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Theoretical study on the off-resonant polarizabilities of linear, square-lattice and dendritic molecular aggregates

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Abstract

We investigate the intermolecular-interaction effects on the off-resonant polarizabilities (α) of fractal-dimensional (dendritic), one-dimensional (linear) and two-dimensional (square-lattice) aggregate models in order to elucidate the structure-property relation in α . As a fractal-dimensional system, we consider a D25-like dendritic molecular-aggregate model, which involves chromophores at the position of acetylene units of a phenylacetylene dendrimer D25. It is found for a dendritic aggregate that intermolecular-interaction effects more enhance the contribution to α in the core region than that in the periphery region.

Keywords: Semi-empirical models and model calculations, Dendritic and/or fractile surfaces, Polarizability, Dipole-dipole interaction, Exciton model

1. Introduction

Recently, several phenylacetylene dendrimers have attracted a great deal of attention because of the remarkable light-harvesting ability [1–4]. The directional energy transfer from the periphery to the core was actively investigated. In our previous paper [4], we reported a theoretical analysis of the exciton migration of a dendritic molecular-aggregate model involving molecules at the position of acetylene units of a phenylacetylene dendrimer. However, the polarizabilities (α) of dendritic systems have not been much investigated. In this study, we calculate a nonperturbative α of a D25-like dendritic molecular-aggregate model (D25) shown in Fig. 1. As references, we calculate the α of *J*-aggregate model (L25J), *H*-aggregate model (L25H) and square-lattice model (S25) shown in Fig. 1. We elucidate the difference in the intermolecular-interaction effects on the off-resonant α among these systems.

2. Calculation method

We consider four types of molecular-aggregate models (Fig. 1) composed of two-state monomers, which possess a transition energy, 38000 cm⁻¹, and a transition moment, 5 D.

We consider the dipole-dipole interaction among monomers. In our previous paper [5], we developed an analysis method visualizing the spatial contribution of exciton generation to α of molecular aggregates. This method utilizes the following expression of α :

$$\alpha(-\omega, \omega) = \frac{p(\omega)}{\varepsilon(\omega)} = \sum_{a>b}^N \alpha_{a-b} = \sum_k^N \frac{2 \operatorname{Re}[\mu_k \rho_{0k}(\omega)]}{\varepsilon(\omega)}, \quad (1)$$

where $p(\omega)$ and $\varepsilon(\omega)$ present polarization and electric field amplitude, respectively. The α_{a-b} represents the contribution of virtual or real one-exciton generation to α represented by the basis pair $a-b$. The μ_k and ρ_{0k} are the transition moment and the density matrix element between the ground and the k -th exciton state, respectively. N is the number of dipole units.

Since our calculation method of α is presented in detail in our previous papers [4–5], we here provide its outline. At first, we can obtain a new exciton-states model by diagonalizing the one-exciton Hamiltonian for the aggregate model, which is written by the sum of a noninteracting Hamiltonian for monomers and a dipole-dipole interaction Hamiltonian. Next, the time evolution of the exciton density matrix is performed involving the

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relaxation processes in the Markoff approximation under the irradiation of a laser field ($\omega = 3000 \text{ cm}^{-1}$ and the intensity is 10 MW/cm^2). It is noted that only the transition moments between the ground and the one-exciton states exist in the present model. The density matrix representation in the molecular aggregate basis is calculated to examine the contribution of each dipole unit. Finally, we perform the Fourier transformation of $p(t)$ and calculate α by Eq. (1). We obtain α values with and without intermolecular interaction. The difference between those α values can elucidate the intermolecular-interaction effects on α .

3. Results and discussion

The intermolecular-interaction contribution of each dipole unit in L25J and L25H to α are shown in Fig. 2. The J -aggregate-type interaction is known to reduce the transition energy, while H -aggregate-type interaction is known to enhance it. Namely, the J -aggregate-type interaction tends to enhance α , while the H -aggregate-type interaction tends to reduce it. This supports the feature that the enhancement (reduction) of J (H)-aggregate model occurs except for both-end regions (Fig. 2).

Figure 3 shows the intermolecular-interaction contribution of each dipole unit in D25 and S25 to α . It is found for S25 that the contributions in the middle region are more enhanced in the column direction, while those are

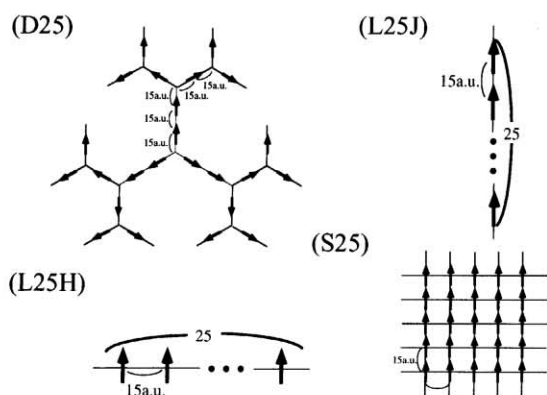


Fig. 1. Four types of molecular aggregate models: (D25) dendritic aggregate model, (L25J) J -aggregate model, (L25H) H -aggregate model and (S25) square-lattice model. Each arrow represents a dipole unit.

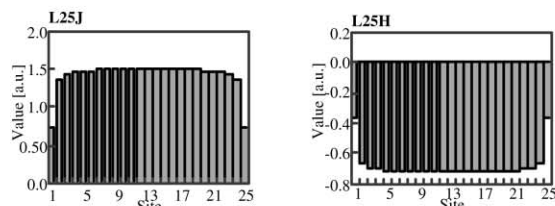


Fig. 2. Intermolecular-interaction contribution of each dipole unit to α of J -aggregate model (L25J) and H -aggregate model (L25H).

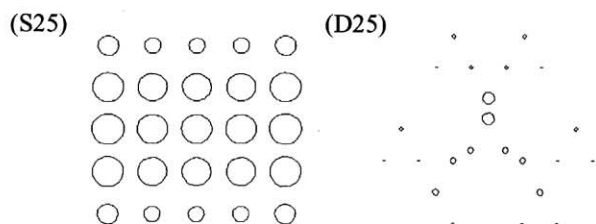


Fig. 3. Intermolecular-interaction contribution of each dipole unit to α of square-lattice model (S25) and D25-like dendritic aggregate model (D25).

somewhat more reduced in the row direction. This spatial variation in the intermolecular-interaction contribution can be well explained by considering the features observed in L25J and L25H. In contrast, the magnitude of intermolecular-interaction contributions to α of D25 enhances as going from the periphery to the core. This feature originates in the fractal structure of D25 where the each generation is well decoupled and the lengths of J -aggregate-type linear legs more enlarge in the internal generations.

4. Conclusion

The present study elucidates that the intermolecular-interaction effects on the contribution of one-exciton generation to off-resonant α for dendritic systems causes the difference in the magnitude of contribution among the generations: the contribution in the internal generations tend to be more enhanced than those in the outer generations. Such difference in the contribution to α among generations is not observed in other conventional aggregate systems, in which the spatial variation appears continuously in the whole region of the aggregate. This work suggests a novel structure-response property relation for fractal-dimensional (dendritic) systems.

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