

DFT Calculation Results of Merocyanine-Dye Cationic and Anionic Radicals

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An alkylated merocyanine dye, $C_{18}DS$, forms J-aggregates in Langmuir and Langmuir-Blodgett films. Using the electron spin resonance (ESR) technique, Kuroda et al. [Thin Solid Films **99** (1983) 21] found that two intrinsic spin species, i.e., Species A and B, are generated in the J-aggregates of the dye. Their intensive ESR study provided insights into the nature of the spin species, especially of Species A. However, it has been difficult to assign these spin species to the radicals of $C_{18}DS$. In the present work, the spin distribution over the cationic and anionic radicals of an analogue of $C_{18}DS$ with a shorter alkyl chain, C_4DS , has been calculated based on the density functional theory (DFT). By comparison of the calculation results and the reported properties of Species A, it has been assigned to the cation radical.

Key words: Merocyanine dye, J-aggregate, charge transfer, hyperfine coupling, DFT, ESR

1. INTRODUCTION

Dye aggregates are self-assembled nano-structures [1], in which the electronic properties of the dyes are modified from those in the isolated states. This modification of the electronic properties is the origin of the characteristic functions of those nano-structures. For example, the electronic absorption bands of the dyes shift toward the low energy side upon the J-aggregation; and besides their bandwidths are largely reduced. Because of such characteristics, J-aggregates are used as optical sensitizers and moreover are expected to be useful in optoelectronic devices. Therefore, the modification of the electronic properties of dyes due to J-aggregation has been attracting much attention of researchers.

A long-chain substituted merocyanine dye, 3-carboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone, hereafter abbreviated as $C_{18}DS$, forms J-aggregates in its Langmuir (L) films prepared under appropriate experimental conditions [2,3]. The J-aggregates of $C_{18}DS$ can be transferred onto solid substrates by means of Langmuir-Blodgett (LB) method. Many researchers have studied various aspects of the $C_{18}DS$ aggregates in the L and LB films [2-30].

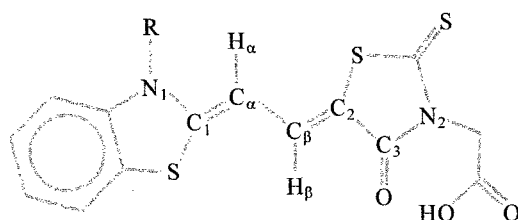


Fig. 1 $C_{18}DS$ ($R = C_{18}H_{37}$) and C_4DS ($R = C_4H_9$).

Among the various studies on the $C_{18}DS$ J-aggregates, those performed by using the electron spin resonance (ESR) technique [4-16] occupy a unique place. Actually, Kuroda et al. found:

- i) Two intrinsic spin species with different relaxation times are generated in the $C_{18}DS$ J-aggregate.
- ii) The ESR signal due to the spin species with the shorter relaxation time (Species A) shows a triplet structure, while that with the other spin species (Species B) is structureless.
- iii) The triplet structure reflects the hyperfine coupling between the electron spin and the nuclear spin ($I = 1$) of the nitrogen atom in the benzothiazolylidene group.
- iv) The anisotropy in the ESR signal due to Species A is orthorhombic and the triplet structure is most clearly observed when the external magnetic field is perpendicular to both of the normal axis of the film plane and the dipping direction of the substrate.
- v) Irradiation of light generates two photo-induced spin species that provide the same ESR lineshape as the intrinsic species.
- vi) One radical spin accompanies with several hundred dye molecules, etc.

Based on these experimental results, Kuroda et al. proposed a charge-transfer model of the $C_{18}DS$ J-aggregate [5,7]. In this model, the $C_{18}DS$ dye is considered as a pair of electron donor and acceptor (DA) and then an intramolecularly charge-transferred state, i.e., a zwitterionic state (D^+A^-), is assumed for the dyes in the J-aggregate. However, dyes at the ends of aggregates may be sometimes truly charged and consequently long-distance intermolecular charge transfer can be realized as



This model predicts that the interaction between the cationic and anionic radical spins is negligible and then consistent with the observed ESR. Furthermore, this model explains the observed photo-generation of the spins. However, the experiments could not clearly assign the spin species A and B to DA^- or D^+A .

