

Direct Observation of the Intramolecular Triplet–Triplet Energy Transfer in Poly(aryl ether) Dendrimers

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A series of benzophenone (BP) and naphthalene (NA) labeled poly(aryl ether) dendrimers (BP-Gn-NA), generations 1–4, were synthesized, and their photophysical properties were examined. Flash photolysis demonstrates that the triplet energy in BP-Gn-NA can be transferred from the peripheral BP chromophores to the core NA group with the efficiencies of ca. 0.97, 0.96, 0.88, and 0.54 and with the rate constants of 1.4×10^8 , 1.2×10^8 , 9.5×10^7 , and 1.3×10^7 s⁻¹ at room temperature for generations 1–4, respectively. The transient absorption spectra of BP-Gn-NA show clearly the formation of the triplet NA absorption along with the decay of the triplet BP one with an isosbestic point at 475 nm, which gives direct evidence of the triplet energy transfer from the periphery BP chromophores to the core NA group. The phosphorescence of the NA group attached to the focal point was observed when the periphery BP chromophores were selectively irradiated in BP-G1-NA at 77 K. The triplet energy transfer occurs at 77 K with the efficiencies of 1.0, 0.16, 0.17, and 0.21 for generations 1–4, respectively. The intramolecular triplet energy transfer is proposed to proceed mainly via a through space mechanism.

Introduction

Studies on the natural photosynthetic systems revealed that the structure of a photosynthetic unit is a central reaction center surrounded by light-harvesting complexes.¹ The remarkable character of the photosynthetic system is that the energy of any photon absorbed by antenna complexes is transferred to the reaction center with unit efficiency.² Dendrimers are regularly and hierarchically branched macromolecules with numerous chain ends all emanating from a single core. The chromophores can be accurately located at the core, the focal point, the periphery, or even at each branching point of the dendritic structure. The specific structure of a dendrimer makes it a mimic of a light-harvesting system, where the antenna chromophores surround the central reaction center.³

The energy transfer in dendrimers has been extensively examined by several groups.^{4–9} Most of the studies¹⁰ on the intramolecular energy transfer between the periphery chromophores and the core in dendrimers are related to singlet states only; the energy transfer proceeds via the Förster mechanism, which is a through-space dipole–dipole interaction, and the donor–acceptor (D–A) orbital overlap is not required.¹¹ This allows chromophores to be separated by a relatively large distance (10–100 Å). Within dendritic structures, the distance between D and A is less than several tens of angstroms, even when D and A are located at the periphery and the core, respectively, in high generations. Thus, it is expected that the energy transfer via the Förster mechanism can occur efficiently

from the periphery to the core in dendritic structures and the experimental results confirm this hypothesis.^{5,8,9} The triplet–triplet energy transfer is the most common and most important type of energy transfer involved in chemical and biochemical processes.¹² The mechanism for triplet energy transfer is usually described by Dexter electron exchange interaction¹³ and may be visualized in terms of two electron-transfer processes or one electron-transfer and one hole-transfer processes. Generally, this electron exchange requires a strong D–A orbital overlap, and therefore, the rate constant of the energy transfer in this case decreases exponentially with increasing D–A distance. Thus, one might expect that the rate constant of the triplet energy transfer will become negligibly small as the D–A distance increases beyond 10 Å¹² unless the energy transfer occurs via a “through-bond mechanism” in conjugated or rigid systems.¹⁴ Up to now, only a few examples of the application of intramolecular energy transfer of dendrimers deal with triplet states.^{15,16} Furthermore, the intramolecular triplet energy transfers in poly(aryl ether) dendrimers have rarely been studied directly in liquid solution.

In the previous study,¹⁶ we used a photochemical reaction as the probe to detect the occurrence of the triplet–triplet energy transfer. Now, we create another dendritic system (BP-Gn-NA) by using a photophysical probe to observe the triplet state formation of the acceptor via the triplet–triplet energy transfer. In BP-Gn-NA, benzophenone (BP) chromophores and naphthalene (NA) group are attached to the periphery and the core of a poly(aryl ether) dendrimer, respectively. Fréchet dendron only acts as a scaffold to hold D and A in a desired spatial arrangement, and its antenna role is not studied since we excite at lower energy compared to dimethoxybenzene S1 state. The dendrimers are synthesized up to the fourth generation, as shown in Figure 1. In these molecules, the BP chromophores can be selectively excited. After intersystem crossing with 100%

