

Dynamics simulation of a π -conjugated light-harvesting dendrimer

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 365242

(<http://iopscience.iop.org/0953-8984/19/36/365242>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 04:38

Please note that [terms and conditions apply](#).

Dynamics simulation of a π -conjugated light-harvesting dendrimer

Yasunobu Kodama, Soh Ishii and Kaoru Ohno

Department of Physics, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Received 16 June 2007, in final form 17 June 2007

Published 24 August 2007

Online at stacks.iop.org/JPhysCM/19/365242

Abstract

Carrying out a semi-classical Ehrenfest dynamics simulation based on the time-dependent density functional theory, we investigate the light-harvesting property of a π -conjugated dendrimer, star-shaped stilbenoid phthalocyanine (SSS1Pc) with oligo (*p*-phenylenevinylene) peripheries and show that an electron and a hole transfer from the periphery to the core through a π -conjugated network when an electron is selectively excited in the periphery. The one-way electron and hole transfer occurs more easily in dendrimers with a planar structure than in those with steric hindrance because π -conjugation is well maintained in the planar structure. The present results explain recent experiments.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Dendrimers are special organic molecules with dendritic structures on the nanometer scale. Some types of dendrimer, namely the so-called light-harvesting dendrimers, have attracted considerable interest because the optical energy absorbed in the periphery is transferred to the core, and a significant amount of energy can be concentrated at the core [1, 2]. This light-harvesting property would be useful for realizing molecular-based devices such as low-threshold lasers [3], light frequency converters [4], optical switches [5–7], and biomimetic systems for photosynthesis [8–10]. Despite this high level of interest, the mechanism of the light-harvesting mechanism has not been understood completely, and no first-principles dynamics simulation has been performed so far on this subject. Historically, the Förster mechanism [11], which is based on the long-range dipole–dipole interaction between molecules, is well known for explaining the exciton energy transfer; however, it cannot explain the fact that the increase in the core photoluminescence (PL) is significantly faster than the decay of the periphery PL in π -conjugated light-harvesting dendrimers [12, 13].

In our previous study, we performed a semi-classical Ehrenfest dynamics simulation based on the local density approximation of the time-dependent density functional theory and

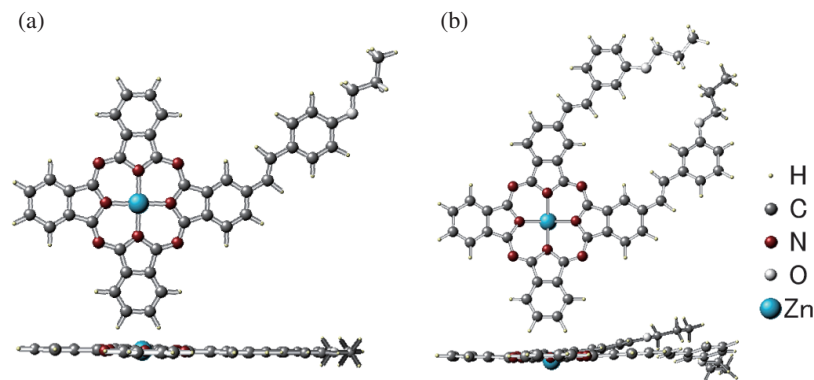


Figure 1. Structure of (a) SSS1Pc-1 and (b) SSS1Pc-2. In both (a) and (b), the upper figures show the front view and the lower figures show the side view. The structure of SSS1Pc-2 (b) is three-dimensional due to steric hindrance between the peripheries.

showed that a model nano-composite, a methane–lithium system, exhibits a light-harvesting property [14]. As demonstrated in that paper, the mechanism of the one-way electron and hole transfer is analogous to the mechanism of a p–n junction in semiconductors and is described as follows: if the energy gap in the periphery is larger than and enclosing the energy gap in the core, an electron excited in the periphery automatically moves toward the lower empty level in the core, and a hole created in the periphery automatically moves toward the higher occupied level in the core.

