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Possible Anomalous "Monomer Shifts" of Merocyanine Dyes in their Aggregates – an Analytical Study

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To investigate the so-called monomer shifts in aggregates of merocyanine dyes that bear a donor-acceptor type chromophore, a simple model has been introduced to describe the electronic structure of such a chromophore. This model can be solved analytically and the obtained solution tells us that the physical quantities relating to the optical properties of the system, i.e., the excitation energy, the transition dipole moment, the static dipole moment at the ground state, and the static dipole moment at the excited state strongly depend on the extent of the bond alternation in the chromophore, which includes seven atomic p_z orbitals. Based on this model, as a consequence, possibility of anomalous monomer shifts in the merocyanine J-aggregates has been demonstrated.

Key words: Merocyanine dye, J-aggregate, twitterionic state, bond alternation, electronic excitation

1. INTRODUCTION

J-aggregates [1] are self-assembled nano-structures that are attracting much attention because of their optical functions. Most of the dyes forming J-aggregates are based on symmetric chromophores, but merocyanine dyes shown in Fig. 1 (a), called "MS family" in this paper, are exceptions [2,3]: their common chromophore is a donor-acceptor type. Therefore, J-aggregates of these dyes possibly exhibit exotic properties or functions that can be used in future industrial applications.

Aggregation of dyes leads to shifts of their electronic absorption bands by two ways. One is the path through the non-secular terms of the interaction Hamiltonian, and the other through the modification of the secular terms. The former is related to the energy transfer within the aggregates and has been well studied by many researchers. On the contrary, the latter, named "monomer shift", has not intensively been investigated so far because it should be trivial in aggregates of symmetric dyes such as cyanine and oxonol. However, monomer shifts in aggregates of donor-acceptor type dyes can be very large, partially because the photo-excitation may largely modifies the molecule's static dipole moment, and partially because the aggregation modifies the balance between the neutral and twitterionic Lewis structures in the ground and excited states of the chromophore.

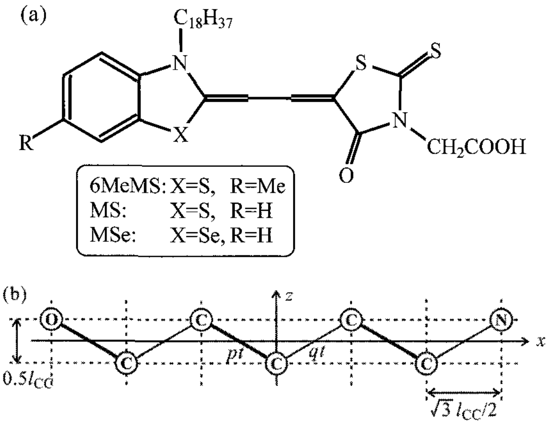

Fig. 1 (a) Merocyanine dyes MS, 6MeMS and MSe and (b) a model atomic arrangement of their common chromophore.

This paper aims at demonstrating the possibility of such anomalous monomer shifts basing on a simple model for MS family's chromophore, which can be solved analytically.

2. MODELING

Although the free-electron model well describes the optical properties of cyanine [1], a quite successful family of dyes, it is not applicable to merocyanine dyes, which have bond alternation character in their chromophore. Therefore, in this study, a rigid-lattice tight-binding model with the Hückel approximation has been adopted to analyze the electronic structure of the merocyanine dyes' polymethine chromophore including seven atoms, i.e., O=C–C=C–C=C–N: (Fig. 1 (b)). According to the usual procedure, the system's one-electron wavefunction of $|\psi\rangle$ is written by a linear combination of the atomic p_z orbitals of $|\chi_k\rangle$ (k = 1, 2, …, 7) as

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$$|\psi\rangle=\sum_{k=1}^{7} c_k |\chi_k\rangle \,. \tag{1}$$

That is, on the one hand, the orbital of the lone pair at N is taken into account, but, on the other hand, those at O are not because they are sp and p_y orbitals.

