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We investigate a rapid energy transfer (ET) process and its temperature dependence in a star-shaped stilbenoid phthalocyanine (SSS1Pc) dendrimer having π-conjugated light-harvesting (LH) antennas. In SSS1Pc, intense core-photoluminescence is observed under selective excitation on the LH-antenna as a result of the highly efficient ET from the LH-antenna. Pump-probe experiments show that ET occurs rapidly with a rising time constant (~ 250 fs). To understand such rapid ET, we employ a simplified ET model through a π-conjugated network between the LH-antenna and the core that takes into account the steric hindrance between the LH-antenna subunits. Our model reveals that the highly efficient ET at room temperature in SSS1Pc takes place through the π-conjugated network mediated by a thermally activated torsional vibration of the aromatic ring subgroup in the LH-antenna.

1 Introduction In light-harvesting (LH) dendrimers, light energy absorbed in LH-antennas transfers highly efficiently to central chromophore (core) at room temperature (RT) [1, 2]. In the case of hyper-branched dendrimers, aromatic rings in the LH-antenna are connected to each other by a long ether-type subgroup ($-OCH_2-$). Because of the isolation of the aromatic rings by the long and π un-conjugated subgroup, an absorption band of the LH-antennas appears in the ultraviolet light region (> 4 eV) [3]. In order to expand the spectral region of the LH-antenna to the visible light region, we have to choose LH-antenna systems having more extended π-conjugating molecular orbitals (MOs).

On the other hand, through measurements of the temperature dependence of photoluminescence (PL) in LH-dendrimers, we have demonstrated that the freezing of molecular vibrations quenches energy transfer (ET) at temperatures below ~ 100 K [4,5]. This clearly implies that the

highly efficient ET at RT is realized with the assistance of thermally activated molecular vibrations.

In this study, we employ π-conjugated oligo-phenylene-vinylene (OPV) subunits for the LH-antenna and investigate ET processes in a dendrimer having such OPV-antennas. The ultrafast dynamics of ET from the photo-excited antenna to the core is measured with ~ 100 fs time resolution. We discuss the ultrafast dynamics and the temperature dependence of the ET process in connection with relevant molecular vibrations.

2 Experimental Figure 1 shows the chemical structures of a star-shaped stilbenoid phthalocyanine dendrimer (SSS1Pc [6]) and of its component molecules. Zinc phthalocyanine (ZnPc) and OPV1 is the core unit and the antenna component of SSS1Pc, respectively. For comparison with SSS1Pc, we also prepared a solution (Mix 1) containing these component molecules. To measure ultrafast
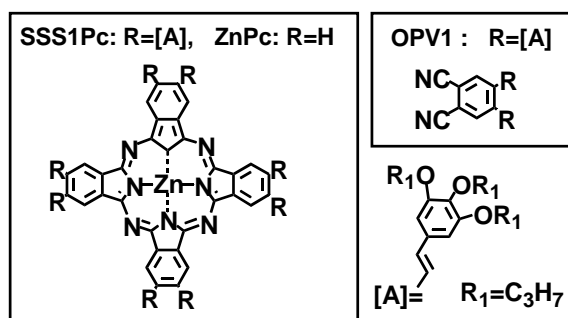
Figure 1 Chemical structures of SSS1Pc and its component molecules ZnPc, OPV1.
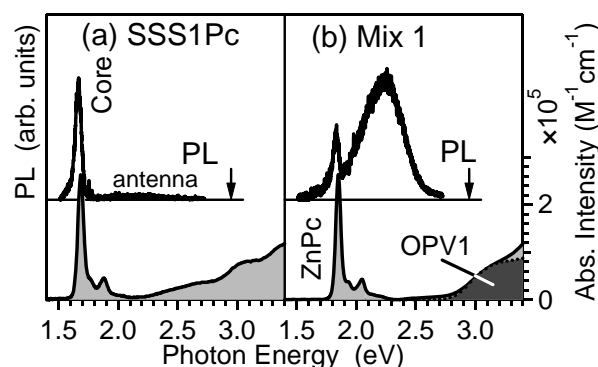

Figure 2 Optical spectra of SSS1Pc (a) and Mix1 (b). Grayish and solid line spectra denote the absorption and PL spectra, respectively. The dark grayish spectrum represents the absorption of the OPV1. Downward arrows indicate the excited energy position for each PL spectrum.

ET dynamics, we employed real-time pump-probe imaging spectroscopy implemented on a single shot basis [7]. A WinMOPAC package based on MOPAC97 was used with the PM3 Hamiltonian [8] for quantum chemical simulations.

