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Exciton Migration Pathways in Dendritic Molecular Aggregates

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The energies and transition moments of exciton states for dendritic molecular aggregates are calculated using a model Hamiltonian involving dipole-dipole interaction. Exciton pathways are found to be remarkably influenced by the constituent monomer units.

Keywords: dendrimer; exciton; aggregate; dipole-dipole interaction

INTRODUCTION

A large molecular antenna with an ordered geometry and ordered energetics has attracted much attention because of its high light-harvesting ability [1]. For example, it has been shown that a series of dendritic structures, i.e., Bethe-lattice structure, composed of phenyl rings and acetylene units exhibit a structurally symmetry and ordered exciton funnel with a well-directed energy gradient [2]. These molecules involve the legs composed of linearly connected diphenylacetylene units and the meta-branching points (phenyl rings). It is known that the individual linear legs are electronically decoupled and the electron-hole pair (exciton) is localized within each linear leg region. These individual linear legs are known to construct multi-step energy states, which cause the directed migration of excitons from the periphery to the core. In this study, we alternatively consider molecular aggregates in which the monomer is assumed to be a dipole unit (a two-state molecular model) arranged as modeled after the above dendrimer. Firstly the transition energies and transition properties of this aggregate are

calculated by a dipole-dipole coupled model in one-exciton case. We next perform the exciton migration dynamics of this system after irradiation of laser field with relevant frequency. The time-dependent variation in the exciton population at each site is visualized and thus the migration pathways of excitons are elucidated. We also examine the effects of an introduction of a different dipole unit, e.g., a transition metal compound, on the exciton migration pathways. Finally, on the basis of the present results, we discuss a possibility of the control of exciton migration pathway by changing resonant field frequency and by introducing different monomer species.

CALCULATION METHODS AND AGGREGATE GEOMETRIES

We consider model aggregates (A) and (B) (Fig. 1) composed of two-state monomers (chromophores), which are arranged as modeled after a dendritic structure referred to as D25 [2]. The kth 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

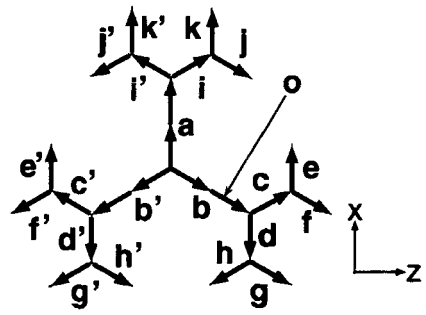

FIGURE 1 Structures of molecular aggregates (A) (composed of all the same dipole units) and (B) (involving a different dipole unit O). For aggregate (A), the transition energy and transition moment are assumed to be 38000 cm^{-1} and 5 D, respectively. The transition energy and transition moment of a different dipole unit, O, are 36000 cm^{-1} and 3 D, respectively. The intermolecular distance is assumed to be 15 a.u.

direction of applied field for this new state-model are calculated. It is noted that only the transition moment between the ground and exciton states exist in the one-exciton model.

The time evolution of a molecular aggregate model is described by the following density matrix formalism [3]:

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

where $\rho(t)$ indicates the total molecular density matrix at time t. It is noted that the relaxation term is omitted since we only investigate the exciton migration pathway. The total Hamiltonian $H(t)$ is expressed by the sum of the aggregate Hamiltonian, H_{agg}, and aggregate-field interaction, $V(t)$:

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

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. 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 $\{|\varphi^1_{i_1}\varphi^2_{i_2}\cdots\varphi^N_{i_N}\rangle\}$ at time t is also calculated.

EXCITON MIGRATION PATHWAYS IN AGGREGATES

The dendritic molecular aggregate (A) shown in Fig. 1 involves all the same dipole units. The transition energy and transition moment of the dipole unit (a two-state monomer) is assumed to be 38000 cm^{-1} and 5 D, respectively. The transition energies and the magnitude of transition moments between the ground and the one-exciton states for this aggregate is obtained as shown in Figs. 2(A-1) and 2(A-2). There are found to be some different groups of one-exciton states (See I and II shown in Fig. 2(A-1)), which include degenerate states and are close to each other in a group. The dominant transition moments are shown to exist in the one-exciton states below the monomer transition energy (38000cm^{-1}) since the *J*-aggregate-type interaction is dominant in the present system. It is expected from Fig. 2(A-1) that the individual exciton pathways exist for the exciton distributions of the one-exciton-state groups I and II, repectively. These exciton pathways are elucidated by performing dynamics (Eq. (2)) after the irradiation of the electric field with different frequencies, which are nearly resonant with the one-exciton states of groups I and II, respectively. Such dynamics is performed in the following procedure. Firstly, we perform the time-evolution of aggregate system coupled with time-dependent electric field with a frequency by using Eq. (2). Next, we search the time t_0, at which the ground state population nearly vanishes, and then turn off the external field at that time. The diagonal density matrix $\rho_{i_1,i_2,\ldots,i_N;i_1,i_2,\ldots,i_N}(t)$ in the aggregate basis (which represents exciton population) are calculated and the time-evolution of exciton population at appropriate dipole sites are investigated. We consider two types of frequencies of the external fields, which are resonant with exciton states 5 and 6 in group I and states 11 and 12 in group II, respectively. The time-evolution of exciton population (after t_0) of aggregate (A) in appropriate region for each field is shown in Figs. 3(A-I) and 3(A-II). In the case of the first field, we can detect two types of characteristic oscillations of the exciton population. Namely, it is found that the first exciton migration pathway exists between regions c(c') and d(d'), while the second pathway does between regions c(c') and i(i')-a-b(b'). In contrast, in the case of the second field, there are found to be a dominant oscillation of exciton migration between regions j(j')-k(k') and g(g')-h(h') via region e(e')-f(f') though an oscillation with a slight amplitude for the exciton distribution is also detected in region e(e')-f(f'). Namely, the second field is found to cause a half-circular exciton migration pathway over the outermost dipole units.

