Different J-Aggregates of an Amphiphilic Cyanine Dye in Monolayers at the Air−Water Interface[†]

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J-Aggregates of the amphiphilic symmetrical cyanine dye 5,5′-6,6′-tetrachloro-1,1′-diethyl-3,3′-dioctadecyl-benzimidazolocarbocyanine toluenesulfonate are formed in monolayers of the pure dye at the air−water interface as well as in mixtures with the coaggregates hexadecane (HD) and methyl octadecanoate (MOD), respectively, at a molar ratio of dye/coaggregate of 1:1. The monolayers have been characterized by surface pressure−area and surface potential−area isotherms as well as reflection spectroscopy. The position of the J-aggregate band that is red-shifted with respect to the monomer band depends on the kind of coaggregate. This in the case of symmetrical cyanines surprising phenomenon was analyzed by applying the extended dipole model according to the model of two-dimensional "brickstone" structure assuming that the coaggregate MOD in contrast to HD modifies chromophore packing.

1. Introduction

Amphiphilic cyanine dyes can be organized into J-aggregates in monolayers at the air−water interface by mixing the dye with molecules such as hexadecane that assist an appropriate arrangement in the process of monolayer formation.[1] J-Aggregates are characterized by a very narrow and intense absorption band shifted to longer wavelengths (bathochromic) with respect to the monomer absorption band and by a sharp emission band with very little Stokes shift.[2,3] The position of the J-aggregate band has been rationalized by the "brickstone" structure[4] using the extended dipole model of cyanine dyes.[5] Due to the unusual photophysical properties and rapid motion of the coherent exciton,[6,7] the excitation energy of about 10.000 molecules is transferred to a single molecule of an appropriate energy acceptor in the J-aggregate,[8] demonstrating that these associates may be particularly efficient light-harvesting systems. The dynamics of such systems of donor J-aggregate and energy acceptor has been investigated theoretically based on the model of the coherent exciton.[9] A more detailed knowledge of the relation between dye organization (J-aggregate geometry) and spectroscopic properties of such aggregates is required in view of their potential application in devices for light harvesting as well as for transport of energy and/or charge in ultrathin films. Reflection spectroscopy[10,11]

proved to be an extremely useful method for studying J-aggregate formation in monolayers at the air−water interface.

We have investigated aggregate formation in pure and mixed monolayers at the air−water interface of the amphiphilic cyanine dye 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-dioctadecyl-benzimidazolocarbocyanine toluenesulfonate (OB6, structure shown in Chart 1) with hexadecane (HD) and methyl octadecanoate (MOD), respectively. Monolayers of this symmetrical cyanine dye have been used in the investigation of spectral sensitization of silver bromide,[12] of epitaxial attachment to fresh gypsum surfaces,[13] and of nonradiative decay of excited molecules near a metal surface.[14] The extended dipole model was used to calculate the wavelength of the absorption maximum. The interaction integral J_{ij} between the extended dipoles in the monolayer was determined for selected geometries, and the energy shift between the J-aggregate and monomer absorption maximum ($\Delta E_{ag} - \Delta E$) was calculated following the procedure given in ref 15. By comparison with the experimental energy shifts obtained from the reflection spectra, the minimum aggregation number N_{min} and the slip angle α (see Chart 1b) were estimated.

2. Experimental Section

2.1. Materials. The amphiphilic cyanine dye OB6 (the first sample has kindly been provided by D. O'Brian, Eastman Kodak Research Laboratories) was obtained from R. Steiger (Ciba-Geigy Photochemie Ltd.). HD, reference for gas chromatography, and MOD, reference for gas chromatography, were purchased from Merck and used without further purification. The solvent chloroform (99.8%), HPLC grade, was purchased from Baker. The water was purified in a Milli-Q filtration unit of Millipore Co., with a resistivity of 18 MΩ cm.

