Dyes and Pigments 109 (2014) 21–33

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Dimers, tetramers, and octamers of mono- and trimethyne thiacarbocyanine dyes. Structure, formation energy, and absorption band shifts

Vitaly G. Avakyan [a,*], Boris I. Shapiro [b], Mikhail V. Alfimov [a]

[a] Photochemistry Center of the Russian Academy of Sciences, 7A Novatorov Str., Moscow 117421, Russia
[b] M.V. Lomonosov State University of Fine Chemical Technology, Pr. Vernadskogo 86, Moscow 119571, Russia

ARTICLE INFO

Article history:
Received 28 February 2014
Received in revised form
14 April 2014
Accepted 16 April 2014
Available online 30 April 2014

Keywords:
Aggregates of cyanine dyes
Structure of dimers, tetramers, and octamers
DFT-D calculations
Frontier orbitals of dimers and tetramers
Transition energies at CIS, TD DFT, and ZINDO/S approach
Driving forces of aggregation

ABSTRACT

Quantum-chemical calculations for monomers, dimers, and tetramers of 3-ethyl-2-[(1E,3E)-3-(3-ethyl-1,3-thiazol-2(3H)-ylidene)prop-1-en-1-yl]-1,3-thiazol-3-ium chloride and 3-ethyl-2-[(E)-(3-ethyl-1,3-benzothiazol-2(3H)-ylidene)methyl]-1,3-benzothiazol-3-ium chloride were performed. Both dyes were found capable of forming two kinds of π-stacking-dimers with various degree of overlap. Three kinds of tetramers: four-deck ladder, three-deck brickwork, and two-deck linear, can be formed without destruction of the dimers of the cyanine dyes. The energy of tetramer formation was found to decrease in the order brickwork > linear > ladder configurations. For dimers of the first dye and its tetramer (brickwork, ladder and linear) configurations, the energies of the first $S_0 \rightarrow S_1$ singlet transitions, oscillator strengths, and structures of frontier MO have been calculated. The spectral shifts in dimers and tetramers were found to depend only on mutual orientation of components: brickwork and linear tetramers show red shift ($+\Delta\lambda$) while ladder tetramers, blue shift ($-\Delta\lambda$) of absorption bands (with respect to monomer).

1. Introduction

A remarkable property of cyanine dyes (CDs) is their capability of self-assembling into nanosized H- and J-aggregates in solution [1,2]. Compared to monomers, their absorption bands are shifted either to shorter (H-aggregates, $-\Delta\lambda$) or longer (J-aggregates, $+\Delta\lambda$) wavelengths [3,4]. Due to strong absorption in the visible and high quantum yield of charge carries, J-aggregated CDs are regarded as promising materials for use in photosensors, chemical indicators, photovoltaic devices, OLED-monitors, optical information storage/retrieval systems, and in nano optoelectronics [3,5]. Structural data for thirty monomer CDs are included in the Cambridge database (CSD) [6] and the absorption/emission properties of two free and solvated 3,3′-diethyl-benzothiazolotrimethynecyanines have been predicted by standard methods of quantum chemistry [7].

Dimers and tetramers (primary H- and J-aggregates) belong to the next, supramolecular level of self-assembling. To date, reliable data have been reported for both dimers of crystalline 1,1′-diethyl-2,2′-thiazoline carbocyanine iodide (Refcode ETAZCY) [8a] and 5,5′,6,6′-tetrachloro-1,1′-bis(3-carboxypropyl)-3,3′-dioctylbenzimida-carbocyanine in dimethylsulfoxide solvate (Refcode QAJPIA) [8b].

The band shapes in the absorption spectra of dimers of 1,1′-diethyl-2,2′-cyanine chloride, (also known as pseudoisocyanine, PIC chloride) dye were simulated using a combination of an empirical molecular force field for the ground state with quantum-chemical calculations (CNDO/S) of the electron excitation energy as a function of mutual shift of chromophores relative to each other. If the monomers in dimer are positioned with plane-parallel (*face-to-face*) configuration a large *hypsochromic* shift of the 0–0-transition band is observed. If the monomers are strongly shifted relative to each other, the small *bathochromic* shift of the 0–0 transition band is predicted [9]. Calculation of exciton interaction energies was performed for 3,3′-dimethyl-benzothiasolotrimethynecyanine dimer taken in initial *face-to-face* configuration, mutual orientation of monomer dipoles being not indicated. Then one molecule was translated relative to the other in directions perpendicular and parallel to the chromophore planes. Calculations are carried out at semiempirical, *ab initio* Hartree–Fock, and *ab initio* configuration interaction-singles levels using the sum over Coulombic interactions between atomic transition charges. Calculations

* Corresponding author. Tel.: +7 (495) 9350205; fax: +7 (495) 9361255.
E-mail addresses: avak@photonics.ru, boyev@mail.ru (V.G. Avakyan).