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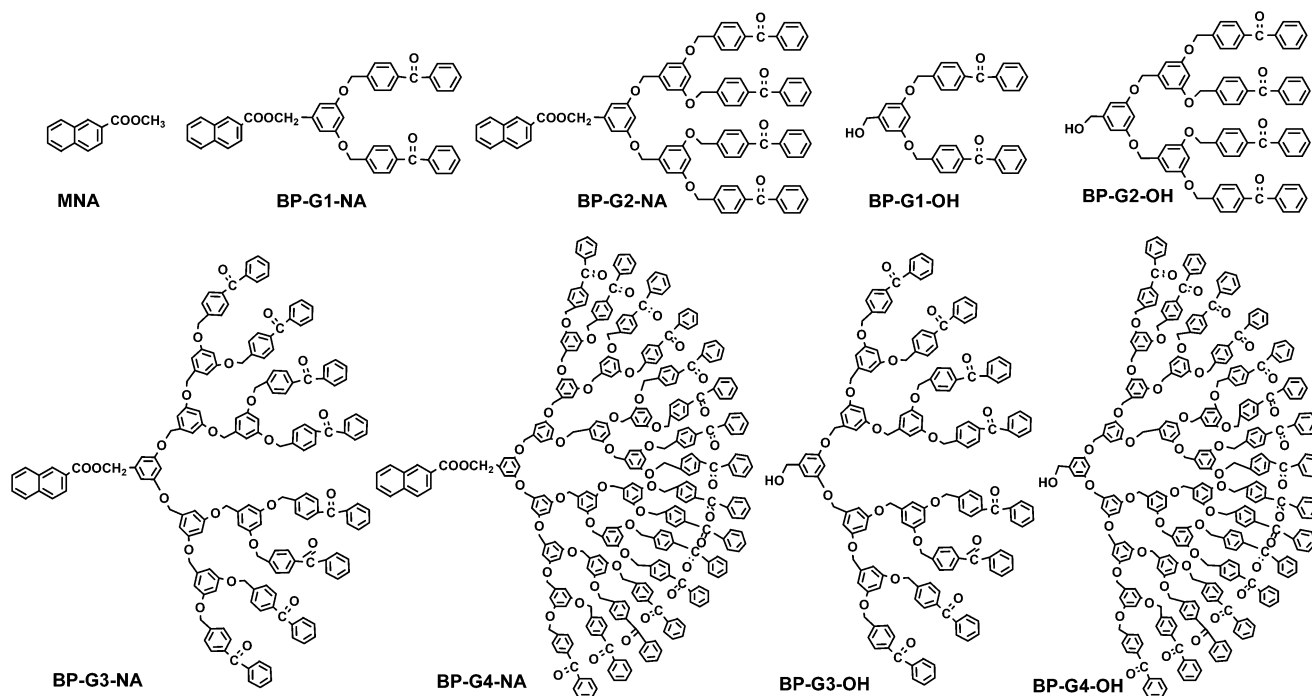


Figure 1. Structures of the acceptor model compound MNA, the donor model compounds BP-*Gn*-OH, and the target compounds BP-*Gn*-NA.

efficiency, the triplet energy of BP is transferred to NA. The transient process of the triplet energy transfer was detected by the transient absorption measurement, and the efficiencies and the absolute rate constants of the intramolecular triplet energy transfer were examined by steady-state and transient spectroscopies. These findings give a direct observation of the intramolecular triplet energy transfer in poly(aryl ether) dendrimers.

Results and Discussion

Synthesis and Characterization of the Dendrimers. Dendritic benzyl alcohols (BP-*Gn*-OH, $n = 1-4$), the donor model compounds, were synthesized with Fréchet's method¹⁷ and were described elsewhere.¹⁶ The target compounds, BP-*Gn*-NA ($n = 1-4$), were synthesized with BP-*Gn*-OH and 2-naphthoyl chloride. The details of the synthesis and the characterization of BP-*Gn*-NA ($n = 1-4$) are described in the Experimental Section. All the compounds have been purified by column chromatography. The compounds were characterized by ¹H NMR, IR, mass spectrometry (MALDI-TOF or EI), and HPLC.

Absorption and Phosphorescence Studies on the Intramolecular Triplet Energy Transfer from the Benzophenone Chromophores to the Naphthalene Group in BP-*Gn*-NA. The absorption spectra of dendrimers, BP-*Gn*-NA, the models for donor BP-*Gn*-OH, and the model for acceptor methyl 2-naphthoate (MNA) were measured in dichloromethane (CH₂Cl₂). Figure 2 illustrates the absorption spectra of BP-G1-NA, BP-G1-OH, and MNA in CH₂Cl₂. No measurable interaction between the NA and BP chromophores of BP-*Gn*-NA in the ground state can be observed from the absorption spectra. Significantly, the absorption of the BP chromophores extends to longer wavelength than that of the NA group, which suggests that the singlet-singlet energy transfer from the excited BP chromophore to the NA group is endothermic and, consequently, unlikely. Furthermore, we can selectively excite the BP moieties in BP-*Gn*-NA systems above 350 nm.

The emission spectra of BP-*Gn*-NA and BP-*Gn*-OH were studied in glassy 2-methyltetrahydrofuran (MTHF) at 77 K.

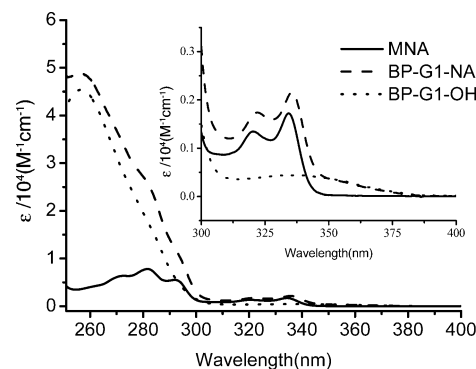


Figure 2. Absorption spectra for the acceptor model compound MNA, the donor model compound BP-G1-OH, and the target compound BP-G1-NA.