In the present paper, we extend our previous approach to a more realistic π -conjugated light-harvesting dendrimer. For the π -conjugated light-harvesting dendrimer, we consider here a star-shaped stilbenoid phthalocyanine (SSS1Pc) composed of a zinc phthalocyanine (ZnPc) core and oligo (*p*-phenylenevinylene) (OPV1) peripheries [15], which was experimentally studied by Akai *et al* [12, 13] and quite recently by Ishida *et al* [16]. According to their analysis, it has been found that the rate of energy transfer is low (high) at low (high) temperatures. They suggested that dynamic propagation of the electron–hole excitation from the periphery to the core is mediated by torsional vibrations of the phenyl group at the vinylene joint in the periphery.

In order to explore this interesting behavior theoretically, we consider a SSS1Pc with one periphery, which we call SSS1Pc-1, and a SSS1Pc with two peripheries, which we call SSS1Pc-2. The optimized structure of SSS1Pc-1 obtained by using the Gaussian 03 package [17] is two-dimensional (figure 1(a)) and that of SSS1Pc-2 is three-dimensional (figure 1(b)) induced by the steric hindrance between the peripheries. Below, we will show that energy transfer is suppressed by the steric hindrance between the peripheries. This explains the experimental behavior that the efficiency of the electron and hole transfer increases with temperature, because the periphery and the core come more frequently into the same plane instantaneously due to torsional vibration.

In this work, we perform a semi-classical Ehrenfest dynamics simulation, in which the time-dependent local density approximation (TDLDA), i.e. the adiabatic LDA [18] of the time-dependent density functional theory (TDDFT) for electrons [19], is used together with the Newtonian equation of motion for nuclei. The method is essentially the same as that adopted in our previous work [14].

2. Methodology

The time-dependent Kohn–Sham (TDKS) equation within the TDLDA [20] is given by

$$i\hbar(\partial/\partial t)\psi_j(\mathbf{r}, t) = H(t)\psi_j(\mathbf{r}, t), \quad (1)$$

where $H(t)$ is the electronic part of the Hamiltonian and $\psi_j(\mathbf{r}, t)$ denotes the wavepacket of the j th level. We use the spectral method to integrate accurately the TDKS equation with respect to time [21, 14]. In this method, we use the eigenstates and eigenvalues that satisfy

$$H(t)\phi_k(\mathbf{r}, t) = \epsilon_k(t)\phi_k(\mathbf{r}, t). \quad (2)$$

The wavepackets $\psi_j(\mathbf{r}, t)$ are expanded in terms of the eigenstates as

$$\psi_j(\mathbf{r}, t) = \sum_k c_{jk}(t)\phi_k(\mathbf{r}, t). \quad (3)$$

Within the time interval Δt in which the Hamiltonian is almost unchanged, we can integrate the TDKS equation as

$$\psi_j(\mathbf{r}, t + \Delta t) = \sum_k \exp[-i\epsilon_k(t)\Delta t]c_{jk}(t)\phi_k(\mathbf{r}, t). \quad (4)$$

Here, we use the all-electron mixed basis approach [21, 14] in which $\psi_j(\mathbf{r}, t)$ and $\phi_k(\mathbf{r}, t)$ are expressed as linear combinations of both (numerical) atomic orbitals (AOs) and plane waves (PWs). For SSS1Pc-1, we use 302 (374 for SSS1Pc-2) AOs and 24405 PWs corresponding to a cutoff energy of 7.0 Ryd. In contrast to the usual LCAO (linear combination of atomic orbitals) approaches, this basis can almost span the entire space of the system, as required in the spectral method.

For the dynamics, we perform the time-dependent simulation of the electron and hole transfer from the periphery to the core of SSS1Pc-1 and SSS1Pc-2 after exciting an electron from the P(periphery)-HOMO (highest occupied molecular orbital) level to the P(periphery)-LUMO (lowest unoccupied molecular orbital) level. The initial electronic states are self-consistently determined on the adiabatic surface of the optically excited state, and therefore include the exciton configuration and the related long-range interaction beyond linear response [22]. The TDKS equation for electrons coupled with the Newtonian equation of motion for nuclei is integrated stepwise with the basic time step $\Delta t = 0.25$ fs. The total energy including the electronic part of the energy, the potential energy between nuclei, and the kinetic energy of nuclei is conserved in this simulation.

