained dye monomers, which aggregate after being added. The spectrum shows the four subbands again, but with different intensity ratios and markedly larger half-width. The latter indicates a lower degree of molecular order within these *J*-aggregates.

It has been demonstrated recently, that water-soluble and insoluble alkanols such as methanol and decanol, respectively, have a strong effect on the molecular structure of the C_8O_3

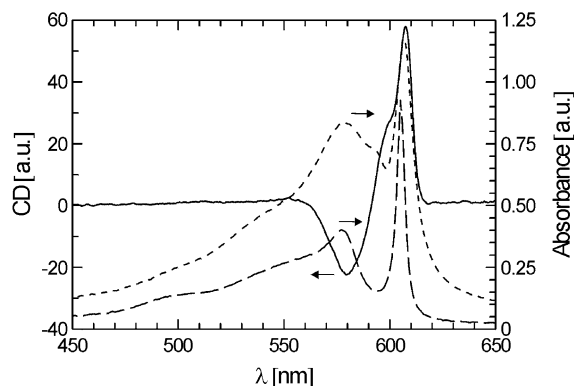


Figure 4. Absorption spectrum (right ordinate, long dashes) of a mixed 1-decanol/ C_8O_3 solution ($[C_8O_3] = 7.1 \times 10^{-4}$ mol/L, molar [1-decanol]/ $[C_8O_3]$ ratio = 2) prior to the addition of PVA and absorption (right ordinate, short dashes) and CD (left ordinate, solid line) spectra of a solid film on a glass slide prepared by the casting method from a mixed PVA/1-decanol/ C_8O_3 solution.

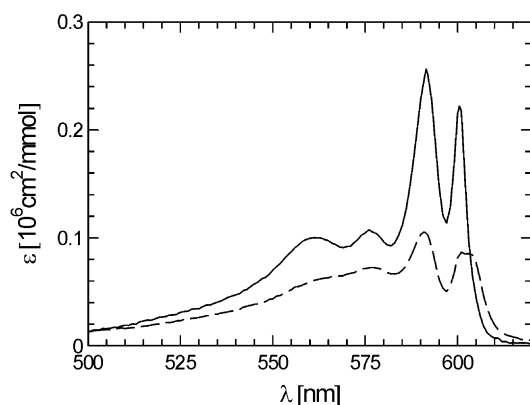


Figure 5. Absorbance of (i) C_8O_3 aggregates in the presence of PVA ($R = 3$) 3 days after mixing (solid line) and (ii) absorbance of this solution after 12 weeks of storage (dashed line). $[C_8O_3] = 3.0 \times 10^{-4}$ mol/L. The shape of the absorption spectrum of mixed PVA/ C_8O_3 solutions remains nearly unaltered upon long-term storage.

aggregates, as is reflected by the absorption and CD spectra.³² Therefore, the interesting question arises whether these alcohols can be exchanged by subsequent adding of polymeric alcohols such as PVA. To answer the question, an aggregated aqueous C_8O_3 solution was first mixed with 1-decanol producing a 2-fold split absorption spectrum with peaks at 577 and 605 nm shown in Figure 4 (long dashes). In the second step, this 1-decanol/ C_8O_3 solution was mixed with a 3 wt % PVA solution, and in the third step, a thin film was prepared by casting the solution on a glass slide. After the film was dried, the absorption (short dashes) and CD spectra (solid line) presented in Figure 4 were measured. The surprising finding was that PVA had almost no effect on the 2-fold split spectrum, except a small shoulder at ~ 593 nm (appearing after storage of the mixed PVA/1-decanol/ C_8O_3 solution for 1 day). This finding clearly demonstrates that a modification of the molecular packing by the PVA is suppressed because the interface between the J -aggregate and the surrounding solvent is saturated by the 1-decanol molecules. The presence of alcohols during sample preparation by the "alcoholic route" could therefore explain the independence of the C_8O_3 absorption spectra with respect to PVA observed by Spitz et al. in their recent studies.^{14,17}

In the PVA/1-decanol/ C_8O_3 mixed solutions, after a period of about 8 days precipitation was observed, indicating an enhanced tendency for agglomeration of these aggregates. This could be related to the enhanced self-assembly of alkanol-