Examples of the emission spectra for generation 1 and 3 are presented in Figure 3. No fluorescence from these compounds was observed with the excitation at the absorption of BP (350 nm), while phosphorescence characteristic of benzophenone with maxima at 416, 445, 480, and 519 nm was detected for BP-*Gn*-OH and BP-*Gn*-NA except for BP-G1-NA. No emission from BP was detected in BP-G1-NA, and only a weak phosphorescence characteristic of naphthalene with maxima at 483, 518, and 560 nm was observed. The overall intensities of the BP phosphorescence for BP-*Gn*-NA ($n = 2-4$) are less than those of the corresponding model compounds BP-*Gn*-OH, ca. 16% for G2, 17% for G3, and 21% for G4. This finding indicates that the phosphorescence of BP is quenched by the NA group in BP-*Gn*-NA, and the quenching efficiency for BP-G1-NA is ca. 100%. Time-resolved phosphorescence measurements in MTHF give the BP phosphorescence lifetimes of BP-*Gn*-OH and BP-*Gn*-NA, which allow the calculation of the quenching efficiencies. The values of the quenching efficiency obtained from the phosphorescence lifetimes for G2-G4 are consistent with those from the phosphorescence efficiency measurements.

To clarify the reason for the intramolecular quenching of BP phosphorescence by the NA group in BP-*Gn*-NA, we calculated the free energy change involved in an electron-transfer process

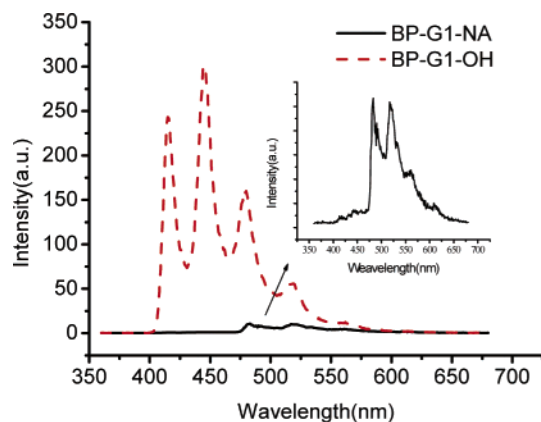


Figure 3. Phosphorescence spectra of BP-*Gn*-NA and BP-*Gn*-OH (*n* = 1, 3) in MTHF at 77 K (λ_{ex} = 350 nm). Concentrations computed with benzophenone are both 6.0×10^{-5} M.

from the NA group to the BP chromophore by the Rehm–Weller equation:¹⁸

$$\Delta G \text{ (kcal/mol)} = 23.06[E(D^{\bullet+}/D) - E(A/A^{\bullet-}) - e^2/r\epsilon] - E_{00} \text{ (kcal/mol)} \quad (1)$$

The redox potentials of MNA $E(\text{MNA}^{\bullet+}/\text{MNA})$ and BP $E(\text{BP}/\text{BP}^{\bullet-})$ were determined in dichloromethane to be 1.38 and -2.40 V, respectively, with respect to Ag/Ag^+ . E_{00} is the excited-state energy and in this study represents the triplet state energy of the 4-substituent benzophenone, which is 69 kcal/mol.¹⁹ $e^2/r\epsilon$ represents the Coulombic energy associated with bringing separated radical ions at a distance r in a solvent of dielectric constant ϵ ($r = 5\text{--}7$ Å; estimated from the molecular modeling). Calculation according to eq 1 gives the free energy change ΔG to be about 12 kcal/mol for BP-*Gn*-NA (*n* = 1–4), suggesting that the electron transfer from NA to the triplet state BP group would be very inefficient had it occur at all. On the other hand, benzophenone ($E_T = 69$ kcal/mol)–naphthalene ($E_T = 60$ kcal/mol)²⁰ is a typical exothermic triplet–triplet energy transfer pair.¹² Therefore, the triplet–triplet energy transfer from the triplet excited BP chromophore to the NA group should be responsible for the intramolecular quenching of the BP phosphorescence in BP-*Gn*-NA. As a consequence of the triplet–triplet energy transfer, the phosphorescence of NA should be observed. In the phosphorescence measurements we could only observe the distinct phosphorescence emission of NA in BP-G1-NA. The lower concentration and smaller emission quantum yield of NA than that of BP²⁰ and the relative lower triplet energy transfer efficiency at higher generations should be the main causes of no obvious detection of the NA phosphorescence in BP-*Gn*-NA (*n* = 2–4). The weak phosphorescence from NA is covered by the strong phosphorescence emission of BP in BP-*Gn*-NA (*n* = 2–4). Time-resolved phosphorescence measurements verify the existence of the naphthalene phosphorescence in BP-*Gn*-NA (*n* = 2–4). The excitation wavelength was 355 nm, and the phosphorescence decay was monitored at 445 and 518 nm. A lifetime ca. 3–4 ms was obtained at both 445 and 518 nm for G2–G4, which is assigned to BP. Despite the BP phosphorescence decay, a decay profile with a long lifetime (ca. 2 s) is also detected at 518 nm for G1–G4, which is assigned to NA by reference to the lifetime of MNA. The existence of the naphthalene decay validates the occurrence of the triplet–triplet energy transfer from BP to NA in BP-*Gn*-NA.

