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Chiral J-Aggregates Formed by Achiral Cyanine Dyes[**]

Stefan Kirstein,*[a] Hans von Berlepsch,[a]
Christoph Böttcher,[b] Christian Burger,[a] Andre Ouart,[c]
Günter Reck,[d] and Siegfried Dähne[d]

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Self-organization of molecular species into chiral supramolecular structures is a fundamental building principle in living materials and found in various systems ranging from double-stranded DNA to complex structures like the tobacco mosaic virus. In all natural systems, only one type of the two possible enantiomers is found, namely they are enantiomerically pure. Although this observation has attracted much research interest during the last decades, two basic questions are still open: How is the chiral structure of the molecular building block transmitted into a chiral superstructure of large, sometimes micrometer sized, molecular assemblies, and what was the reason for the spontaneous break in symmetry between the two possible enantiomeric structures, which in ancient times must have happened in nature? Both questions are currently addressed by investigating various artificial systems; for example, the spontaneous break in symmetry was mostly studied on crystals formed by nonchiral molecules.[1, 2] Recently, for liquid crystals, a spontaneous formation of macroscopic chiral domains from achiral molecules was reported.[3] Many other systems are known where macroscopic chirality is induced by chirality of the molecules, such as helicenes,[4, 5] helical metal complexes,[6] block copolymers,[7] gemini surfactants,[8] or the coiled aggregates of (crown ether

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[a] S. Kirstein,[+] H. von Berlepsch, C. Burger
Max-Planck-Institute for Colloids and Interfaces
Am Mühlenberg 2, 14476 Golm/Potsdam (Germany)
Fax: (+49) 30-2093-7832
E-mail: kirstein@physik.hu-berlin.de

[b] C. Böttcher
Freie Universität Berlin
Takustrasse 3, 14195 Berlin (Germany)

[c] A. Ouart
Federal Institute for Materials Research and Testing
Rudower Chaussee 5, 12489 Berlin (Germany)

[d] G. Reck, S. Dähne
Institute of Chemistry
Humboldt-Universität zu Berlin
Hessische Strasse 1 – 2, 10115 Berlin (Germany)

[+] Current address:
Institute of Physics
Humboldt-Universität zu Berlin
Invalidenstr. 110, 10115 Berlin (Germany)

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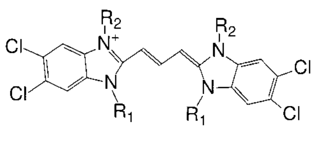
phthalocyaninato) polysiloxanes,[9] to name a few. Other systems which have attracted particular interest within this context are Langmuir monolayers, where the influence of the chirality of lipid molecules on the structure formation of crystalline domains has been investigated,[10] where spontaneous chiral segregation from a racemic mixture of lipids was observed.[11] In all cases, the resulting meso- or macroscopic structure is determined by various intermolecular interactions, such as van der Waals and electrostatic forces, covalent and hydrogen bonding, and, in the case of amphiphilic molecules, hydrophobic interactions[12] to include the interactions with surrounding solvent molecules. Therefore, it is a nearly impossible task to predict the structure and morphology of aggregated systems from the molecular structure in spite of the substantial progress made in molecular modelling.

Self-organisation in polar solutions is a common feature of dye molecules which contain extended planar π-electron systems.[13] Compared to surfactants, in dyes the complexity of the intermolecular force balance is increased by very strong dispersion forces, which are induced by fluctuation of the delocalized π-electrons. A peculiar class of aggregating dyes is represented by the cyanine dyes, which form J-aggregates in polar solvents.[14–18] These aggregates are characterized by a new optical absorption band, which is red-shifted and significantly narrowed with respect to the monomeric absorption, accompanied by an intense and nearly resonant fluorescence emission. The spectroscopic behavior of J-aggregates has been extensively investigated[19–21] and is now well understood in terms of molecular excitons.[22, 23] However, the structure and morphology of J-aggregates in solution is still unknown. Structure determinations published so far were performed on J-aggregates immersed into polymeric films[24] or adsorbed on solid/air[25] or liquid/air interfaces.[26] Only very recently the mesoscopic structure of J-aggregates of certain amphiphilic cyanine dyes has been revealed by cryo-transmission electron microscopy (cryo-TEM).[27, 28] Here, helical J-aggregates are presented, which are spontaneously formed by a nonchiral amphiphilic cyanine dye in aqueous sodium hydroxide solution. The reason for the induced chirality is revealed by X-ray structure analysis of a single crystal.