In the case of the dendritic aggregate (B) involving a different

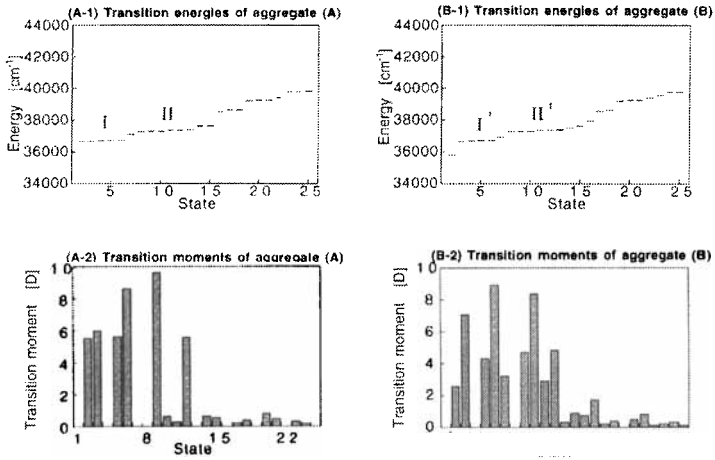

FIGURE 2 Transition energies and transition moments of aggregates (A) and (B) shown in Fig. 1.

monomer unit in leg region b, similar multi-step energy states andtransition dipole moments are obtained as shown in Figs. 2(B-1) and 2(B-2). To compare with the exciton migration in aggregate (A), we examine exciton dynamics using a field with a frequency which is nearly resonant with one-exciton states in group I' (Fig. 2(B-1)). As shown in Fig. 3(B-I'-1), the main exciton pathway is asymmetric and vanishes in the region of the different dipole unit though an existing exciton pathway (c'-d') is similar to pathway (c+c')-(d+d') observed in Fig. 3(A-I). We also found from Fig. 3(B-I'-2) that there is a faster oscillation of exciton distributions between b' and a compared to that between c' and b', in contrast to aggregate (A-I) case. These features seem to be caused by the changes in the exciton distributions in regions b and b' of the energy states in group I' of aggregate (B) due to the introduction of the different dipole unit.

SUMMARY

In this study, we elucidated exciton pathways for dendritic molecular aggregate. In this aggregate, we found two types of exciton migration pathways, one of which exists in the internal leg region, the other exists in the outermost half-circular region. These pathways are found to be generated by tuning external field frequency. Also, the introduction of a different dipole unit, e.g., transition metal compound, was found

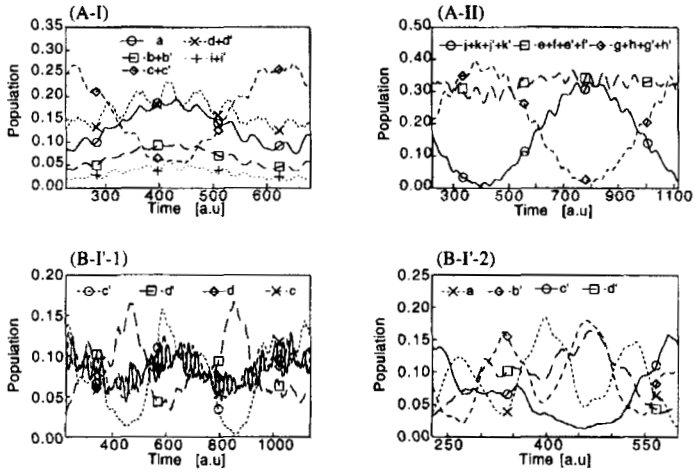

FIGURE 3 (A-I) and (A-II) show exciton population dynamics using the resonant frequency for states 5 and 6 of aggregate (A) and that using the resonant frequency for states 11 and 12 of aggregate (A), respectively. (B-I'-1) and (B-I'-2) show the exciton population dynamics using the resonant frequency for state 6 of aggregate (B). The intensity of electric field is assumed to be 10000 MW/cm^{-1}.

to cause remarkable effects on exciton migration pathways. These results suggest a possibility of controlling exciton migration pathway in such dendritic molecular aggregates by the change in the external field frequency and the chemical modification of the leg region.

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