2.2. Methods. Surface pressure−area and surface potential−area isotherms were measured in a rectangular trough made

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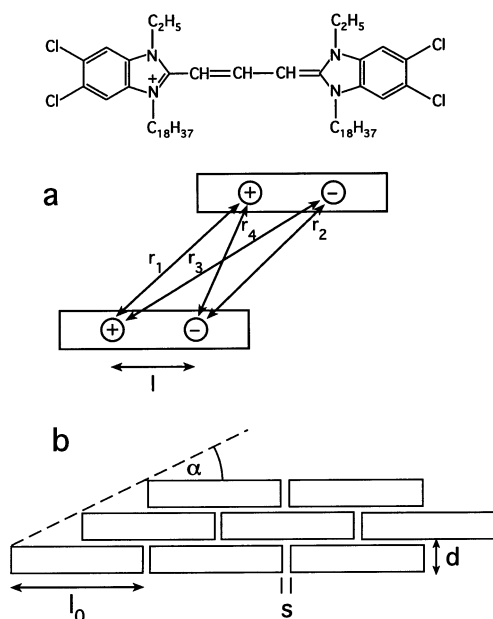(11) Orrit, M.; Möbius, D.; Lehmann, U.; Meyer, H. *J. Chem. Phys.* **1986**, *85*, 4966−4979.
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Chart 1. Chemical Structure of the Dye OB6 (Top, Anion Toluenesulfonate); Geometry and Parameters for the Calculation of the Interaction Energy J (a) and Structural Model of the J-Aggregate with Relevant Parameters (b)

Figure 1. Surface pressure–area (a) and surface potential–area (b) isotherms of monolayers of pure OB6 (1), OB6/HD = 1:1 (2, dashed), OB6/MOD = 1:1 (3), and MOD (4, dotted, here area per MOD molecule), measured by continuous compression; the data of discontinuous monolayer compression are represented by markers: pure OB6 (circles) and OB6/MOD = 1:1 (squares).

from poly(tetrafluoroethylene) with the dimensions 36 cm (length), 11 cm (width), and 1 cm (depth). The trough was thermostated at 20 °C and enclosed in a box. A Wilhelmy balance provided with a 15 mm wide filter paper as a plate was used for the measurement of the surface pressure. The surface potential was measured with a vibrating plate condensor of the type described earlier.[16] As counter electrode, a quadratic Pt plate of length 3 cm was placed at the bottom of the trough. Volumes of 30–40 μL of spreading solutions of ca. 1 mM concentration were delivered to the initial surface of 363 cm², and after about 10 min of relaxation, the monolayers were compressed at an average speed of 16.2 cm² min⁻¹ (continuous mode). Since the surface pressure π decreased during the measurement of reflection spectra at constant area A, π–A isotherms were also measured discontinuously, allowing the monolayer to relax at constant area for ca. 10 min after decreasing the area. Although relaxation may not have been completed (depending on the area), the next compression step was performed in order to finish the measurement in reasonable times (i.e., 5–6 h) in the view of dye stability.

Reflection spectra were measured at constant monolayer area with a modified instrument of the type described earlier,[11] using a rectangular trough of the same dimensions as given above. At the rear end, a small section with a clean water surface was separated by a fixed barrier serving as the reference section for the optical measurements. This trough was also thermostated and enclosed in a box, which was flushed with nitrogen in order to reduce possible photochemical damage of the dye during the series of measurements. The monolayer was compressed to a selected area, and the reflection spectrum was measured at constant area (time required was ca. 6 min) as the difference ΔR of the reflectivities in the presence and absence of the monolayer, respectively.

3. Results and Discussion

3.1. Surface Pressure–Area and Surface Potential–Area Isotherms. The surface pressure–area (π–A) and surface potential–area (ΔV–A) isotherms of the monolayers at the air–water interface, measured in the continuous mode (lines) and discontinuously (markers), are shown in Figure 1. The isotherms of the pure OB6 monolayer and the mixed monolayers of OB6/HD and OB6/
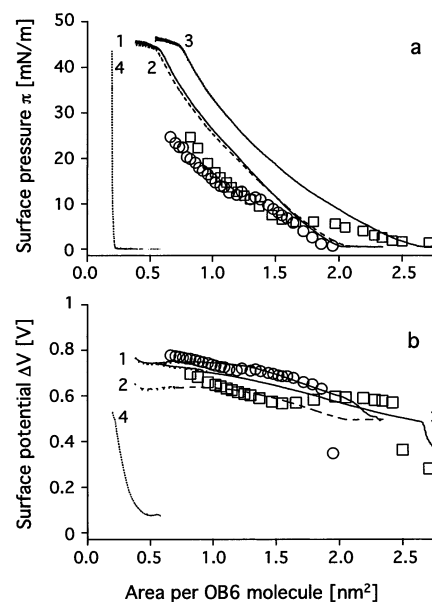
MOD, respectively, molar ratio 1:1, are plotted versus area per OB6 molecule, and those of MOD (dotted curves 4) are plotted versus area per MOD molecule.

