

Chiral Dimers of a Chiral Pentamethine Cyanine Dye and of an Achiral Pentamethine Cyanine Dye in γ -Cyclodextrin as Chiral Host

Volker Buß*^a and Christian Reichardt^b

^a Fachgebiet Theoretische Chemie, Universität Duisburg, D-4100 Duisburg, Germany

^b Fachbereich Chemie, Universität Marburg, D-3550 Marburg, Germany

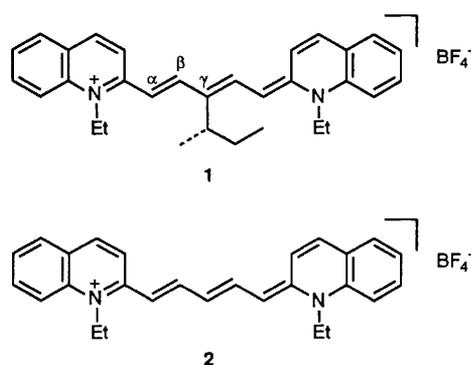
Chiral dimers are formed from the chain-substituted chiral pentamethine cyanine dye **1** at low temperatures and from the corresponding unsubstituted achiral dye **2** in γ -cyclodextrin as chiral host; the geometry of both dimers, on the basis of UV-VIS and circular dichroism (CD) spectroscopy, are quite similar corresponding, presumably, to a twisted sandwich.

The UV-VIS spectral changes accompanying the concentration or low-temperature promoted aggregation of dyes represent one of the most fundamental manifestations of molecular interactions. Theories accounting for both the shifts in absorption maxima and the changes of intensities have been developed at different levels of approximation, with basic relations between experimental data and aggregate structure well established.¹ In this communication we describe a chiral dimer formed from the chirally substituted cyanine dye **1**. Support for the structure claimed for the dimer of **1** comes from spectral evidence concerning the dimerization of the unsubstituted achiral dye **2** in γ -cyclodextrin.

The UV-VIS spectrum of a 3×10^{-6} mol dm⁻³ solution of the chiral γ -*sec*-butyl substituted pentamethine cyanine dye **1**² in methanol-ethanol shows the main absorption at $\lambda_{\max} = 704$ nm and bands of lower intensities at 647, 600 and 760 nm (Fig. 1). At lower temperatures, the vibrational progression sharpens resulting in reduced widths and increased heights of all these bands. In a more concentrated 3×10^{-5} mol dm⁻³ solution of **1** lowering the temperature below -140°C gives

rise to a new absorption band with $\lambda_{\max} = 635$ nm at the expense of the band at 704 nm.

We assume that this new absorption band results from dimerization of the chiral dye **1**; this is substantiated by the corresponding CD spectra (Fig. 2). In an 8×10^{-5} mol dm⁻³



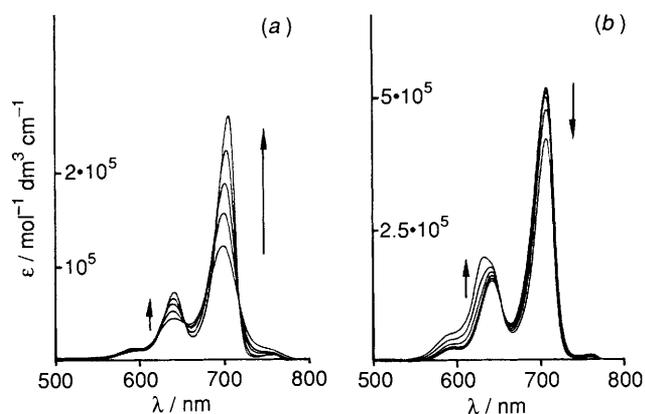


Fig. 1 Temperature-dependent UV-VIS spectra of **1** in ethanol-methanol (4:1). Concentrations are $3 \times 10^{-6} \text{ mol dm}^{-3}$ (a) and $3 \times 10^{-5} \text{ mol dm}^{-3}$ (b). Temperatures vary between $+20$ and -160°C (a) and between -120 and -160°C (b). The arrows indicate the changes caused by lowering the solution temperatures.

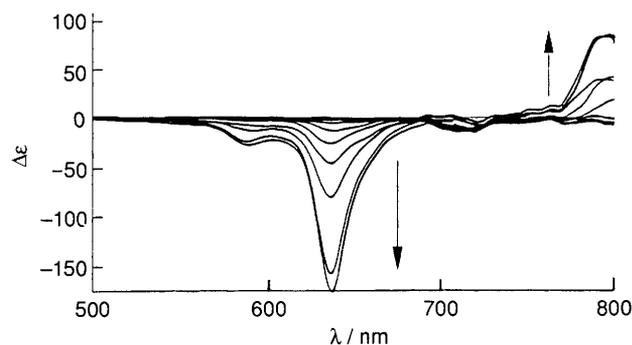


Fig. 2 Temperature dependent CD spectra of **1** ($c 8 \times 10^{-5} \text{ mol dm}^{-3}$) in ethanol-methanol (4:1). Temperatures vary between $+20$ and -80°C with intervals of 20°C and between -100 and -160°C with intervals of 10°C .

solution of **1** a negative band develops at 635 nm that reaches at -160°C an amplitude of $-170 \text{ l mol}^{-1} \text{ cm}^{-1}$ and a positive band around 790 nm , which is close to the limiting wavelength of our spectrometer, with an amplitude of $+85 \text{ l mol}^{-1} \text{ cm}^{-1}$. The rotational strengths associated with both bands assuming a symmetrical shape of the latter incomplete one are -150 and $+90 \times 10^{-40} \text{ cgs}$ units, respectively. The mean of the absorption energies of the two bands is $14\,203 \text{ cm}^{-1}$, which corresponds exactly to the absorption maximum of monomeric **1**.