Laser Flash Photolysis Evidence for the Intramolecular Triplet Energy Transfer in BP-*Gn*-NA. The evidence for the intramolecular triplet–triplet energy transfer in BP-*Gn*-NA

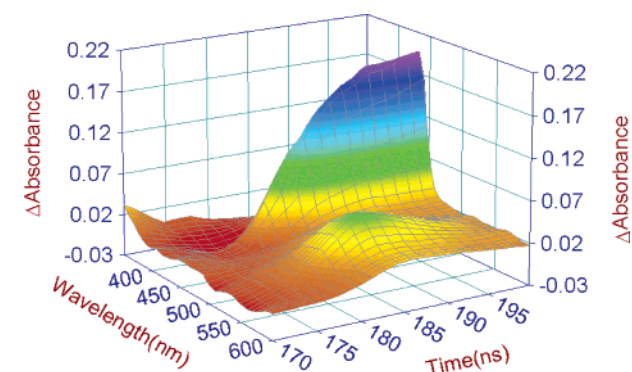
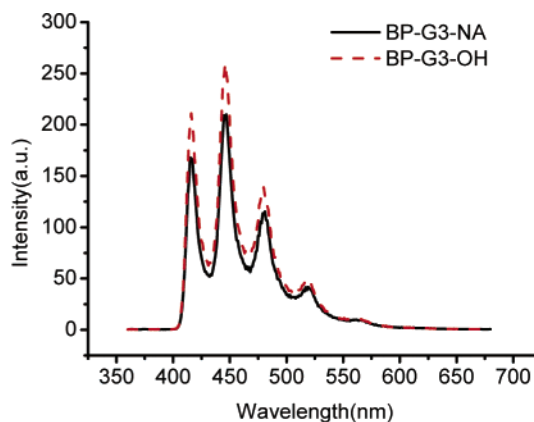


Figure 4. Transient absorption spectra of the triplet states formed upon laser photolysis of BP-G3-NA in CH_2Cl_2 (λ_{ex} = 355 nm, $[\text{BP}] = 1 \times 10^{-3}$ M).

based on phosphorescence efficiency is further strengthened by laser flash photolysis study. Pulsed-laser photolysis of the model compounds, BP-*Gn*-OH, and the target compounds, BP-*Gn*-NA, was performed in deaerated CH_2Cl_2 by using 355 nm excitation light, giving rise to a strong transient absorption spectra with maximum at 536 nm for both BP-*Gn*-OH and BP-*Gn*-NA. Besides the transient absorption at 536 nm a new transient absorption band with maximum at 430 nm forms in BP-*Gn*-NA, which increases with the decay of the transient absorption at 536 nm. The typical transient absorption spectra for BP-G3-NA are depicted in Figure 4.

The transient absorption for BP-*Gn*-OH and BP-*Gn*-NA at 536 nm is assigned to the lowest triplet state of BP by reference to the transient absorption of the triplet state of 4-substituent benzophenone^{16,21} Furthermore, this absorption is rapidly quenchable by O_2 . The transient absorption at 430 nm in BP-*Gn*-NA is assigned to the lowest triplet state of NA on the basis of the following observations. First, this absorption is essentially identical with that of the naphthalene triplet state.²² Second, the 430 nm species is quenched by 1,3-pentadiene and O_2 . Upon irradiation of BP-*Gn*-NA at 355 nm, only the BP chromophores absorb the light under this condition; the detection of the triplet state of NA must be attributed to the triplet energy transfer from the BP chromophores to the NA group. The transient absorption spectra of BP-*Gn*-NA show clearly the buildup of the NA absorption along with the decay of BP with an isosbestic point at 475 nm. This gives a direct observation of the intramolecular triplet energy transfer in poly(aryl ether) dendrimers.

Taking the transient spectra of BP-*Gn*-OH and BP-*Gn*-NA at 536 nm as a function of time gives the decay curves of compounds. All the decay curves can be fitted monoexponen-

TABLE 1: Triplet-State Lifetime of BP for Donor Model Compounds BP-*Gn*-OH and Target Compounds BP-*Gn*-NA, All Measured in CH₂Cl₂ by Flash Photolysis

compd	τ_1/ns	a_1	τ_2/ns	a_2	τ or $\tau(\text{av})/\text{ns}$	χ^2
BP-G1-OH					1339	0.9989
BP-G2-OH	127	0.90	358	0.10	150	0.9989
BP-G3-OH	53	0.77	179	0.23	82	0.9977
BP-G4-OH	36	0.80	238	0.20	76	0.9984
BP-G1-NA					7	0.9555
BP-G2-NA					8	0.9630
BP-G3-NA					9	0.9871
BP-G4-NA	13.4	0.92	329	0.08	38	0.9747