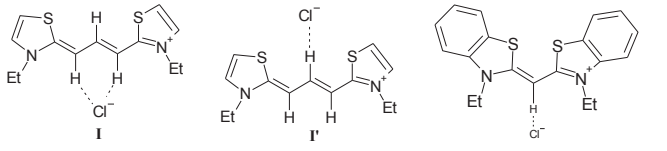
http://dx.doi.org/10.1016/j.dyepig.2014.04.026
0143-7208/

demonstrate the validity of the above approach and lowering exciton interaction energies against an increase in perpendicular and parallel translations of chromophores [10]. Aggregation of 3,3′-diethylbenzothiazolomonomethynecyanine dye was modeled using the reference interaction site model (RISM) and supramolecular approach in water. The hydrated H-dimers are obtained to be more stable than the hydrated J-dimers. However, the complexes consisting from more than four monomers changed their arrangement while self-assembling in water and formed ladder-like structures characteristic of H-aggrerates [11]. The structure and absorption spectrum for dimers and tetramers of 3,3′-disulfopropyl-5,5′-dichloro-9-ethylbenzothiazolotrimethynecyanine (THIATS) have been obtained by quantum-chemical calculations [12].

Nanosized particles formed upon aggregation of the above supramolecular structures represent the next, third level of this hierarchy. Depending on the type of starting supramolecular ensembles, these can be 1D fibrils, 2D strips, 3D rods, nanotubes, 2D Langmuir–Blodgett films, aggregates on the surface of silver halides, etc [4]. Resonance light scattering (RLS) spectrum of J-aggregated meso-tetrakis-(4-sulfonatophenyl) porphyrin in solution was reported. The highest spectroscopic aggregation number (12.9) was determined for the J-aggregate with a hydrodynamic radius of 56 ± 10 nm [13]. From the differential absorption spectra measured by the femtosecond pump and probe experiment, exciton energies of the lowest and second lowest states of merocyanine J-aggregates in LB films have been derived. Exciton delocalization size of 2D J-aggregates have been determined as 26 × 40 molecules [14]. The incoherent size of oxacyanine and thiacyanine dyes in LB films are about 2000 [15]. The mean length of a pseudoisocyanine (PIC) aggregate in $12.5 \cdot 10^{-3}$ M aqueous solution is above 350 nm, which corresponds to about 3000 molecules in an aggregate and a branch diameter of around 2.3 nm [4].

The first step of aggregation is known [2b,16] to be reversible dimerization of dye molecules into larger conglomerates existing in dynamic equilibrium with dimers. One of effective methods for synthesis of J-aggregates is the so-called modular assembling from CD dimers in aqueous solutions [5]. Detailed spectroscopic studies [17] on equilibrium between dimers and J-aggregates have demonstrated that the primary J-aggregates of four dye molecules are formed by two dimers [16,5a]. As derived from absorption spectroscopy data, the so-called optical size [4] of such an aggregate is around four units. However, sometimes the aggregation process is terminated at dimerization step [18].

Since the dimers and tetramers of CDs have been studied inadequately, in this paper we report some results of our DFT and DFT-D quantum-chemical calculations for the first two stages of aggregation of trimethynecyanine 3-ethyl-2-[(1E,3E)-3-(3-ethyl-1,3-thiazol-2(3H)-ylidene)prop-1-en-1-yl]-1,3-thiazol-3-ium chloride (I) and monomethynecyanine 3-ethyl-2-[(E)-(3-ethyl-1,3-benzothiazol-2(3H)-ylidene)methyl]-1,3-benzothiazol-3-ium chloride (**II**) (Fig. 1) resulting in dimer and tetramer formation. In addition, using *ab initio* CIS/6-31**, TD DFT/PBE, and ZINDO/S methods, we calculated the energies of optical $S_0 \rightarrow S_1$ transitions,



(a) 3-ethyl-2-[(1E,3E)-3-(3-ethyl-1,3-thiazol-2(3H)-ylidene)prop-1-en-1-yl]-1,3-thiazol-3-ium chloride (**I**)

(b) 3-ethyl-2-[(E)-(3-ethyl-1,3-benzothiazol-2(3H)-ylidene) methyl]-1,3-benzothiazol-3-ium chloride (**II**)

Fig. 1. The dye structures used in calculations.