The π–A isotherms of pure OB6 (Figure 1, curve 1) and OB6/HD = 1:1 (Figure 1, curve 2, dashed), measured in the continuous mode, are almost identical; however, they present small but significant differences. At low surface pressures, the mixture OB6/HD = 1:1 (dashed curve 2) occupies a slightly larger area per OB6 molecule than the pure OB6, and for $\pi > 12$ mN/m the mixture occupies a smaller area. This may be due to slightly different packing of the hydrocarbon chains with HD filling the free space left by the hydrocarbon chains of OB6 on top of the chromophore for $\pi > 12$ mN/m (Figure 1), thereby causing a stronger attractive interaction between the hydrocarbon chains than in the pure OB6 (where the hydrocarbon chains may be disordered) and leading to a reduction of the occupied area.[1,17] Below $\pi \approx 12$ mN/m (i.e., $A \geq 1.48$ nm² per OB6 molecule), the area occupied by the mixture OB6/HD is somewhat larger, presumably because not all molecules of HD are shifted on top of the chromophores between the hydrocarbon chains of the dye molecules. This interpretation is supported by the reflection spectra, vide infra. The positioning of HD on top of the chromophore between the dye hydrocarbon chains leads to an area per OB6 in the monolayer OB6/HD = 1:1 that is almost identical to that occupied by OB6 in absence of HD. Therefore, the isotherm of OB6/HD = 1:1 is very similar to that of pure OB6.

The π–A isotherm of OB6/MOD = 1:1 (Figure 1, curve 3) measured continuously presents a profile similar to those discussed previously with the difference that it is displaced to larger area per OB6 molecule. The increase of pressure begins at $A = 2.65$ nm² per OB6 molecule, for OB6 at 2.00 nm²/molecule, and 2.10 nm² per OB6 molecule for the mixture OB6/HD. The coaggregate MOD forms

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stable monolayers at the air–water interface (dotted curves 4 in Figure 1). Therefore, this area increase with regard to the isotherm of pure OB6 may be attributed to anchoring of the MOD molecules to the water, in contrast to those of HD. This phenomenon is surprising, since MOD as well as molecules of the even more strongly anchored octadecanoic acid are shifted on top of the chromophores in the case of different symmetrical amphiphilic cyanine dyes, such as dioctadecyl-oxacyanine and dioctadecyl-thiacyanine, respectively.[18] In the case of carboxylic acids, this shifting of the coaggregate on top of the chromophore might be attributed to ion pair formation of the cationic chromophore and the fatty acid anion. An anchoring of the second component in the monolayer at the water surface may laterally separate the chromophores thereby preventing the formation of J-aggregates or at least changing the optical properties of the aggregate due to modified interactions between the chromophores.

The usual way of characterizing monolayers by measuring π–A isotherms by continuous compression may lead to erroneous conclusions if slow reorganization processes occur in the monolayer. In such cases, the compression curves are no isotherms in the thermodynamic sense. Due to the fact that a decrease of the surface pressure π has been observed during the measurement of reflection spectra at constant monolayer area, we measured π–A isotherms in a discontinuous way, providing ca. 10 min time for relaxation after each step of area decrease. The circles in Figure 1 show the π–A isotherm obtained for pure OB6, and the squares that of OB6/MOD = 1:1. Clearly, these curves differ from the curves measured by continuous compression. In the case of pure OB6, the surface pressure starts rising upon compression at $A = 1.95$ nm^2, and the surface pressure values are always lower than during continuous compression (Figure 1a, curve 1). A discontinuity with indication of a short plateau is now seen starting at $A = 1.4$ nm^2 and $\pi = 11$ mN/m which may indicate a phase transition. At areas $A < 0.8$ nm^2, the monolayer becomes unstable as indicated by fluctuations of the surface potential. This is reasonable considering the chromophore dimensions of length $l_0 \approx 2.04$ nm and a thickness of about 0.4 nm resulting in $A_{\text{chromo}} = 0.82$ nm^2.