TABLE 2: Energy Transfer Efficiency and Rate Constant for Compounds BP-*Gn*-NA

compd	$k_{\text{ET}}/\text{s}^{-1}$	Φ_{ET}	$\Phi_{\text{ET}}^{\text{OD}}$
BP-G1-NA	1.4×10^8	0.99	0.95
BP-G2-NA	1.2×10^8	0.95	0.98
BP-G3-NA	9.8×10^7	0.89	0.87
BP-G4-NA	1.3×10^7	0.50	0.57

tially or double-exponentially with acceptable χ^2 values, which are consistent with the data reported by Fréchet⁸ and us.¹⁶ Fréchet and co-workers proposed that the flexible nature of the dendrimers was responsible for the non-monoexponential behavior. The conformational freedom of the dendritic backbone creates a variety of local microenvironments for the individual dyes. Since the photophysical properties of BP are not very sensitive to the environment, the change of the local microenvironment induced by the dendrimer conformations would not affect the triplet-state lifetime of the individual BP dramatically in our system. Taking into account the flexibility of the dendrimer backbone and more than one BP chromophore in a dendrimer molecule, we infer that the intramolecular triplet-triplet (T-T) annihilation between the benzophenone chromophores is the main cause of the non-monoexponential behavior as we proposed in the previous work.¹⁶ An excited BP chromophore may encounter another triplet BP due to the dynamic motion of the dendrimer backbone within its lifetime, which induces the occurrence of the triplet-triplet annihilation. The entire set of acquired data is summarized in Table 1. It should be pointed out that the number of the exponentials used is not intended to signify the exact number of distinct processes being observed.

The average lifetime of BP-*Gn*-OH decreases as the generation increases, which should be mainly induced by the triplet-triplet annihilation. The shorter average lifetime of the BP triplet state for BP-*Gn*-NA in comparison with that of the corresponding BP-*Gn*-OH indicates that an intramolecular triplet-triplet energy transfer from BP to NA in BP-*Gn*-NA occurs. The rate constant (k_{ET}) and efficiency (Φ_{ET}) for the energy transfer can be calculated from the average lifetime of BP-*Gn*-NA (τ_{NA}) and BP-*Gn*-OH (τ_{OH}) according to eqs 2 and 3, respectively. The results are shown in Table 2. The rate constant k_{ET} does not decrease dramatically with the generation increase, which is consistent with what we observed in the previous work,¹⁶ and the result is discussed in the mechanism of the energy transfer section below.

$$k_{\text{ET}} = 1/\tau_{\text{NA}} - 1/\tau_{\text{OH}} \quad (2)$$

$$\Phi_{\text{ET}} = 1 - \tau_{\text{NA}}/\tau_{\text{OH}} \quad (3)$$

We expected non-monoexponential decays for BP-*Gn*-NA as BP-*Gn*-OH. However, the decay curve of BP-*Gn*-NA ($n = 1-3$) can be well-fitted monoexponentially. Comparison of the rate constant of T-T annihilation (k_{TT}) and the rate constant of the

triplet energy transfer reveals this divergency. Considering the T-T annihilation as the main cause of the BP-*Gn*-OH lifetime change with the generation increase by ignoring the nonirradiation from the dendrimer backbone, k_{TT} is estimated to be of 10^6-10^7 s^{-1} magnitude in dendritic systems, which is much lower than the value reported for the intermolecular T-T annihilation of benzophenone.¹² For generations 1-3, $k_{\text{ET}} = \sim 10^8 \text{ s}^{-1}$, which is at least 1 order of magnitude higher than the corresponding k_{TT} . The T-T annihilation in BP-*Gn*-NA ($n = 1-3$) can be ignored, which results in the monoexponential decay. For BP-G4-NA, k_{ET} is comparable with k_{TT} (10^7 s^{-1}), which leads to a non-monoexponential profile. This result shows us a protocol for designing an efficient dendritic light-harvesting system. By selection of an efficient donor-acceptor pair, the energy dissipation via the interaction between the periphery chromophores can be reduced.

The energy transfer efficiency, Φ_{ET} , decreases only 10% from generations 1 to 3 but 50% for BP-G4-NA. Usually, the increase in the donor-acceptor separation that occurs as the dendrimer generation increases is thought to be the reason for the decrease in energy transfer efficiency. In this work, the triplet-triplet annihilation of the BP chromophores could be the main cause of the decrease of the energy transfer efficiency because k_{ET} did not decrease exponentially with the generation increase. The smaller decrease of the energy transfer efficiency from generations 1 to 3 is due to the rapid energy transfer in comparison with the T-T annihilation.

The triplet state of NA was generated from the triplet energy transfer from BP to NA in BP-*Gn*-NA during the pulsed-laser photolysis. Therefore, we can also calculate the energy transfer efficiency from the intensity of the T-T absorption of NA in BP-*Gn*-NA by using benzophenone actinometry. The transient absorption band of NA was observed at 430 nm after the laser flash photolysis of benzophenone ($1 \times 10^{-3} \text{ M}$) and methyl 2-naphthoate (MNA) ($1 \times 10^{-3} \text{ M}$) in deaerated CH₂Cl₂ ($\Delta\text{OD}_{430} = 0.119$). Laser flash photolysis of benzophenone ($1 \times 10^{-3} \text{ M}$) gives $\Delta\text{OD}_{536} = 0.073$. Assuming all the triplet energy of benzophenone transferred to MNA, the molar absorption coefficient of MNA at 430 nm ($\epsilon_{\text{T-T(NA)}}$) was estimated to be $1.18 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ by using $\epsilon_{\text{T-T(BP)}} = 7220 \text{ M}^{-1} \text{ cm}^{-1}$ ²³ from eq 4.

