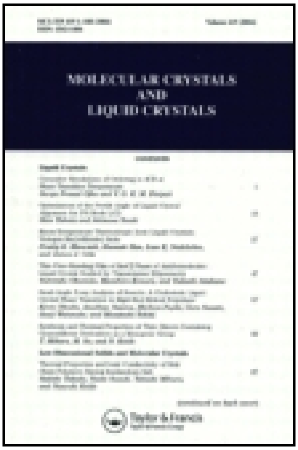

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Polarizabilities of Dendritic Molecular Aggregates: Contribution of Exciton Generation

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The spatial contributions of exciton generation to polarizabilities (α) are elucidated for two types of molecular aggregate models with a dendritic structure, one of which involves a different type of dipole units such as transition metal compounds.

Keywords: dendrimer; exciton; aggregate; polarizability

INTRODUCTION

Recently, dendrimeric supermolecules with fractal antenna structures have attracted a great deal of attention due to their remarkable light-harvesting ability [1,2]. Such molecular systems have a large number of terminal groups originating in a focal point (core) with at least one branch at each repeat unit. There is predicted to be a directional energy transfer from the periphery to the core. Such efficient excitation energy cascades to the core is known to be caused by the fractal antenna (dendritic) structure, which provides an ordered energy states. On the other hand, dendritic molecular aggregate systems are also known to exhibit similar ordered energy states and directional energy transfer [3]. Although such energy transfer process has been investigated actively, the optical processes such as (non)linear optical polarization have not been elucidated well. At the first stage, therefore, we investigate the features of off-resonant polarizability (α) for a dendritic molecular aggregate, in which the monomer (chromophore) is assumed to be a dipole unit (a two-state molecular model) arranged as modeled after the Bethe-tree type structure [2]. Two types of aggregates are examined: one is composed of all the same dipole units and the other involves different dipole units. Using the one-exciton model, the time evolution of density matrix is performed in a numerically exact manner, i.e., numerical Liouville approach (NLA) [3]. To elucidate the difference in α between these two types of aggregates, we develop a visualization method of the spatial contribution of virtual exciton generation to α.

CALCULATION METHODS AND AGGREGATE STRUCTURES

We consider model aggregates (A) and (B) (Fig. 1) composed of two-state monomers, which are arranged as modeled after a dendritic structure referred to as D25 [2]. The *k*th monomer possess a transition energy, $E_{21}^k (\equiv E_2^k - E_1^k)$, and a transition moment, μ_{12}^k. The monomer is approximated to be a dipole. This approximation is considered to be acceptable if the intermolecular distance (R_{kl}) is larger than the size of a monomer. The angle between a dipole k and a line drawn from the dipole site k to l is θ_k. The Hamiltonian for the aggregate model is written by

$$H_{\mathrm{agg}} = \sum_{k}^{N} \sum_{i_k}^{2} E_{i_k}^k a_{i_k}^+ a_{i_k} +$$

$$\frac{1}{4\pi\varepsilon_0} \sum_{k<l}^{N} \sum_{\substack{i_k, i_k', \\ i_l, i_l'}}^{2} \mu_{i_k i_k'}^k \mu_{i_l i_l'}^l [(\cos(\theta_k - \theta_l) - 3\cos\theta_k \cos\theta_l) / R_{kl}] a_{i_k}^+ a_{i_k'} a_{i_l}^+ a_{i_l'} . \quad (1)$$

In Eq. (1), $E_{i_k}^k$ is an energy of state i_k for monomer k, and $\mu_{i_k i_k'}^k$ is a magnitude of a transition matrix element between states i_k and i_k' for monomer k. The $a_{i_k}^+$ and a_{i_k} represent respectively the creation and annihilation operators for state i_k of monomer k. The matrix representation of H_{agg} is obtained using the basis for the aggregate $\{ |\varphi_{i_1}^1 \varphi_{i_2}^2 \cdots \varphi_{i_N}^N \rangle \}$ (N is the number of monomers), which is constructed by a direct product of a state vector for each monomer $\{ |\varphi_{i_k}^k \rangle \}$. By diagonalizing this Hamiltonian matrix, we can obtain a new state-model with eigenenergies $\{ E_i^{\mathrm{agg}} \}$ and eigenstates $\{ |\psi_i^{\mathrm{agg}} \rangle \}$ (i = 1, ..., M), where M is the size of the basis used. The transition dipole matrix elements (μ_{ij}^{agg}) in the direction of the field applied to this new state-model are calculated. It is noted that only the transition moments between the ground (1) and exciton states ($i(\neq 1)$) exist in the one-exciton model.