3. Results

3.1. Ground state

The calculated energy levels and wavefunctions at the ground state of SSS1Pc-2 are shown in figures 2 and 3, respectively. Here, it is convenient to distinguish between the levels associated with the core (C) and those associated with the periphery (P), because the wavefunctions in P and C are almost separated in space, as shown in figure 3. The wavefunctions of the HOMO level and the doubly degenerate LUMO, LUMO + 1 levels are spread over the C region. Therefore, we refer to the HOMO level as the C-HOMO level, and the LUMO, LUMO + 1 levels as C-LUMO levels. Similarly, the wavefunctions of the almost doubly degenerate HOMO-2, HOMO-1 levels and the doubly degenerate LUMO + 2, LUMO + 3 levels are spread only over P, and they are termed P-HOMO and P-LUMO levels, respectively. The ground-state electronic structure of SSS1Pc-1 is similar to that of SSS1Pc-2. The only difference between SSS1Pc-1 and SSS1Pc-2 is that both P-HOMO and P-LUMO levels are

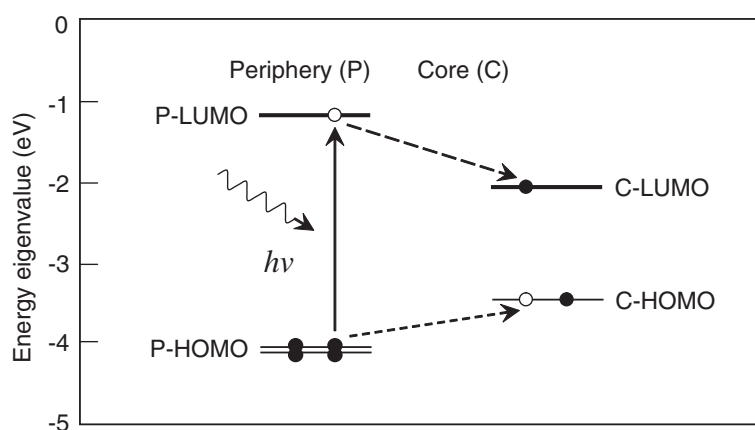


Figure 2. The energy eigenvalues of SSS1Pc-2. Black and white circles denote electrons and holes, respectively. First, an electron is excited from the (almost doubly degenerate) P-HOMO levels to the (doubly degenerate) P-LUMO levels on the periphery side (solid line with an arrow). Then, the electron is transferred from the P-LUMO levels to the (doubly degenerate) C-LUMO levels (dashed line with an arrow) and the hole is transferred from the P-HOMO levels to the C-HOMO level (dotted line with an arrow).

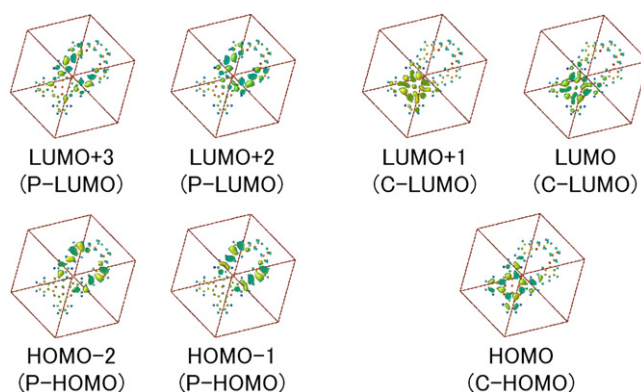


Figure 3. Amplitude of the wavefunction at the ground state of SSS1Pc-2. The cubes are the unit cells. For each level, the points at the center and the upper-right side show the core and the periphery, respectively. Gray and black areas denote the positive and negative values of the wavefunction, respectively.