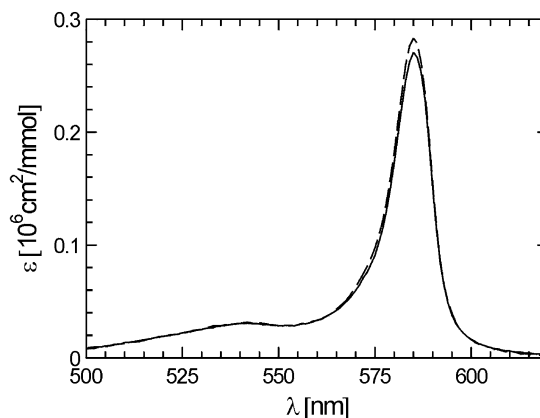


Figure 6. Absorbance of (i) C_8O_4 aggregated in 1 mM NaOH (solid line) and (ii) this solution after adding PVA to a mixing ratio of $R = 100$ (dashed line). $[C_8O_4] = 5.2 \times 10^{-4}$ mol/L. The addition of PVA to aggregated C_8O_4 solutions has a negligible effect on absorbance.

containing J -aggregates into thick ropelike bundles.³² Precipitation is also observed for PVA/ C_8O_3 solutions without further additives but in that case only in the course of several weeks. It is accompanied by a broadening of the subbands as demonstrated in Figure 5 for a 12-week-old solution.

Figure 6 shows the absorption spectra of a C_8O_4 solution in 1 mM NaOH prior to and after the addition of PVA ($R = 100$), respectively. In contrast to C_8O_3 , the measurement does not reveal PVA-induced modifications, reminiscent of the behavior observed when ionic surfactants have been added into aggregated C_8O_4 solutions.³⁰ The packing of the dye molecules within these J -aggregates is obviously not strongly influenced by the adsorbed PVA. The solutions are stable for some days before precipitates appear.

Linear Dichroism. To further elucidate the molecular structure of the aggregates, polarized absorption spectra were recorded on samples oriented in a streaming viscous flow. The aggregated C_8O_3 solutions possess a rather pronounced linear dichroism (LD) spectrum:

$$LD = OD_{\parallel} - OD_{\perp}$$

Here OD_{\parallel} and OD_{\perp} represent the optical density of the sample measured with light polarized parallel and perpendicular with respect to the flow direction, respectively. According to the cryo-TEM data, the C_8O_3 J -aggregates are linear ropelike assemblies of tubular strands with a total thickness on the order of a few tens of nanometers and hundreds of nanometers length.¹³ Considering their geometrical shape, a preferential alignment of those aggregates with their long axis parallel to the flow direction can be expected.

The measurement of the alignment of aggregates as a function of the flow rate revealed maximum alignment at relatively low flow rates. Saturation in alignment is reached at a flow rate of about $0.5 \text{ cm}^3/\text{s}$ or a flow velocity of 50 cm/s, by taking into account the width and thickness of the flow cell, which are 10 mm and 0.1 mm, respectively.

All measurements presented here were performed for maximum alignment of the samples, that is, at a flow rate of about $2 \text{ cm}^3/\text{s}$. In Figure 7, the steady-state absorption spectra for light polarized parallel (short dashes) and perpendicular (long dashes) to the flow direction of a pure C_8O_3 solution (a) and of a PVA/ C_8O_3 mixture ($R = 10$) (b) are plotted. For comparison, the absorption spectra of the isotropic samples (solid lines), that is, with the flow switched off, are added.

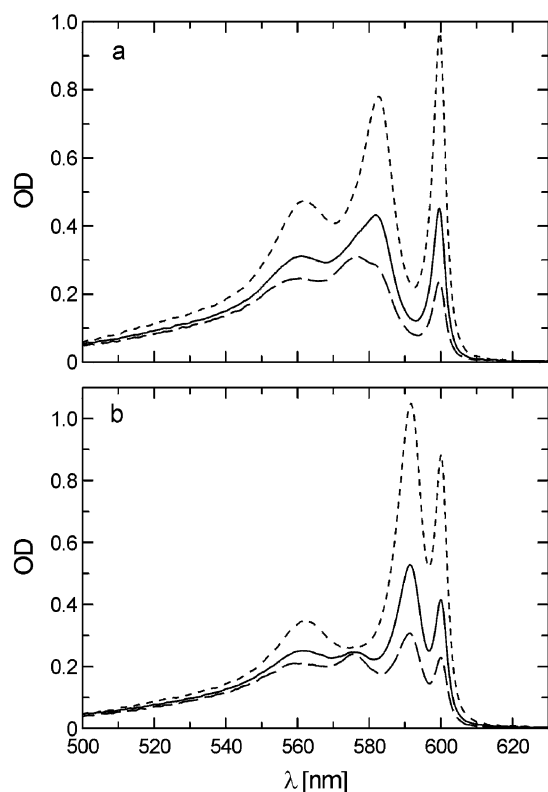


Figure 7. Absorption spectra for light polarized parallel (short dashes) and perpendicular (long dashes) to the flow direction of (a) pure C_8O_3 solution (2.5×10^{-4} mol/L) and (b) PVA/ C_8O_3 solution ($[C_8O_3] = 1.73 \times 10^{-4}$ mol/L, $R = 10$). Flow rate ≈ 2 cm³/s. The solid lines represent the absorption spectra of the isotropic samples (flow switched off).

