# Dexter Type Energy Transfer in *Meta*-Linked Branching Dendrimers

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We investigated rapid energy transfer (ET) processes in dendrimers having *meta*-linked branching light harvesting antennas. It was found that, at room temperature (RT), the rapid ET occurs efficiently from the antennas to the core and gives rise to intense core-PL bands under the selective excitation on the antenna. However, the ET efficiency impairs at lower temperatures than ~100 K.

For understanding these experimental results, we analyzed molecular vibrations and molecular orbitals of a simple model molecule. From these analyses, it was demonstrated that the torsional vibration of the entire antenna subunit is excited sufficiently at RT and the rapid ET in phDG$n$ dendrimer is realized via the $\pi^*$-conjugated network mediated by thermal activation of this torsional vibration.

## §1.  Introduction

Light-harvesting (LH) dendrimers have attracted much interest because they exhibit highly efficient energy transfer (ET) from LH antennas to cores.[1] In large hyper-branched dendrimers, aromatic rings in the LH antenna are connected to each other by $\pi$-unconjugated spacer subunits. Owing to the isolation of the aromatic rings by these spacer subunits, the ET processes have been simplified to a Förster mechanism.[2,3]

Recently, it has been found that ET occurs rapidly prior to achieving quasi-equilibrium in the photoexcited state of the LH antenna in a star-shaped stilbenoid phthalocyanine dendrimer (SSS$n$Pc).[4] In addition, it has been also clarified that the ET quantum efficiency improves at temperatures higher than $\sim$ 100 K. These results imply that highly efficient ET occurs at higher temperatures through the $\pi$-conjugated network mediated by the thermally activated torsional vibration of the LH-antenna subunit.

In this paper, we investigate the ET process in phenylene-based dendrimers (phDG$n$, $n = 1, 2.5$)[5] having *meta*-linked branching LH-antenna and demonstrate that the ET process is analogous to that of SSS$n$Pc dendrimers. In phDG$n$, the ET occurs more rapidly than the case of the Förster type ET. The ET efficiency degrades at lower tempratures than ~100 K. For understanding these results, the ET mechanisms are discussed on the basis of the quantum chemical simulations.

## §2.  Experimental

Figure 1 indicates chemical structures of the phenylene-based dendrimers phDG$n$ ($n = 1, 2.5$).[5] Subunits Ant$n$ ($n = 1, 2.5$) are LH-antennas for these dendrimers. A subunit Ant1-1 is an antenna for a model molecule phDG1-1 discussed in Section 4. Ant$n$ ($n = 1, 2.5$) depicted in Fig. 1 are component molecules of antenna subunits, in which the bonding sites are terminated trimethylsilane. In optical measurements, these molecules were diluted in anhydrous tetrahydrofuran (THF) to concentrations in the range $10^{-5} \sim 10^{-6}$ M. In the steady-state photoluminescence (PL) experiments, samples were excited with the frequency-doubler output from an optical parametric oscillator pumped by the third harmonic generation of a pulsed Nd:YAG laser system. For the time-resolved PL measurements, the second harmonic output from an optical parametric amplifier (OPA) pumped by a Ti:sapphire regenerative amplifier system was used for the selective excitation of the antenna subunits. The fundamental output of the OPA was also used for the direct excitation of the core subunit. For investigation of the temperature dependence, a sealed quartz tube filled with the sample solution was prepared. The freezing point of THF is about 165 K. The MOPAC2009[6] was employed for quantum chemical calculations by using the PM6 Hamiltonian.[7] Molecular orbitals were visualized with the Jmol[8] software.
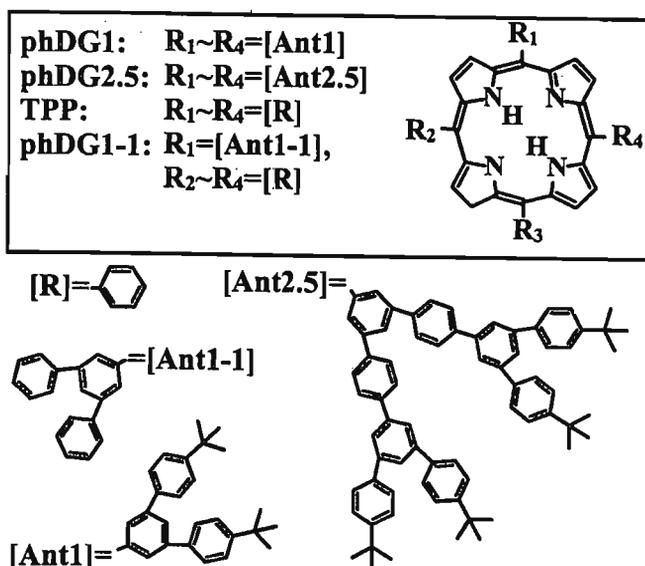