3 Results As shown in Figure 1, aromatic rings in antenna subunits ([A] in Figure 1) are connected to the core by a π-conjugated vinylene joint. This π-conjugation bridges the π-MOs of the aromatic rings between the LH-antenna subunit and the phthalocyanine core. Owing to the direct interactions between these π-MOs, a highly efficient ET occurs in the SSS1Pc dendrimer under the selective excitation of the LH-antenna [9].

The light-gray spectra in Figure 2 are the absorption spectra of SSS1Pc and Mix1 solutions. Q absorption bands of the phthalocyanine core appear at the lowest energy side of the entire absorption. The LH-antenna gives rise to a broad absorption band at energies above 2.5 eV and has sufficient LH-facilities in the visible light region (< 500 nm). The dark-gray spectrum in Mix 1 (Figure (b)) is the absorption spectrum of the antenna component molecule OPV1. In the energy region from 2.8 to 3.2 eV, the absorption intensity of OPV1 is much stronger than that of ZnPc. This fact guarantees that the LH-antenna subunit in SSS1Pc can be excited selectively in this energy region.

By such selective excitation on the LH-antenna, the SSS1Pc dendrimer yields a significantly different PL spectrum from that of Mix 1, as shown in Figures 2 (a) and (b). In SSS1Pc (Figure (a)), an intense core-PL band appears instead of a antenna-PL band. This transposition of the dominative PL is a clear evidence of highly efficient energy transfer from the LH-antenna to the core in the SSS1Pc dendrimer. From a quantitative analysis of PL quantum yields of the core-PL in ZnPc and SSS1Pc, a high quantum efficiency of 51 % has been obtained at RT.

Very recently, Y. Kodama *et al.* applied time-dependent density functional theory to model molecules of SSS1Pc and showed that one-way ET from the LH-antenna to the core occurs through the π-conjugated network between the

LH-antenna and the core [10]. According to their simulations on the completely planar model molecule SSS1Pc-1, which only has one [A]-subgroup in SSS1Pc, wave packets of excited electrons and holes in the LH-antenna propagate ($\sim$10 fs) to the core ultra-rapidly.

On the other hand, our ultrafast pump-probe experiments reveal an ET having a slightly delayed rising component. Gray traces in Figures 3 (a) and (b) denote temporal responses of absorption bleaching on the Q-band in ZnPc and SSS1Pc, respectively. The dotted line in Figure (a) shows the temporal profile of the pumping pulse. The Q-band bleaching of ZnPc rises sharply in the temporal profile of the pumping pulse, as shown in Figure (a). In contrast, a rising component is found in the temporal response of the Q-band bleaching in SSS1Pc, as shown in Figure (b). As a guide for the eye, the rising behavior of ZnPc is also shown (see dashed line in Figure (b)). On the basis of a deconvolution analysis, the rising time constant $\tau_{\text{SSS1Pc}}^{\text{rise}}$ of SSS1Pc is estimated to be $\sim$ 250 fs. The fitted result is plotted by open circles in Figure (b).

4 Discussion Although a slightly delayed rising behavior is found in the ET in SSS1Pc, this rising time constant is much shorter than the decay time constant $\tau_{\text{ant.PL}}^{\text{decay}}$ ($\sim$400 ps) of the antenna-PL in SSS1Pc. As shown in the PL spectra in Figure 2, the antenna-PL (2.0$\sim$2.6 eV) in SSS1Pc and Mix 1 appears with a large Stokes shift. This fact implies that the antenna-PL occurs after deep vibrational relaxations in the LH-antenna. By considering rapid ET in advance of such deep vibrational relaxations, one can understand the disagreement between $\tau_{\text{SSS1Pc}}^{\text{rise}}$ and $\tau_{\text{ant.PL}}^{\text{decay}}$ [9].