$$\epsilon_{\text{T-T(NA)}}/\epsilon_{\text{T-T(BP)}} = \text{OD}_{(\text{NA})}/\text{OD}_{(\text{BP})} \quad (4)$$

For laser flash photolysis of BP-*Gn*-NA in deaerated CH₂Cl₂ by using 355 nm excitation light under the same condition ($[\text{BP}] = 1 \times 10^{-3} \text{ M}$), ΔOD_{430} was obtained to be 0.113, 0.117, 0.104, and 0.068 for generations 1-4, respectively. Assuming the absorption coefficient of NA at 430 nm in BP-*Gn*-NA ($n = 1-4$) is the same as that of MNA at 430 nm. The concentration of the triplet state NA was calculated to be 9.58×10^{-6} , 9.91×10^{-6} , 8.81×10^{-6} , and $5.76 \times 10^{-6} \text{ M}$ for generations 1-4, respectively. The number of laser photons (N_p) absorbed by BP-*Gn*-NA was measured to be $N_p = 1.01 \times 10^{-5} \text{ einstein L}^{-1}$

from the actinometry using the triplet–triplet absorption of benzophenone as a standard. The quantum yield for the formation of the triplet NA in BP-*Gn*-NA, which is also the triplet–triplet energy transfer efficiency of BP-*Gn*-NA, was estimated to be 0.95, 0.98, 0.87, and 0.57 for generations 1–4, respectively ($\Phi_{\text{ET}}^{\text{OD}}$, shown in Table 2). The triplet energy transfer efficiencies obtained from the transient absorption of NA agree with the results calculated by the triplet lifetimes of BP (Φ_{ET}).

The rise time of naphthalene in BP-*Gn*-NA can be estimated by analysis of the transient absorption at 430 nm as a function of time, and they are 5–6 ns for generations 1–3 and 12 ns for generation 4. The rise time of the naphthalene triplet state is consistent with the decay time of the benzophenone triplet state for generations 1–3. The difference between the acceptor rise time and the donor decay time in the forth generation should be caused by the T–T annihilation, which is consistent with the observation of the non-monoexponential decay in BP-G4-NA. The lifetime of the naphthalene triplet state increases with the generation, and they are 24, 29, 35, and 63 μs for generations 1–4, respectively.

Mechanism of the Intramolecular Triplet–Triplet Energy Transfer from the BP to NA Groups in BP-*Gn*-NA. The studies on the phosphorescence spectroscopy and the flash photolysis reveal that the excitation of the BP chromophore in BP-*Gn*-NA results in an intramolecular triplet–triplet energy transfer from the BP to NA groups. The efficiencies of such triplet–triplet energy transfer at room temperature are ca. 0.97, 0.96, 0.88, and 0.54 (the average of Φ_{ET} and $\Phi_{\text{ET}}^{\text{OD}}$), and the rate constants are ca. $1.4 \times 10^8 \text{ s}^{-1}$, $1.2 \times 10^8 \text{ s}^{-1}$, $9.5 \times 10^7 \text{ s}^{-1}$, and $1.3 \times 10^7 \text{ s}^{-1}$ for generations 1–4, respectively.

It has been well established that the triplet–triplet energy transfer proceeds via the Dexter electron exchange mechanism, and its rate constant decreases exponentially with the increasing of the distance between D and A.¹² The triplet energy transfer is normally expected to become very inefficient as the D–A distance increases beyond 10 Å unless it occurs via a “through-bond mechanism” in a conjugated or a rigid system. The through-bond mechanism has been excluded due to the smaller change of k_{ET} with the generation. Although the detailed three-dimensional structures of dendrimers are not well-understood, theoretical²⁴ and experimental results²⁵ suggest that a dendrimer with a flexible backbone will take a folded conformation, especially at higher generations. We also inferred that the poly(aryl ether) dendrimers took the folding-back conformation and the triplet energy transfer proceeded via the closest donor and the acceptor groups in our previous study.¹⁶ Computation by using MM+, the Polak–Ribiere algorithm (HyperChem 6.0 program), shows that the lowest energy conformation of BP-*Gn*-NA is folded, while optimizing the conformation the solvent effect could not be taken into account due to the limitation of the program. Therefore, we propose that the intramolecular triplet–triplet energy transfer in BP-*Gn*-NA mainly proceeds via a through-space mechanism. After the BP chromophore is selectively excited, the intersystem crossing occurs with 100% efficiency. When the excitation happens on the BP chromophore in proximity of the core NA group, the energy transfer occurs directly. If the distance between the excited BP chromophore and the NA group is out of the range for the effective triplet energy transfer, there are two ways to make the energy transfer occur: a movement of the excited BP chromophore toward the NA group within its lifetime and an energy migration to the closest BP. Because the movement of the molecular moieties is prohibited at 77 K, the energy transfer efficiency at 77 K is

much lower than that at room temperature for BP-*Gn*-NA ($n = 2$ –4). The high energy transfer efficiency for BP-G1-NA at 77 K is due to the proximity of the donor and the acceptor. The magnitude of the rate constant for the triplet energy transfer in this work (10^7 – 10^8 s^{-1}) is consistent with the results reported in the literatures (10^7 – 10^{10} s^{-1}), where BP and NA are linked by a flexible spacer and the triplet energy transfer proceeds via a through-space mechanism.²⁶

