

Optical excitations in diphenylacetylene based dendrimers studied by a coupled exciton model with off-diagonal disorder

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(Received)

Abstract

A phenomenological coupled exciton model is proposed in order to characterize optical excitations in extended dendrimers. An onsite exciton state is assigned at each phenyl rings and a nearest neighbor hopping integral which obeys the Gaussian distribution is considered between the exciton states. The decreasing optical excitation energy with respect to the dendrimer size indicates the presence of exciton funnels along the backbone of the dendrimers. Therefore, the extended dendrimers can work as artificial fractal antenna systems which capture energy of light. Dynamics of an exciton is also investigated by solving time development of a wavefunction of optical excitations. It is shown that a damping term with a certain magnitude is necessary in order that optical excitations captured at the outer edge of the supermolecule

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move to the central areas of the molecule.

PACS numbers: 36.20.Kd, 71.35.Cc, 31.50.+w, 78.66.Qn

I. Introduction

Recently, the dendrimer supermolecules with antenna structures have been investigated extensively. After capture of light at the outer edges of the molecule, generated excitons migrate along the legs of the molecular structures and carry energy obtained from light. Then, the excitons move to a certain core to localize there, or move to the center of the supermolecule in order to emit light by recombination of electrons and holes. Because energy of light is captured and the energy is transferred by excitons, the supermolecules might act as artificial molecular antenna. Therefore, the design of the molecular structures and their optical properties are quite attractive in view of scientific interests as well as their potential for technological applications.

One example of antenna supermolecules has dendrimeric structures. It is a family of molecules composed of phenyl rings and acetylene units, namely, extended dendrimers [1-5]. Their geometrical structures are illustrated in Fig. 1. Figure 1 (a) shows the diphenylacetylene with its abbreviated notation. Figure 1 (b) shows the family of extended dendrimers: D4, D10, D25, D58, and D127. The number in their names means the number of phenyl rings in the molecules. In the D4 and D10 dendrimers, each leg is composed of two single bonds and one triple bond. In D25, three central legs are made of one phenyl rings and two short legs (shown as Fig. 1 (a)). In D58, three central legs are composed of two phenyl rings and three short legs (Fig. 1 (a)). The next connecting legs via the phenyl vertex are like the central legs of D25. In D127, the three central legs are made of three phenyls and four short legs (Fig. 1 (a)). In this way, the extended dendrimers have fractal molecular structures, and the length of the central legs becomes longer as the size of the dendrimer becomes larger.

Optical experiments of the extended dendrimers [3-5] show that the optical gap decreases as the dendrimer size becomes larger. The optical spectra have features which can be understood as contributions from legs of phenylacetylene oligomers. The energy of each feature agrees with that of oligomers. The excitation energy becomes smaller as the length of the legs becomes larger. Therefore, the presence of exciton migration pathways along the legs or the backbone

of the supermolecules has been concluded.

Another example of the antenna supermolecules has structures with four zinc-containing tetraarylporphyrins linked to a central, unmetallated porphyrin through ethyne bonds [6]. They show migration characters of excitons, and are interesting as light harvesting antennas. Such alternative molecular designs, replacement of molecules at the vertexes, different structure of leg chains, and so on, have been investigated intensively. Although various molecular structures are of interests, we would like to concentrate upon optical excitation properties of the extended dendrimers in this paper because of the varieties of possible structures which will require much more theoretical efforts in future.

Theory of optical excitations in the dendrimers has not been reported so often, and for example energy transfer has been investigated by solving phenomenological probability process equations [7]. The rates of the excitation flow along the legs of the dendrimer have been introduced, and the mean passage time has been obtained theoretically.

The first purpose of this paper is to propose a phenomenological coupled exciton model and characterize optical excitations in extended dendrimers. By sample average over sets of off-diagonal disorder, we will obtain a decreasing optical excitation energy with respect to the dendrimer size, and show exciton funnels are present along the backbone of the dendrimers. The second purpose is to simulate flows of excitons by looking at time development of a wavefunction of optical excitations. We will show an importance of a damping term with a certain magnitude in order that optical excitations captured at the outer edge of the supermolecule move to the central areas of the molecule. We note that a part of this paper – characterization of the parameters for excitons – has been reported in the short communication [8].