From Figure 7a, it can clearly be seen that the apparent 3-fold split spectrum of the pure C_8O_3 aggregates is a superposition of four bands, numerated 1 to 4 starting at the lowest wavelength (cf. Figure 7). The two components 2 and 3 of the band around 580 nm have a different polarization behavior: band 3 at 582 nm is polarized parallel to the long axis of the aggregates, while band 2 at 577 nm either is polarized perpendicular to the axis or represents an isotropically oriented transition. The latter cannot be discriminated clearly from the spectra presented in Figure 7a. However, frequency-resolved polarization-selective pump–probe data³⁴ reveal photoinduced bleaching at around 577 nm in the case when the probe light is polarized perpendicular to the flow direction, while the bleaching is absent in the case of parallel-polarized probe light. This strongly indicates that band 2 represents a transition that is oriented perpendicular to the long axis of the aggregates. The remaining two bands (1 and 4) are due to transitions that are clearly polarized parallel to the aggregate axis.

All of these features result in the LD spectrum plotted in Figure 8a (solid line) with three maxima centered at 562, 583, and 600 nm and a minimum at around 573 nm. The maxima of the LD spectrum match well with the absorption maxima of the isotropic sample (dashed line), while the minimum corresponds to the position of the shoulder of its middle subband. Furthermore, from the direction of alignment of the aggregates, it follows that the three peaks in the LD spectrum reveal transitions oriented parallel to the long axis of the aggregates. The minimum corresponds to the position of peak 2 in the absorption spectrum measured with perpendicularly polarized light. As it was stated above, this transition represents a perpendicularly polarized state, which because of its low

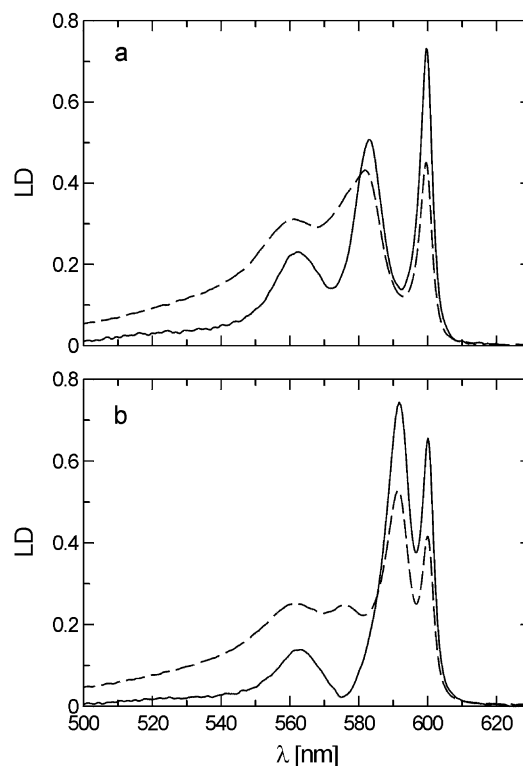


Figure 8. Linear dichroism spectra (solid lines) calculated from the measured dichroic absorption spectra shown in Figure 7 for (a) pure C_8O_3 solution and (b) PVA/ C_8O_3 solution. The dashed lines represent the absorption spectra of the isotropic samples (flow switched off).

oscillator strength and large overlap between the much stronger parallel transitions does not result in negative values of the linear dichroism.

One has to note that even at a flow rate of 2 cm³/s, that is, well above the saturation in alignment of the aggregates, the absorption for perpendicularly polarized light is still substantial over the whole spectral range: the parallel-polarized transitions are only reduced by approximately 75% in the perpendicularly polarized spectra. This can only be due to incomplete orientation of the aggregates or due to transitions that are oriented in a direction that is neither parallel nor perpendicular to the long axis of the aggregates. The details will be discussed elsewhere.³⁵