nondegenerate in SSS1Pc-1 and doubly degenerate in SSS1Pc-2. This is because SSS1Pc-1 has one periphery, while SSS1Pc-2 has two peripheries of the same molecule. When the periphery absorbs light, an electron is excited from the P-HOMO level to the P-LUMO level. The calculated energy gaps are consistent with the experimental optical absorption energies (~ 1.7 eV for the ZnPc core and ~ 3.0 eV for the OPV1 peripheries) [12, 13]. Since the stability of the electron (hole) increases with decreasing (increasing) energy, the one-way energy transfer occurs from the periphery to the core.

3.2. Dynamics

If we fix the position of nuclei during simulation, we find that nothing happens in the electronic states. This is because the initial electronic states are the steady-state solutions of the TDKS

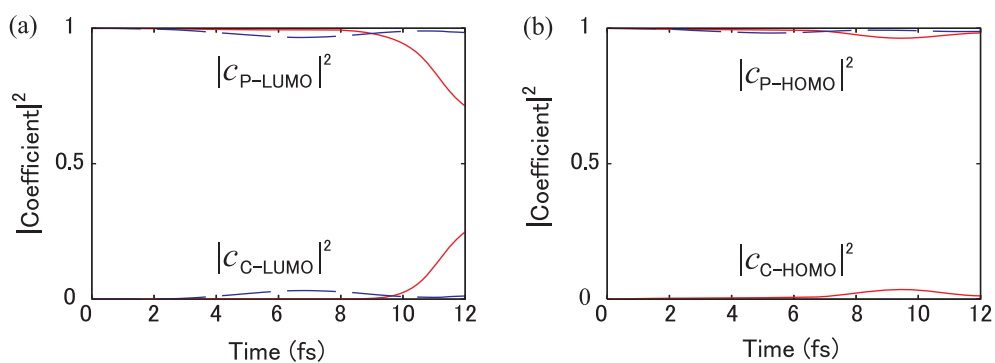


Figure 4. Time evolution of the absolute squared coefficients for the P- and C-eigenstates in the wavepacket of (a) the P-LUMO level and (b) the P-HOMO level. The upper (lower) curves correspond to the P-LUMO (C-LUMO) eigenstates for (a) and the P-HOMO (C-HOMO) eigenstates for (b). The solid and dashed curves denote SSS1Pc-1 and SSS1Pc-2, respectively.

equation. On the other hand, if we relax the constraint of the atomic positions, we see in the wavepacket of the P-LUMO level, $\psi_{\text{P-LUMO}}$, that the excited electron transfers from the periphery to the core. Similarly, in the wavepacket of the P-HOMO level, $\psi_{\text{P-HOMO}}$, we see that the hole created by the electron excitation transfers from the periphery to the core. The results are as follows.

The wavepacket of the P-LUMO level, $\psi_{\text{P-LUMO}}$, coincides with the pure eigenstate, $\phi_{\text{P-LUMO}}$, at $t = 0$ and, at later times, becomes a linear combination of the eigenstates of the P-LUMO and C-LUMO levels as $c_{\text{P-LUMO}}\phi_{\text{P-LUMO}} + c_{\text{C-LUMO}}\phi_{\text{C-LUMO}}$. Figure 4(a) represents the time evolution of the absolute square of the coefficients of the two eigenstates, $|c_{\text{P-LUMO}}|^2$ and $|c_{\text{C-LUMO}}|^2$, in the components of the P-LUMO wavepackets of SSS1Pc-1 (solid curves) and SSS1Pc-2 (dashed curves). The two eigenstates are mixed in the wavepackets of SSS1Pc-1 and SSS1Pc-2 after 9 fs and around 4–10 fs, respectively. This implies that there exists a net probability of the electron transfer from the P-LUMO level to the C-LUMO level. The mixing of the states in SSS1Pc-1 is considerably larger than that in SSS1Pc-2, reflecting that the transfer probability is higher in SSS1Pc-1 than in SSS1Pc-2. This characteristic can be attributed to the steric hindrance in SSS1Pc-2.