Table 1
Formation energies (kcal/mol) for dye **I** and its aggregates as calculated by DFT-D method.

	ΔH_0	ΔH_0 (2 dimers)	ΔE_{vdW}	ΔE_{vdW} (2 dimers)
I′	0	–	–	–
I	−14.2	–	–	–
$2\mathbf{I}_{st}$	−32.6	–	−25.5	–
$2\mathbf{I}_{bw}$	−28.1		−13.8	–
$4\mathbf{I}_{bw}$ C_i[a]	−99.9	−43.6	−48.0	−20.5
$4\mathbf{I}_{bw}$ C_2	−79.8	−24.1	−55.4	−27.9
$4\mathbf{I}_{ladder}$ C_i	−86.5	−21.2	−78.2	−27.1
$4\mathbf{I}_{bw\text{-}linear}$ C_i[a]	−89.4	−33.1	−45.7	−18.2
$4\mathbf{I}_{bw\text{-}linear}$ C_2	−84.5	−28.2	−62.6	−35.1

[a] Symmetry group.

the values and signs of absorption shifts ($\pm\Delta\lambda$) for dimers and tetramers of dyes **I** and **II** as a function of the shift angle α between chromophore planes, oscillator strengths, and structures of frontier molecular orbitals. The questions to be answered are as follows: (i) whether free dye monomers in the absence of solvent are capable to form primary dye aggregates such as dimer and tetramer, (ii) what geometry of dimer and tetramer is more thermodynamically stable, (iii) whether standard quantum-chemical methods are capable to predict the sign reversal for $\Delta\lambda$ observed in spectra of the series monomer–dimer–H- or J-tetramer, (iv) if capable, what orbital structure impels the dyes to display these spectral and structural properties.

2. Computational details

The dyes **I** and **II** selected as objects are members of thiacarbocyanine dye family forming a subclass of numerous polymethine dyes capable to form J- and H-aggregates (Fig. 1) [4]. The former is the simplest specimen of trimethyne dyes, whereas the latter is a monomethyne dye with more extended benzothiacarbocyanine chromophore. Since, dye absorption properties depend mainly on a chromophore structure, we minimized number of substituents surrounding chromophores in order to diminish a size of aggregates to be calculated.

Geometry optimization of monomers, dimers, and tetramers of dyes **I** and **II** with account of zero point energy (ZPE) was carried out by using the DFT method with the PBE functional [19] with three-exponent basis 3ζ [20] (DFT method, Priroda program suite [21]). Contribution from the van der Waals (vdW) interaction to the aggregation energy as well as optimization of monomers, dimers, and tetramers of dyes **I** and **II** was performed using DFT-D/PBE [22a] method with correction on dispersion (DFT-D method) [22b] on the Ahlrichs basis [22c] with software package ORCA, version 2.6.71b. Basis nomenclature: H atoms [4s1p]/2s1p{31/1}, second-period atoms [7s4p1d]/3s2p1d{511/31/1}, S atoms [10s7p1d]/4s3p1d {5311/511/1} [22c]. The energy of aggregation was determined as follows. The energy of dimerization was found as shown in equation (1) while the energy of tetramerization, as follows from equations (2) and (3).

$$\Delta E_{dimer} \equiv \Delta H_0 = E_0(\text{dimer})_n - 2E_0(\text{monomer}),\ n = \text{st, bw} \qquad (1)$$

$$\Delta E_{tetramer} \equiv \Delta H_0 = E_0(\text{tetramer})_{brickwork} - 2{*}E_0(\text{dimer})_{bw} \qquad (2)$$

$$E_{tetramer} \equiv \Delta H_0 = E_0(\text{tetramer})_{ladder} - 2E_0(\text{dimer})_{st},$$
$$E_0 = E_{total(DFT-D)} + \text{ZPE}_{DFT} \qquad (3)$$

The results are presented in Tables 1 and 2.

It is noteworthy that the aggregation formation energies, ΔH, calculated here should be considered as energetic trends in the