In the case of the PVA/ C_8O_3 mixtures, the difference between the absorption for parallel and perpendicular polarization of the light (Figure 7b) is much more pronounced. Despite the four-banded structure of the absorption spectrum of the isotropic sample, only three bands are visible in the absorption spectrum when the light is polarized parallel to the flow direction (short dashes). In contrast, for light polarized perpendicular to the flow (long dashes), the absorption spectrum has a well-resolved four-band structure. Three out of the four bands, that is, the subbands 1, 3, and 4 are situated at wavelengths in agreement with the absorption maxima for parallel polarization, while the position of band 2 peaked at around 578 nm shows a similar behavior as described above for the pure C_8O_3 yet more pronounced. In the isotropic spectrum, as well as in the spectrum recorded with perpendicularly polarized light, band 2 shows up with the same intensity, while the absorption at around 578 nm for parallel polarization is slightly but definitely higher. This indicates that the band 2 either is polarized perpendicular to the long axis of the aggregates or represents an isotropically oriented transition. However, like in the case of the pure C_8O_3 sample, frequency-resolved polarization-selective pump–probe data³⁴ reveal that the transition is oriented perpendicular to the long axis of

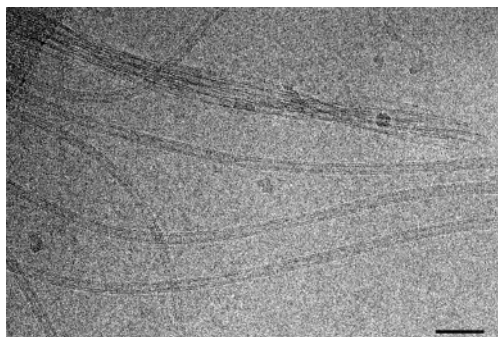


Figure 9. Cryo-TEM image of a 3.0×10^{-4} M C_8O_3 solution in 10 mM NaOH 1 day after the addition of PVA ($R = 3$). The dark spots are due to surface contamination. Bar = 50 nm.

aggregate. The LD spectrum given in Figure 8b yet again has a three-banded structure revealing three transitions oriented parallel to the long axis of aggregates. As in the case of the pure C_8O_3 sample, the low oscillator strength of the perpendicular transition and the overlap of bands 1 and 3, which represent parallel transitions, result only in a pronounced minimum but not in a negative band in the LD spectrum at around 575 nm.

In addition, we measured LD spectra of PVA/ C_8O_3 mixtures ($R = 10$) in which the PVA had different molecular masses ($M_w = 190\,000$ g/mol and $205\,000$ g/mol). The results showed that both the absorption spectrum of isotropic samples and the LD spectra remain unchanged. This means that the molecular mass of PVA has obviously no effect on the spectral properties of the aggregates. Because the spectral properties are closely related to the molecular structure of aggregates, one can expect no effect of the polymer chain length on the latter as well.

In summary, these investigations revealed that the tubular aggregates of C_8O_3 are characterized by four electronic transitions, where three are polarized along the long axis of the aggregate and one is polarized in parallel. In previous works, Knoester et al. have evaluated the principal features of the excitonic spectrum of cylindrical molecular aggregates.^{14,20,21} The optical spectrum of the bilayer-walled tubular *J*-aggregate has been ascribed to six exciton transitions (three per layer), which are pairwise degenerated.¹⁴ According to this model, the two short wavelength transitions at 561 and 582 nm should be polarized perpendicular to the long axis of the aggregates while the long wavelength transition at 600 nm should be polarized parallel to it. Here, the short wavelength transitions represent circular excitations of the inner and outer chromophore layers of the double-walled molecular cylinder. The discrepancy between these findings and the present observations clearly show the demand for further theoretical investigations assuming more complex molecular arrangements within a tubular structure.

Morphology of Aggregates. A representative cryo-TEM micrograph of a PVA/ C_8O_3 solution after 1 day of mixing ($R = 3$) is shown in Figure 9. Besides isolated tubules, which are slightly bent and typically several hundreds of nanometers long, a few bundles of helically twisted tubules can be seen. The amount of isolated tubules clearly predominates over the twisted assemblies. This is opposite to the situation of pure aggregated C_8O_3 solutions, in which nearly no isolated aggregates are found. It appears obvious that the penetrating polymer molecules disrupt most of the superhelical bundles and stabilize isolated tubular aggregates. Because the polymer chains are not visible in the cryo-TEM micrographs, it cannot be decided whether the few bundled ropelike assemblies are residual unmodified aggregates coexisting with the PVA-modified species or whether

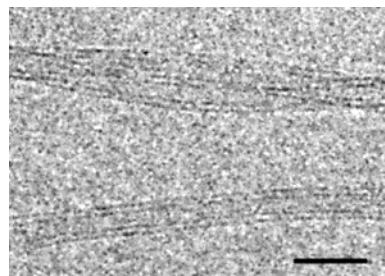


Figure 10. Cryo-TEM image of a PVA/ C_8O_3 solution showing a single tubular and a twisted double-stranded *J*-aggregate at large magnification. Bar = 25 nm.

they are the result of incomplete separation or reassembly or both. Although the mixing ratio ($R = 3$) was smaller than the saturation limit ($R \approx 8$), that is, unmodified and modified aggregates should coexist according to their absorption spectrum, the long-time studies discussed below will rather support a reassembly of the modified tubules into bundles.

