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# Spectroscopic studies of $\beta$ -cyclodextrin-complexed cyanine dyes

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## Abstract

We have studied the interaction of a homologous series of symmetrical thiacyanine dyes (DTCI, DTDCI, DTTCI) with  $\beta$ -cyclodextrin. From absorption spectra we infer that all three dyes form  $\beta$ -CD complexes, either as dye cation monomer or dimer. Higher aggregates, e.g. H-aggregates, are observable in water alone for both DTDCI and DTTCI, as is well-known. The H-aggregate formed from DTTCI in water provides evidence of a unique pathway for thermalization of photoexcitation energy; excited aggregate ejects excited dye monomer.  $\beta$ -CD complexes of all three dyes exhibit technologically useful levels of second-order hyperpolarizability, measured by Hyper-Rayleigh scattering, and we assign the non-linear optical response to dimer complex. Second-order scattering is observed, however, only when the saturation concentration of dye monomer in water is exceeded; at lower concentrations we infer that complexes do not form. Computational modelling, carried out for DTCI, suggests that the dimer forms endergonically with a structure that both locks in a significant degree of bond alternation, as well as allowing considerable freedom for torsional relaxation.

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**Keywords:** Symmetrical cyanine dyes; Computational modelling;  $\beta$ -CD complexes; Hyper-Rayleigh scattering

## 1. Introduction

Cyanine dyes are well-known chromophores with high transition probabilities. They are of significant utility in photography, cytofluorimetry, photodynamic therapy, DNA labelling, in laser technology, and in non-linear optics [1]. Their photophysics have been of ongoing interest in our laboratory for the past decade [1–7].

Cyanine dyes would be of greater interest for non-linear optical applications if significant hyperpolarizabilities could be demonstrated for them. A priori no second-order hyperpolarizability would be expected for symmetrical cyanine dyes, though second-order hyperpolarizability tensors,  $\langle\beta\rangle \leq 50 \times 10^{-30}$  esu, have been reported under certain conditions for  $N,N'$ -diethyl-2,2'-dithiacyanine iodide (DTI;  $n = 0$ ),  $N,N'$ -diethyl-2,2'-dithiacarbocyanine iodide (DTCI,  $n = 1$ ),  $N,N'$ -diethyl-2,2'-dithiadibenzocarbocyanine iodide (DTDCI,  $n = 2$ ), but not for the higher analogue,  $N,N'$ -diethyl-2,2'-

dithiatricarbocyanine iodide (DTTCI,  $n = 3$ ) [7]. We associated these signals with transient asymmetrical structures proposed to occur as a result of activation of coherently coupled bond stretching modes of the polymethine chains of the dyes (bond alternation coordinate) [8]. It occurred to us that these transient, charge-localized, asymmetrical structures might be stabilized on complexation of the cyanine chromophore in an asymmetric environment.

Cyclodextrin complexation of cyanine dyes appeared to offer such a possibility. Cyanine dye-cyclodextrin complexes were first reported in 1987 using both  $\beta$ - and  $\gamma$ -cyclodextrins (but not  $\alpha$ -cyclodextrin), with promotion of cyanine dye dimer formation [9]. That such complexation should provide a non-centrosymmetric chromophore was demonstrated using circular dichroism spectroscopy on a complex of (symmetrical)  $N,N'$ -diethyldioxadibenzocarbocyanine iodide and  $\gamma$ -cyclodextrin [10]. Subsequently, it was shown that cyclodextrin complexation enhanced the light stability of cyanine chromophores, hence enhancing the dyes' utility, e.g. in a Q-switching application or as fluorescent probes [11,12]. Reduction in dye sensitized singlet oxygen quantum yields also

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accompanies this enhanced stability [11], suggesting that the complexes may be less attractive than free dye for application in photodynamic therapy [13]. This work was extended to synthesis of  $\beta$ -cyclodextrin-cyanine chromophore conjugates [14], and two isomers of a cyanine dye- $\alpha$ -cyclodextrin rotaxane have recently been synthesized with the objective of enhanced fluorescence efficiency, as well as light stability [15]. Two relevant reviews of cyclodextrin complexes have appeared [16,17].

The purpose of the present work is two-fold. We undertake characterization of  $\beta$ -cyclodextrin inclusion complexes of DTCl, DTDCI and DTTCl in aqueous media, and we evaluate these complexes for second-order hyperpolarizability using the Hyper-Rayleigh scattering (HRS) technique [18,19].

## 2. Experimental details

The complexing agent,  $\beta$ -cyclodextrin ( $\beta$ -CD), was obtained from Aldrich Chemical Co. (USA) and used as received. Dyes, products of commerce, were also used as received from their respective suppliers: DTCl (H.W. Sands Co., Jupiter, FL, USA), DTDCI (Eastman Kodak Co., Rochester, NY, USA) and DTTCl (Aldrich Chemical Co., Milwaukee, WI, USA). Purity of the dyes in these samples had been established by thin layer chromatography and optical spectroscopy in previous studies in this series [5–7]. Solutions were made up in ion-exchange purified water.

Fluorescence spectra (wavelength uncorrected) were recorded on a Hitachi-Perkin-Elmer MPF44B fluorescence spectrophotometer, equipped with Hitachi 944 photomultiplier tubes to enable detection of near-infrared emission. Independently by actinometry [20], we estimated an optical power of ca.  $1 \text{ mJ cm}^{-2}$  for the exciting beam at its focal point in the probed solution. We infer that this power is too low to effect significant photochemical changes in the samples under investigation on the time scale of our measurements. In order to obtain and selectively excite particular species in solution, it was necessary to carry out fluorescence spectroscopy on solutions of optical density higher than normally used for this purpose. Relative fluorescence intensities thus obtained were accordingly unreliable and not suitable for, e.g. estimation of fluorescence quantum efficiencies. Absorption spectra were recorded on a Shimadzu UV-265 diode array spectrophotometer.

Technique for HRS measurement, tests for signal purity, and data analysis are reported in accounts of previous studies from our laboratory employing this method [7,21,22]. We selected a fundamental wavelength of 840 nm and monitored second harmonic at 420 nm, finding that dye absorption did not appear to overlap either of these wavelengths with DTCl, DTDCI or DTTCl. For estimation of  $\langle\beta\rangle$ , the experimental set-up was calibrated using *p*-nitroaniline, which is well accepted as a standard for hyperpolarizability measurements, and for which  $\langle\beta\rangle = 35 \times 10^{-30} \text{ esu}$  [23].

Computational studies [24] on monomer and dimer were carried out at the AM1 level of approximation with geometry optimization. The starting geometry for individual monomers was provided by Merck Molecular Force Field calculations. Electronic charge distribution in the final structures was inferred from Mulliken population analysis.