The bond alternation can explicitly be introduced into this model by giving different values to the overlap integrals of the nominally single and double bonds. For simplicity's sake, however, the differences in the potential among the atoms (O, C and N) are neglected. Thus, three energetic parameters, E_{atom}, t and γ are used in this model, which are defined as follows:

$$\langle \chi_k |H| \chi_k \rangle = E_{\text{atom}} \,, \tag{2}$$

$$\langle \chi_1 |H| \chi_2 \rangle = \langle \chi_3 |H| \chi_4 \rangle = \langle \chi_5 |H| \chi_6 \rangle = -t\cos\gamma \,, \tag{3}$$

and

$$\langle \chi_2 |H| \chi_3 \rangle = \langle \chi_4 |H| \chi_5 \rangle = \langle \chi_6 |H| \chi_7 \rangle = -t\sin\gamma \,, \tag{4}$$

where H is the one-electron Hamiltonian of the chromophore, and $t > 0$ is assumed.

Because for an eigenfunction of $|\psi\rangle$ the variation principle requires

$$\frac{\partial}{\partial c_k}\langle \psi |H| \psi \rangle = 0 \,, \tag{5}$$

the linear combination coefficients c_k must satisfy the simultaneous equation of

$$\begin{bmatrix} \omega & p & 0 & 0 & 0 & 0 & 0 \\ p & \omega & q & 0 & 0 & 0 & 0 \\ 0 & q & \omega & p & 0 & 0 & 0 \\ 0 & 0 & p & \omega & q & 0 & 0 \\ 0 & 0 & 0 & q & \omega & p & 0 \\ 0 & 0 & 0 & 0 & p & \omega & q \\ 0 & 0 & 0 & 0 & 0 & q & \omega \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ c_7 \end{bmatrix} = 0 \,. \tag{6}$$

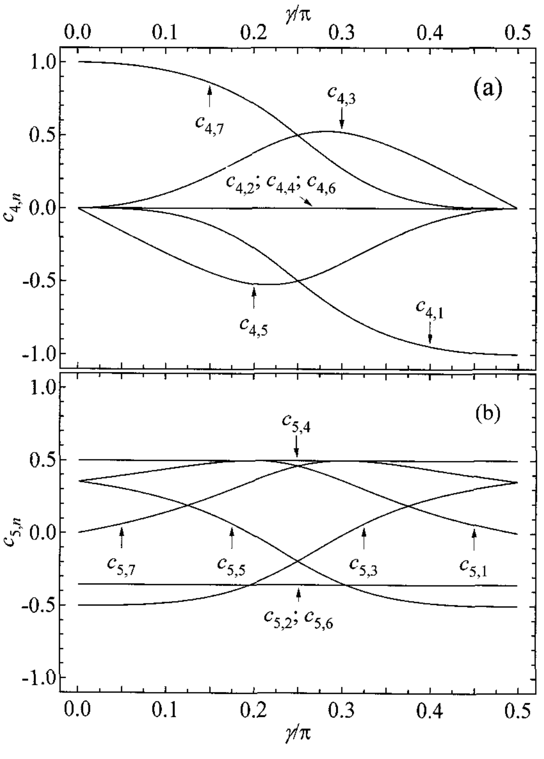

Fig. 2 The LCAO (Linear Combination of Atomic Orbitals) coefficients for (a) $|\psi_4\rangle$ and (b) $|\psi_5\rangle$ as a function of the bond-alternation parameter of γ.