To understand the effect of PVA on the morphology of the *J*-aggregates, it is important to note that PVA is able to form complex compounds or association products with several ions such as borate, cupric, and vanadate ions^{36–38} or certain azo dyes.^{39–41} This complexation is assumed to be the result of a binding between the hydroxyl groups of the polymer and functional groups of the complexation reagents, which are capable of hydrogen bonding. Moreover, PVA can form hydrogen bonds with other PVA molecules and by itself.³⁸

The strong adsorption of PVA on the dye aggregates could thus be explained by hydrogen bonding between the hydroxyl groups of the PVA and the carboxyl groups of the dye. In an earlier study,¹³ we assumed that the structure of the dye aggregate itself is stabilized by hydrogen bonds between dye molecules. The PVA-induced changes of the molecular packing within the aggregates, as reflected by the spectral changes, could be due to a rearrangement of these hydrogen bonds from dye–dye bonds into dye–PVA bonds. Quite similar spectral effects have been observed for alkanols,³² and they have also been considered to be the result of a delicate change of the molecular packing due to adsorption of the added alcohol molecules at the aggregate–solvent interface. The strong effect of additives on the molecular construction is a striking characteristic of the C_8O_3 aggregates and presumably connected with packing constraints due to the extreme curvature of the tubular geometry. For the flat ribbonlike C_8O_4 *J*-aggregates, a similarly strong spectral and structural effect is not observed.³⁰

The polymer-coated tubules are stabilized against assembly into ropelike bundles by entropic repulsion forces emerging from the adsorbed polymer chains—a mechanism that is known as steric stabilization.⁴² A similar mechanism has recently been proposed to explain the debundling and stabilization of single-wall carbon nanotubes in aqueous solution by gum arabic⁴³ or in an organic solvent by PVA.⁴⁴ Looking for other polymers suitable for stabilizing, we checked the effect of a polysaccharide (Dextran T 500) and of poly(ethylene glycol) ($M_w = 23\,000$ g/mol) on the absorption spectrum of the aggregates. However, neither of the two showed any spectral effect. Interaction with the C_8O_3 *J*-aggregates has thus been excluded, and structural investigations were not undertaken.

The morphology of the isolated tubules is very similar to those found in the pure C_8O_3 system,¹³ as well as in the C_8O_3 system in the presence of alkanols.³² The micrograph reproduced in Figure 10 shows a single tubule, as well as a twisted double-stranded aggregate at larger magnification. The wall of the

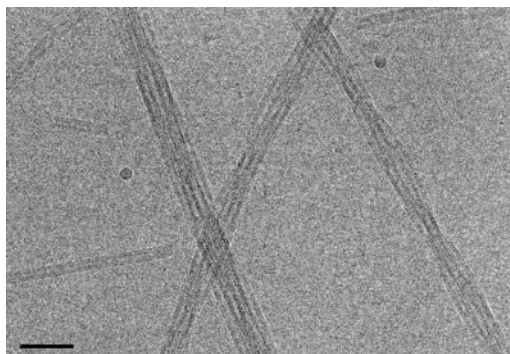


Figure 11. Cryo-TEM image of a 3.0×10^{-4} M C_8O_3 solution in 10 mM NaOH 10 days after the addition of PVA ($R = 3$). Bar = 50 nm. As compared to Figure 9, the number of twisted multiple stands has increased.

tubules with a thickness of 4.0 ± 0.5 nm is clearly observable. The constituting monolayers of chromophores appear as dark lines, while the intercalating octyl chains between exhibit less contrast. The mean total diameter of an individual tubule is about 11.5 ± 1 nm and thus only insignificantly enlarged as compared to the pure C_8O_3 system or in the presence of alkanols. The invariable diameter and the ability to assemble into ropelike superhelical bundles discriminate all of these alcohol-modified tubular C_8O_3 aggregates from those generated upon the incorporation of sodium dodecyl sulfate (SDS).²⁹

To check for morphological changes occurring on the mesoscopic scale during storage a PVA/ C_8O_3 mixed solution was studied 10 days after its preparation by cryo-TEM. Figure 11 shows a representative micrograph. Isolated tubules can be seen as described before, but the amount of ropelike bundles has again markedly increased, indicating that a slow process of reassembly occurred. The underlying mechanism is not clear. A possible explanation of the renewed self-assembly could be a cooperative “zippering” between PVA-coated tubules by the formation of polymer-mediated hydrogen bonds. A similar cooperative binding effect has recently been discussed to explain the collapse of interpenetrating polymer networks of acrylic acid/acrylamide copolymer gels.⁴⁵ At first sight, this mechanism seems to contradict the above-discussed stabilizing effect, but the well-known cross-linking ability of PVA and the relatively slow kinetics are features that could support the concept of a cooperative polycomplexation.