Another important insight deduced from the ESR study concerns the molecular arrangement in the $C_{18}DS$ J-aggregates [6-11]. Since it was empirically known that the hyperfine splitting due to a nitrogen atom becomes the largest along the $p\pi$ orbital axis, the orientation of the normal axis of the $C_{18}DS$ chromophore plane was estimated: it lies in the film plane and makes 60–65° with the dipping direction of the substrate. Taking into account that the flow-orientation effect aligns the long axis of the J-aggregate to the dipping direction [31], the angle between the long axis of the J-aggregate and the long axis of the $C_{18}DS$ chromophore was estimated at 25-30°. However, the planarity of the $C_{18}DS$ radicals and relationship between the molecular axes and the principal axes of the hyperfine coupling have not been verified.

The purpose of the present work is to resolve the remaining problems mentioned in the last two paragraphs by means of computer chemistry. Recent progress both in the hard and software has enabled us to perform this kind of work without devoting too much time and cost. Particularly, the density functional theory (DFT) largely

reduces the calculation tasks required to take into account the electron-electron correlations, which must crucially affect the distribution of the spin density in the radicals. Actually, the DFT vibrational calculations of the pristine and ^{13}C -substituted C_4DS (C_α in Fig. 1 is substituted) well reproduced the infrared (IR) spectra experimentally observed for chloroform solutions of the pristine and substituted $C_{18}DS$, respectively [26]. This fact implies that DFT calculations of isolated merocyanine molecules can satisfactorily describe the electronic state of the dye. Therefore, we have applied the DFT method to the cationic and anionic radicals of C_4DS and compared the calculation results with the reported experimental facts.

2. METHOD

The DFT calculations were performed for the cationic and anionic radicals of a model molecule, C_4DS , in which the alkyl chain is truncated from an octadecyl group to a butyl one to avoid wasting CPU time for uninteresting part. All DFT calculations were based on the B3LYP model [31] and performed by using Gaussian 98 Rev. A9 [32] through Quantum Chemistry Grid/Gaussian Portal user interface program [33,34].

The radical ions were assumed to be surrounded by a dielectric medium with the dielectric constant of 2.5, whose effect was taken into account by the Onsager model with the solute radii recommended by the Hatree-Fock calculation for the neutral C_4DS , 5.83 Å [26].

3. RESULTS AND DISCUSSION

In the DFT calculations, firstly, the structures of the cationic and anionic C_4DS radicals have been optimized using a relatively large basis set, 6-31+G(d') [32]. This calculation level has been proved enough for the structural optimization, that is, the vibrational calculation at this level well reproduced the infrared spectra of the pristine and ^{13}C -substituted $C_{18}DS$ in the neutral state [26]. However, 6-311++G(2d,p) [32], a much larger basis set, was used for calculating the electronic states of the radicals because their wavefunctions may be more diffusive than those of the neutral closed-shell molecule.

Figure 2 shows the shape of the chromophore calculated for the C_4DS radicals. Here, the xy -plane is defined so that the standard deviation of the atomic positions from that plane, $\sigma = \sqrt{\sum z^2/N}$, becomes minimum. The σ value is approximately 0.01 nm in the both cases, showing good planarity of the DS chromophore even in the charged state.

In this report, the x -axis is defined so that the electric dipole moment, μ , of the cationic C_4DS lies in the xz -plane. The projection of μ onto the xy -plane is shown in the figure for both of the cationic and anionic cases. (Since the carboxyl group and alkyl chain are not in the xy -plane, the z -component of μ is not zero, but it is small