This paper is organized as follows. In Sec. II, the coupled exciton model with off-diagonal disorder is explained. Section III is devoted to characterization of optical excitations by comparison of the theory with experiments. In Secs. IV and V, we study dynamics of exciton flow in the supermolecules. Equilibrium and nonequilibrium dynamcses are studied in Secs. IV and V, respectively. The paper is summarized in Sec. VI.

II. Formalism

In this section, we give rise to a new theoretical model composed of coupled exciton states with off-diagonal disorder. We note that the theoretical model of dipole moments [9] has been used in order to characterize optical excitations of the photosynthetic unit of purple bacteria, which is the biological analog of the dendrimeric supermolecule. In the present model, an onsite exciton state is assigned at each phenyl ring. There are two possibilities for the nearest neighbor interactions: (1) When the interactions occur by dipole-dipole couplings, the direction of the transition dipole moment is by no means parallel with the electric field of light and cannot be spatially correlated. Interaction strengths between neighboring dipole moments may vary among positions of dipole pairs. They can be looked as randomly distributed. Therefore, we assume that the nearest neighbor interactions obey the Gaussian distribution function. (2) The second candidate of the interaction between neighboring exciton states is an exciton flow characterized with the strengths $t_e t_h / \Delta_{\text{ex}}$ by perturbation, where t_e and t_h are hopping integrals of electrons and holes, Δ_{ex} is the excitation energy of the electron hole pair. We assume that the mean value of the interaction is zero and the standard deviation of the interaction J is one of theoretical parameters in the Gaussian distribution. Another theoretical parameter in the model is the site energy E which specifies the central energy position of excitons in the optical spectra. The following is our tight binding model:

$$H = E \sum_i |i\rangle\langle i| + \sum_{\langle i,j \rangle} J_{i,j} (|i\rangle\langle j| + \text{h.c.}), \quad (1)$$

where i means the i th site of the phenyl ring, $|i\rangle$ is an exciton state at the site i , the sum with $\langle i,j \rangle$ is taken over neighboring pairs of sites, and the distribution of $J_{i,j}$ is determined by the Gaussian function,

$$P(J_{i,j}) = \frac{1}{\sqrt{4\pi}J} \exp\left[-\frac{1}{2}\left(\frac{J_{i,j}}{J}\right)^2\right]. \quad (2)$$

Here, the disorder effects appear in the off-diagonal matrix elements of the hamiltonian. Such the disorder model is named as ‘‘off-diagonal’’. When the disorder effects appear in the diagonal

matrix elements, the terminology “diagonal disorder” is used. In other words, the off-diagonal disorder model which modulates couplings of bonds is called as “bond disorder”, and the diagonal disorder model which perturbs site energies is named as “site disorder”. Though detailed theoretical treatments are not the same altogether, the related exciton models have been used for the photosynthetic unit of purple bacteria [9] and the J-aggregate systems [10-12]. The diagonalization of eq. (1) gives energies of one exciton states measured from the energy of the ground state.

III. Optical absorption

The model eq. (1) is diagonalized numerically for the five types of the extended dendrimers: D4, D10, D25, D58, and D127. The lowest eigenvalue always gives the energy position of the optical absorption edge because the state with the lowest energy is always allowed for dipole transition from the ground state. This is checked by looking at the parity of the wave function for each dendrimer. In TABLE I, we show the energy of the absorption edge as a function of the parameters E and J . Here, the number of disorder samples is 10000, and this gives the well converged average value of the optical excitation energy.

Figure 2 shows one example of the comparison of the calculation with experiments for the parameters $E = 37200\text{cm}^{-1}$ and $J = 3552\text{cm}^{-1}$. We find fairly good agreement between the experiments and calculations. Two results have the trend that the lowest optical excitation energy decreases as the dendrimer size becomes larger. Therefore, it is clarified that the presence of exciton migration funnels is well described by the present coupled exciton model with off-diagonal disorder. The interaction strength J is one order of magnitudes larger than that of the purple bacteria [9], indicating the stronger contact between neighboring exciton states. When the flow of excitons occur by hopping of electrons and holes, the interaction strength is characterized as $t_e t_h / \Delta_{\text{ex}}$ by perturbation. With assuming $t_e \sim t_h \sim 0.5t$ and $\Delta_{\text{ex}} \sim 2t$ where t is the resonance integral of the π orbitals of the phenyl ring, we obtain a characteristic

magnitude: $|J| \sim 0.1t$. This quantity is also of the same order of magnitudes with the above parameter $J = 3552\text{cm}^{-1}$, because $t \sim 2\text{eV} \sim 25000\text{cm}^{-1}$. Thus, our theoretical parameter can characterize exciton flows along the legs of dendrimers very well.