Here, ω denotes the normalized one-electron energy of $(E-E_{\text{atom}})/t$, and p and q represents $\cos\gamma$ and $\sin\gamma$, respectively. The secular equation can be solved analytically and the eigenvalues are obtained as

$$\omega = 0, \quad \pm\sqrt{1-\sqrt{\tfrac{1}{2}}\sin 2\gamma}, \quad \pm 1, \quad \pm\sqrt{1+\sqrt{\tfrac{1}{2}}\sin 2\gamma} \,. \tag{7}$$

To distinguish the different wavefunctions, we number them from the lowest energy state to the highest as $|\psi_j\rangle$ (j = 1, 2, ... , 7) and the corresponding linear combination coefficients are rewritten as $c_{j,k}$. Since the system contains eight electrons, i.e., one electron from O and each C plus two electrons from N, from $|\psi_1\rangle$ to $|\psi_4\rangle$ are occupied at the ground state, and at the lowest excitation moves one electron from $|\psi_4\rangle$ to $|\psi_5\rangle$. The coefficients $c_{4,k}$ and $c_{5,k}$ are plotted as a function of γ, respectively, in Fig. 2 (a) and (b). From these plots, it can be seen that when $\gamma \approx 0$ (or $\pi/2$), $|\psi_4\rangle$ well corresponds to the lone pair's orbital at the N (or O) atom and $|\psi_5\rangle$ is the antisymmetric orbital of the usual 6π-electron system having three nodes. In contrast, when $\gamma = \pi/4$, $|\psi_4\rangle$ becomes an antisymmetric orbital with three nodes and $|\psi_5\rangle$ becomes a symmetric orbital with four nodes. It should be noted that the latter case corresponds to the electronic structure of the cyanine and oxonol dyes' chromophores. For the merocyanine dye, γ should be around $\pi/4$, since otherwise the chromophore would be insensitive to light irradiation, but the assertion of $\gamma = \pi/4$ may be difficult to be justified.

Based on the present model, the physical quantities relating to the optical properties of the chromophore are obtained as the followings.

- Excitation energy:

$$\Delta E_{\text{mol}}(\gamma) = t\sqrt{1-\sqrt{\tfrac{1}{2}}\sin 2\gamma} \tag{8}$$

- Transition dipole moment:

$$\mu_{\mathrm{tr}} = \sqrt{2}e\sum_{k=1}^{7} r_k c_{4,k} c_{5,k} \tag{9}$$

- Static dipole moment at the ground state:

$$\mu_{\mathrm{g}} = e\left[r_7 + \sum_{k=1}^{7} r_k\left(1-2\sum_{j=1}^{4} c_{j,k}^2\right)\right] \tag{10}$$

- Static dipole moment at the excited state:

$$\mu_{\mathrm{e}} = \mu_{\mathrm{g}} - e\left[\sum_{k=1}^{7} r_k\left(c_{5,k}^2 - c_{4,k}^2\right)\right] \tag{11}$$

Here, r_k denotes the position of the k-th atom (1st is O and 7th is N) and e is the absolute value of the elementary charge. Due to the spin degeneracy, the factor of $\sqrt{2}$ appears in eq. (9) [1,4].

3. DISCUSSION

3.1 Estimation of parameters

By giving r_k's as shown in Fig. 1 (b) the normalized dipole moments $\mu_{\mathrm{tr}}/el_{\mathrm{cc}}$, $\mu_{\mathrm{g}}/el_{\mathrm{cc}}$ and $\mu_{\mathrm{e}}/el_{\mathrm{cc}}$ are obtained as a function of γ (Fig. 3), where l_{cc} is the bond length in the model. In addition, from the reported crystallographic data [5] we can appropriately assume the value of l_{cc} as 0.138 nm, resulting in el_{cc} of 6.63 Debye. With this value of l_{cc}, the γ value in the MS family displayed in Fig. 1 is roughly estimated at $\pi/5$ because it exhibits $|\mu_{\mathrm{tr}}|$ of about 10 Debye in dilute chloroform solution.

In evaluation of the value of t, the absorption wavelengths of the cyanine and oxonol dyes based on the polymethine chromophore with the same length as that treated in this study are good references. Since our target is the MS family (Fig. 1 (a)), the absorption wavelengths of the cyanine dye bearing benzothiazol as an auxochrome and the oxonol dye bearing rhodanine, 557 and 542 nm, respectively, are referred and t is estimated at 33600 cm^{-1} when $\gamma = \pi/4$. However, there is no reason to assume that t is independent from γ. In fact, with $\gamma \approx \pi/5$ and t = 33600 cm^{-1} eq. (8) predicts too large excitation energy for the MS family.