## 3. Results and discussion

### 3.1. Absorption spectra

The absorption spectra of DTCl at several different concentrations in water are shown in Fig. 1a. Principal absorption bands occur at 556 nm (shoulder at 522 nm), associated with the free, monomeric dye cation in solution, and at 514 nm, which has been proposed to correspond to a dimer [25,26]. From the maximum absorption observable at the longer peak wavelength we infer that free monomer solubility does not exceed ca.  $1.7 \times 10^{-5} \text{ M}$ . When absorption spectra are taken of the dye over the same concentration range in 0.011 M aqueous  $\beta$ -CD (Fig. 1b), maxima are observed at 554 nm (shoulder at 524 nm) and at 516 nm. The former more-or-less corresponds to the longer wavelength band observed in water alone. Given the precedent for incorporation of cyanine dyes in cyclodextrin hosts as dimers [9,10], we assign the 516 nm absorption to DTCl dimer, either free in solution or in  $\beta$ -CD complex, consistent with the assignment of Khairutdinov and Serpone [26].

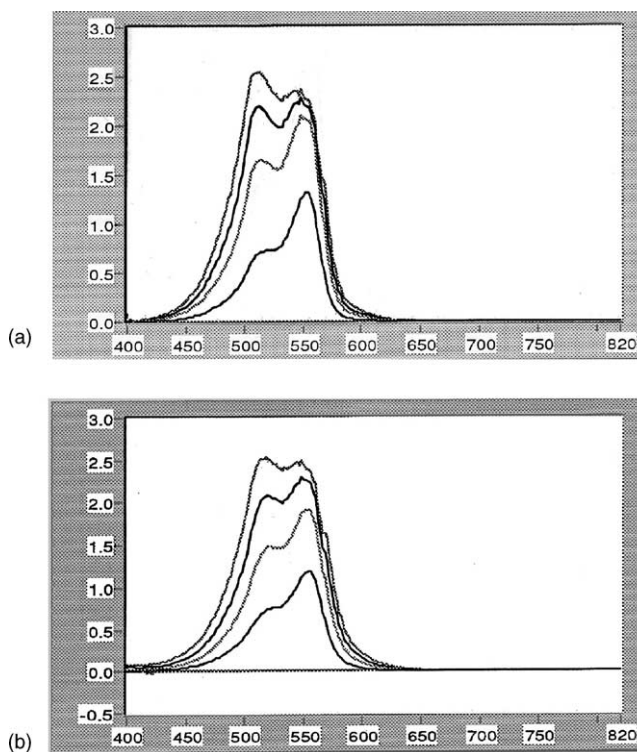


Fig. 1. Absorption spectra of DTCl (a) in water, (b) in 0.011 M aqueous  $\beta$ -CD. Concentrations of DTCl are  $1 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $3 \times 10^{-5}$  and  $4 \times 10^{-5} \text{ M}$  (bottom–top).

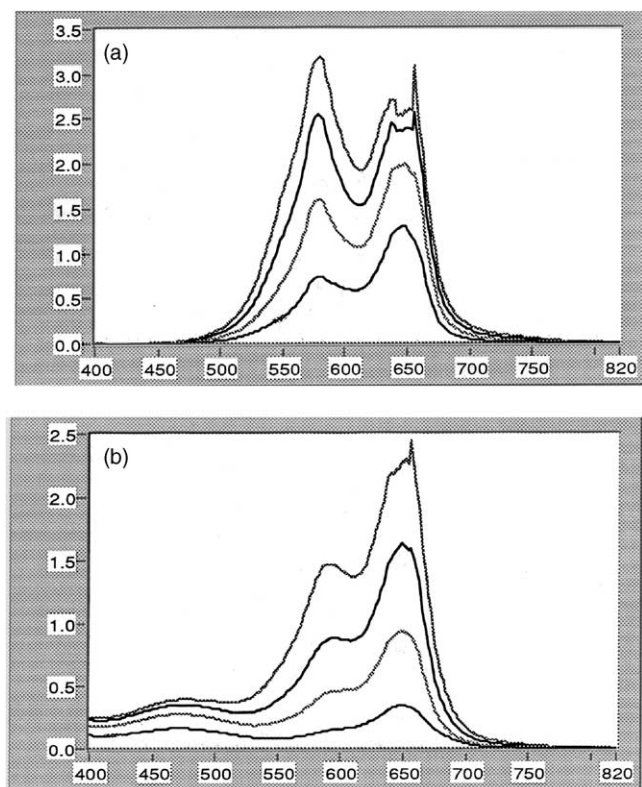


Fig. 2. As Fig. 1 for DTDCI.

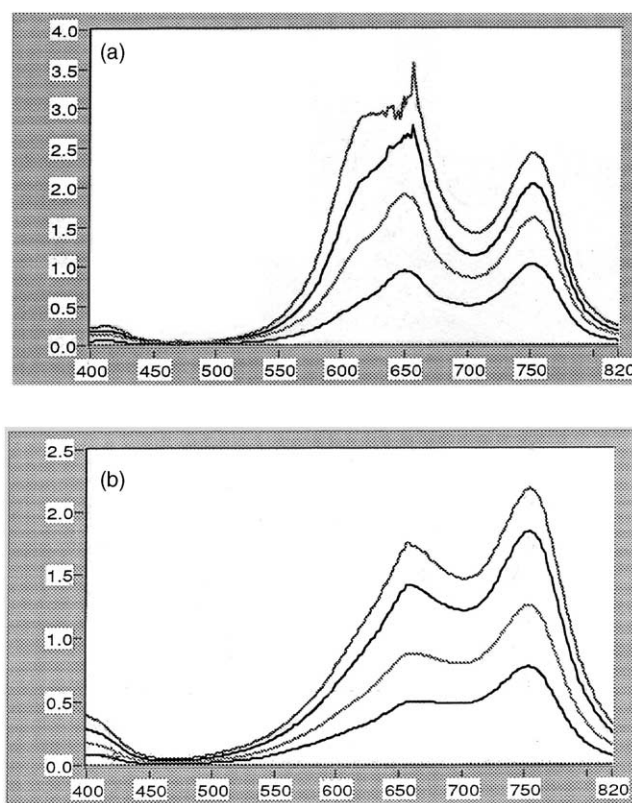


Fig. 3. As Fig. 1 for DTTCI.

Fig. 2a and b provide the analogous spectra for DTDCI in water and in aqueous  $\beta$ -CD. For this dye, the free monomer absorbs at 648 nm (water) or 650 nm ( $\beta$ -CD). The aqueous solution is saturated in free dye at a concentration of ca.  $2.5 \times 10^{-5}$  M, as inferred from the maximum observable absorption at 648 nm. Higher concentrations in water alone lead to increase in the intensity of a band at 578 nm, close to the wavelength assigned by Rebane et al. for a trimer [27]. Unlike the case of DTICI, with DTDCI this shorter wavelength band is present in aqueous solutions at all concentrations studied. When  $\beta$ -CD is present, the shorter wavelength band is shifted to 596 nm, corresponding to absorption of dimer according to Rebane et al. [27]. Because of the considerable overlap between the dimer band and that of the trimer, the presence of dimer in water alone cannot be excluded and is, in fact likely, given the behaviour of DTICI, above, and DTTICI, below.