Fig. 1.  Chemical structures of phDG$n$ ($n =$1,2.5) dendrimers. [Ant1-1] is an LH antenna subunit in a model molecule (phDG1-1) discussed in Section 4.

## §3.  Results

### 3.1.  *Rapid energy transfer*

Figure 2 indicates optical spectra of the phDG$n$ dendrimers. In the porphyrin core, optical transitions from $\pi$- to $\pi^*$-MOs give rise to a weak Q- and an intense Soret-absorption band in the energy region below 3.3 eV. On the other hand, the broad absorption bands above 3.7 eV can be assigned to the optical transitions from $\pi$- to $\pi^*$-MOs in antenna subunits, because the antenna component molecules AnG$n$ also provide the same bands displayed with broken lines in insets of Fig. 2, where the absorption intensities of AnG$n$ are indicated in the four times enlarged scale for comparison.
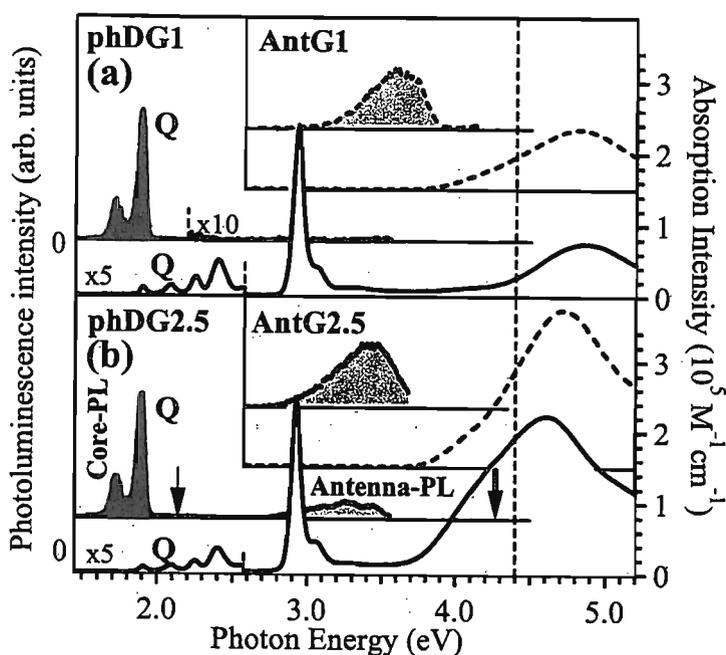


Fig. 2.  Optical spectra of the phDG$n$ dendrimers and the antenna component molecules AntG$n$ at room temperature. The vertical broken line indicates the exciting energy position for the steady-state PL measurements. The exciting energy positions for the time-resolved PL measurements (see Fig. 3) are marked by downward arrows in (b).

By using an exciting light of 4.4 eV (vertical broken line in Fig. 2), we can excite the antenna subunits in each dendrimer. Under such selective excitation, intense antenna-PL bands appear in AnG$n$ as displayed with gray spectra in insets of Fig. 2. By contrast, in phDG$n$, intense core-PL bands (black spectra) are observed dominantly instead of the antenna-PL owing to highly efficient ET from the photo-excited antenna.