Conclusions

Flash photolysis demonstrates that the triplet energy in BP-*Gn*-NA can be transferred from the peripheral BP chromophores to the core NA group with the efficiencies of ca. 0.97, 0.96, 0.88, and 0.54 and with the rate constants of 1.4×10^8 , 1.2×10^8 , 9.5×10^7 , and $1.3 \times 10^7 \text{ s}^{-1}$ at room temperature for generations 1–4, respectively. The triplet energy transfer from BP to NA is observed in transient absorption spectroscopy with an isosbestic point at 475 nm for generations 1–4, which gives direct evidence of the triplet energy transfer. We infer that BP-*Gn*-NA takes a folded conformation and the intramolecular triplet energy transfer in BP-*Gn*-NA proceeds mainly via a through-space mechanism involving the closest donor and acceptor groups. The triplet energy transfer can also occur at 77 K with efficiency of ca. 1.0, 0.16, 0.17, and 0.21 for generations 1–4, respectively. The energy transfer efficiency for BP-*Gn*-NA at 77 K is much lower than that at room temperature except for generation 1, which is caused by the prohibition of the molecular moieties movement, and the spatial proximity of BP and NA in BP-G1-NA leads to a high energy transfer efficiency. This work gives direct experimental evidence for the triplet–triplet energy transfer from the periphery chromophores to the core in poly(aryl ether) dendrimers.

Experimental Section

Materials. Reagents were purchased from Aldrich or Acros and were used without further purification, unless otherwise noted. Tetrahydrofuran (THF) was distilled over Na/Benzophenone under argon atmosphere. Acetone was dried with anhydrous K_2CO_3 and distilled. Spectral-grade 2-methyltetrahydrofuran (MTHF) and dichloromethane (CH_2Cl_2) were used for absorption and emission spectra and flash photolysis measurements.

Instrumentation. ^1H NMR spectra were recorded on either a Varian Gemini 300 MHz or a Bruker 400 MHz spectrometer. IR spectra were run on a Bio-Rad Win IR spectrometer. MALDI-TOF mass spectrometry was performed on a Bruker BIFLEX III spectrometer. Melting points were determined on a XT4A apparatus and were uncorrected. HPLC was recorded at a Hitachi system with an Alltima LC-Si 5 μm column (4.6 mm i.d., 25 cm) and a UV–vis detector. Steady-state absorption spectra and phosphorescence spectra were measured by a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively.

Phosphorescence Measurements. Phosphorescence studies were performed in 2-methyltetrahydrofuran at 77 K with the excitation wavelength at 350 nm. For comparison of the emission efficiency of BP-*Gn*-NA with BP-*Gn*-OH, the spectra were run by using solutions with identical optical density at the excitation wavelength. The relative emission efficiencies were measured from the peak areas of the emission spectra.

Time-Resolved Spectroscopic Measurements. Millisecond phosphorescence decay processes were recorded with the single photon counting technique on an Edinburgh FLS920 phosphorescence lifetime system. Naphthalene phosphorescence decay

was detected by a 0.3 m spectrometer and a photomultiplier tube (PMT) coupled to a 32-bit microprocessor-based data acquisition and spectrometer controller module (NCL Electronics Interface, Acton Research Corp.) and computer with the third harmonic output (355 nm, 10 kHz, 5 mW) of a diode pumped Q-switched Nd:YAG laser (AmbeiUV-5AQ, Guoke Laser Co.) as the excitation source. The decay process was recorded after the laser was cut off. Nanosecond transient absorption spectra were performed on a LP-920 pump-probe spectroscopic setup (Edinburgh). The excited source was the unfocused third harmonic (355 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum surelite II), and the probe light source was a pulse-xenon lamp. The signals were detected by an Edinburgh analytical instrument (LP900) and recorded on a Tektronix TDS 3012B oscilloscope and computer.

Redox Potentials of Benzophenone and MNA. The redox potentials of benzophenone and MNA were determined by cyclic voltammetry in dichloromethane, using a 10 μ m platinum microelectrode and a Ag/Ag⁺ (the concentration of Ag⁺ is 0.01 M) reference electrode in the presence of 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

General Procedure for the Synthesis of the BP-Gn-NA System. These reactions were carried out on scales of about 300 mg. A mixture of the appropriate dendritic benzyl alcohol, BP-Gn-OH, (1.00 equiv), 2-naphthoyl chloride (**1**) (3.00 equiv), and 4-(dimethylamino)pyridine (0.1 equiv) in dry CH₂Cl₂ was stirred under nitrogen for 24 h. For generations 3 and 4, a large excess amount of **1** was required to complete the reaction. The reaction mixture was diluted by CH₂Cl₂ and partitioned into water and CH₂Cl₂ layers. The aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layers were dried over MgSO₄ and evaporated to dryness. The crude product was purified as outlined in the following text.