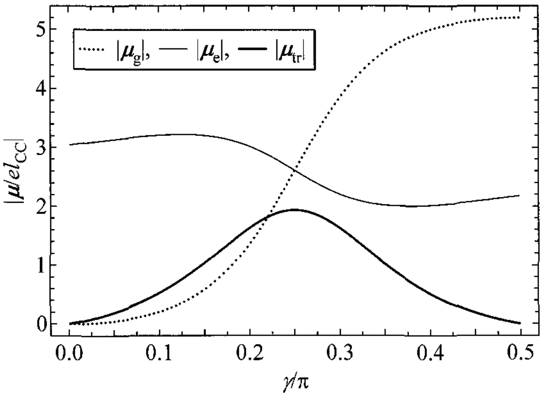

Fig. 3 Normalized dipole moments as a function of γ.

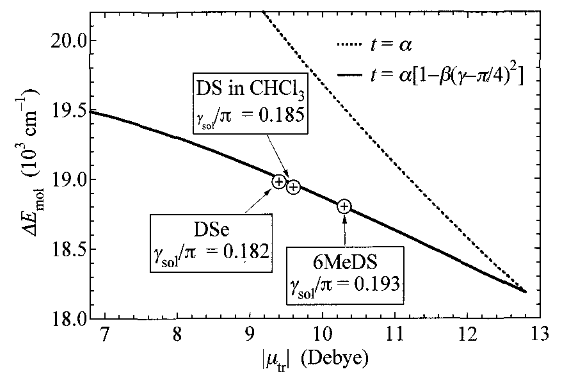

Fig. 4 Correlation between ΔE_{mol} and $|\mu_{\mathrm{tr}}|$. The parameters of α and β are set to 33.6 × 10^3 cm^{-1} and 1.15 respectively.

Rather, since the system is symmetrical with respect to $\gamma = \pi/4$, according to the general consideration,

$$t = \alpha\left[1-\beta\left(\gamma-\pi/4\right)^2\right] \tag{12}$$

with $\beta > 0$ can be supposed for the $|\gamma - \pi/4| << 1$ case. The combination of eqs. (8), (9) and (12) with α = 33600 cm^{-1} and β = 1.15 well reproduces the optical properties of the MS family in chloroform (Fig. 4). Furthermore, the γ parameter at the solution state, γ_{sol}, can be estimated at 0.185π, 0.193π and 0.182π for MS, 6MeMS and MSe, respectively.

3.2 Monomer shifts

As shown by eq. (11), in the merocyanine-dye case μ_{e} can be different largely from μ_{g}, and as a consequence, the electrostatic energy of a dye chromophore in an aggregate is modified through the optical excitation. This mechanism is the same as that known for aggregates of usual symmetrical dyes, but its magnitude can be much larger than those usual cases. In this paper, we call this mechanism type A.

To evaluate the type A monomer shift, the electrostatic energies of the chromophore at the ground

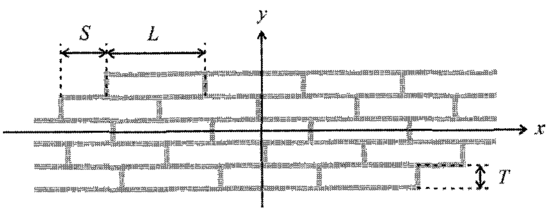

Fig. 5 Molecular arrangement of the J-aggregate of 6MeDS.