From the temporal response of the core- and antenna-PL intensities, we can confirm that the highly efficient ET process occurs rapidly prior to achieving quasi-
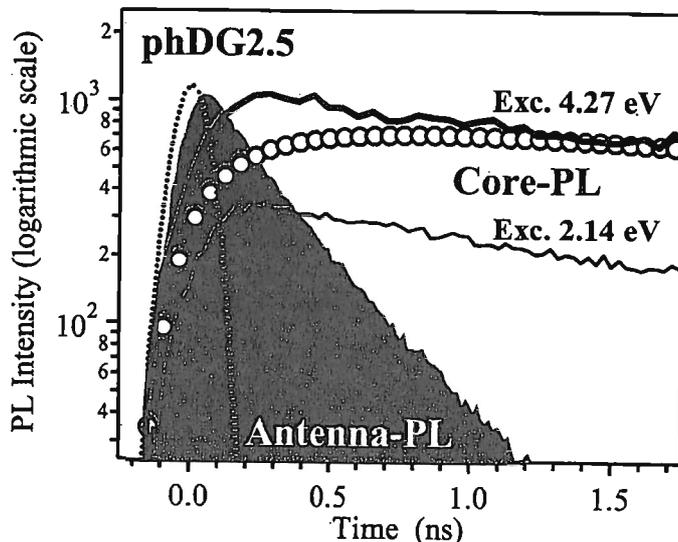
Fig. 3. Temporal profiles of the PL intensities of phDG2.5 dendrimer. The gray profile and solid
curves indicate those of antenna-PL and core-PL, respectively. The dotted curve around 0 ns
means the temporal profile of the exciting laser pulse.

equilibrium in the photoexcited state of the LH antenna. The thick solid curve in
Fig. 3 indicates the result for phDG2.5 with selective excitation of the LH antenna
(4.27 eV: thick downward arrow in Fig. 2 (b)). The gray profile denotes the temporal
profile of the antenna-PL intensity under the same exciting condition. The open
circles show a simulation result obtained by deconvolution analysis by assuming that
the rising time constant for the acceptor state (core) for the ET is equivalent to the
decay time constant of the energy donor state (LH antenna: gray profile). However,
the core-PL intensity rises more rapidly than this simulation result, as Fig. 3 shows.
In addition, the same rising response is observed under the direct excitation of the
core (2.14 eV: thin downward arrow in Fig. 2 (b)) as displayed by the thin solid
curve in Fig. 3. Such rapid rising of the ET is commonly observed in the temporal
profiles of the core-PL intensities for phDG1. These results clearly demonstrate that
the rising time for ET in phDG$n$ dendrimers is less than the limited time resolution
($\sim 50$ ps) and is much faster than the decay time constant of the PL of the antennas.

### 3.2. *Temperature dependence*

Although the aromatic rings in the antenna and the porphyrin core have rigid
structures, the adjoining bonds among them have a great flexibility for the internal
molecular vibration. In a $\pi$-conjugated LH dendrimer, we have reported that the
quantum efficiency of the rapid ET increases with heating from 4 K to $\sim 200$ K[4]
and the thermally activated torsional vibration of the antenna subunit mediates the
highly efficient rapid ET at room temperature (RT).

In phDG$n$ dendrimers, a similar temperature dependence of the ET efficiency
is observed. For investigation of the temperature dependence of the ET efficiency,
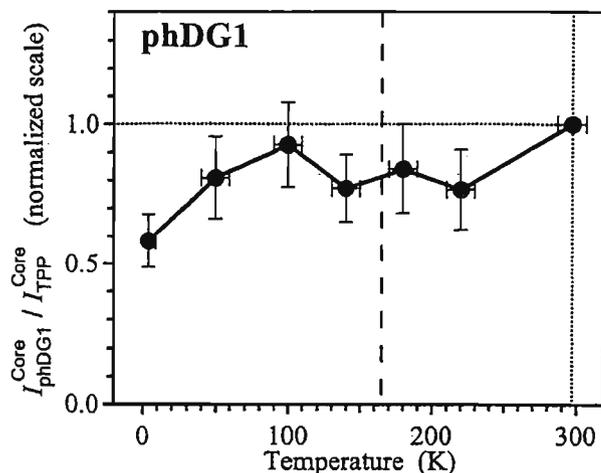
Fig. 4. Temperature dependence of the core-PL intensity ratio $I_{\text{phDG1}}^{\text{Core}}/I_{\text{TPP}}^{\text{Core}}$.