The dye molecule **C8O3** (5,5′,6,6′-tetrachloro-1,1′-dioctyl-3,3′-di-(3-carboxypropyl)-benzimidacarbocyanine; Scheme 1) combines structure formation abilities known from soluble surfactants with the outstanding optical properties of J-aggregates. The molecule is related to the more prominent dye **TDBC** (5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-di-(4-sulfobutyl)-benzimidacarbocyanine; Scheme 1). From these dyes, it is known that their J-aggregates exhibit very strong coupling between the transition dipole moments of neighboring molecules and hence, very strong exciton delocalization over at least ten molecules at room temperature[29] and about 100 molecules at 1.5 K.[20] The J-aggregates of **C8O3** show exciton splitting of the J-absorption band combined with optical activity.[30] In Figure 1, the absorption and CD spectra of a 6.5 μM solution of **C8O3** are shown. The J-aggregate is characterized by three strong absorption bands located at 600, 580, and 562 nm, respectively. The J-aggregate spectrum of **TDBC**, indicated by the dashed line, shows a small peak around 520 nm, caused by residual monomers.



Scheme 1. Chemical structure of the chromophore of the cyanine dyes. ***C8O3****:* $R_1 = C_8H_{17}$, $R_2 = C_3H_6COOH$; ***TDBC****:* $R_1 = C_2H_7$, $R_2 = C_4H_8SO_3^-$.

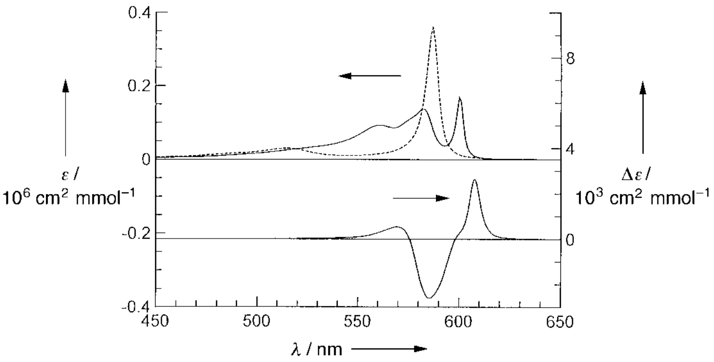


Figure 1. Absorption (left scale) and CD spectrum (right scale) of a 6.5 μM solution of ***C8O3*** *dissolved in 0.01 M NaOH. Crystalline material was dissolved directly by stirring for 24 h. The absorption spectrum of* ***TDBC*** *at same concentration is shown by the dashed line as a reference.*

The CD spectra of different solutions always showed the same sign of the bands, whereas the total intensity fluctuated between samples. Two positive bands are present with maxima at 610 and 570 nm and one negative band at 585 nm. The position of CD bands are not identical to the maxima of the absorption bands, which indicates that the CD spectrum is caused by chirality and not by linear dichroism of partially oriented samples. In the latter case, differently polarized absorption bands would appear as positive and negative bands in a CD spectrum, with their maximum at the same position as in the absorption spectrum.[31]

The occurence of the three bands in the absorption spectra of **C8O3** is caused by exciton splitting of the J-aggregate band. The observed optical activity must be due to excitonic coupling between several molecules of a chiral or helical aggregate. The intensity of the CD signal $\Delta\varepsilon$, normalized to the extinction coefficient ε, is in the order of $\Delta\varepsilon/\varepsilon \approx 10^{-3}$ and suggests a nonracemic mixture of right- and left-handed aggregates with a large excess of one type. However, the CD strength varied between samples, to indicate that the aggregate solutions cannot be enantiomerically pure. It is also not possible to conclude unambiguously from the CD spectra on the sense of the helicity because the sign of the CD couplet also depends on the sign of the intermolecular coupling energy and, hence, on the geometrical arrangement of the molecules.[31] Although the molecular structure is still unknown, one can assume from the red-shifted J-aggregate band that an acute angle is formed between the molecular transition moments, which contribute to the chiral excitonic transition.[32] In this case, right-handed aggregates would be predicted from the positive CD couplet at 610 and 585 nm.