In the case of DTTICI shown in Fig. 3a and b, the situation is more clear-cut. In both water and  $\beta$ -CD aqueous solution free dye absorbs at 754 nm. The maximum observed absorption at this wavelength suggests saturation at a dye concentration of ca.  $3 \times 10^{-5}$  M in water. With increasing concentration, bands are observed at 657 nm both with and without  $\beta$ -CD. In absence of the complexing agent, however, a third absorption centered on 600 nm can also be resolved. Consistent with our interpretation of the spectra of DTICI and DTDCI and the report of Soper et al. [28] we assign the 657 nm band as DTTICI dimer; we then identify the 600 nm band unambiguously with H-aggregate. Note that the blue shifts associated with DTTICI

dimer and aggregate formation are much larger than observed with DTICI and DTDCI.

From the absorption spectroscopy we can infer that all three dyes form  $\beta$ -CD complexes, either as dye cation monomer or dimer. Given the similarity in width and maximum of the absorption bands assigned to dye-CD complexes to those observed in free solution, we might expect that complexation would not involve geometrical isomerization of the chromophores. These dyes normally exist in solution in all-*trans* conformations, but relax by *trans*-*cis* isomerization [2,4,8,29]. This pathway could, however, be constrained on either aggregate formation or complexation [14,15]. As will be discussed below, computational chemical studies do not fully bear out these expectations.

### 3.2. Fluorescence spectroscopy

Fluorescence spectroscopy was carried out on aqueous solutions  $1 \times 10^{-5}$  and  $4 \times 10^{-5}$  M in dye, without and with 0.011 M  $\beta$ -CD. Excitation wavelengths were selected to allow selective excitation of the various species present in the solutions. The resulting spectra are presented in Figs. 4–6, and the experimental conditions and figure legends are provided in Table 1.

Fig. 4a and b shows the emission spectra obtained from DTICI in water alone and in the presence of  $\beta$ -CD, respectively. In both cases the results are qualitatively the same. Ex-

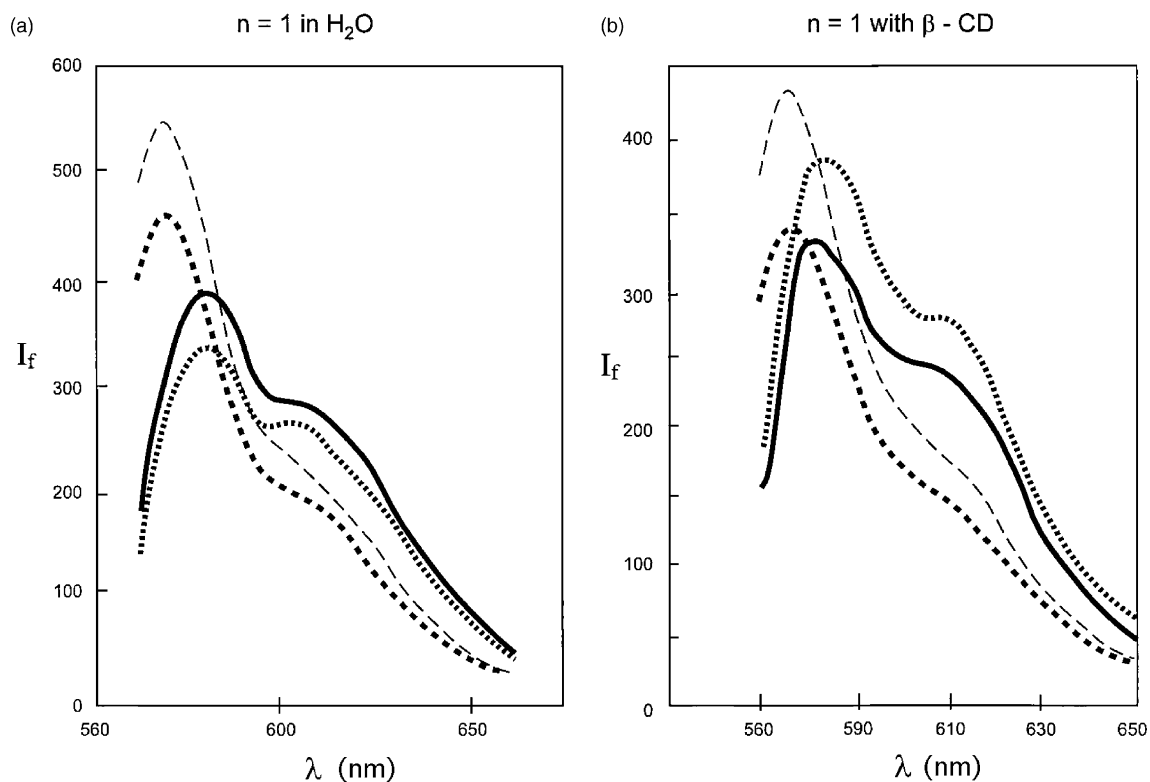


Fig. 4. Fluorescence spectra for DTICI (a) in water, (b) in 0.011 M aqueous  $\beta$ -CD. For conditions and key see Table 1.