The appearance of two oppositely signed CD bands symmetrically displaced from the monomer absorption is a clear indication that we are indeed dealing with a dimeric aggregate of **1**. Additional evidence comes from the aggregation behaviour of cyanine dye **2**, which resembles **1** without the chiral γ -substituent. Dye **2** has its main absorption maximum at 709 nm , shifted slightly to the red as compared with **1**. As expected the tendency of **2** to dimerize is significantly higher than that of **1** owing to the missing bulky chain substituent. In a highly diluted $3 \times 10^{-6} \text{ mol dm}^{-3}$ solution of **2** at -160°C the dimer band at 632 nm is already completely developed (not shown). The spectral distance between the monomer and dimer band of **2** is 1740 cm^{-1} , which is close to the 1545 cm^{-1} observed for **1**.

The dimer of **2** is necessarily achiral. In a chiral environment, however, it may become chiral provided the chiral discrimination is sufficient. As for other cyanine dyes³ γ -cyclodextrin enhances the dimerization of **2** as can be seen from the UV spectrum [Fig. 3(a)]. The CD spectrum of **2**

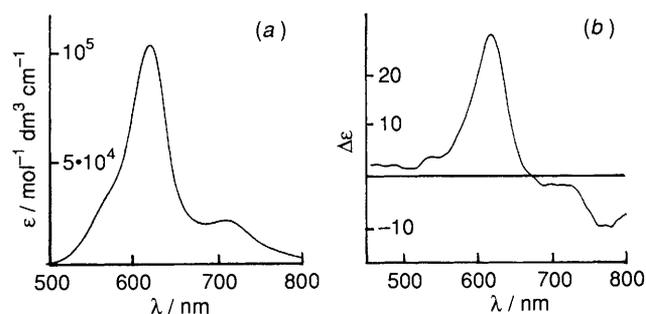


Fig. 3 (a) UV-VIS spectrum of **2** ($2 \times 10^{-5} \text{ mol dm}^{-3}$) in 15% ethylene glycol-water with $10^{-2} \text{ mol dm}^{-3}$ of γ -cyclodextrin added. (b) CD-spectrum of the same solution.

[Fig. 3(b)] shows a positive band with a maximum at 615 nm (UV-VIS: 620 nm) and a negative band at 780 nm . Here again, as in Fig. 2, the long-wavelength band is cut off owing to the limitation of the spectrometer. Except for the mirror-like behaviour of the CD-spectra and the broader bandshapes, which may be a consequence of the different solvents used, the spectra of dimeric **1** and **2** are remarkably alike. The reversal of chirality is purely accidental since the sources of dissymmetry, *i.e.* the asymmetric carbon in **1** and the chirality of the carbohydrate host, are not related to each other.

The very low UV-VIS extinction of the dimers in the region of the low-energy band as compared with the intense high-energy band suggests an almost parallel geometry of the two dye molecules in the aggregate. For a twist angle 2α between the transition moments the ratio of intensities between the two bands goes with $\cos^2\alpha/\sin^2\alpha$. For $\alpha = 5^\circ$, the long-wavelength band should already obtain 3% of the intensity of the allowed band, which according to the spectra represents an upper limit of the twist.

There are only very few reported instances with CD exciton states that are non-overlapping and so clearly resolved as in Figs. 2 and 3, the most recent also concerned cyanine dyes.⁴ With non-overlapping CD-bands the rotatory strengths associated with each transition can be obtained rigorously and compared with theoretical results. The transition moment of dye **1** varies with temperature between 10.2 and 12.3 D . Modelling this transition by an extended dipole with the length of 70 pm the interaction between two such moments 35 pm apart and twisted by 10° against each other gives two states with absorptions at 789 and 735 nm and rotatory strengths of $\pm 125 \times 10^{-40} \text{ cgs}$. The satisfactory agreement of these calculated values with the experimental ones indicates that the twisted dimer proposed is plausible; whether more accurate calculations yield other information remains to be seen.

There is another peculiar aspect of these CD spectra. According to theory⁵ and in agreement with innumerable experiments⁶ the two exciton states should have equal but opposite rotatory strengths. This is obviously not the case. In the CD spectra shown both in Figs. 2 and 3 the 790 nm band affords significantly less rotatory strength than the one at 635 nm . There are several possible explanations for this deviating behaviour of **1** and **2**. We have excluded the possibility that the spectrometer gave spurious results by repeating the measurements of Fig. 2 with another instrument and obtained essentially identical spectra. The zero sum rule might break down if the excitation states are not sufficiently separated from other excited states of the system. In that case one would expect the higher and the lower exciton states to interact differently with the environment leading to asymmetric exciton bands. The extremely long wavelength absorptions of the dimer appear to rule out this explanation. Higher aggregation of the dye molecules should significantly influence the shape of the UV and CD spectra of **1** and **2**. This factor is difficult to rule out completely.⁷ The negative CD absorption around 580 nm in Fig. 2 might indicate the

presence of such higher aggregated forms. There is, however, one other possibility we would like to point out.

A necessary condition for the zero sum rule to be valid for CD exciton states is that the monomers forming the aggregate are achiral themselves (a condition that cannot be met in any chiral aggregate). If, as a consequence of the interaction in the aggregate, the dye molecules are losing their planarity and assuming distorted geometries, this could lead to the observed deviation since in one of the exciton states the chirality is increased owing to the internal twist, whereas in the other state it is diminished. More rigorous calculations have to be performed in order to test this hypothesis.

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- 7 Higher aggregation of the cyanine dye DODC in or on the γ -cyclodextrin host is in light of the present result almost certainly responsible in part for the spectra attributed by one of us, V. Buß, *Angew. Chem.*, 1991, **103**, 889; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 869, to the dimer only.