The extended dendrimers are the rare example where π -conjugated electron systems are present along the acetylene based legs. In most of dendrimers (see the recent review [13] for example), the systems are composed of σ -bondings rather than π -bonds. Owing to the presence of exciton funnels composed of π -bonds, the extended dendrimers can work as an artificial fractal antenna which captures energy of light.

In the compact dendrimers (the another form of diphenylacetylene based dendrimers), the optical absorption edge less depends on the molecule size [3]. This might come from the very huge steric repulsions among neighboring legs, and therefore the mutual interactions between legs are hindered easily by geometric effects. The nearly constant absorption edge with respect to the dendrimer size indicates that values of the interaction strengths $J_{i,j}$ of the compact dendrimers are much smaller than those of the extended dendrimers when the present coupled exciton model is applied to. Such the difference of the parameter values can characterize the different dependence on the system size of the extended and compact dendrimers.

IV. Equilibrium dynamics

After the characterization of the optical absorption spectra in the previous section, we shall study exciton propagations in dendrimers by looking at time development of wavefunctions in the following two sections. We will focus on the largest dendrimer D127, hereafter. This supermolecule is of most interests among the five dendrimers.

A. Exact time development

The dynamics of an exciton which is located at the site 1 at the time $t = 0$ (see Fig. 1 (b) for the site numbers in D127) can be solved exactly. When the eigenstates $|\mu\rangle$ and their energies

ω_μ for a disorder set are obtained, the initial wavefunction $|\Psi_0\rangle$ of the exciton is expanded as:

$$|\Psi_0\rangle = \sum_{\mu} a_{\mu} |\mu\rangle. \quad (3)$$

At the time t , this wavefunction becomes

$$|\Psi\rangle = e^{-iHt} |\Psi_0\rangle \quad (4)$$

$$= \sum_{\mu,i} a_{\mu} b_{\mu,i} e^{-i\omega_{\mu}t} |i\rangle, \quad (5)$$

where $b_{\mu,i}$ is an expansion coefficient in the site representation, $|\mu\rangle = \sum_i b_{\mu,i} |i\rangle$. The probability amplitude at the site i is calculated as

$$\left| \sum_{\mu} e^{i\omega_{\mu}t} a_{\mu} b_{\mu,i} \right|^2 = \sum_{\mu} a_{\mu}^2 b_{\mu,i}^2 + \sum_{\mu \neq \nu} 2 \cos[(\omega_{\mu} - \omega_{\nu})t] a_{\mu} a_{\nu} b_{\mu,i} b_{\nu,i}. \quad (6)$$

The total energy

$$\langle \Psi | H | \Psi \rangle = \sum_{\mu} a_{\mu}^2 \omega_{\mu} \quad (7)$$

conserves, and this is checked, too.

Figure 3 shows the exact time development of probabilities at twelve sites (the site numbers are indicated for D127 in Fig. 1 (b)) of a wavefunction of the exciton. Sample average over disorder has been also performed as before. Probability amplitudes in Figs. 3 (a) and (b) are displayed in the logarithmic and linear scales, respectively. Hereafter, time is measured in the units of $1/J$. Series of plots are not labeled by the site numbers, but it is clear that all the series of plots for the sites 1, 2, ... and 12, are ordered from the top to the bottom in Fig. 3 (a). The same symbols are used for the identical sites 1-12 in Figs. 3-6.

The probability at the site 1 decreases within the time of $t = 1(1/J)$, and is nearly constant with the small oscillation at longer time. As shown clearly in Fig. 3 (b), the decrease around $t = 0$ is parabolic. The coherence of the exciton at the site 1 is lost within the time scale $1(1/J) = 1.4946$ fs. In the course of time development, the exciton tends to have more amplitudes at the site 2, 3, and so on. However, the values of the probability saturate finally, and small oscillations continue in time afterward. The saturated value at the site 1 is about 0.5, and it

never becomes smaller than that of the site 2. The probability at site 2 is larger than that at the site 3. Therefore, we find that the initial optical excitation captured at the outer edge of the dendrimer does not move into central regions of the molecule in the treatment of the equilibrium dynamics, although the time scale of 1.4946 fs seems reasonable for intramolecular optical processes in organic systems. Some kind of nonequilibrium effects would be necessary for exciton migrations to occur.