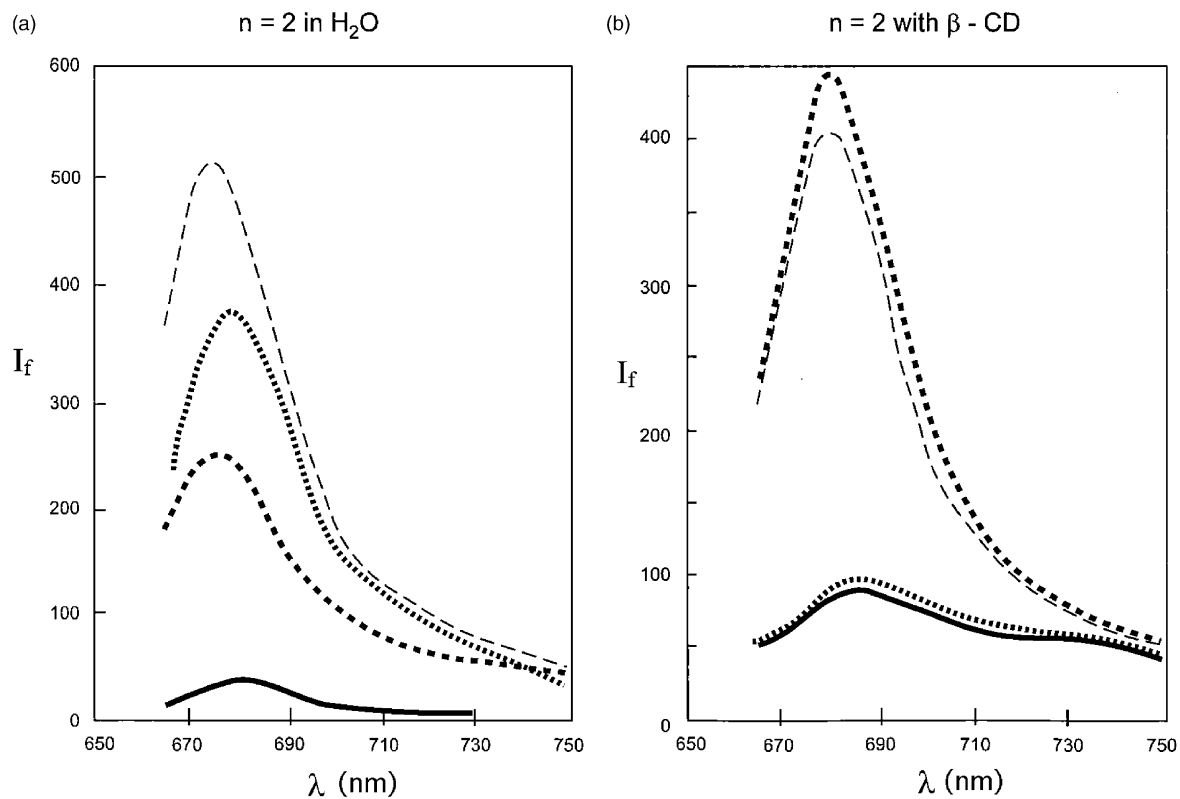


Fig. 5. Fluorescence spectra for DTDCI (a) in water, (b) in 0.011 M aqueous  $\beta$ -CD. For conditions and key see Table 1.



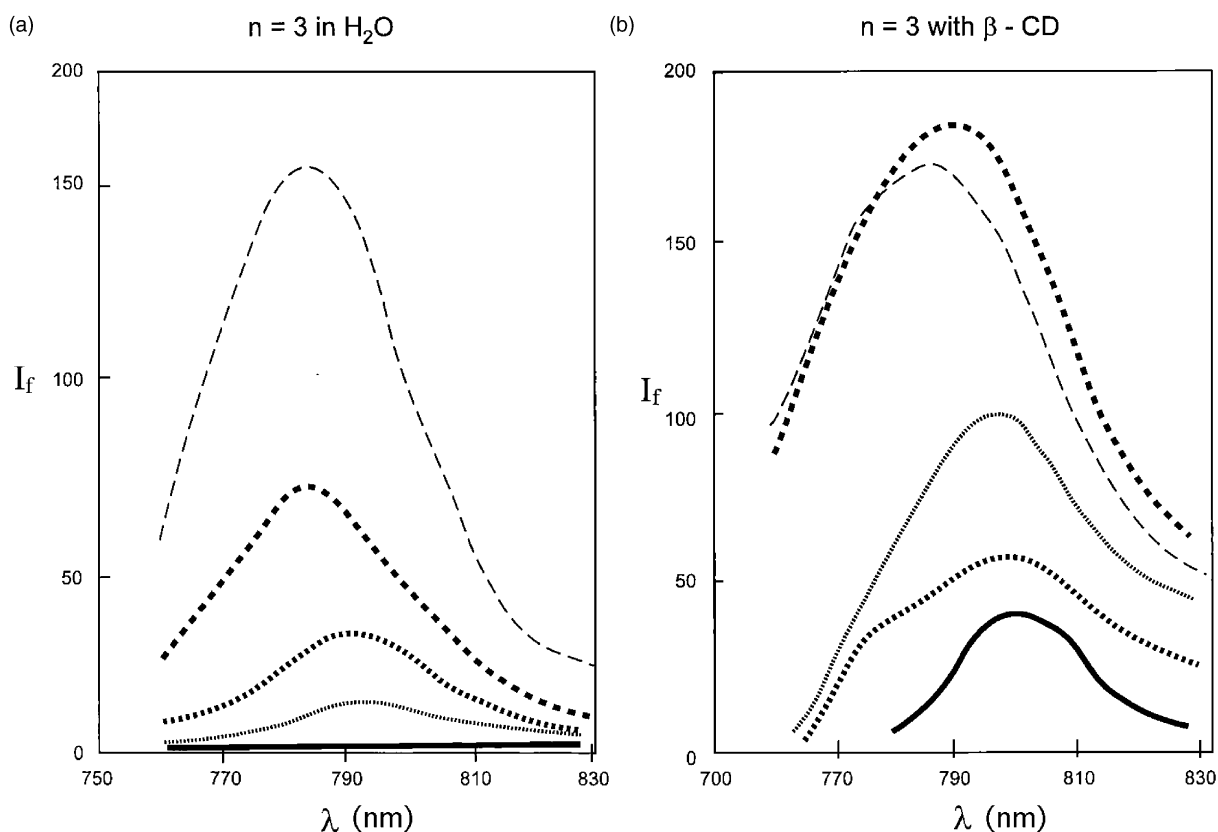


Fig. 6. Fluorescence spectra for DTTCI (a) in water, (b) in 0.011 M aqueous  $\beta$ -CD. For conditions and key see Table 1.

Table 1  
Conditions for fluorescence spectroscopy, including key for Figs. 4–6

In H <sub>2</sub> O		With $\beta$ -CD		
$\lambda_{\text{ex}}$ (nm)	[Dye] (M)	$\lambda_{\text{ex}}$ (nm)	[Dye] (M)	
$n = 1$		$n = 1$		
554	$1 \times 10^{-5}$	554	$1 \times 10^{-5}$	
510	$1 \times 10^{-5}$	520	$1 \times 10^{-5}$	
554	$4 \times 10^{-5}$	554	$4 \times 10^{-5}$	
510	$4 \times 10^{-5}$	520	$4 \times 10^{-5}$	
$n = 2$		$n = 2$		
656	$1 \times 10^{-5}$	656	$1 \times 10^{-5}$	
575	$1 \times 10^{-5}$	590	$1 \times 10^{-5}$	
656	$4 \times 10^{-5}$	656	$4 \times 10^{-5}$	
575	$4 \times 10^{-5}$	590	$4 \times 10^{-5}$	
$n = 3$		$n = 3$		
750	$1 \times 10^{-5}$	750	$1 \times 10^{-5}$	
650	$1 \times 10^{-5}$	650	$1 \times 10^{-5}$	
750	$4 \times 10^{-5}$	750	$4 \times 10^{-5}$	
650	$4 \times 10^{-5}$	650	$4 \times 10^{-5}$	
600	$4 \times 10^{-5}$	700	$4 \times 10^{-5}$	

citation into either the monomer or dimer absorption yields more-or-less the same spectral distribution of emission. The monomer emission is seen at 575 nm in water, essentially the same as observed in methanol [4]. Excitation of monomer emission when the dimer band is excited may be explained by overlap of monomer and dimer absorption bands. In the presence of  $\beta$ -CD the emission is slightly blue shifted to