In the case of OB6/MOD = 1:1 (squares in Figure 1a), the values of the discontinuous isotherm measurement are considerably shifted to smaller area or lower surface pressure values, respectively, as compared to those of the continuous isotherm (Figure 1a, curve 3). A plateau upon compression is seen in the range of 2.0 nm$^2 > A > 1.55$ nm^2 (recall that A is the area per OB6 chromophore in the two-component monolayer). Between $A = 1.5$ nm^2 and $A = 1.3$ nm^2, the surface pressure is even smaller than for the pure OB6 monolayer. Below $A = 1.3$ nm^2 ($\pi = 11$ mN/m), the area per OB6 molecule is larger in the presence of MOD than in the absence. For example, at $\pi = 20$ mN/m the area is $A = 0.82$ nm^2 for pure OB6 and $A = 0.96$ nm^2 in the presence of MOD. We tentatively attribute the shift of the discontinuous isotherm of OB6/MOD = 1:1 to larger areas as compared to that of pure OB6 to the fact that the MOD molecules (at least a large fraction of them) are located with their headgroups in contact with the water surface, thereby separating the chromophores. Direct and unambiguous information on molecular aggregation in the monolayers supporting this view is obtained by reflection spectroscopy (vide infra).

The surface potential–area isotherms of the monolayers, measured simultaneously with the π–A isotherms,
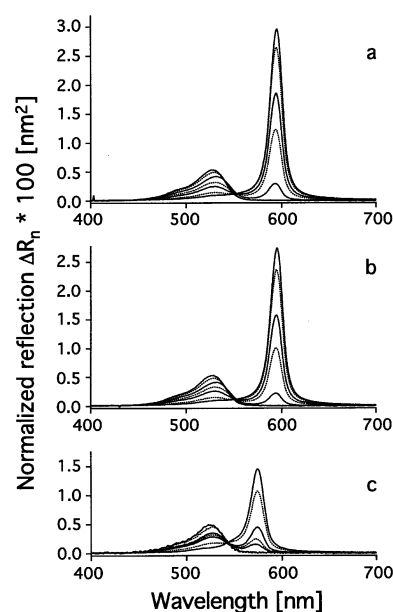
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Figure 2. Reflection spectra of monolayers plotted as reflection ΔR_n normalized with respect to the surface density of OB6: (a) pure OB6; (b) OB6/HD = 1:1; (c) OB6/MOD = 1:1. The spectra presented alternately as full and dotted lines, respectively, were measured at different constant areas per OB6: 2 nm^2 (full), 1.7 nm^2 (dotted), 1.4 nm^2 (full), 1.3 nm^2 (dotted), 1.2 nm^2 (full), 1 nm^2 (dotted), 0.8 nm^2 (full) (OB6 and OB6/HD = 1:1); 2.5 nm^2 (full), 2 nm^2 (dotted), 1.7 nm^2 (full), 1.6 nm^2 (dotted), 1.5 nm^2 (full), 1.2 nm^2 (dotted), 0.8 nm^2 (full) (OB6/MOD = 1:1). With decreasing area, the band of the monomer around 527 nm decreases and the strong and narrow band at longer wavelengths increases.

are shown in Figure 1b. Again, these isotherms are plotted versus area per OB6 molecule, except in the case of MOD (curve 4). The surface potential ΔV of the pure OB6 monolayer (curve 1) is rather positive in the whole area range, as expected for an amphiphile with a positively charged headgroup. The continuously measured ΔV–A isotherm of OB6/HD = 1:1 (curve 2) is seen at a slightly less positive potential, and the corresponding isotherm of the mixture OB6/MOD = 1:1 (curve 3) is between the former two isotherms. The values of ΔV measured discontinuously are shown as circles (pure OB6) and squares (OB6/MOD = 1:1). An interpretation of these values in the view of monolayer organization is rather ambiguous since the orientation of the dipole of the carbonyl group of MOD may play a significant role in the case of OB6/MOD = 1:1. The normal component μ_n of the apparent dipole moment per OB6 (not shown here), calculated as usual (μ_n/D = $2.65 A$/nm$^2 \times \Delta V$/V), decreases during compression from $\mu_n = 3.11$ D at $A = 1.86$ nm^2 to $\mu_n = 1.6$ D at $A = 0.79$ nm^2 for the pure OB6 monolayer. This may be attributed to the contribution of the electric double layer changing with surface charge density.