B. Numerical time development

Here, time is divided with a mesh of the width Δt , and time development of a wavefunction of an exciton is calculated numerically. The expansion $e^{-iH\Delta t} \simeq 1 - iH\Delta t + O((\Delta t)^2)$ is retained up to the first order of Δt . The results are compared with those of the exact dynamics. We need such kind of the numerical treatment for nonequilibrium dynamics that will be studied in the next section. Therefore, we perform numerical calculations of dynamics here in order to compare with the exact results.

Figure 4 shows time developments of exciton propagation calculated with the mesh $\Delta t = 0.0001J$. Sample average over disorder has been done also. Figures 4 (a) and (b) are for the short and long time dynamics, respectively. The time variations of Fig. 4 (a) are quite similar to those of Fig. 3 (a), even though the absolute magnitudes of the saturated probabilities are somewhat different due to the linearized numerical treatment. In the long time behaviors show as Fig. 4 (b), the probabilities of all the sites simply continue oscillating. The values of the probabilities tend to be larger when the site number is smaller. Such the qualitative results remain the same as those of Fig. 3. In this sense, we can also use the numerical time developing treatment when the nonequilibrium effects are considered. We note that energy of the system is kept constant while the simulation is continued within time of Fig. 3 (b). Numerical errors do not seem developing as far as we look at the total energy.

V. Nonequilibrium dynamics

In this section, a positive damping factor Γ is introduced as $J_{i,j} \rightarrow J_{i,j} - i\Gamma$ in the hamiltonian H , and time developments are investigated numerically with the time mesh $\Delta t = 0.0001J$. In a toy model of an exciton dimer with the coupling $J_0 - i\Gamma$ ($J_0 > 0$), the two eigenvalues are $\pm(J_0 - i\Gamma)$. In the course of time developments, there are two factors, $e^{-iJ_0t - \Gamma t}$ and $e^{iJ_0t + \Gamma t}$. They mean that the probability of the wavefunction of the higher energy state decreases and the energy of the system moves to the lower energy state. The introduction of a finite Γ takes into account of damping of energy as in this toy model. Such the nonequilibrium dynamics will generate motion of excitons from the outer edge to central areas in the dendrimers. The purpose of this section is to demonstrate the exciton flow in D127.

The similar method of including a damping term has been used in the optical model of particle scattering to the target nucleus [14]. The optical model has been proposed in 1950's, and has been known in scattering problems. The imaginary damping term is added to the hamiltonian. And, this term describes well the effect that the incident particle is absorbed by the target with decreasing energy.

Development of a wavefunction of the exciton is simulated numerically for the two damping factors: $\Gamma = 0.1J$ and $0.5J$. The results are summarized in Figs. 5 and 6, respectively. Figs. 5 (a) and 6 (a) show behaviors in the short time scale $0 \leq t \leq 4(1/J)$. The decay of the exciton becomes a little bit faster than that of Fig. 4 (a), though the main trend remain similarly. The dramatic differences are seen in the long time behaviors. In Fig. 5 (b) for $\Gamma = 0.1J$, the probability at the site 1 becomes smaller than that of site 2 at the time larger than $40(1/J)$. The exciton at the outer edge begins motion in the direction of the molecular center due to the damping effects. However, the probability at the site 3 does not become larger than that of the site 1, even though the probabilities at the sites with large numbers are enhanced from those of $\Gamma = 0$ apparently. Figure 6 (b) displays the case of the stronger damping $\Gamma = 0.5J$. The probability at the site 1 becomes smaller than that of the site 2 at time about $3(1/J)$. It even

becomes smaller than that of the site 12 (the center of the dendrimer) at the time $\sim 40(1/J)$. Furthermore, the probabilities of the site 2 and 3 become smaller than those of the sites 4 and 5 which are located in the course of the optical path. We thus find that *the migration of an exciton really occurs owing to the damping effects*.