Cryo-TEM of a sample that was stored for 12 weeks (cf. the spectrum given in Figure 5) did not reveal other morphological changes but bundling. The amount of thick ropelike bundles markedly increased at the expense of individual tubules. Hence, it can be assumed that the thick fibers, visible by optical microscopy in such stored solutions, consist of agglomerated bundles and eventually form the precipitate. In this respect, the long-time behavior does not differ from that of C_8O_3 solutions containing alkanols^{32,33} instead of PVA.

Referring to the above discussion it should be pointed out that the occurring reassembly into multiple bundles during the long-time storage is accompanied by a broadening of the subbands of the absorption spectrum but not by qualitative changes of the spectral shape (Figure 5). This demonstrates that the interaction between the excited states of adjacent tubules is obviously too small to have a significant effect on the optical spectra. The PVA-induced spectral changes therefore cannot be explained by the decomposition of the ropelike aggregates into single tubules. In fact, they are caused by modifications of the packing of dye molecules within the single tubular aggregates.

Separation and complexation effects as described for C_8O_3

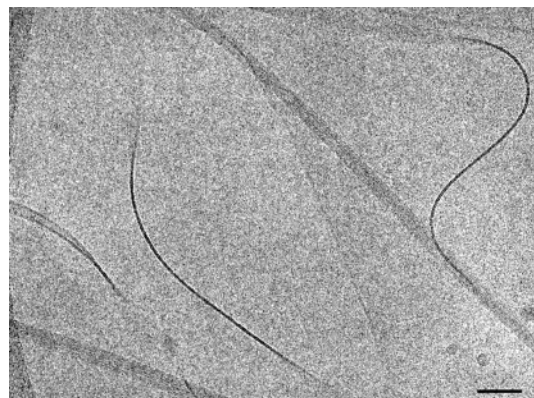


Figure 12. Cryo-TEM image of a 4.4×10^{-4} M C_8O_4 solution in 1 mM NaOH 4 days after the addition of PVA ($R = 8$). Bar = 50 nm.

should be expected to occur also for the *J*-aggregates of other carboxyalkyl-substituted tetrachlorobenzimidacarbocyanine derivatives. In particular, we expected a separation of the stacked C_8O_4 *J*-aggregates¹³ into individual bilayer ribbons. Figure 12 shows a typical cryo-TEM micrograph. Besides multilayered *J*-aggregates that are identified by their high contrast and the typical pattern of stripes, which are due to stacking,^{13,30} single bilayers can be seen. When vitrified in top view orientation, the contrast of the single bilayer ribbons for the traversing electrons is low. However, when embedded “on edge”, its contrast is strongly enhanced and the ribbons are clearly visible, allowing an estimation of the thickness. A total bilayer thickness of about 3.8 ± 0.8 nm was obtained. It can be concluded that the suggested separation mechanism is indeed operative, but as in the case of the C_8O_3 *J*-aggregates, separation is incomplete. Complete separation into single ribbons could be accomplished by anionic surfactants as shown recently,³⁰ demonstrating that in this case the surfactants are more effective dispersing agents than PVA. The absorption spectra remain nearly unaffected by both kinds of additives.

IV. Summary and Conclusions

The influence of poly(vinyl alcohol) on the morphology and spectroscopy of *J*-aggregates of the benzimidacarbocyanine dye C_8O_3 was investigated in detail. Absorption spectra were recorded upon addition of increasing amounts of PVA to a solution of dye aggregates. Above a critical PVA concentration on the order of 8 polymer repeat units per dye molecule ($R \approx 8$), the absorption spectra are independent of PVA concentration and molecular mass. The absorption spectrum is characterized by four well-resolved subbands. C_8O_3 *J*-aggregates dispersed in PVA thin films reveal the same four-banded spectrum. The effect of PVA on the spectra can be suppressed when the interface of the aggregates to the surrounding solvent is saturated by alkanols. The presence of short-chain alkanols during sample preparation (“alcoholic route”) explains why Spitz et al. did not observe the four-banded spectrum in their former studies on PVA-dispersed C_8O_3 *J*-aggregates.¹⁴

The linear dichroism measurement on oriented samples revealed that the *J*-aggregates of the pure C_8O_3 and PVA-modified aggregates are both characterized by four transitions, where three of them are polarized parallel to the long axis of the aggregates while one is polarized perpendicular to it. The spectra of the two types of aggregates differ by the position of only one of the parallel polarized bands and the ratio of their respective intensities. Accordingly, the linear dichroism spectra show the three maxima of the parallel polarized bands, which match well with the absorption maxima of the isotropic samples.