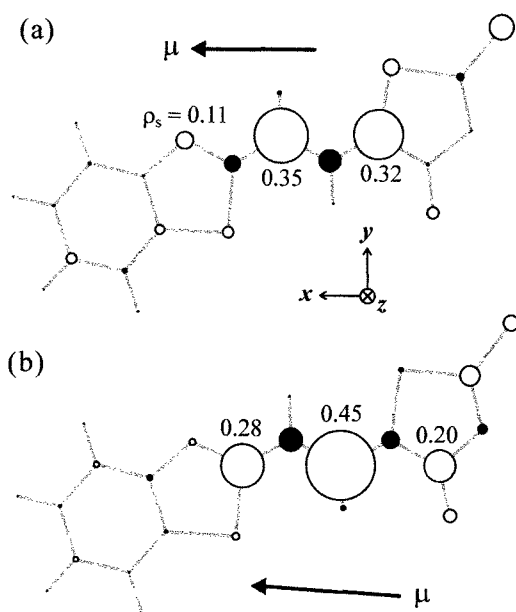


Fig. 2 Optimized shape of the main part of the chromophore of C_4DS in the (a) cationic and (b) anionic radical state. The spin density (ρ_s) on each atom is represented by the radius of the circle (open and closed circles stand for positive and negative spin densities, respectively).

and negligible in this work.) The spin density (ρ_s) on each atom is also displayed in Fig. 2.

Comparing the shapes in the cationic and anionic states with each other, the structural difference between them can be recognized, but it is found to be small. On the contrary, the distribution of the spin density is largely different between the two cases. On one hand, ρ_s 's on N_1 , C_α and C_2 atoms are relatively large in the cationic case. On the other hand, ρ_s on C_1 , C_β and C_3 atoms are relatively large in the anionic case.

As for the spin species A, Kuroda et al. [4-10] found that the most remarkable structure (triplet lines) in the ESR spectrum observed for the J-aggregates of $C_{18}DS$ reflects the hyperfine splitting due to the nitrogen atom (bearing a nuclear spin of 1). They proved that N_1 is the cause of the triplet structure by showing that the structure becomes doublet lines when N_1 is substituted by ^{15}N [11,12]. Furthermore, they experimentally estimated ρ_s on the N_1 atom, $\rho_s(N_1)$, at 0.14 by analyzing the ESR spectra [13]. The present DFT calculation predicts that $\rho_s(N_1)$ in the cationic $C_{18}DS$ is as large as 0.11, while $\rho_s(N_1)$ in the anionic $C_{18}DS$ and $\rho_s(N_2)$ in both of cationic and anionic $C_{18}DS$ are less than 0.06. Namely, it is suggested that Species A originates from the cationic radical of $C_{18}DS$.

Strictly speaking, the hyperfine coupling depends not only on the volume-integrated spin density that is discussed in the last paragraph, but also on the form of the wavefunction and the orbital angular momentum. Then, the principal axes and the principal values of the hyperfine couplings in the C_4DS radicals have been calculated for each atom. In this calculation, nitrogen, carbon, and hydrogen atoms were assumed to be ^{14}N , ^{13}C , and 1H , respectively. The calculation results for some important atoms are listed in Table I. In this table the calculated principal values and the orientation of the principal axes (ξ , η , ζ) are combined and expressed as a vector in the xyz -coordination system defined in Fig. 2 (signs are neglected).

We note again that the hyperfine splitting due to the N_1 atom calculated for the cationic case is as large as that expected from the triplet structure observed in the ESR spectrum of Species A. On the contrary, that calculated for the anionic case and those for the N_2 atom in the both cases are small, when compared with the observed triplet structure. Thus, Species A can be assigned to the cationic radical of $C_{18}DS$.

Moreover, the present calculation predicts that the hyperfine splitting due to the N_1 atom is quasi uniaxial and the axis along which the splitting becomes maximum is approximately parallel to z -axis, i.e., $p\pi$ -orbital axis of the chromophore plane. This result reinforces the basis on which Kuroda et al. [6-11] discussed the molecular orientation of $C_{18}DS$ in its J-aggregates. Actually, they used a spin Hamiltonian with the hyperfine principal values of $A_z = 5.4$ gauss and $A_x = A_y = 1.1$ gauss, which