3.2. Reflection Spectroscopy. The reflection of light by dye containing complex monolayers at the air–water interface depends on the organization and the density of the dye in the monolayer. Transition moments oriented parallel to the monolayer plane give rise to an enhancement ΔR of the reflection of light at normal incidence in the range of the dye absorption band as compared to the reflection of the clean water surface.[10,11] The reflection spectrum, therefore, characterizes the particular organization of the dye monolayer.

Figure 2 shows the reflection spectra of monolayers of pure OB6 (a) and of the mixtures OB6/HD = 1:1 (b) and OB6/MOD = 1:1 (c) for different areas as specified in the

figure caption. The spectra were measured at constant area. All spectra are normalized with respect to the surface density of the chromophore (i.e., the normalized reflection signal is $\Delta R_n = \Delta R\, A$). The normalized reflection spectrum remains constant during monolayer compression if the density only is varied. Therefore, any variation of the orientation and/or molecular association giving rise to changes of the transition moments is clearly visible in the normalized reflection spectrum.

All three types of monolayers show a broad band at large areas per chromophore, $A \geq 2$ nm², with the maximum at $\lambda_{max} = 527$ nm corresponding to the monomer band (in ethanol solution $\lambda_{max} = 517$ nm). With decreasing area, the normalized intensity ΔR_n of the band of the dye monomer decreases and a new band is observed at larger wavelengths. This narrow (full width at half-maximum = 16 nm in the case of pure OB6 and 17 nm for OB6/MOD = 1:1) and intense band is attributed to the J-aggregate of OB6. The wavelength of the maximum of this narrow band depends on the monolayer composition. This maximum is at $\lambda_{max} = 594$ nm in the case of the monolayers of pure OB6 (Figure 2a) and of the mixture OB6/HD = 1:1 (Figure 2b). The close similarity of the spectra in these two series supports the view that HD is shifted on top of the OB6 chromophores without influencing chromophore packing. Different from these two monolayers, $\lambda_{max} = 574$ nm is observed for the mixture OB6/MOD = 1:1 (Figure 2c). Further, the intensity of this band is reduced as compared to the former cases. After the measurement at the smallest area value, the monolayers were expanded to the area of the initial measurement, and again a reflection spectrum was measured. For monolayers of OB6 and OB6/HD = 1:1, these spectra were identical with the initial spectrum within experimental error, indicating that no loss of dye, for example, by photochemical degradation, has occurred. In the case of OB6/MOD = 1:1, some J-aggregate is still seen as a band of lower intensity than the monomer band. Obviously, the disintegration of the J-aggregate is much slower in this monolayer than in the former ones.

Since the transition moment of OB6 chromophores should be oriented parallel to the water surface in all monolayers studied here independent of the area (as long as no collapse occurs), the decrease of the monomer band is due to a change of the equilibrium between monomer and J-aggregate. The isosbestic point observed in all three series of spectra is evidence for an equilibrium of two species. The values of the normalized reflection at the maxima, that is, $\Delta R_{n,max}$, taken from the spectra in Figure 2 are plotted versus area per OB6 molecule in Figure 3. The decrease of the monomer band (Figure 3a) and the increase of the J-aggregate (Figure 3b) band with decreasing area are very similar for the monolayers of pure OB6 (circles) and OB6/HD = 1:1 (triangles). A different course is observed for OB6/MOD = 1:1 (squares) with the decrease of the monomer and increase of the J-aggregate bands upon compression starting at a larger area than in the other cases. Further, the intensity of the J-aggregate band here is smaller than in the case of pure OB6 and of OB6/HD = 1:1. These observations reflect the close similarity of the $\pi-A$ isotherms measured continuously for pure OB6 and OB6/HD = 1:1 and the obvious difference in the isotherms measured discontinuously for pure OB6 and for OB6/MOD = 1:1, respectively.

Since the molecules of MOD obviously do occupy an area in addition to that of the chromophores for $A < 1.3$ nm², MOD is not shifted on top of the chromophores upon
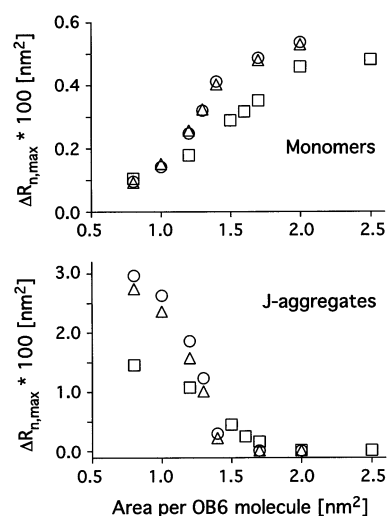