The time evolution of a molecular aggregate model is described by the following density matrix formalism [4]:

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[H(t),\rho(t)]-i\Gamma\rho(t), \tag{2}$$

where $\rho(t)$ indicates the total molecular density matrix and the second term on the right-hand side of Eq. (2) represents the relaxation processes in the Markoff approximation. The total Hamiltonian $H(t)$ is expressed by the sum of the aggregate Hamiltonian, $H_{\rm agg}$, and the aggregate-field interaction, $V(t)$:

$$H(t)=H_{\rm agg}+V(t)=\sum_{j=1}^{M}E_j^{\rm agg}b_j^+b_j-\sum_{i,j=1}^{M}\mu_{ij}^{\rm agg}(F\cos\omega t)b_i^+b_j, \tag{3}$$

where F is an external-field amplitude in the direction of x (See Fig. 1) since the incident field is assumed to be a plane wave with frequency ω and wave vector $\boldsymbol{k}$ travelling perpendicular to the molecular plane and the polarization vector is parallel to x axis. The b_j^+ and b_j represent respectively the creation and annihilation operators for state j of aggregate state-model. The concrete matrix elements of relaxation term ($-(\Gamma\rho(t))_{ij}$) in Eq. (2) are presented in our previous paper [4]. We perform a numerically exact calculation to solve Eq. (2) by the fourth-order Runge-Kutta method. The density matrix representation $\rho_{i_1,i_2,\ldots,i_N;i'_1,i'_2,\ldots,i'_N}(t)$ in the aggregate basis $\{\left|\varphi^1_{i_1}\varphi^2_{i_2}\cdots\varphi^N_{i_N}\right\rangle\}$ at time t is also calculated. Using this density matrix, the polarization $p(t)$ is calculated by

$$p(t)=\sum_{\substack{i_1,i_2,\ldots,i_N,\\ i'_1,i'_2,\ldots,i'_N}}^{M}\mu_{i_1,i_2,\ldots,i_N;i'_1,i'_2,\ldots,i'_N}\,\rho_{i'_1,i'_2,\ldots,i'_N;i_1,i_2,\ldots,i_N}(t). \tag{4}$$

Here, the transition matrix element $\mu_{i_1,i_2,\ldots,i_N;i'_1,i'_2,\ldots,i'_N}$ is represented by

$$\mu_{i_1,i_2,\ldots,i_N;i'_1,i'_2,\ldots,i'_N}=\sum_{l=1}^{N}\mu'^{\,l}_{i_l i'_l}\left(\prod_{n\neq l}^{N}\delta_{i_n i'_n}\right), \tag{5}$$

where $\mu'^{\,l}_{i_l i'_l}$ represents a transition dipole matrix element (in the direction of applied field) between states i_l and i'_l of monomer l.

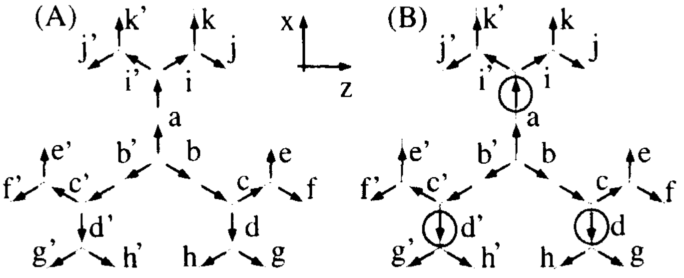


FIGURE 1 Spatial configuration of dendritic molecular aggregates. Each arrow represents a dipole unit. The dipole unit circled in aggregate (B) represents a different dipole unit. The intermolecular distance is assumed to be 15 a.u.

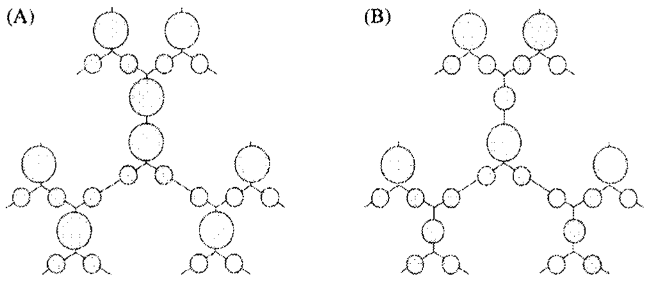
Using the external-field amplitude $\varepsilon(\omega)(=F/2)$, the Fourier transformed polarization $p(\omega)$, and Eq. (4), the nonperturbative $\alpha(-\omega;\omega)$ for the molecular aggregate is calculated by

$$\alpha(-\omega;\omega)=\frac{p(\omega)}{\varepsilon(\omega)}=\sum_{a>b}^{M}\alpha_{a-b}=\sum_{a>b}^{M}\frac{2\mu_{ab}\rho_{ba}^{\mathrm{real}}(\omega)}{\varepsilon(\omega)}, \tag{6}$$

where a and b indicate the aggregate basis $\{\,|\varphi_{i_1}^{1}\varphi_{i_2}^{2}\cdots\varphi_{i_N}^{N}\rangle\,\}$, and $\rho_{ba}^{\mathrm{real}}(\omega)$ is a real part of density matrix element in the aggregate basis. The partitioned α_{a-b} represents the contribution of virtual or real one-exciton generation represented by base pair a-b. In one-exciton case, either a or b is $|11\ldots1\rangle$ (1:the ground state of monomer), so that we can elucidate the spatial contribution of one-exciton generation to α by showing the one-exciton distribution, e.g., $|121\ldots1\rangle$ (2: the excited state of monomer).