The existence of three transitions oriented parallel and one oriented perpendicular to the long axis of the aggregates cannot be explained by the simple exciton model presented earlier.¹⁴

The typical morphology of the C₈O₃ J-aggregate is the superhelical bundle of individual tubular strands. Cryo-TEM revealed that upon addition of PVA most of the bundles are separated into isolated tubular strands. These are polymer-coated tubular aggregates, which are stabilized against assembly into multiple bundles by entropic repulsion forces emerging from adsorbed polymer chains. The mean total diameter of such an individual tubule is about 11.5 ± 1 nm and only insignificantly enlarged as compared to that of the additive-free C₈O₃ system,³ or when low molecular weight alcohols³² are incorporated.

The fact that the tubular morphology is not changed by the presence of PVA besides a slight increase in diameter and accompanied by only moderate changes of the optical spectra has been ascribed to the adsorption of the polymer at the surface of the aggregates. For polymer/dye mixing ratios exceeding the amount of about 8 polymer repeat units per dye molecule, saturation of the surface of the aggregates with PVA molecules has been spectroscopically determined. The polymer is suggested to bind to the dye molecules via hydrogen bonding. The binding of PVA molecules to dye molecules leads to distinct changes of their orientation or position or both within the aggregate. This rearrangement is manifested in the energy shift of only one of the four excitonic transitions observed.

Acknowledgment. The authors thank Professor S. Dähne for the generous gift of some of the C₈O₃ dye samples used and A. Ouart for purification of these samples. Further, we would like to express our gratitude to Professors J. Knoester and K. Duppen for many stimulating discussions. The CD spectra were measured at the MPI für Kolloid- und Grenzflächenforschung that is gratefully acknowledged. R.H., A.P. and C.D. are grateful to the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). H.v.B., S.K., and C.B. thank the Deutsche Forschungsgemeinschaft (Grant SFB 448 "Mesoskopisch strukturierte Verbundsysteme") for financial support, and S.K. appreciates funding from the EU (EFRE) and generous support from Professor J. Rabe.