570 nm. This result indicates that at concentrations studied, monomer may be present in the form of a  $\beta$ -CD complex, and that complexation constrains the relaxation process associated with the Stokes shift for this dye. This relaxation is presumably torsional; torsional relaxation in the polymethine chain has been understood for some time to be the principal pathway for thermalization of excitation energy in cyanine chromophores (see literature cited in Ref. [2]). A similar result has been obtained with rotaxane encapsulated cyanine dyes, and similarly interpreted [14].

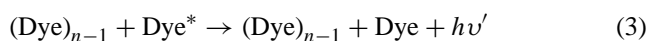
The dimer fluorescence is observed centered on 610 nm; no corresponding emission is seen for this dye in solvents, which do not promote aggregation, e.g. methanol [4]. From the basic theory of the electronic structure of cyanine dye aggregates [30,31] we would expect that the red-shift of the dimer fluorescence, compared to monomer fluorescence, should be equal, energetically, to the blue-shift in the absorption spectrum. For the present dye, both shifts correspond to  $0.15 \pm 0.01$  eV.

The situation in the case of DTDCI, shown in Fig. 5a and b for water and  $\beta$ -CD respectively, is quite different. Essentially only monomer emission is observed in any case, centered on 675 nm (water) or 680 nm ( $\beta$ -CD), corresponding to the fluorescence observed in methanol solution [4], though there is a suggestion of a longer wavelength component to the fluorescence observed at higher dye concentration in the presence of  $\beta$ -CD. In water alone, at higher dye concentra-

tion, irradiation into the well-resolved aggregate absorption yields little or no monomer emission, as well. We infer that the aggregate formed from this dye at higher concentration in aqueous solution is fluorescence inactive and possesses a pathway for radiationless deactivation which is not revealed by our present strategy.

The fluorescence observed from DTTCI is shown in Fig. 6a and b for water alone and  $\beta$ -CD, respectively. At lower dye concentrations the emission envelope looks essentially the same as that observed for free dye in methanol solution [4], and is correspondingly centered on 785 nm. In the presence of  $\beta$ -CD, irradiation into the dimer absorption band (650 nm) selectively excites a fluorescence at 800 nm. In this case the red-shift, compared to monomer emission, is much smaller than would be expected on the basis of dimer excitation energy and simple theory [25,30,31]. Thus there is a much smaller Stokes shift associated with the dimer than with the monomer, which would be the case if only the dimer, and not the monomer, were complexed by  $\beta$ -CD.

The emission from DTTCI in water alone represents a particularly interesting case. Only monomer emission is observed, regardless of whether the monomer or the H-aggregate absorption band is irradiated, as was the case with DTDCI. The mode is slightly red-shifted at the higher concentration studied. When the aqueous solution is irradiated at 650 nm, corresponding to dimer absorption, no emission is observed. Therefore we cannot account for monomer emission when the H-aggregate absorption band is irradiated in terms of overlapping absorptions. We accordingly propose a mechanism whereby excited aggregate dissociates, during excitation lifetime, to yield ground state aggregate and excited monomer.



This mechanism accounts for observation of monomer fluorescence on selective excitation of H-aggregate. It may not have been observed with dimers and/or aggregates of the lower homologues of DTTCI insofar as the monomer-aggregate absorption shift may be energetically insufficient to drive dissociation of the aggregate. Conceivably the lack of aggregate-based emission from DTDCI, above, can be accounted for by a similar mechanism in which, however, ground state, rather than excited dye monomer is ejected from the excited aggregate. Khairutdinov and Serpone [26] have suggested that thermal energy leading to aggregate dissociation, e.g. to smaller aggregate plus monomer, may represent a significant pathway for energy disposal from photoexcited dye aggregates.

In summary fluorescence spectroscopy has suggested that DTDCI is complexed by  $\beta$ -CD in both monomeric and dimeric forms. Only dimer complexes seem to form for DTTCI. The H-aggregate formed from DTTCI in water provides evidence of a pathway for thermalization of photoexcitation energy, namely excited aggregate ejects excited dye monomer. Within the series of dyes studied this pathway appears to be unique to DTTCI, insofar as this dye is the only one forming a well-defined H-aggregate under our conditions.

### 3.3. HRS estimation of hyperpolarizability

We monitored second harmonic scattering of 840 nm fundamental for all three dyes over a concentration range of  $4 \times 10^{-6}$  to  $1 \times 10^{-4}$  M, overlapping the saturation concentrations for each of the dyes. These data are shown in Figs. 7–9 for DTDCI, DTDCI and DTTCI, respectively. For DTTCI, as can be seen from inspection of Fig. 3, there is significant light absorption both at the second harmonic (420 nm) and, presumably, the fundamental (840 nm) wavelengths. It was therefore necessary to correct the raw data using [19]:

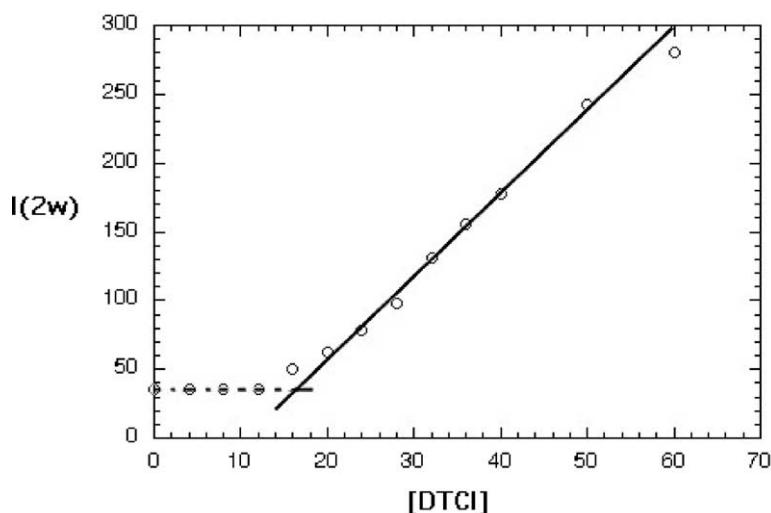


Fig. 7. HRS signals (counts) for DTDCI in 0.011 M aqueous  $\beta$ -CD; [DTDCI] in (mol dL<sup>-3</sup> × 10<sup>6</sup>).

