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Exciton Migration Dynamics of D58-like Dendritic Molecular Aggregate

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We report the exciton population dynamics of D58-like dendritic molecular-aggregate model involving chromophores at the position of acetylene units of a phenylacetylene dendrimer D58. It is found that the relaxation effect is essential for exciton migration from the periphery to the core.

Keywords: phenylacetylene dendrimer; exciton migration; molecular aggregate; energy transfer; dipole-dipole interaction

INTRODUCTION

Recently, some phenylacetylene dendrimers (Fig. 1) have attracted much attention due to their remarkable light-harvesting property.[1] A series of these dendrimers is composed of many phenyl-ring and acetylene units, and is known to exhibit an efficient directional energy transfer from the periphery to the core. Such transfer relates closely to the multi-step energy structure caused by decoupling π-electron conjugation between generations at the meta branching points (phenyl rings).[1,2] In a previous paper,[3] we reported the exciton migration from the periphery to the core of D25-like dendritic molecular-aggregate model that has molecules at the position of acetylene units of a relatively small-size dendrimer D25. We here consider a larger-size aggregate, i.e., D58 (Fig. 1) -like aggregate model (Fig. 2), to examine whether similar migration is observed. The exciton dynamics of this model is investigated using coupled-dipole one exciton model.

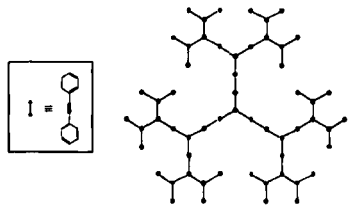

Fig.1 Example of phenylacetylene dendrimer (D58).

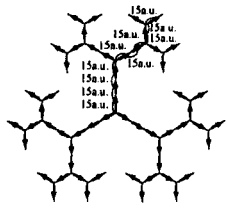

Fig.2 Dendritic aggregate model. Each arrow represents a dipole unit.

CALCULATION METHOD

Since details of our calculation method are presented in our previous paper,[3] we provide its outline. We here consider an aggregate model (Fig. 2) composed of two-state monomers, which possess transition energy, 38000 cm^{-1}, and transition moment, 5 D. The molecules are assumed to be dipoles coupled mutually by the dipole-dipole interaction. The Hamiltonian for this aggregate model is written by the sum of a noninteracting Hamiltonian for monomers and a dipole-dipole interaction Hamiltonian. By diagonalizing the Hamiltonian matrix for the aggregate model, we can obtain a new exciton-states model. We also calculate the transition moments among these states. It is noted that only the transition moments between the ground and the exciton states exist in the present model.

The time evolution of the exciton density matrix is performed using the following density matrix formalism:

$$i\hbar\frac{\partial}{\partial t}\rho(t) = [H(t), \rho(t)] - i\Gamma\rho(t), \qquad (1)$$

where $\rho(t)$ represents the density matrix element and the second term on the right-hand side of Eq. (1) represents the relaxation processes in the Markoff approximation. The total Hamiltonian $H(t)$ is expressed by the sum of the Hamiltonian for the aggregate model and the electric field. The electric field amplitude in the direction of x axis is 10 MW/cm^2. The frequency of the incident beam coincides with the transition energy between the ground and exciton states (26,27). Details of the relaxation terms in the Markoff approximation are presented in our previous paper.[3] We perform a numerically exact

calculation to solve Eq. (1) by the fourth-order Runge-Kutta method. Since we examine the contribution of each dipole unit, the density matrix representation in the molecular-aggregate basis is calculated.

RESULTS AND DISCUSSION

Transition energies and moments of the molecular aggregate-model (Fig. 2) are obtained as shown in Fig.3. It is found that there is a multi-step exciton energy states. Some states are degenerated with each other due to the symmetric structure of D58. This aggregate model is found to possess five exciton states (states (2,3) (6,7) (12,13) (21,22) and (26,27)) with significant transition moments. Some spatial distributions of exciton states are shown in Fig. 4. It is found that exciton population for higher energy states is distributed in the periphery region, while that for lower energy states is distributed in the core region.

We perform the exciton population dynamics with and without relaxation terms among exciton states after the irradiation in the direction of x axis. The three segments connected at the core are referred to as generation 1 (G_1). Also, the segment connected to G_n is referred to as G_{n+1}. Exciton population dynamics of each generation are shown in Fig. 4. Without the relaxation effect, the exciton population migration between generations is not observed. However,

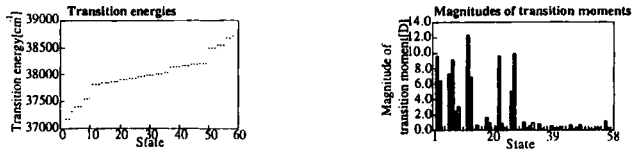

Fig.3 Transition energies and moments of the D58-like aggregate model.

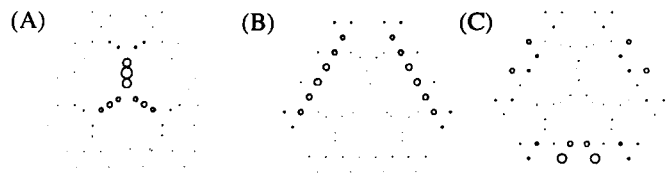

Fig.4 Spatial distribution of exciton states (A) 2,3 (B) 12,13 and (C) 26,27.

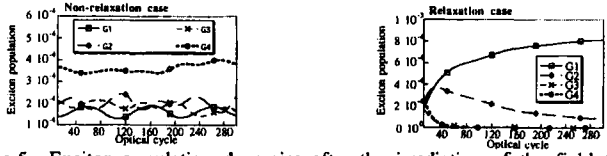

Fig.5 Exciton population dynamics after the irradiation of the field (0-10 optical cycle) with and without the relaxation terms among the ground state and the exctiton states.

including the relaxation effect, efficient exciton migration from the periphery to the core is observed (Fig. 5).

SUMMARY

In this study, we found the multi-step energy structure of D58-like dendritic molecular-aggregate model. The exciton migration from the periphery to the core is observed only in the case of including the relaxation terms. Those are similar to the features observed in the D25-like aggregate model.[3] It is concluded that larger aggregate model including relaxation effects exhibit a similar exciton migration. In order to better elucidate the structure-relaxation relations, exciton dynamics with a weak exciton-phonon coupling will be investigated at the next step.

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