Similarly, the wavepacket of the P-HOMO level, $\psi_{\text{P-HOMO}}$, coincides with $\phi_{\text{P-HOMO}}$ at $t = 0$ and, at later times, becomes a linear combination of the eigenstates of the P-HOMO and C-HOMO levels as $c_{\text{P-HOMO}}\phi_{\text{P-HOMO}} + c_{\text{C-HOMO}}\phi_{\text{C-HOMO}}$. Figure 4(b) shows the time evolution of the absolute square of the coefficients of the two eigenstates, $|c_{\text{P-HOMO}}|^2$ and $|c_{\text{C-HOMO}}|^2$, in the components of the P-HOMO wavepackets of SSS1Pc-1 (solid curves) and SSS1Pc-2 (dashed curves). In the case of SSS1Pc-1, the two eigenstates are slightly mixed in the wavepacket around 8–12 fs. However, in the case of SSS1Pc-2, the mixing is negligibly small. This implies that the steric hindrance in SSS1Pc-2 interrupts the hole transfer.

4. Discussion

From these results, we find that the one-way electron and hole transfer occurs separately from the periphery to the core of SSS1Pc. For both SSS1Pc-1 and SSS1Pc-2, the net probability of the electron transfer is larger than that of the hole transfer. This is because the overlap between the wavefunctions of two molecules is larger in the LUMOs than in the HOMOs. The probability of the electron and hole transfer is higher in SSS1Pc-1 than in SSS1Pc-2.

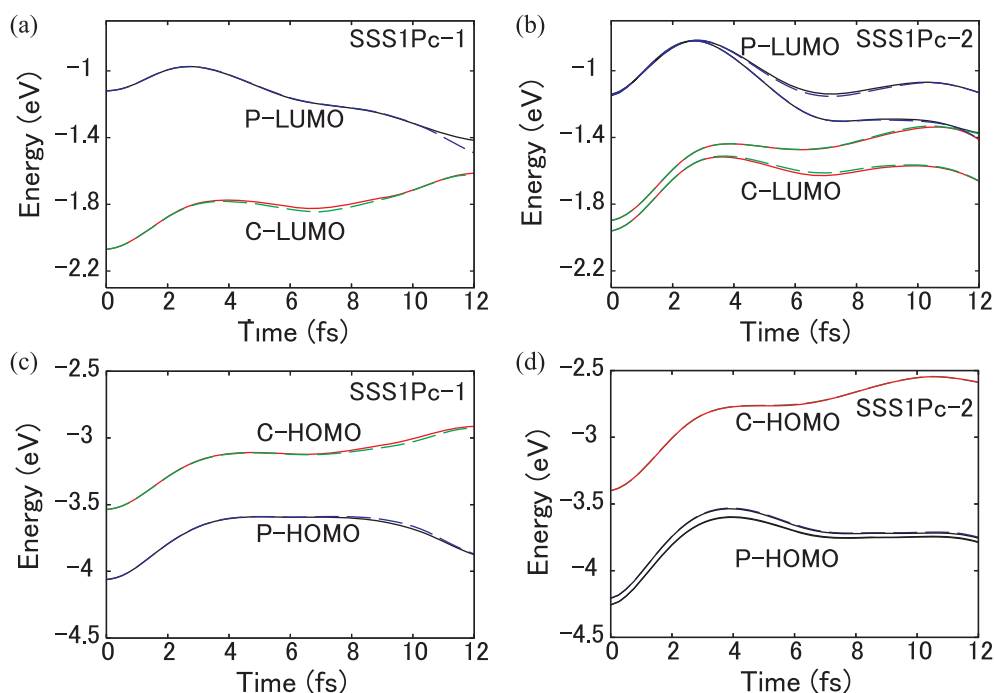


Figure 5. Time evolution of the energy eigenvalues (solid curves) and energy expectation values (dashed curves): (a) and (b) show the P-LUMO (black curves) and C-LUMO (gray curves) levels of SSS1Pc-1 and SSS1Pc-2, respectively; (c) and (d) show the P-HOMO (black curves) and C-HOMO (gray curves) levels of SSS1Pc-1 and SSS1Pc-2, respectively.