we measured the temperature dependence of the core-PL intensity $I_{\text{TPP}}^{\text{Core}}$ of the core-component molecule (TPP: tetraphenylporphyrin) and the core-PL intensity $I_{\text{phDG1}}^{\text{Core}}$ of the selectively excited phDG1 on the antenna. The ratios of $I_{\text{phDG1}}^{\text{Core}}$ to $I_{\text{TPP}}^{\text{Core}}$ are plotted as a function of temperature by closed circles in Fig. 4, where the values are normalized with that at RT. As Fig. 4 clearly shows, the ratio $I_{\text{phDG1}}^{\text{Core}}/I_{\text{TPP}}^{\text{Core}}$ decreases at lower temperatures than 140 K. This result clearly demonstrates that the rapid ET in phDG1 degrades at lower temperatures, and suggests that the thermal activation of molecular vibrations with low frequencies mediate the highly efficient ET at higher temperatures than 140 K.

## §4. Discussion

### 4.1. *Energy diagram of optimized structure*

To discuss the rapid ET and its temperature dependence in phDG1, we employ a simple model molecule phDG1-1 and analyze it using the MOPAC2009 software. Although phDG1-1 only has one antenna subunit as seen in Fig. 1, one can evaluate the steric structure and the molecular vibration of the antenna subunit.

Figure 5 shows an energy diagram from HOMO−4 to LUMO+4 states of the optimized structure for phDG1-1. The molecular orbitals from HOMO-1 to LUMO+1 are localized within the porphyrin ring and can be assigned as the $\pi$- and $\pi^*$-MOs of the porphyrin core as described in Ref. 9). On the other hand, $\pi$- and $\pi^*$-MOs of the antenna subunit are assigned as the HOMO−2 $\sim$ −3 and LUMO+3 $\sim$ +4, respectively, because their MOs are localized within the antenna subunit as shown in Fig. 5. However, it should be noted that another $\pi^*$-MO (LUMO+2) of the porphyrin ring is located nearby the $\pi^*$-MOs (LUMO+3 $\sim$ +4) of the antenna subunit (quasi-degeneracy) as shown in Fig. 5.
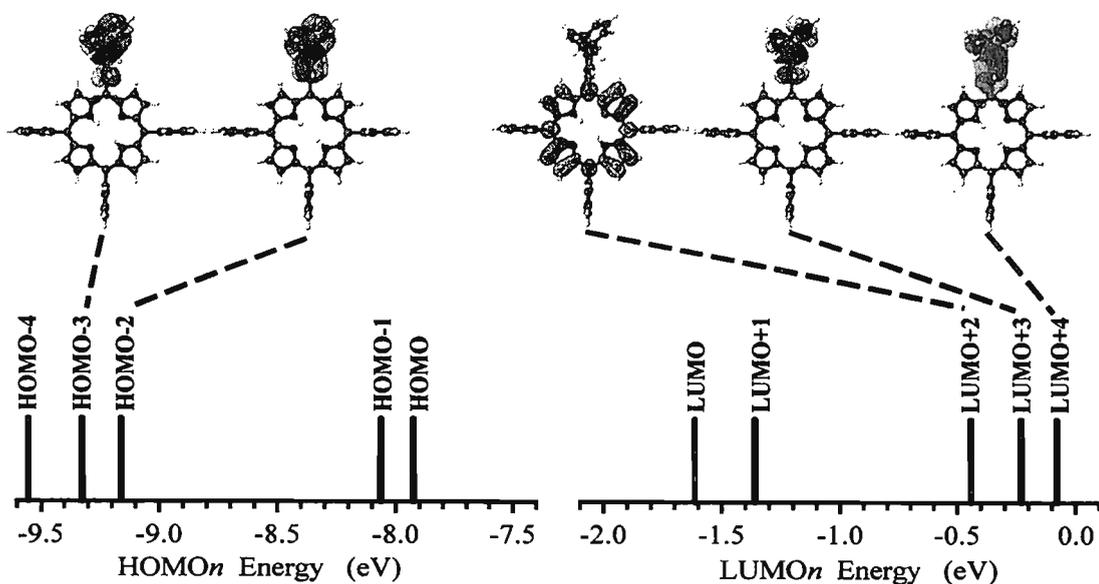
Fig. 5. Energy diagram and molecular orbitals of a simple model molecule phDG1-1 (see Fig. 1).

