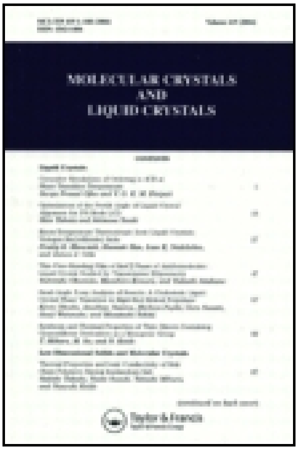

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Theoretical Study on the Polarizabilities of Two-Dimensionally-Grown Dendritic Molecular Aggregates: The Artichitecture- and Size-Dependency

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Theoretical Study on the Polarizabilities of Two-Dimensionally-Grown Dendritic Molecular Aggregates: the Artichitecture- and Size-Dependency

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We investigated the architecture- and size-dependences of polarizabilities of various molecular aggregates. As examples, we considered several sizes of dendritic (fractal dimensional), linear (one-dimensional) and square-lattice (two-dimensional) aggregates.

Keywords dendrimer; exciton; aggregate; polarizability

INTRODUCTION

Recently, several dendritic supramolecules with fractal antenna structures have attracted a great deal of attention due to their remarkable light-harvesting ability.[1] Such molecular system has many terminal groups originating in a focal point (core) with at least one branch at each repeat unit. It is predicted that there is a directional energy transfer from the periphery to the core.[2-4] Although the first-order optical processes, i.e., absorption and emission of light, have been investigated actively, response properties have not been elucidated yet. In this study, we elucidate the features of polarizability α of dendritic molecular aggregates, in which monomer is assumed to be a dipole unit arranged as modeled after Bethe-lattice type structure. As references, we also examine α values of conventional one- and two-dimensional molecular aggregates with non-fractal structures. On the basis of these results, we discuss the architecture- and size-dependences of α.

CALCULATION METHOD AND AGGREGATE STRUCTURES

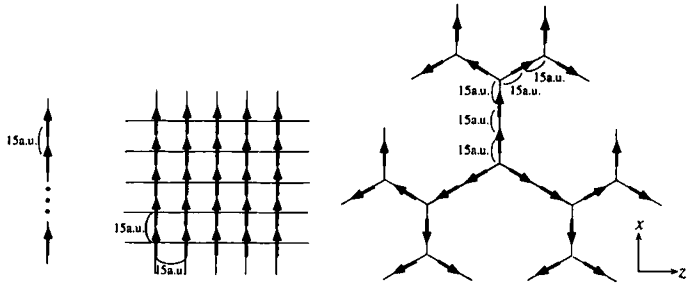
We consider model aggregates (Fig. 1) composed of two-state monomers, which are arranged as linear (L), square-lattice (S) and dendritic (D) structures. The k-th monomer possesses a transition energy, $E_{21}^k (\equiv E_2^k - E_1^k) = 38000\ \mathrm{cm}^{-1}$, and a transition moment, $\mu_{12}^k = 5\ \mathrm{D}$. 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_l}. The Hamiltonian for the aggregate model is written by

$$\begin{aligned} H_{\mathrm{agg}} = & \sum_{k}^{N} \sum_{i_k}^{2} E_{i_k}^k a_{i_k}^+ a_{i_k} + \\ & \frac{1}{4\pi\varepsilon_0} \sum_{k<l}^{N} \sum_{\substack{i_k, i_k', \\ i_l, i_l'}}^{2} \mu_{i_k i_k'}^k \mu_{i_l i_l'}^l [(\cos(\theta_{k_l} - \theta_{l_k}) - 3\cos\theta_{k_l} \cos\theta_{l_k}) / R_{kl}^3] a_{i_k}^+ a_{i_k'} a_{i_l}^+ a_{i_l'} . \end{aligned} \qquad (1)$$

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. By diagonalizing this Hamiltonian matrix, we can obtain a new state-model with eigenenergies { E_i^{agg} } and eigenstates { $|\psi_i^{\mathrm{agg}}\rangle$ } (i = 1, ..., M), where M represents the size of the basis used. The time evolution of a molecular aggregate model is described by the density matrix equation including the relaxation processes in the Markoff approximation. Details of the relaxation factors are presented in our previous paper.[5] The field is applied in the direction of x (See Fig. 1). We perform a numerically exact calculation to solve this equation by the fourth-order Runge-Kutta method. Using the external field amplitude $\varepsilon(\omega)$ and the Fourier transformed polarization $p(\omega)$, the nonperturbative $\alpha(-\omega;\omega)$ for a molecular aggregate is calculated by $\alpha(-\omega;\omega) = p(\omega)/\varepsilon(\omega)$.

ARCHITECTURE- AND SIZE-DEPENDENCES ON α

Figure 2(a) shows the size-dependences of α ($\omega = 3000\ \mathrm{cm}^{-1}$) for models (L), (S) and (D). It is found that the size-dependences of α for (L) and (S) are nearly equal to each other, while they are larger than those for (D). This feature can be explained by the fact that all the dipoles in (L) and (S) are parallel to the polarization vector of the applied field in contrast to the case of (D), where partial dipoles are parallel to the polarization vector of the applied field. The intermolecular-interaction effects on the size-dependence of α are shown in Fig. 2(b). The intermolecular-interaction effects are shown to enhance the size-dependences of α in the order of enhancement: (L) > (S) > (D). Since it is well-known that the J-aggregate-type interaction decreases the allowed excitation energies, those intermolecular-interaction effects on the size-dependences of α are closely related to the number of J-aggregate-type interaction pairs involved in each model.



L25 (N=25) S25 (N=25) D25 (N=24)

FIGURE 1 Structure of linear (L25), square-lattice (S25) and dendritic (D25) molecular aggregates. N represents the number of monomers.

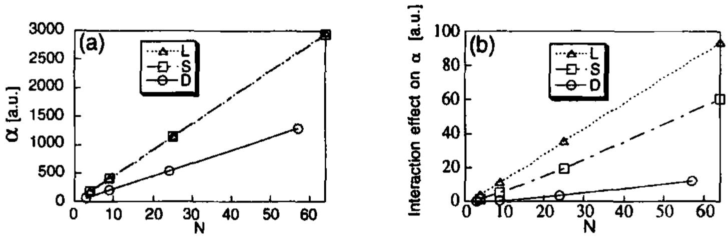


FIGURE 2 Size dependences of α [a.u.] (a) and their intermolecular-interaction effects (b) for systems (L), (S) and (D). N represents the number of monomers.

SUMMARY

It is found that the configurations of dipoles with respect to the polarization vector of applied field determine the size-dependences of off-resonant α, while the number of J-aggregate-type interactions involved in each system relates to the size-dependences of intermolecular-interaction enhancement of α.

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