On the other hand, the rising behavior of the ET observed in SSS1Pc (Figure 3 (b)) can presumably be explained by considering the molecular structure of SSS1Pc.
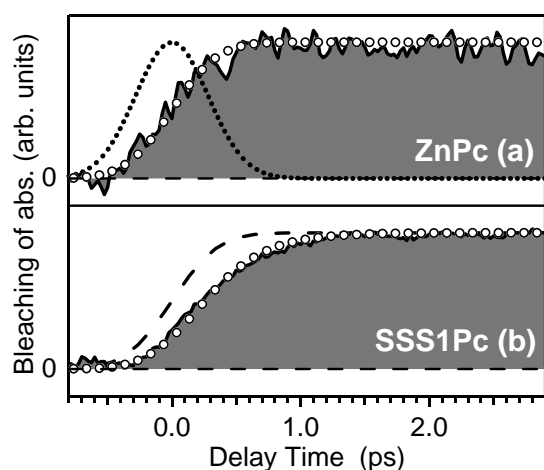
Figure 3 Ultrafast responses of the bleaching of the Q-absorption in ZnPc (a) and SSS1Pc (b). The dotted line in (a) shows the time profile of the instrumental response function. Fitted results with respective rising components are plotted with open circles. The dashed line in (b) indicates the fitted result in ZnPc (open circles in (a)) as a guide for the eye.

Although the aromatic rings have a rather rigid structure, the aromatic ring subgroup in the LH-antenna subunit ([A] in Figure 1) is allowed to tilt at the bond alternating vinylene joint. In order to determine the tilting of the aromatic rings, we obtained an optimized structure (Figure 4 (a)) of the LH-antenna subunit (OPV1). As seen in Figure 4 (a), in response to the steric hindrance between the terminating subgroups (-OR$_1$ in Figure 1), the aromatic rings in the LH-antenna are tilted against the plane of the aromatic ring in the phthalocyanine core. Such degradation of the co-planarity between the aromatic rings of the LH-antenna and the phthalocyanine core is expected to suppress ET processes mediated by the π-conjugation network between them and lead to the rising behavior of ET in SSS1Pc.

In addition, by considering molecular vibrations of the aromatic rings in the LH-antenna, we can understand appropriately the temperature dependence of ET in SSS1Pc. A normal coordinate analysis of the optimized structure yields the torsional vibration of the aromatic rings in the LH-antenna ([A] in Figure 1) as the lowest normal vibrations mode (~ 8 cm^{-1}). In this mode, the aromatic rings in the LH-antenna vibrate at the vinylene joint changing the tilt angle against the plane of the aromatic ring in the phthalocyanine core. At higher temperature, the co-planarity between the aromatic ring in the LH-antenna and the core changes dynamically due to the sufficiently high thermal activation of this torsional vibration. To characterize the temperature dependence of ET in SSS1Pc, we employ a simplified model taking into account such torsional vibration.

Figure 4 (b) schematizes the adiabatic potentials of the ground and excited state in the LH-antenna subunit. In this
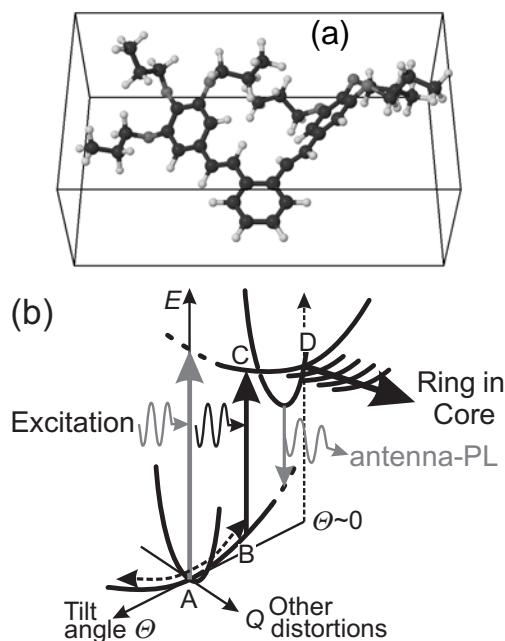

Figure 4 (a) Optimized structure of the LH-antenna sub unit in SSS1Pc. (b) Schematic diagram of the adiabatic potentials of the ground and excited states considering the torsional vibration (tilt angle Θ) and other normal mode vibrations (Q).

diagram, two coordinates are introduced for the portrayal of the adiabatic potentials. The first is the tilt angle Θ between the aromatic rings in the LH-antenna and the core. The curvature of the adiabatic potential along Θ is gentle reflecting the low frequency of the torsional vibration. The second is the configuration coordinate Q, which represents all other normal coordinates vibrating with high frequencies.

In the ground state, a potential minimum (point A in Figure 4 (b)) is located at a large tilt angle Θ due to the steric hindrance between the antenna subunits as mentioned before. However, in the excited states (based on π^*-MOs), the potential minimum is different. The quasi-equilibrium point on Θ in the excited state is thought to be located near $\Theta \sim 0$ (point D in Figure (b)) [11], because, in the excited state, the bond alternation at the vinylene joint is partially released owing to the extension of the π^*-MOs [11]. As a result of the relaxation along Θ on the adiabatic potential, a planar structure ($\Theta \sim 0$, D in Figure (b)) is more feasible in the excited state. It is expected that in such a planar structure, a highly efficient ET would occur by the π-conjugated network [10] as indicated by the thick solid arrow in Figure (b).