BP-G1-NA (2). This was prepared from BP-G1-OH and 2-naphthoyl chloride (**1**), purified by column chromatography eluting with CH₂Cl₂, gradually increasing to 1/30 ethyl ether/CH₂Cl₂, and recrystallized from 50% hexanes/CH₂Cl₂ to give **2** as white crystals: yield 86%; mp 150–151 °C; retention time t_R = 10.5 min in HPLC (10/1 acetonitrile/THF); IR ν 1733, 1712, 1658, 1597, 1448, 1375, 1317, 1278, 1151, 1052 cm⁻¹; ¹H NMR (CDCl₃) δ 5.18 (s, 4H, PhCH₂-), 5.99 (s, 2H, -COOCH₂-), 6.63 (s, 1H, ArH), 6.76–6.77 (d, 2H, ArH), 7.46–7.60 (m, 12H, PhCO- and naphthalene ring 2H), 7.79–7.97 (m, 11H, -COPh- and naphthalene ring 3H), 8.06–8.09 (d, 1H, naphthalene ring 1H), 8.65 (s, 1H, naphthalene ring 1H); MS for C₄₆H₃₄O₆ m/z 682 (M⁺), 440, 195, 119, calcd m/z 682.76.

BP-G2-NA (3). This was prepared from BP-G2-OH and 2-naphthoyl chloride (**1**), purified by column chromatography eluting with CH₂Cl₂, gradually increasing to 1/30 ethyl ether/CH₂Cl₂, and recrystallized from 50% hexanes/CH₂Cl₂ to give **3** as white solid: yield 85%; mp 111–113 °C; retention time t_R = 14.4 min in HPLC (10/1 acetonitrile/THF); IR ν 1734, 1710, 1657, 1596, 1447, 1373, 1317, 1277, 1148, 1046 cm⁻¹; ¹H NMR (CDCl₃) δ 5.02 (s, 4H, ArCH₂-), 5.13 (s, 8H, PhCH₂-), 5.36 (s, 2H, -COOCH₂-), 6.58–6.72 (m, 9H, ArH), 7.46–7.62 (m, 22H, PhCO- and naphthalene ring 2H), 7.78–7.95 (m, 19H, -COPh- and naphthalene ring 3H), 8.05–8.10 (d, 1H, naphthalene ring 1H), 8.63 (s, 1H, naphthalene ring 1H); MS (MALDI-TOF) for C₈₈H₆₆O₁₂ m/z 1338 (M + Na⁺), 1354 (M + K⁺), calcd m/z 1315.46.

BP-G3-NA (4). This was prepared from BP-G3-OH and 2-naphthoyl chloride (**1**) and purified by column chromatography eluting with CH₂Cl₂, gradually increasing to 1/30 ethyl

ether/CH₂Cl₂, to give **4** as a colorless glassy solid: yield 80%; retention time t_R = 30.6 min in HPLC (10/1 acetonitrile/THF); IR ν 1732, 1709, 1656, 1595, 1446, 1373, 1317, 1277, 1147, 1045 cm⁻¹; ¹H NMR (CDCl₃) δ 4.96–4.98 (d, 12H, ArCH₂-), 5.10 (s, 16H, PhCH₂-), 5.33 (s, 2H, -COOCH₂-), 6.54–6.69 (m, 21H, ArH), 7.44–7.60 (m, 42H, PhCO- and naphthalene ring 2H), 7.77–7.94 (m, 35H, -COPh- and naphthalene ring 3H), 8.00–8.01 (d, 1H, naphthalene ring 1H), 8.61 (s, 1H, naphthalene ring 1H); MS (MALDI-TOF) for C₁₇₂H₁₃₀O₂₄ m/z 2603 (M + Na⁺), 2619 (M + K⁺), calcd m/z 2580.86.

BP-G4-NA (5). This was prepared from BP-G4-OH and 2-naphthoyl chloride (**1**) and purified by column chromatography eluting with CH₂Cl₂, gradually increasing to 1/20 ethyl ether/CH₂Cl₂, to give **5** as a colorless glassy solid: yield 68%; retention time t_R = 10.4 min in HPLC (2.5/1 acetonitrile/THF); IR ν 1700, 1657, 1596, 1448, 1374, 1316, 1277, 1152, 1051 cm⁻¹; ¹H NMR (CDCl₃) δ 4.88–4.90 (m, 28H, ArCH₂-), 5.04 (s, 32H, PhCH₂-), 5.30 (s, 2H, -COOCH₂-), 6.49–6.65 (m, 45H, ArH), 7.40–7.55 (m, 82H, PhCO- and naphthalene ring 2H), 7.72–7.83 (m, 67H, -COPh- and naphthalene ring 3H), 7.94–7.98 (d, 1H, naphthalene ring 1H), 8.54 (s, 1H, naphthalene ring 1H); MS (MALDI-TOF) for C₃₄₀H₂₅₈O₄₈ m/z 5135 (M + Na⁺), calcd m/z 5111.66.

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Supporting Information Available: HPLC traces for BP-Gn-NA (n = 1–4), phosphorescence spectra of BP-Gn-NA and BP-Gn-OH, transient absorption spectra of BP-Gn-NA, and molecular modeling of BP-Gn-NA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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