Figure 3. Normalized reflection values at the band maxima (taken from the reflection spectra in Figure 2) of the monomer (a) and the J-aggregate (b) plotted vs area per OB6 for monolayers of pure OB6 (circles), OB6/HD = 1:1 (triangles), and OB6/MOD = 1:1 (squares).

compression, or a small fraction of the MOD molecules only are shifted up. The onset of J-aggregate formation is at larger areas in the presence of MOD than in the other two cases. This may be interpreted as an initiation of aggregate formation by MOD due to stronger adhesion of the chromophores in the presence of MOD. The fact that the disintegration of the J-aggregate upon expansion of the monolayer is much slower in the presence of MOD than in its absence or in the presence of HD points to the same conclusion. The difference of the spectral position of the J-aggregate band maximum then has to be due to modified chromophore interactions and has to be reflected by a structural model of the J-aggregates. The observation of different J-aggregates of the same dye due to the presence of the coaggregate octadecane has been reported for monolayers of 1,1′-dioctadecyl-2,2′-cyanine transferred to glass plates.[19] In that case, the maximum of the J-aggregate formed by the pure dye was at $\lambda_{max} = 552$ nm, whereas $\lambda_{max} = 578$ nm was observed for monolayers of dye/octadecane, with a molar ratio of 1:1. The observations were rationalized by different structural models for the two J-aggregates based on the extended dipole approximation of H. Kuhn and co-workers.[5]

To our knowledge, for floating monolayers of amphiphilic symmetrical cyanine dyes, no observation has been reported of spectral shifts of the J-aggregate band due to the nature of a coaggregate, although a large variety of additives have been used. In the case of an amphiphilic merocyanine dye, we have recently reported such a phenomenon.[20] Here, we will interpret the new observations with OB6 on the basis of the extended dipole model and propose slightly different structural models for the two J-aggregates.

3.3. Structural Models for the Different J-Aggregates of OB6. In the extended dipole model of aggregates, the transition moments of the dye molecules are replaced by the classical extended dipoles with length *l* and charge $+q$ and $-q$. The charge q and the dipole

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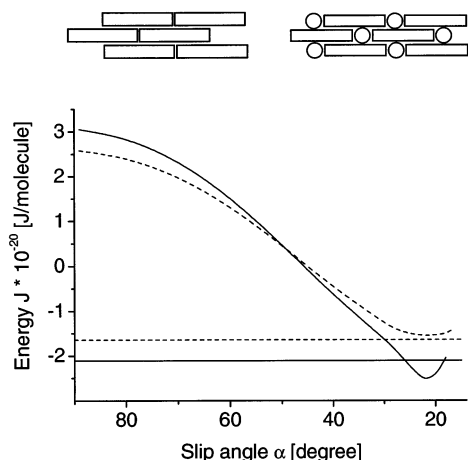
Figure 4. Total chromophore interaction energy J in J-aggregates of the brickstone structures shown schematically on top for pure OB6 (left) and OB6/MOD = 1:1 (right) calculated with the extended dipole model as a function of the slip angle α (see Chart 1b) for the number of chromophores $N = 49$ and with the parameters $d = 0.40$ nm and $s = 0$ for OB6 and OB6/HD = 1:1 (full curve) and parameters $d = 0.48$ nm and $s = 0.48$ nm for OB6/MOD = 1:1 (dashed curve). The horizontal lines represent the shift of the J-aggregate band with respect to the monomer for J-aggregate $\lambda_{max} = 594$ nm (full line) and $\lambda_{max} = 574$ nm (dashed line); the minima of the calculated curves occur at the slip angles $\alpha \approx 22°$.