The mesoscopic structure of the J-aggregates was resolved with cryo-TEM. Ropelike structures with lengths of several micrometers and diameters ranging from 20 to more than 50 nm were found as presented in Figure 2. The aggregates consist of multiple "strands" twisted around each other. The number of strands was constant within a single aggregate but varied between aggregates from three and more than ten. Occasionally, the splitting of an aggregate into two bundles was observed. At the lower edge of Figure 2 a rarely observed single strand is visible; its shape can be clearly identified as a cylindrical structure.

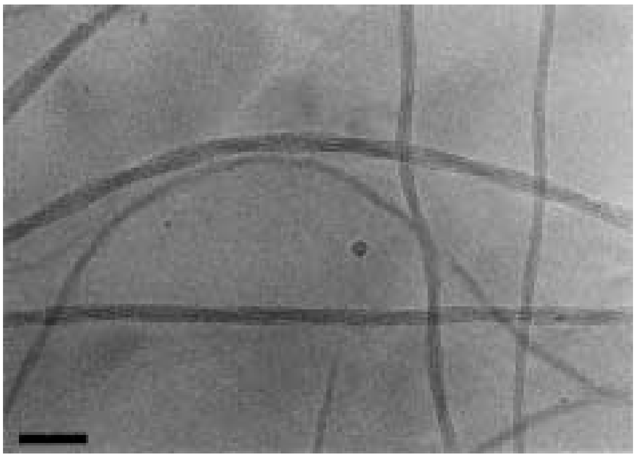


Figure 2. *Cryo-TEM picture of a 2.8 × 10^{-4}* M *solution of* ***C8O3***. *Ropelike aggregates containing different numbers of individual strands can be identified. The scale bar corresponds to 100 nm.*

The appearance of the aggregates in the TEM pictures was qualitatively modeled by computer simulations. The projection of the electron density of a model superhelix was calculated, which consists of five single hollow cylinders (tubules) with diameters of approximately 10 nm, arranged on a trigonal lattice, and with a left-handed twist around a helical axis. The left-handed helicity was chosen arbitrarily; the same projected view could also be obtained for right-handed aggregates. For this example, the total pitch, defined as the distance over which all cylinders have rotated fully, is in the range of 400 nm. In Figure 3, the original TEM picture (a) of a single superhelix having five single strands is compared with the calculated image (c) obtained from the model (b). The model of a five-stranded superhelix shown here was created by using the same parameters as the model of a four-stranded helix presented in our previous work.[27] The excellent agreement of the calculated and original pictures confirms the validity of the modelling procedure.

The handedness of the aggregates was determined by oblique shadowing of samples after their transfer to solid substrates as described in ref. [27]. A majority of left-handed aggregates was found in most of the pictures, although the right-handed type appeared as well. The existence of predominantly left-handed aggregates seems to contradict the conclusion drawn from the CD measurements, which suggests the existence of right-handed helices. However, it is not unlikely that the optical activity is caused by the arrangement of the molecules in the single strands, whose sign might have the opposite sense compared to the mesoscopic structure of the superhelices. A similar behavior has recently been reported for a system of chemically linked porphyrins[9] and is a general feature found in twisted ropes.

Figure 3. *a) Cryo-TEM picture of one* ***C8O3*** *J-aggregate that consists of five single strands. b) A simple model, that consists of a bundle of tubules that are packed on a trigonal lattice and twisted around each other. c) The calculated image of the J-aggregate, derived from the model in (b). The scale bar corresponds to 50 nm.*

To understand the ultimate origin of the spontaneous generation of chiral helices from nonchiral molecules, a detailed structure analysis on a molecular scale would be required. Although no such data are available, valuable information can be drawn from the X-ray structure analysis of a single crystal of **C8O3**;[33] see Figure 4. The triclinic unit cell is composed of two slightly different conformers, A and B, and their centrosymmetric mirror images, A′ and B′. The molecules A and B (A′ and B′) are paired with an average interplanar distance of the chromophores of 3.54 Å, which is a typical value for molecular packing in J-aggregates.[21] The conjugated π-electron system (colored in blue) of the A-type molecules is strictly planar; all dihedral angles are less than 1.7°. However, the B-type chromophores are twisted along the trimethine backbone by an angle of approximately 18° with left-handed symmetry for B but right-handed symmetry for B′. This torsion angle is indicated in Figure 4b by the twisted position of the four green chlorine atoms and is