Figure 7 shows the variations of the total energy of the system D127 as functions of time. The plots indicate the total energy after the mean energy E is subtracted. The squares, circles, and triangles are for $\Gamma = 0$ (Fig. 4), $0.1J$ (Fig. 5), and $0.5J$ (Fig. 6), respectively. The energy of the $\Gamma = 0$ case is constant as we described before. However, in the cases of the finite Γ , the energy first decreases near $t = 0$ and then increases, and become decreasing again. The time, where the energy begins decreasing secondly of the case $\Gamma = 0.5J$, is about $40(1/J)$. This is near to the time when the two curves for the sites 1 and 12 cross in Fig. 6 (b). The crossover between the states located at the outer edge and the states in the central area of the supermolecule *really occurs* in the time development. Such the crossover to the lower energy states is actually brought about by the damping effects of the term Γ . This theoretical fact demonstrates the necessity of the finite damping term in order that the dendrimer can act as a molecular antenna of energy from light.

VI. Summary

We have proposed the coupled exciton model with off-diagonal disorder in order to characterize optical excitations in the extended dendrimers. The decreasing optical excitation energy with respect to the dendrimer size indicates the presence of exciton pathways along the backbone of the dendrimers. The theoretical parameters are reasonable in view of the electron and hole hopping processes, and also of the exciton decay time scale.

Next, dynamics of an exciton has been investigated by solving time development of a wavefunction of optical excitations. We have shown that a damping term with a certain magnitude is necessary in order that optical excitations captured at the outer edge of the supermolecule

move to the central areas of the molecule. It has been discussed that the damping term gives rise to the crossover from states located at the outer edge to the states in the central area of the supermolecule in the time development.

Acknowledgements

Useful discussion with the members of Condensed Matter Theory Group (<http://www.etl.go.jp/~theory/>), Electrotechnical Laboratory is acknowledged. Numerical calculations have been performed on the DEC AlphaServer of Research Information Processing System Center (RIPS), Agency of Industrial Science and Technology (AIST), Japan.

References

- [1] Z. Xu and J. S. Moore, *Acta Polym.* **45**, 83 (1994).
- [2] C. Devadoss, P. Bharathi, and J. S. Moore, *J. Am. Chem. Soc.* **118**, 9635 (1996).
- [3] R. Kopelman, M. Shortreed, Z. Y. Shi, W. Tan, Z. Xu, J. S. Moore, A. Bar-Haim, and J. Klafter, *Phys. Rev. Lett.* **78**, 1239 (1997).
- [4] M. R. Shortreed, S. F. Swallen, Z. Y. Shi, W. Tan, Z. Xu, C. Devadoss, J. S. Moore, and R. Kopelman, *J. Phys. Chem.* **101**, 6318 (1997).
- [5] S. F. Swallen, Z. Y. Shi, W. Tan, Z. Xu, J. S. Moore, and R. Kopelman, *J. Lumin.* **76&77**, 193 (1998).
- [6] R. W. Wagner, T. E. Johnson, and J. S. Lindsey, *J. Am. Chem. Soc.* **118**, 11166 (1996).
- [7] A. Bar-Haim and J. S. Klafter, *J. Lumin.* **76&77**, 197 (1998).
- [8] K. Harigaya, *Phys. Chem. Chem. Phys.* **1**, 1687 (1999).
- [9] T. Ritz, X. Hu, A. Damjanović, and K. Schulten, *J. Lumin.* **76&77**, 310 (1998).
- [10] F. C. Spano, J. R. Kuklinski, and S. Mukamel, *Phys. Rev. Lett.* **65**, 211 (1990).
- [11] F. C. Spano, J. R. Kuklinski, and S. Mukamel, *J. Chem. Phys.* **94**, 7534 (1991).
- [12] T. Kato, F. Sasaki, S. Abe, and S. Kobayashi, *Chem. Phys.* **230**, 209 (1998).
- [13] “Dendrimers”, ed. F. Vögtle (Springer, Berlin, 1998).
- [14] L. D. Landau and E. M. Lifshitz, “Quantum Mechanics, 3rd ed.” (Pergamon Press, Oxford, 1977), p. 610.

TABLE I. The energy of the lowest optical excitation.

Dendrimer	Absorption edge
D4	$E - 1.6037J$
D10	$E - 2.3346J$
D25	$E - 2.8078J$
D58	$E - 3.1588J$
D127	$E - 3.4338J$