This result strongly suggests that the electron and hole transfer is caused by the π -conjugation and suppressed by the steric hindrance of molecular structure. That is, the efficiency of the energy transfer depends on the steric hindrance of molecular structure in accordance with the experiments [12, 13, 16], in a sense that the electron and hole transfer is caused by π -conjugation and cannot be explained by the Förster mechanism [11].

Figures 5(a) and (b) show the energy eigenvalues (solid curves) and the energy expectation values (dashed curves) of the P-LUMO and C-LUMO levels of SSS1Pc-1 and SSS1Pc-2, respectively. First of all, we note that the energy eigenvalues and the energy expectation values change smoothly and that ΔE is ~ 0.1 eV at most, which suggests that there is no rapid change in the electronic density and that the present TDLDA treatment is valid. Next, we notice that the net probability of the electron transfer increases with the difference between the energy eigenvalues and the energy expectation values, $\Delta E = |\varepsilon_k - \langle \psi_k | H | \psi_k \rangle|$. Moreover, when the eigenvalues of the P-LUMO (black curves) and C-LUMO (gray curves) levels approach each other, the net probability of the electron transfer increases. These behaviors are well understood by the mixing of the states when the electron transfer takes place from the periphery to the core. On the other hand, although the difference between the eigenvalues of the P-LUMO and C-LUMO levels of SSS1Pc-2 becomes less than that of SSS1Pc-1, the net probability of the electron transfer in SSS1Pc-1 is larger than that in SSS1Pc-2. Obviously, this is due to the effect of the steric hindrance in SSS1Pc-2.

Similarly, figures 5(c) and (d) show the energy eigenvalues and energy expectation values of the P-HOMO and C-HOMO levels of SSS1Pc-1 and SSS1Pc-2, respectively. In this case also, the net probability of the hole transfer increases as the difference ΔE between the energy

eigenvalues and the energy expectation values increases. Again, these figures show that the energy eigenvalues and the energy expectation values change smoothly and that ΔE is ~ 0.1 eV at most, and therefore there is no rapid change in the electronic density and that the present TDLDA treatment is valid.

During the simulation, the average distance between hydrogen atoms and carbon atoms increases very slightly by 0.072 Å in SSS1Pc-1 and by 0.094 Å in SSS1Pc-2 in 12 fs. Within this short time interval, the structures of SSS1Pc-1 and SSS1Pc-2 do not vibrate, but each atom moves unidirectionally. Thus, we observed clearly that such a very small atomic motion can induce the electron and hole transfer. However, for longer timescales, the atomic motion becomes large and the semi-classical Ehrenfest dynamics breaks down. Therefore, a more elaborated simulation such as surface hopping [23, 24] would be required in the future study.

We also performed a similar simulation for a phenylene-based dendrimer (phDG2) first synthesized by Kimura *et al* [25]. Although we do not show the details here, we also found that the electron and hole transfers occur from the periphery to the core [26].

5. Concluding remarks

In summary, by performing the first-principles molecular dynamics simulation using the TDKS equation on the basis of the TDDFT, we have investigated the light-harvesting mechanism of SSS1Pc, when an electron is selectively excited in the periphery. We found that the one-way electron and hole transfer occurs from the periphery to the core through a π -conjugated network during very slight motion of the molecules. Moreover, by comparing two structures without and with steric hindrance of these dendrimers (SSS1Pc-1 and 2), we found that the electron and hole transfer occurs more easily in dendrimers with a planar structure than in those with steric hindrance, because π -conjugation is well maintained in the planar structure. The present results explain well the recent experiment conducted by Akai *et al* [12, 13] and Ishida *et al* [16].