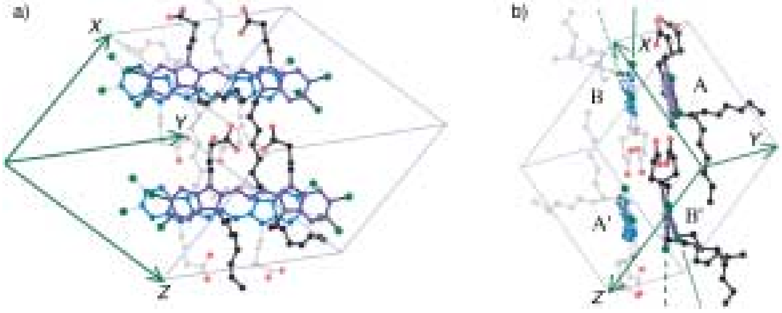


*Figure 4. Molecular structure of a single crystal of **C8O3** of dimensions 0.4 × 0.25 × 0.2 mm^3, as revealed by X-ray diffraction analysis. The triclinic unit cell (a = 16.581, b = 17.340, c = 19.245 Å, α = 64.45, β = 76.62, γ = 64.18°) consists of four molecules, in which two (A′, B′) are point symmetric with respect to the other ones (A, B). a) A view normal to the molecular plane, defined by the π-conjugated chromophore system (marked blue). The molecules in the background are colored in light blue. b) A view on the small edge of the molecular plane. The planar structure of the molecules A, A′ and the twisted structure of B and B′ are clearly visible from the green chlorine atoms and indicated by dashed lines. The average distance between the planes of molecule A to B and A′ to B′ is 3.54 Å. The DMSO molecules, which are also found in the crystal, are not shown here.*

emphasized by the dotted lines. It is important to note that, within the crystal lattice, this molecular twist occurs in a strictly racemic ratio. The coexistence between planar and twisted molecular structures indicates that the activation energy of dihedral torsions along the polymethine chain is low and, thus, the molecules can be easily twisted if it is favorable for the molecular packing.

The reason for the occurance of planar and twisted structures in the crystal lattice is the position and orientation of the carboxy groups. In case of the A type molecules, the carboxy groups are pointing towards a uniform direction, which alternates between A and A′ molecules. The distance between the carboxy groups of A and A′ in two neighboring unit cells is 2.97 Å, which enables *intermolecular* hydrogen bonding. The carboxy groups of the B molecules are directed with their oxygen atoms towards each other, forming *intramolecular* hydrogen bonds. In order to bring the carboxy groups to a close proximity, the trialkyl chains of the B molecules have to be arranged in an antisymmetric orientation, as seen in Figure 4 b. It seems that this out-of-plane orientation of the carboxypropyl chains is responsible for the twist of the chromophores. This is supported by a recent investigation of the aggregates and crystallites of a slightly modified molecule, in which these chains are enlarged by one methylene group: In this case, no chirality was observed within the aggregates.[34] It is assumed that the longer carboxybutyl chains are more flexible and, thus, the intramolecular hydrogen bonds between the carboxy groups can be formed without disturbing the planarity of the molecules.

Due to the peculiarities of the aqueous environment, many of the structural features of the crystals may be lost in solution. For example, in the crystal lattice, the octyl chains are packed closely to the carboxypropyl groups in order to bring the chromophoric planes close together in a pairwise arrangement. In aqueous solutions, the preferred structures have the hydrophobic chains covered by hydrophilic moieties, as it is the case of surfactant micelles.[12] Therefore, the amphiphilic dye **C8O3** is expected to form bilayers or micellar structures in solution. However, a micellar structure cannot be judged from the TEM pictures presented in Figure 3, since a 10 nm tubule diameter is contradictory to the assumption of a cylindrical micelle filled with an alkyl chain. Such a model was proposed in our earlier work for similar dyes with longer alkyl chains.[34, 35] Here, the molecular architecture of the aggregates must be more complex than it is expected from models of simple surfactant systems.