Table I The hyperfine splitting due to N_1 and N_2 (assumed to be ^{14}N), C_α and C_β (assumed to be ^{13}C), and H_α and H_β (assumed to be 1H) calculated for the cationic and anionic C_4DS radicals. The principal values (unit: gauss) associated with the principal axes, ξ , η , and ζ , are projected to the xyz -coordination system displayed in Fig. 2.

atom	axis	cation			anion		
		x	y	z	x	y	z
N_1	ξ	1.66	0.75	0.05	0.99	0.64	0.01
	η	0.78	1.72	0.02	0.68	1.05	0.05
	ζ	0.07	0.07	3.71	0.05	0.10	2.43
N_2	ξ	0.15	0.01	0.01	0.50	0.21	0.06
	η	0.00	0.05	0.00	0.23	0.56	0.01
	ζ	0.01	0.00	0.20	0.12	0.03	1.15
C_α	ξ	6.41	5.95	0.02	3.39	0.32	0.01
	η	6.12	6.60	0.02	0.21	2.20	0.06
	ζ	0.06	0.00	17.75	0.00	0.15	5.62
C_β	ξ	4.13	0.22	0.04	7.99	6.34	0.18
	η	0.15	2.83	0.00	6.38	8.04	0.10
	ζ	0.07	0.00	6.97	0.17	0.38	20.45
H_α	ξ	3.66	0.15	0.04	1.48	0.01	0.01
	η	0.17	4.38	0.05	0.00	0.46	0.02
	ζ	0.01	0.01	0.72	0.00	0.05	1.02
H_β	ξ	2.10	0.32	0.02	4.26	0.07	0.06
	η	0.15	1.04	0.29	0.08	4.89	0.05
	ζ	0.05	0.28	1.00	0.01	0.01	0.63

coincide approximately with the values listed in Table I

They also experimentally examined the spin density on the C_α atom by the ^{13}C -substitution technique [14]. As their expectation, this isotope substitution brought about an additional splitting in the ESR spectrum of the J-aggregates. Interestingly, the additional splitting can be seen only in the spectrum of Species A, showing that $\rho_s(C_\alpha)$ is larger in the cationic state than in the anionic state. Hence, the present calculation result (Fig. 2) is qualitatively consistent with that experimental result.

However, a quantitative agreement between the experimental and DFT results was not obtained. That is, Kuroda et al. [14] deduced the hyperfine principal values of $A_z = 8.5$ gauss and $A_x = A_y = 4$ gauss for $^{13}C_\alpha$ atom in the cationic case, while they were estimated at twice larger (Table I) in the DFT calculations.

A similar discrepancy is noted between the calculated hyperfine splitting due to the hydrogen atoms in the central methine chain, H_α and H_β in Fig. 1, and the ESR spectrum observed for the J-aggregates of the pristine $C_{18}DS$. The present calculation predicts that the hyperfine splitting due to H_α (in the cationic case) or H_β (anionic case) reaches up to 3.7–4.9 gauss in the xy -plane, but the corresponding doublet structures are seen in the ESR spectra of neither Species A nor B.

Both of these discrepancies show that the real spin

density in the central methine chain is much smaller than the DFT calculation result. Here, it must be noted that the calculation is performed by assuming the radicals are isolated, while the ESR signals may come from radicals included in the J-aggregate. The previous IR study [26-29] indicated that the charge density in the central methine chain decreases when the dye forms the J-aggregate. Taking these facts into account, a part of the disagreement between the ESR experimental results and the DFT calculation results can be ascribed to the difference in the electronic state between the J-aggregated and isolated C₁₈DS dyes.

4. SUMMARY

The DFT calculations have been performed for the cationic and anionic radicals of C₄DS. The calculation results have indicated that what is called Species A, which is one of the two intrinsic spin species found in the J-aggregate of C₁₈DS, can be assigned to the cationic radical of the dye. This result supports the intermolecular charge-transfer model of Kuroda et al., and their estimation of the molecular arrangements in the J-aggregate as well, although the calculation performed for the isolated radicals could not well reproduce the decrease in the charge density in the central methine chain due to the J-aggregate.

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