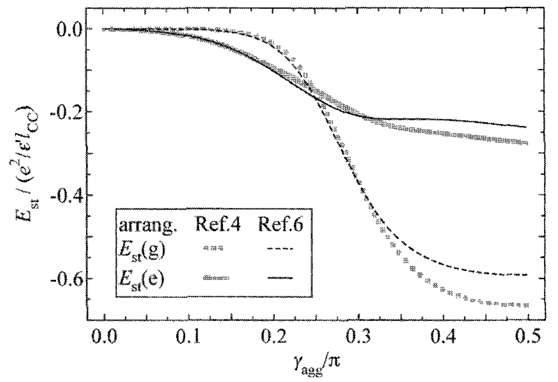

Fig. 6 Electrostatic energy of a chromophore at the ground (E_{st}(g)) and excited states (E_{st}(e)) calculated for 6MeDS J-aggregate with assuming the molecular arrangements proposed in Refs. [4] and [7].

and excited states, E_{st}(g) and E_{st}(e), respectively, are calculated with the present model. To do this, the chromophore is put at the center of a large J-aggregate whose molecular arrangement is shown in Fig. 5. The set of the arrangement parameters (L, T and S) given in refs. [4] and [6], i.e., (1.63, 0.35 and 0.81 nm) and (1.57, 0.38 and 0.71 nm), respectively, are used. The electrostatic interaction between chromophores can be evaluated by adopting the extended dipole model [1] with the magnitude of the point charge being fixed at e. The results normalized by $e^2/\varepsilon' l_{cc}$ are plotted in Fig. 6 as a function of γ_{agg}, where γ is the parameter characterizing the chromophore in the aggregate, and ε' is the relative dielectric constant of the molecule. These plots reveal that the type A monomer shift can be negative and positive, depending on γ_{agg}.

In addition to type A, the increase in the γ parameter upon the J-aggregation, which has been strongly suggested in the merocyanine case by the infrared spectroscopic studies [4,7,8], gives rise to another shift of the electronic absorption band. The shift due to this mechanism, which we call type B in this paper, is quite exceptional as a monomer shift, but cannot be ignored in the merocyanine case. The type B monomer shift is simply given by the difference between $\Delta E_{mol}(\gamma_{agg})$ and $\Delta E_{mol}(\gamma_{sol})$. However, since eq. (12) is applicable only for the $|\gamma-\pi/4| \ll 1$ case, the range of γ within which the calculation is reliable is limited.

Figure 7 displays the calculation result for the type B monomer shift, together with those of the type A with ε' = 2.5 (accepted value for hydrocarbons) and the total. It is clearly realized that in the merocyanine J-aggregates monomer shift can have extremely large magnitude and both of negative and positive signs.

In conclusion, we have theoretically demonstrated that anomalous monomer shifts possibly appear in the J-aggregates of merocyanine dyes. The authors are grateful to Prof. M. Sugi for his valuable suggestions.

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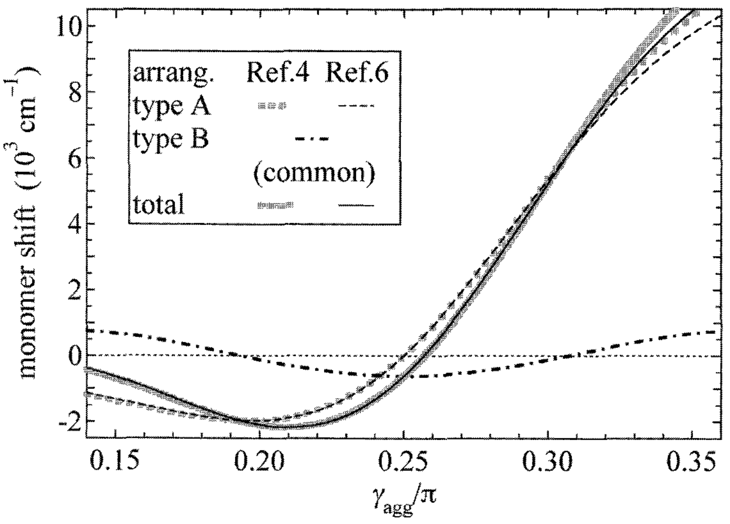

Fig. 7 Type A, B and total monomer shifts in a 6MeDS J-aggregate calculated as a function of γ_{agg}.