## 4.2. *Vibrational analysis*

On account of this quasi-degeneracy of these $\pi^*$-MOs, one can expect that effective mixing between these $\pi^*$-MOs occurs during molecular vibrations due to the change of steric structure.

From the vibrational mode analyses in phDG1-1, we found that the torsional vibration of the entire antenna subunit causes such mixing. Figure 6 shows the result. Since this torsional vibration has rather low frequency ($14.7 \text{ cm}^{-1} = k_B T$ at $T = 21$ K), the torsional vibration is sufficiently activated at higher temperatures than $\sim 140$ K. The solid curve in Fig. 6 (a) shows the adiabatic potential for this torsional vibration. At the energy minimum, the co-planarity between the porphyrin core and the first ring (the aromatic ring adjoining to the porphyrin core) in antenna is quite low ($\theta \sim 82°$). However, at RT, the dihedral angle $\theta$ changes obviously in the wide range from 92° to 73° as shown with the broken line in Fig. 6 (a), where the thermal energy at RT is indicted by the horizontal dotted line.

The renovation of the co-planarity between the planes of the porphyrin and the first ring at smaller dihedral angles ($\theta \sim 73°$) induces an effective interaction between the $\pi^*$-MOs of the core and antenna. Figures 6 (b) and 6 (c) demonstrate the energy changes of the LUMO+2 $\sim$ +3 and the variation of the molecular orbital for LUMO+2 during the torsional vibration. In Fig. 6 (b), one can recognize an anti-crossing like behavior between LUMO+2 ($\pi^*$-MO in porphyrin) and LUMO+3 ($\pi^*$-MO of antenna) on account of the interaction. Furthermore, at smaller dihedral angle ($\theta \sim 73°$) in Fig. 6 (c), one can also find that the LUMO+2 extends to the antenna subunit. Such extension allows the short-range interaction by the spatial overlapping of these $\pi^*$-MOs and guarantees the rapid ET from the antenna to the core through the $\pi^*$-network between them. The temperature dependence of the
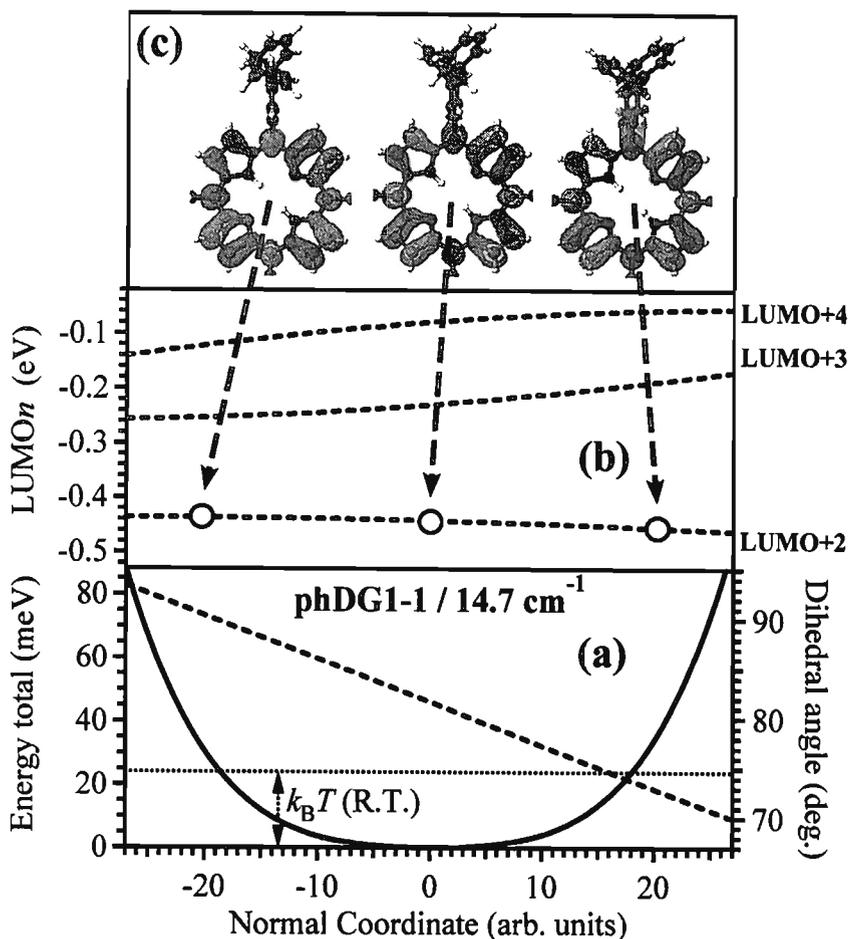
Fig. 6.   (a) Solid curve: adiabatic potential of the torsional vibration of the entire antenna subunit in phDG1-1, broken line: dihedral angle $\theta$ between the planes of the porphyrin and the aromatic ring (the first ring) adjoining to the porphyrin core. (b) Changes of the energies of the LUMO+2 $\sim$ +4 states. (c) Variation of the molecular orbital of LUMO+2 during the torsional vibration.