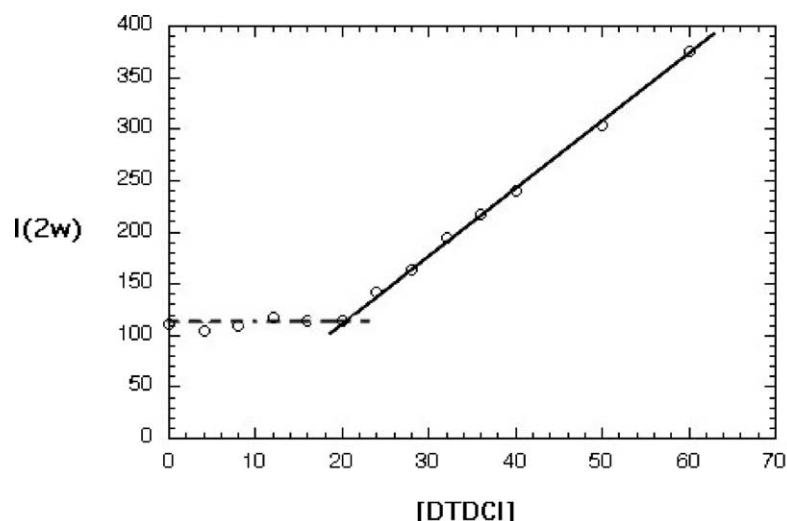


Fig. 8. As Fig. 7 for DTTCI; lock-in amplifier gain is  $3\times$  greater than for data of Fig. 7.

$$I(2\omega) = (I_0 + G\langle\beta\rangle^2[\text{DTTCI}])\exp(-\alpha[\text{DTTCI}]) \quad (5)$$

where  $I(2\omega)$  is the observed HRS signal in the presence of [DTTCI],  $I_0$  the signal in absence of dye,  $G$  a fitting parameter derivable from the calibration experiments with *p*-nitroaniline, and  $\alpha$  an empirical absorption coefficient. For  $[\text{DTTCI}] \leq 2 \times 10^{-5} \text{ M}$  we found that, within experimental error, the signal could be fit to Eq. (5) with the second term set to zero, thereby allowing estimation of  $\alpha = (8.0 \pm 0.2) \times 10^4 \text{ mol}^{-1} \text{ dL}^{-3}$ ; data shown in Fig. 9 are accordingly corrected and reported as  $I(2\omega) \exp(\alpha[\text{DTTCI}])$ .

In water alone we saw no significant second harmonic scattering from any of the dyes, which is different from the results previously obtained in methanol [7]. The finite values of  $I_0$  in  $\beta$ -CD solution are attributed to HRS from the  $\beta$ -CD itself, and are not observed in its absence. From the magnitudes of the signals we infer  $\langle\beta\rangle$  for  $\beta$ -CD about one order of

magnitude less than that for the control, *p*-nitroaniline. (This level of hyperpolarizability is below that which we can estimate quantitatively with confidence under our experimental conditions).

With all three dyes in the presence of  $\beta$ -CD no scattering attributable to dye, i.e. greater than  $I_0$ , was observed until the dye concentration exceeded a threshold, designated  $[\text{Dye}]_0$ . Values of  $[\text{Dye}]_0$  are estimated from the intersection points of the two regression lines shown in each Figure, and are reported in Table 2. The values are consistent with the saturation concentrations estimated from absorption spectroscopy, both in order of magnitude and in the trend toward increasing solubility of dye with increasing polymethine chain length,  $n$ .

Above these levels, scattering signals,  $I(2\omega)$ , increased monotonically with amount of added dye, as expected. From the relative quadratic coefficient,  $dI(2\omega)/d[\text{Dye}] = G\langle\beta\rangle^2$ , we estimated  $\langle\beta\rangle$  for the complexed dye, by comparison

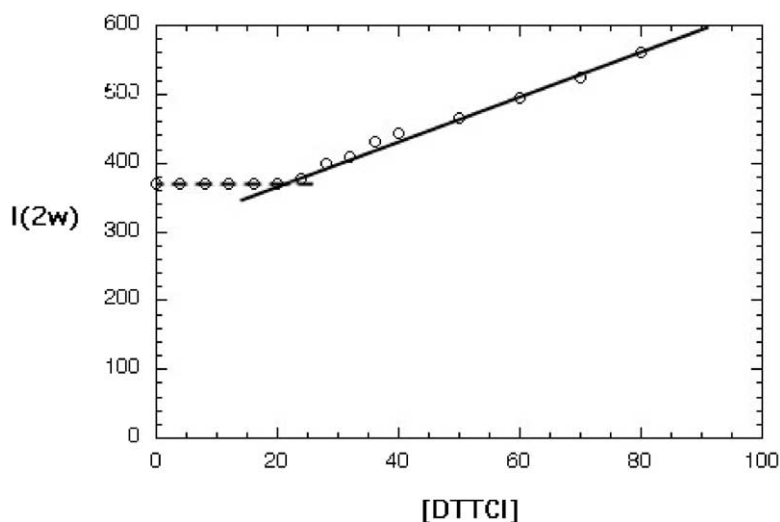


Fig. 9. As Fig. 7 for DTTCI:  $I(2\omega)$  is corrected as described in text using Eq. (5); lock-in amplifier gain is  $10\times$  greater than for data of Fig. 7.



Table 2

Threshold concentrations for observation of HRS,  $[\text{Dye}]_0$  ( $\text{mol dL}^{-3}$ ), relative quadratic coefficients ( $\text{mol}^{-1} \text{dL}^{-3}$ ), hyperpolarizability tensors,  $\langle\beta\rangle$  ( $\text{esu} \times 10^{30}$ ), and correlation coefficients,  $r$ , for HRS data analysis

Dye	$[\text{Dye}]_0$	$dI(2\omega)/d[\text{Dye}]^a$	$\langle\beta\rangle^b$	$r$	$\langle\beta\rangle^c$
<i>p</i> -nitroaniline	–	$8.5 \times 10^5$	$35^d$	0.978	–
DTCI	$1.6 \times 10^{-5}$	$18 \times 10^6$	$(160 \pm 10)$	0.996	$(40 \pm 5)$
DTDCI	$2.0 \times 10^{-5}$	$6.5 \times 10^6$	$(100 \pm 3)$	0.998	$(54 \pm 8)$
DTTCI <sup>e</sup>	$2.4 \times 10^{-5}$	$1.3 \times 10^6$	$(44 \pm 4)$	0.995	$<5$

<sup>a</sup> Quadratic coefficients normalized to amplifier gain used in calibration experiment with *p*-nitroaniline.

<sup>b</sup> As  $\beta$ -CD complexes; this work.