length l are related to the transition moment μ according to

$$ql = \mu \qquad (1)$$

It is assumed that the transition moment of the chromophore is oriented parallel to the long axis of the dye molecule like in the cases of other cyanine dyes with two long-chain substituents.[11] The interaction integral J_{ij} between two dipoles is obtained by

$$J_{ij} = \frac{q^2}{4\pi\epsilon_0\epsilon_r}\left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_3} - \frac{1}{r_4}\right) \qquad (2)$$

where ϵ_r is the dielectric constant of the medium (we are using the value of ϵ_r for the hydrocarbons $\epsilon_r = 2.5$[5]), and r_i is the distance between two charges (Chart 1a). The values of J_{ij} can be calculated by assuming the dipole length $l = 0.99$ nm,[5,7] the length of the long axis of the OB6 $l_0 = 2.04$ nm,[5,4] and a lateral distance between adjacent dipole moments of about $d = 0.40$ nm.[4] This distance d (see Chart 1b) is slightly modified by the coaggregate, since this may be approximated by a column representing a hydrocarbon chain of 0.48 nm diameter. Further, the ends of the chromophores are separated by distance s (Chart 1b) in the presence of the coaggregate MOD inserted here between the chromophores. A location of MOD between the rows of the chromophores would prevent J-aggregate formation. The structural models used in the following are shown schematically on top of Figure 4. The charge $q = 3.84 \times 10^{-20}$ C corresponds to 24% of the elementary electric charge.[5,21]

The excitation energy of the reflection maximum of the aggregate band (ΔE_{ag}) is approximately represented as the sum of the excitation energy of the monomer peak

(ΔE) and the interaction integrals J_{ij}:[5,22]

$$\Delta E_{ag} \approx \Delta E + 2\frac{1}{2}\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}J_{ij} \qquad (i \neq j) \qquad (3)$$

When a J-aggregate consists of a large number of chromophores, eq 3 can be simplified as

$$\Delta E_{ag} \approx \Delta E + 2\sum_{i=1}^{N}J_{ij} = \Delta E + 2J \qquad (i \neq j) \qquad (4)$$

where the jth dye is placed at the center of the J-aggregate.[15] We used the same number of rows and columns for the calculations.

Figure 4 shows the energy J plotted against the slip angle α between the long axis of the aggregate and the extended dipole vector, for the J-aggregate structures in monolayers of pure OB6 and OB6/HD = 1:1 (full curve) and OB6/MOD = 1:1 (dashed curve). The number of chromophores used in both cases is $N = 49$. The other parameters are $d = 0.40$ nm and $s = 0$ nm (full curve) and $d = 0.48$ nm and $s = 0.48$ nm (dashed curve). For larger values of N, the curves follow that of $N = 49$. The minimum of the theoretical curve is slightly more negative than the corresponding experimental value in the case of pure OB6. The slip angle at the minima is $\alpha \approx 22°$ in both cases. The horizontal lines represent the experimental energy shifts ($\Delta E_{ag} - \Delta E$) with respect to the OB6 monomer peak $2 \times (2.10 \times 10^{-20}$ J/molecule) (full line) and $2 \times (1.64 \times 10^{-20}$ J/molecule) (dashed line), corresponding to the values of $\lambda_{max} = 594$ nm of the J-aggregate band in the cases of OB6 and OB6/HD = 1:1 and 574 nm in the case of OB6/MOD = 1:1. The schemes on top represent the structural models used for pure OB6 and OB6/HD = 1:1 (left) and OB6/MOD = 1:1 (right).

For both J-aggregates of the amphiphilic symmetrical cyanine dye OB6, we propose a brickstone structure. The coaggregate MOD modifies chromophore packing since it is located between the ends of adjacent chromophores in each row thereby slightly increasing also the row spacing. The two-dimensional crystals of the J-aggregate formed in the monolayers at the air−water interface, to our regret, could not be observed by Brewster angle microscopy like in the case of other cyanine dyes,[23] presumably due to a size smaller than the lateral resolution of our instrument (a few micrometers). However, scanning force microscopy at the air−water interface might provide a possibility to test the proposed models in the future.

4. Conclusion

The effect of the coaggregates hexadecane and methyl octadecanoate, respectively, on the formation of the J-aggregates of the amphiphilic symmetrical cyanine OB6 was studied in monolayers at the air−water interface. The position of the aggregate band depends on the chemical nature of the coaggregate with hexadecane shifted on top of the chromophores upon monolayer compression. The coaggregate MOD is anchored to the water surface, thereby influencing chromophore coupling by slightly modifying chromophore packing. The chromophore interaction energies of the J-aggregates were calculated using the extended dipole model of aggregates of dye molecules with an

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aggregation number $N_{min} = 49$ yielding a slip angle of $\alpha \approx 22°$ in both cases.

Abbreviations

OB6 = 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-dioctadecyl benzimidazolocarbocyanine

HD = hexadecane

MOD = methyl octadecanoate

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