rapid ET efficiency in Fig. 4 can also be understood from these consideration. At low temperature, the low co-planarity between the porphyrin core and the antenna inhibits the rapid ET from the photo-excited antenna. In contrast, it is expected that the sufficiently activated torsional vibration mediates the highly efficient and rapid ET through the $\pi^*$-network at higher temperatures than $\sim$ 21 K ($=$ 14.7 cm$^{-1}$).

## §5.   Summary

We have investigated the ET process in the phDG$n$ dendrimers having *meta*-linked branching LH-antenna and have discussed the ET mechanism.

In phDG$n$, intense core-PL bands appear under the selective excitation of the antennas due to the highly efficient ET from the antennas to the core. From the rapid

rising of the core-PL intensity under such selective excitation, it is found that a rapid ET occurs from the antennas prior to thermal equilibrium being achieved for the photoexcited state in the LH antennas. On the basis of the temperature dependence of the core-PL intensities of the core component molecule and the phDG1 dendrimer, the temperature dependence of the ET efficiency is evaluated qualitatively, and it is demonstrated that the rapid ET in phDG1 is strongly suppressed by further cooling below $\sim$ 140 K. To explain both the rapid rising behaviour and the temperature dependence of ET, we have analyzed the torsional vibration and the molecular orbitals on the basis of quantum chemistry. From these analyses, it is demonstrated that the torsional vibration of the entire antenna subunit is excited sufficiently at higher temperatures than $\sim$ 20 K and the renovation of the co-planarity between the core- and antenna-planes by this torsional vibration allows the short-range interaction between their $\pi^*$-MOs. Consequently, it is expected that the highly efficient and rapid ET in phDG$n$ dendrimer is realized via the $\pi^*$-conjugated network mediated by thermally activated torsional vibration.

## Acknowledgements

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