By considering thermal behavior in the adiabatic potential of the ground state, we can explain qualitatively the temperature dependence of the ET quantum efficiency β_{ET} in SSS1Pc. The solid line in Figure 5 (a) indicates the adiabatic potential of the torsional vibration (the low-

est mode: 8 cm^{-1}) obtained through calculations of the self-consistent field (SCF) energies of respective vibrating structures. The horizontal dotted line represents the thermal energy at RT. Vibrating Θ is plotted with open circles in Figure (a) as a function of the normal coordinate. At low temperature ~ 0 K, Θ fluctuates in the vicinity of the equilibrium position with small amplitude. In this case, the co-planarity between the aromatic rings in the LH-antenna and the phthalocyanine core is not so good because of the tilting of the aromatic rings in the LH-antenna due to the steric hindrance, and selective excitation of the LH-antenna is only available from point A in Figure 4 (b). The Franck Condon state just above point A is far from the point where $\Theta \sim 0$ (point D).
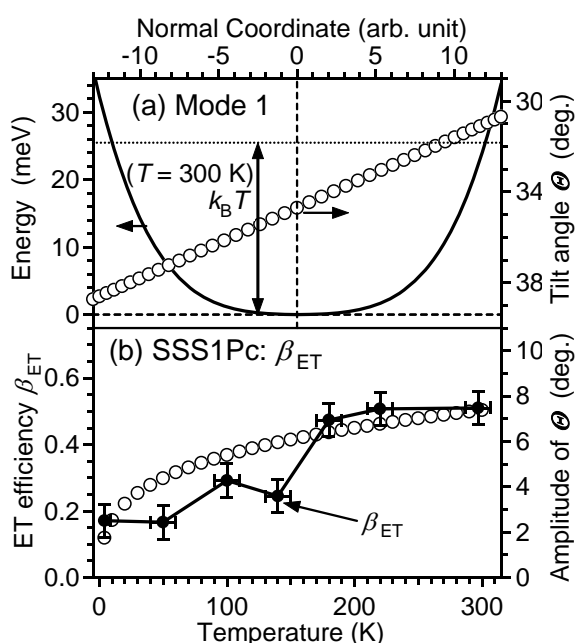

Figure 5 (a) An adiabatic potential (solid line) and the tilt angle Θ (open circles) as functions of the normal coordinate. (b) Temperature dependence of the amplitude of Θ (open circles) and the ET quantum efficiency β_{ET} (closed circles) [4].

On the other hand, at higher temperatures, the amplitude of Θ increases as shown by the open circles in Figure 5 (b), and the probability of higher co-planarity (smaller Θ) increases during the torsional vibration. Thus, excitation from points with a smaller Θ (point B in Figure 4 (b)) is enabled at higher temperatures. After excitation from point B, the Franck Condon state (point C in Figure 4 (b)) relaxes toward the intermediate bottom with $\Theta \sim 0$ (point D), and the excited state can ride on the ET channel to the core effectively. It is expected that during the relaxation along Θ, relaxation due to the other distortions toward the bottom of the adiabatic potentials occurs as well. However, at higher temperatures, since it is possible to excite the Franck Con-

don state near $\Theta \sim 0$, ET is expected to occur satisfactorily in advance of other distortions. As seen in Figure 5 (b), the ET quantum efficiency β_{ET} has a similar temperature dependence [4] as the amplitude of the vibrating Θ. This good agreement implies that the rapid and highly efficient ET at RT is mediated by thermal activated torsional vibrations.

5 Summary We have investigated ET processes in SSS1Pc dendrimers having π-conjugated LH-antenna. Under selective excitation on the LH-antenna, an intense core-PL band appears because of the highly efficient ET from the LH-antenna to the core. In the transient absorption spectra, a rapid rising of the bleaching of the core-absorption is observed with a rising time constant of ~ 250 fs. To understand both such rapid ET and the temperature dependence of the ET, we have considered a simplified model that takes into account the steric hindrance between the LH-antenna subunits and the torsional vibration of the aromatic rings in the LH-antenna. On the basis of the thermal behavior of the torsional vibration in the ground state, it is concluded that the highly efficient ET at RT is realized through the π-conjugated network mediated by the thermally activated torsional vibration.

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