Acknowledgments

We thank professors Jun Takeda, Ichiro Akai, and Mutsumi Kimura for introducing us to this interesting subject and for valuable discussions. This work was supported by the Grant-in-Aid for Scientific Research B (no. 17310067) and Scientific Research on Priority Areas (nos 18036005 and 19019005) from the Japan Society for the Promotion of Science and from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

- [1] Devadoss C, Bharathi P and Moore J S 1996 *J. Am. Chem. Soc.* **118** 9635
- [2] Nakano M, Takahata M, Yamada S, Kishi R, Nitta T and Yamaguchi K 2004 *J. Chem. Phys.* **120** 2359
- [3] Milas S M, Ye J Y, Norris T B, Balogh L P, Baker J R Jr, Hollman K W, Emelianov S and O'Donnell M 2003 *Appl. Phys. Lett.* **82** 994
- [4] Serin J M, Brousmiche D W and Fréchet J M J 2002 *J. Am. Chem. Soc.* **124** 11848
- [5] Archut A, Azzellini G C, Balzani V, Cola L D and Vögtle F 1998 *J. Am. Chem. Soc.* **120** 12187
- [6] Shin H K, Kim J M, Kwon Y S, Park E and Kim C 2002 *Opt. Mater.* **21** 389
- [7] Jung K H, Jung S B, Shin H K, Kim C and Kwon Y S 2005 *Synth. Met.* **152** 285
- [8] Kopelman R, Shortreed M, Shi Z Y, Tan W, Xu Z, Moore J S, Bar-Haim A and Klafter J 1997 *Phys. Rev. Lett.* **78** 1239
- [9] Raychaudhuri S, Shapir Y, Chernyak V and Mukamel S 2000 *Phys. Rev. Lett.* **85** 282
- [10] Gust D, Moore T A and Moore A L 2001 *Acc. Chem. Res.* **34** 40

- [11] Förster T 1948 *Ann. Phys.* **2** 55
- [12] Akai I, Nakao H, Kanemoto K, Karasawa T, Hashimoto H and Kimura M 2005 *J. Lumin.* **112** 449
- [13] Akai I, Okada A, Kanemoto K, Karasawa T, Hashimoto H and Kimura M 2006 *J. Lumin.* **119/120** 283
- [14] Kodama Y and Ohno K 2006 *J. Chem. Phys.* **125** 054501
- [15] Kimura M, Narikawa H, Ohta K, Hanabusa K, Shirai H and Kobayashi N 2002 *Chem. Mater.* **14** 2711
- [16] Ishida A, Makishima Y, Okada A, Akai I, Kanemoto K, Karawasa T, Kimura M and Takeda J 2007 *Proc. 16th Int. Conf. on Dynamical Processes in Excited States of Solids (DPC 07, Segovia, Spain, 2007)*
- [17] GAUSSIAN 03, Gaussian Inc., Wallingford, CT 2004
- [18] Vignale G and Kohn W 1996 *Phys. Rev. Lett.* **77** 2037
- [19] Runge E and Gross E K U 1984 *Phys. Rev. Lett.* **52** 997
- [20] Marques M A L, Ullrich C A, Nogueira F, Rubio A, Burke K and Gross E K U 2006 *Time-Dependent Density Functional Theory* (Berlin: Springer)
- [21] Sawada T and Ohno K 2005 *Chem. Phys. Lett.* **405** 234
- [22] Ohno K 2007 *Mater. Trans.* **48** 649
- [23] Craig C F, Duncan W R and Prezhdo O V 2005 *Phys. Rev. Lett.* **95** 163001
- [24] Tapavicza E, Tavernelli I and Rothlisberger U 2007 *Phys. Rev. Lett.* **98** 023001
- [25] Kimura M, Shiba T, Yamazaki M, Hanabusa K, Shirai H and Kobayashi N 2001 *J. Am. Chem. Soc.* **123** 5636
- [26] Kodama Y, Ishii S and Ohno K 2007 unpublished