<sup>c</sup> In methanol from Ref. [7].

<sup>d</sup> Ref. [23].

<sup>e</sup> Data required correction for self-absorption; see text.

to the quadratic coefficient measured for the standard, *p*-nitroaniline [23]. These data are also reported in Table 2.

Dyes exist in our system as free monomer, dimer and higher aggregates, CD-complexed monomer, **dye-CD**, and CD-complexed dimer, **dye<sub>2</sub>-CD**. From the absence of HRS signals for the dye species in water alone we infer that only complexed dye is contributing to the observed HRS. At the same time, since HRS signals are observed only when  $[\text{Dye}] > [\text{Dye}]_0$  we assume that in this concentration regime,  $d[\text{Dye}] = d[\text{dye-CD}] + 2 d[\text{dye}_2\text{-CD}]$ . From Eq. (5), the relative quadratic coefficient, neglecting self-absorption of second harmonic by dye,  $G\langle\beta\rangle^2 = dI(2\omega)/d[\text{Dye}] = dI(2\omega)/\{d[\text{dye-CD}] + 2 d[\text{dye}_2\text{-CD}]\}$ . With the assumption, consistent with the absorption spectra and the linear behaviour exhibited by Figs. 7–9, that  $[\text{dye-CD}] < [\text{dye}_2\text{-CD}]$ , the quadratic coefficient can be interpreted in terms of the hyperpolarizability of complexed dimer alone, i.e.  $G\langle\beta\rangle^2 = dI(2\omega)/d[\text{Dye}] = dI(2\omega)/2 d[\text{dye}_2\text{-CD}]$ . It must be emphasized that the resulting values of  $\langle\beta\rangle$  are lower-limit estimates, insofar as both assumptions represent approximations, at best.

Accordingly, estimates of the hyperpolarizability tensor are all greater than the estimates for the same dyes in methanol solution [7], included in Table 2 for comparison, and reflect, we believe, the influence of the chiral host. Interestingly and counter-intuitively, estimates of  $\langle\beta\rangle$  for both free dye and dimer complexes decrease monotonically with increasing polymethine chain length.

These hyperpolarizabilities represent technologically useful levels of non-linear optical response, but remain more than an order of magnitude below the second-order hyperpolarizability tensors achieved with the best molecules engineered to optimize this response [32]. Possible applications include biphotonic sensitization of photoeffects [20], e.g. in biphotonic fluorescence microscopy [33].

We summarize these results as follows. To the extent that dye is soluble in water it does not form an inclusion complex with  $\beta$ -CD. Above the saturation concentration, complexes form, consistent with the non-polar character of the cyclodextrin cavity [16]. In the thoroughly studied series of cyclodextrin–viologen complexes it has been found that monocationic guests are only weakly bound to  $\beta$ -CD [17,34]. This inference agrees with that drawn above on the basis

of fluorescence spectroscopy. The complexed chromophore is non-centrosymmetric by virtue of the environmental influence of the chiral host, which gives rise to measurable second-order hyperpolarizability. This interpretation is consistent with observation by circular dichroism spectroscopy of a non-centrosymmetric cyanine dimer trapped in the  $\gamma$ -cyclodextrin cavity [10]. We believe our complexes correspond to similar species.

### 3.4. Computational modelling

The structural properties of cyanine dye aggregates have been studied by-and-large on well-defined surfaces, e.g. Ag(111) [35] and AgBr [36], and in Langmuir–Blodgett monolayers [37]. Under all these conditions the substrate is likely to exert a strong influence on the aggregate structure. Furthermore, most studies have focussed on J-aggregates, owing to their technological importance in photography [38]. A proposal for the structure of the  $\gamma$ -cyclodextrin complex of the dimer of *N,N'*-diethyldioxadibocyanine cation has been offered by Buss [10] on the basis of circular dichroism data.

Accordingly, we sought to clarify our experimental results by semi-empirical quantum chemical calculations at the AM1 level of approximation. Counter-ions were omitted from our simulation. The minimum energy structure for the dimer of DTTCI in the gas phase, i.e. in the absence of solvation effects, is shown in Fig. 10. The slip angle between dye molecules, measured at the *meso*-carbon atoms, is  $64^\circ$ , consistent with an H-aggregate precursor and the blue shift of the dimer absorption band [39]. The AM1 enthalpy of formation of dimer from two dye cation monomers under these conditions is  $79 \text{ kcal mol}^{-1}$ , which implies that dimer formation may be driven by solvation effects, e.g. so-called hydrophobic bonding, and complex formation. In fact we do not see dimer absorption at dye concentrations below the limit to monomer solubility.

It can be seen from Fig. 10 that only one heterocyclic base of each dye molecule is eclipsed with that of its conjugate. It might be expected that this end of the dimer fits into the cyclodextrin cavity, while the other end would protrude and thus be relatively unconstrained. This lack of constraint of the uneclipsed heterocycles provides a number of degrees of

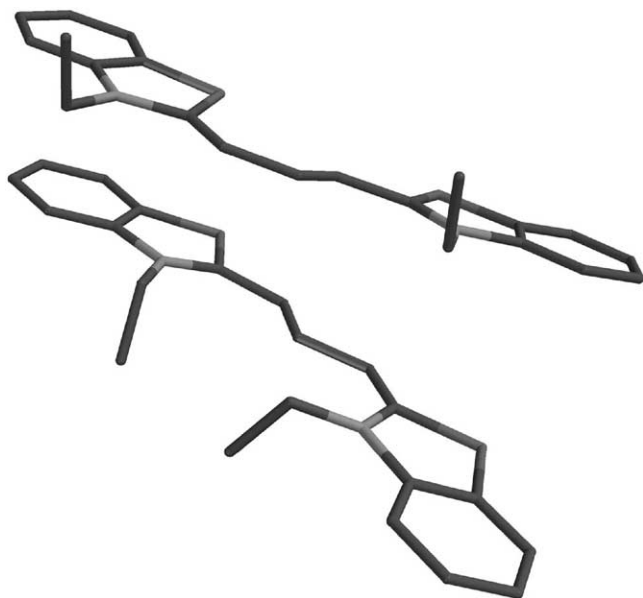


Fig. 10. Structure of DTCl dimer based on AM1 calculation with geometry optimization.

freedom for energy dissipation by torsional relaxation, contrary to the *a priori* expectation, above, for dye complexes, but consistent with the relatively low fluorescence intensities observed in our experimental study, above. Note also that on geometry optimization one of the two dye molecules adopts a *mono-cis* conformation.