References and Notes

- (1) Ritz, T.; Damjanović, A.; Schulten, K. *ChemPhysChem* **2002**, *3*, 243.
- (2) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517.
- (3) van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Scientific: Singapore, 2000.
- (4) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973.
- (5) Scheibe, G. *Angew. Chem.* **1936**, *49*, 563.
- (6) Scheibe, G. *Angew. Chem.* **1937**, *50*, 51.
- (7) Jelly, E. E. *Nature* **1936**, *138*, 1009.
- (8) Jelly, E. E. *Nature* **1937**, *139*, 631.
- (9) Bach, G.; Dähne, S. Cyanine dyes and related compounds. In *RODD's Chemistry of Carbon Compounds*, 2nd Suppl. to 2nd ed.; Sainsbury, M., Ed.; Elsevier: Amsterdam, 1997; Vol. IVB, p 383.
- (10) Knapp, E. W. *Chem. Phys.* **1984**, *85*, 73.
- (11) De Rossi, U.; Moll, J.; Spieles, M.; Bach, G.; Dähne, S.; Kriwanek, J.; Lisk, M. *J. Prakt. Chem.* **1995**, *337*, 203.
- (12) Pawlik, A.; Ouart, A.; Kirstein, S.; Abraham, H.-W.; Dähne, S. *Eur. J. Org. Chem.* **2003**, 3065.
- (13) von Berlepsch, H.; Böttcher, C.; Ouart, A.; Burger, C.; Dähne, S.; Kirstein, S. *J. Phys. Chem. B* **2000**, *104*, 5255.
- (14) Spitz, C.; Knoester, J.; Ouart, A.; Dähne, S. *Chem. Phys.* **2002**, *275*, 271.
- (15) De Rossi, U.; Dähne, S.; Meskers, S. C. J.; Dekkers, H. P. J. M. *Angew. Chem.* **1996**, *108*, 827.
- (16) Pawlik, A.; Kirstein, S.; De Rossi, U.; Dähne, S. *J. Phys. Chem. B* **1997**, *101*, 5646.
- (17) Spitz, C.; Dähne, S.; Ouart, A.; Abraham, H.-W. *J. Phys. Chem. B* **2000**, *104*, 8664.
- (18) Lampoura, S. S.; Spitz, C.; Dähne, S.; Knoester, J.; Duppen, K. J. *Phys. Chem. B* **2002**, *106*, 3103.
- (19) Kirstein, S.; von Berlepsch, H.; Böttcher, C.; Burger, C.; Ouart, A.; Reck, G.; Dähne, S. *ChemPhysChem* **2000**, *1*, 146.
- (20) Bednarz, M.; Knoester, J. *J. Phys. Chem. B* **2001**, *105*, 12913.
- (21) Didraga, C.; Klugkist, J. A.; Knoester, J. *J. Phys. Chem. B* **2002**, *106*, 11474.
- (22) Scheibe, G. In *Optische Anregung organischer Systeme*; Foerst, W., Ed.; Verlag Chemie: Weinheim, Germany, 1966; p 109.
- (23) Scheblykin, I. G.; Varnavsky, O. P.; Verbouwe, W.; De Backer, S.; van der Auweraer, M.; Vitukhnovsky, A. G. *Chem. Phys. Lett.* **1998**, *282*, 250.
- (24) Shklyarevskiy, I. O.; Boamfa, M. I.; Christianen, P. C. M.; Touhari, F.; van Kempen, H.; Deroover, G.; Callant, P.; Maan, J. C. J. *Chem. Phys.* **2002**, *116*, 8407.
- (25) Misawa, K.; Ono, H.; Minoshima, K.; Kobayashi, T. *Appl. Phys. Lett.* **1993**, *63*, 577.
- (26) Kamalov, V. F.; Struganova, I. A.; Yoshihara, K. *J. Phys. Chem.* **1996**, *100*, 8640.
- (27) Lidzey, D. G.; Bradley, D. D. C.; Virgili, T.; Armitage, A.; Skolnick, M. S.; Walker, S. *Phys. Rev. Lett.* **1999**, *82*, 3316.
- (28) Kano, H.; Saito, T.; Kobayashi, T. *J. Phys. Chem. B* **2001**, *105*, 413.
- (29) von Berlepsch, H.; Böttcher, C.; Ouart, A.; Regenbrecht, M.; Akari, S.; Keiderling, U.; Schnablegger, H.; Dähne, S.; Kirstein, S. *Langmuir* **2000**, *16*, 5908.
- (30) von Berlepsch, H.; Regenbrecht, M.; Dähne, S.; Kirstein, S.; Böttcher, C. *Langmuir* **2002**, *18*, 2901.
- (31) Ouart, A. Ph.D. Thesis, Humboldt-Universität, Berlin, 2000. <http://dochostr.rz.hu-berlin.de/dissertationen/ouart-andre-2000-09-28/PDF/Ouart.pdf>.
- (32) von Berlepsch, H.; Kirstein, S.; Böttcher, C. *Langmuir* **2002**, *18*, 7699.
- (33) von Berlepsch, H.; Kirstein, S.; Böttcher, C. *J. Phys. Chem. B*, in press.
- (34) Hania, P. R.; Pugzlys, A.; Duppen, K., manuscript in preparation.
- (35) Didraga, C.; Hania, P. R.; Pugzlys, A.; von Berlepsch, H.; Duppen, K.; Knoester, J., manuscript in preparation.
- (36) Deuel, H.; Neukom, A. *Makromol. Chem.* **1949**, *3*, 113.
- (37) Saito, S.; Okuyama, H. *Kolloid Z.* **1954**, *139*, 150.
- (38) Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I., Eds. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1989; Vol. 17, p 167.
- (39) Dittmar, C.; Priest, W. J. *J. Polym. Sci.* **1955**, *18*, 275.
- (40) Shibayama, M.; Ikkai, F.; Moriwaki, R.; Nomura, S. *Macromolecules* **1994**, *27*, 1738.
- (41) Tsujimoto, M.; Shibayama, M. *Macromolecules* **2002**, *35*, 1342.
- (42) Napper, D. H., Ed. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: Orlando, FL, 1993.
- (43) Bandyopadhyaya, R.; Nativ-Roth, E.; Regev, O.; Yerushalmi-Rozen, R. *Nano Lett.* **2002**, *2*, 25.
- (44) in het Panhuis, M.; Maiti, A.; Dalton, A. B.; van den Noort, A.; Coleman, J. N.; McCarthy, B.; Blau, W. J. *J. Phys. Chem. B* **2003**, *107*, 478.
- (45) Ilmain, F.; Tanaka, T.; Kokufuta, E. *Nature* **1991**, *349*, 400.