The generation of helical aggregates might be explained by the result that part of the molecules are in a twisted state within the crystal (B molecules). Since the molecular chirality is originating from intramolecular hydrogen bonds of the B molecules, it may be conserved even in solution. The twisted molecules may then serve as chiral building units for the growth of helical aggregates. Planar molecules (A molecules) or those of opposite handedness may easily change to the same handedness when they attach to a given aggregate, due to the torsional flexibility of the trimethine chain. However, since the chirality of the B molecules occurs in a strictly racemic ratio, one would expect the growth of J-aggregates with an equal ratio of both handedness and no net CD effect should be observable. Such a racemic ratio of chiral J-aggregates was reported previously for pseudoisocyanine (PIC), whose molecules are strongly twisted due to steric hinderances.[36]

The spontaneous break of symmetry in the formation of J-aggregates from **C8O3** requires an additional explanation. One possibility could be that a certain excess of one enantiomer of the dye is found at the surface of the crystallites, since all solutions are prepared by dissolving crystalline material. In this case, small nuclei are formed from the surface molecules which are dissolved first and, hence, the enantiomeric excess at the crystal surface might be transferred to the aggregate morphology. Another mechanism might be the transfer of chirality from fragments of larger aggregates to newly formed nuclei, as it was proposed for the formation of crystals of sodium chlorate.[1] The suggestion that the chirality of small nuclei is frozen in micrometer long J-aggregates is further supported by the observation that the sense of chirality of the aggregates could not be influenced or reversed by addition of large amounts of enantiomerically pure tartrate.[37] This would require a collective rearrangement of all molecules; however, the energy barrier for such a process is too high and, hence, the initially determined helicity is conserved.

The J-aggregates of **C8O3** presented here are an ideal tool to investigate the influence of the molecular structure and environmental conditions on the asymmetric generation of chiral supramolecular materials. In contrast to other chiral supramolecular systems, the asymmetric generation of helical aggregates is not initiated by chiral auxiliaries. The enantiomeric symmetry is spontaneously broken at a primary state of nucleation which is not hitherto understood. Once generated, the preferred handedness is templated to the J-aggregates during the period of growth to micrometer-long bundles of cylindrical structures. Their morphological complexity was not predictable from the simple one- or two-dimensional J-aggregate models that are usually discussed to describe their optical properties. To our knowledge, it is the first artificial system that shows delocalized excitons and energy migration in a helical arrangement of dye molecules.

Experimental Section

The dye (**C8O3**) was purchased from FEW Chemicals (Wolfen, Germany; Dye S 0250, highest purity available) and used without further purification. The crystalline material was dissolved directly in aqueous sodium hydroxide (1.0×10^{-2} M) by continuous stirring at room temperature for at least 24 h. Aliquots of the 2.5×10^{-2} M stock solution thus formed was diluted by NaOH solution for spectroscopic and cryo-TEM experiments by, typically, a factor of 50. The dye **TDBC** was also purchased from FEW Chemicals (Dye EC 2092) and used without further purification. It was dissolved in aqueous sodium hydroxide at a concentration of 10^{-4} M.

To prepare samples for cryo-TEM, a droplet (5 µL) of the aggregate solution was placed on hydrophilized, perforated, carbon-filmed copper grids. After removal of the excess fluid, an ultrathin layer (100 nm) spanned the holes of the carbon film. These grids were vitrified in liquid ethane (89 K) using a standard plunging device. The vitrified samples were transfered under liquid nitrogen into a TEM (Philips CM12) using the Gatan cryoholder and stage.

Single crystals of **C8O3** were grown from a 100 °C solution of dimethylsulfoxide (DMSO) by slowly cooling to room temperature in a Dewar vessel and stored for several days in a refrigerator. Crystals were investigated at room temperature using a SMART single-crystal diffractometer (Siemens). Absorption spectra were recorded using a spectrophotometer (Varian Cary 4), the CD-spectra from a spectropolarimeter (Jasco J-715).

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