Mulliken population analysis allows us to estimate that the total electrostatic charge on the eclipsed heterocycle of the *mono-cis* dye molecule is +0.43, while the charge on the corresponding heterocyclic moiety of the all-*trans* dye molecule is −0.03. (For purposes of comparison, the charge on the heterocycles in the fully symmetrical, all-*trans* monomeric dye structure is calculated to be +0.18). This disparity in electrostatic charge implies that dimer formation locks in considerable, complementary bond alternation in the two cyanine chromophores. In free dye, such bond alternation is thought to be a transient phenomenon [7,8] on the pathway leading to thermal or photochemical *trans-cis* isomerization. In the dimer it serves to minimize electrostatic repulsion between the two cations. Note that in DTCl, for example, the calculated enthalpy change on *trans-cis* isomerization is only ca. 4 kcal mol<sup>−1</sup> [7].

#### 4. Conclusions

We have studied the interaction of a homologous series of symmetrical thiacyanine dyes (DTCl, DTDCI, DTTCl) with  $\beta$ -cyclodextrin. From absorption spectra we infer that all three dyes form  $\beta$ -CD complexes, either as dye cation monomer or dimer. Higher aggregates, e.g. H-aggregates, are observable in water alone for both DTDCI and DTTCl, as is well-known. The H-aggregate formed from DTTCl in water

provides evidence of a unique pathway for thermalization of photoexcitation energy; excited aggregate ejects excited dye monomer.  $\beta$ -CD complexes of all three dyes exhibit technologically useful levels of second-order hyperpolarizability, measured by Hyper-Rayleigh scattering, and we assign the non-linear optical response to dimer complex. Second-order scattering is observed however, only when the saturation concentration of dye monomer in water is exceeded; at lower concentrations we infer that complexes do not form. Computational modelling, carried out for DTCl, suggests that the dimer forms endergonically with a structure that both locks in a significant degree of bond alternation, as well as allowing considerable freedom for torsional relaxation.

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#### References

- [1] M.R.V. Sahyun, Rec. Adv. Photochem. Photobiol. 1 (2000) 13 See references cited by.
- [2] N. Serpone, M.R.V. Sahyun, J. Phys. Chem. 98 (1994) 734.
- [3] M.R.V. Sahyun, J.T. Blair, J. Photochem. Photobiol. A: Chem. 104 (1997) 179.
- [4] M.R.V. Sahyun, N. Serpone, J. Phys. Chem. A 101 (1997) 9877.
- [5] A.C. Bruce, M. Chadha, A.F. Marks, M.R.V. Sahyun, S.E. Hill, J. Photochem. Photobiol. A: Chem. 119 (1998) 191.
- [6] M.R.V. Sahyun, J. Imaging Sci. Technol. 44 (2000) 229.
- [7] A.F. Marks, A.K. Noah, M.R.V. Sahyun, J. Photochem. Photobiol. A: Chem. 139 (2001) 143.
- [8] A. Sanchez-Galvez, P. Hunt, M.A. Robb, M. Olivucci, T. Vren, H.B. Schlegel, J. Am. Chem. Soc. 122 (2000) 2911.
- [9] K. Kasatani, M. Ohashi, M. Kawasaski, H. Sato, Chem. Lett. (1987) 1633.
- [10] V. Buss, Angew. Chem. Intl. Ed. Engl. 30 (1991) 869.
- [11] Y. Matsuzawa, S.-I. Tamura, N. Matsuzawa, M. Ata, J. Chem. Soc. Faraday Trans. 90 (1994) 3517.
- [12] T.V.S. Rao, J.H. Huff, C. Bieniarz, Tetrahedron 54 (1998) 10627.
- [13] M. Krieg, R.W. Redmond, Photochem. Photobiol. 57 (1993) 472; M. Krieg, J.M. Bilitz, M.B. Sirchai, R.W. Redmond, Biochem. Biophys. Acta 1199 (1994) 149.
- [14] R. Guether, M.V. Reddington, Tetrahedron Lett. 38 (1997) 6167.
- [15] J.E.H. Buston, J.R. Young, H.L. Anderson, Chem. Commun. (2000) 905.
- [16] K.A. Connors, Chem. Rev. 97 (1997) 1325.
- [17] S.A. Nepogodiev, J.F. Stoddart, Chem. Rev. 98 (1998) 1959.
- [18] K. Clays, A. Persoons, Phys. Rev. Lett. 66 (1991) 2980.
- [19] T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt, A. Persoons, J. Am. Chem. Soc. 116 (1994) 9320.

- [20] M.P. Goertz, M.R.V. Sahyun, J. Photochem. Photobiol. A: Chem. 159 (2003) 199.
- [21] A. Rassbach, M.R.V. Sahyun, J. Imaging Sci. Technol. 45 (2001) 254.
- [22] M.R.V. Sahyun, Spectrochim. Acta A 58 (2002) 3149.
- [23] J.L. Oudar, D.S. Chemla, J. Chem. Phys. 66 (1977) 2664.
- [24] W.H. Hehre, SPARTAN, Version 4.0, Wavefunction Inc., Monterey Park, CA, 1997.
- [25] G.R. Bird, K.S. Norland, A.S. Rosenoff, H.B. Michaud, Photogr. Sci. Eng. 12 (1968) 196.
- [26] R.F. Khairutdinov, N. Serpone, J. Phys. Chem. B 101 (1997) 2602.
- [27] M. Drobizhev, C. Sigel, A. Rebane, J. Luminesc. 86 (2000) 107.
- [28] S.A. Soper, Y.Y. Davidson, B.M. Gunn, Proc. SPIE 2388 (1995) 226.
- [29] F. Mommichioli, I. Baraldi, G. Berthier, Chem. Phys. 123 (1988) 103.
- [30] M. Kasha, H.R. Rawls, M.A. El-Bayounni, Pure Appl. Chem. 11 (1965) 371.
- [31] V. Czikkely, H.D. Forsterling, H. Kuhn, Chem. Phys. Lett. 6 (1970) 207.
- [32] F.W. Vance, J.T. Hupp, J. Am. Chem. Soc. 121 (1999) 4047.
- [33] M.R.V. Sahyun, M. Goertz, Proc. SPIE 4963 (2003) 128.
- [34] A. Mirzoian, A.E. Kaifer, Chem. Eur. J. 3 (1997) 1052.
- [35] M. Kawasaki, H. Ishii, J. Imaging Sci. Technol. 39 (1995) 210.
- [36] H. Haefke, U.D. Schwartz, H.J. Güntherodt, F. Fröb, G. Gerth, R. Steiger, J. Imaging Sci. Technol. 37 (1993) 545.
- [37] L. Wolthaus, A. Schaper, D. Möbius, Chem. Phys. Lett. 225 (1994) 322.
- [38] W. West, P.B. Gilman, The Theory of the Photographic Process, 4th edn., Macmillan, New York, 1977, Chapter 10.
- [39] K. Norland, A. Ames, T. Taylor, Photogr. Sci. Eng. 14 (1970) 295.