CONTRIBUTION OF ONE-EXCITON GENERATION TO α

The dendritic molecular aggregate shown in Fig. 1(A) involves all the same dipole units. The transition energy and transition moment of the dipole unit (monomer) is assumed to be 38000 cm^{-1} and 5 D, respectively. On the other hand, the dendritic molecular aggregate shown in Fig. 1(B) involves different dipole units (E_{21}=36000 cm^{-1} and μ_{21}= 3 D) in leg regions a, d and d'. Although both aggregates are found to possess similar multi-step energy states and the transition moments between the ground and the one-exciton states, there are some differences in the



Totel $\alpha = 555.21$ a.u. Totel $\alpha = 465.19$ a.u.

FIGURE 2 α values and their partitioned $\alpha_{|1,1,\ldots,1)-b}$ for aggregates (A) and (B). The size of circle at each dipole site represents the magnitude of $\alpha_{|1,1,\ldots,1)-b}$.

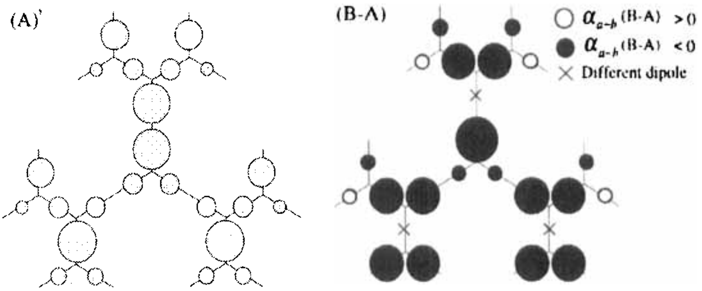


FIGURE 3 Difference between the partitioned α_{a-b} of aggregate (A) and the α of monomer (α_{mono}) on each site is shown in (A)'. Difference between the partitioned α_{a-b} of aggregate (A) and that of aggregate (B) on each site is shown in (B-A). The size of circle at each dipole site represents the magnitude of α_{a-b}-α_{mono} (>0) for (A)' and α_{a-b}(B-A) ($\equiv \alpha_{a-b}$(B)-α_{a-b}(A)) for (B-A), respectively. For (B-A), the circles at different dipole sites are omitted to focus on the effects of dipole-dipole interaction.

exciton distribution and its migration pathway [4]. It is predicted from this result that the spatial contribution of exciton to α for aggregate (A) is somewhat different from that for aggregate (B).

Figure 2 shows off-resonant α values (at ω = 3000 cm^{-1}) and their partitioned $\alpha_{|1,1,\ldots,1)-b}$ (distributed on the exciton site represented by aggregate basis b) for aggregates (A) and (B). It is found that the contributions of virtual exciton states in regions k, k', a, d, d', e and e' for aggregate (A) are dominant. This feature is ascribed to the fact that the direction of dipoles in such regions are paralell to that of the applied field. For aggregate (B), the total α (465.19 a.u.) is shown to be slightly reduced compared to that (555.12 a.u.) of aggregate (A). This tendency is found to mainly originate in the reduction of the contribution of the different dipole units.

The difference between the partitioned α_{a-b} and the α of monomer ($\alpha_{\rm mono}$) on each site is shown in Fig. 3(A)' in order to elucidate the effects of dipole-dipole interaction on α. The present dipole-dipole interaction is shown to enhance the total α. The degree of the enhancement is found to be significant in regions k(k')-i(i')-a and e(e')-c(c')-b(b')-d(d'). This feature can be understood by the *J*-aggregate-type interaction in those regions.

Figure 3(B-A) shows the difference between the partitioned $\alpha_{a-b}$of aggregate (A) and that of aggregate (B) on each site. It is found that the introduction of different dipole units causes not only a remarkable reduction of contribution of the different dipole units (See Fig. 2), but also slight reduction of the neighboring contribution. This feature can be explained by the reduction of the dipole-dipole interaction among the different unit sites and their neighboring sites.

SUMMARY

In this study, we developed an analysis method of visualizing the contribution of exciton generation to $\alpha$for dendritic molecular aggregates. In these aggregates, we found a slight enhancement of total α compared to the case of aggregate composed of non-interacting monomers. The enahncement was found to be mainly caused by dipole units with large *J*-aggregate-type interactions. The present introduction of different dipole units, e.g. transition-metal compounds, was found to reduce the dipole-dipole interaction between the different dipole units and their neighboring sites, and then to reduce the partitioned α_{a-b} in those regions.

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