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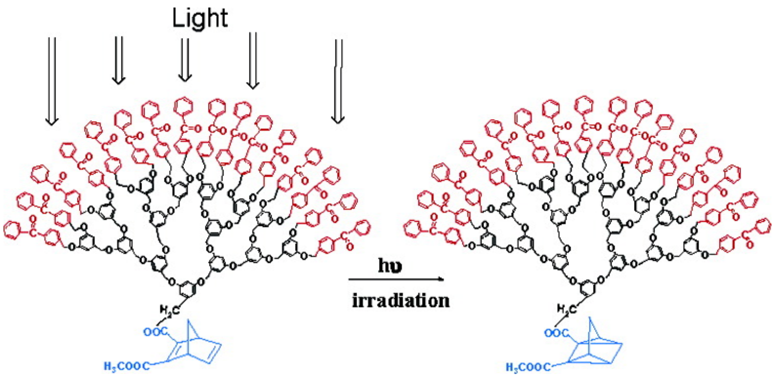

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Light-Harvesting and Photoisomerization in Benzophenone and Norbornadiene-Labeled Poly(aryl ether) Dendrimers via Intramolecular Triplet Energy Transfer

Jinping Chen,[†] Shayu Li,[‡] Lu Zhang,[†] Baining Liu,[†] Yongbin Han,[†]
Guoqiang Yang,*[,‡] and Yi Li*[,†]

Contribution from the Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China, and Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received August 28, 2004; E-mail: yili@mail.ipc.ac.cn (Y.L.); gqyang@iccas.ac.cn (G.Y.)

Abstract: A series of benzophenone (BP) and norbornadiene (NBD)-labeled poly(aryl ether) dendrimers (G*n*-NBD), generations 1−4, were synthesized, and their photophysical and photochemical properties were examined. The phosphorescence of the peripheral BP (donor) chromophore was efficiently quenched by the NBD (acceptor) group attached to the focal point. Time-resolved spectroscopic measurements indicated that the lifetime of the triplet state of the BP chromophore was shortened due to the proximity of the NBD group. Selective excitation of the BP chromophore resulted in isomerization of the NBD group to quadricyclane (QC). All of these observations suggest that an intramolecular triplet energy transfer occurs in G*n*-NBD molecules. The light-harvesting ability of these molecules increases with generation due to an increase in the number of peripheral chromophores. The energy transfer efficiencies are ca. 0.97, 0.54, 0.45, and 0.37 for generations 1−4, respectively, and the rate constant of the triplet−triplet energy transfer is ca. 10^6−10^7 s^{-1}, which decreases inconspicuously with increasing generation. The intramolecular triplet energy transfer is proposed to proceed mainly via a through-space mechanism involving the closest donor (folding back conformation) and acceptor groups.

Introduction

Studies on the natural photosynthetic systems revealed that the structure of the 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, focal point, periphery, or even at each branching point of the dendritic structure. The specific structure of the dendrimer makes it a mimic light-harvesting system, where the antenna chromophores surround the central reaction center.[3]

Recently, the studies of energy transfer in dendrimers have been extensively examined by several groups. Balzani and co-workers initially reported a series of multichromophoric dendrimers with different metal polypyridine complexes as the building block undergoing intramolecular energy transfer.[4] Xu and Moore developed a system based on phenylacetylene dendrimers and showed an energy cascade from the dendrimer to a single perylene, which is the first efficient, unidirectional energy transfer example.[5] Fréchet and co-workers used the poly(aryl ether) as an antenna to harvest the energy then transfer the energy to the ion at the focal point.[6] Jiang and Aida, using a system based on poly(aryl ether) dendrimers, have shown that multiple low-energy photons could be harvested by the dendrimer and transferred to an azobenzene core, accelerating its isomerization from *cis*- to *trans*-azobenzene.[7] The dendrimer-independent energy transfer systems, in which the energy transfer occurs between the peripheral chromophores and the core and the dendrimer backbone acts as a spacer, were also built and studied. A series of laser dye-labeled poly(aryl ether) dendrimers were built by Fréchet and co-workers. The energy transfer efficiency from the periphery to the core in this system was found to be efficient for generations 1−3, with only a slight

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* Authors to whom correspondence should be addressed. Y.L.: 86-010-64865872, phone; 86-010-64865872, fax. G.Y.: 86-010-82617263, phone; 86-010-82617315, fax.

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decreasing for generation 4 (∼93%).[8] Müllen, De Schryver, and their co-workers developed a system in which the donor (D) and the acceptor (A) were separated by rigid polyphenylene dendrimers and found that intramolecular directional Förster resonance energy transfer took place very efficiently.[9]

Up to now, most of the studies and other experiments[10] on intramolecular energy transfer between the periphery chromophores and the core in dendrimers are related to the singlet states only, and the energy transfer proceeds via Förster mechanism. The Förster mechanism is a through-space dipole−dipole interaction, and the D−A orbital overlap is not necessary. This allows the 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 D and A are located at the periphery and the core, respectively, in high generations. It is expected that the energy transfer via the Förster mechanism can occur efficiently from the periphery to the core in the dendritic structure, and the experimental results confirm this hypothesis.[8,9] However, dendrimers capable of light harvesting through the triplet−triplet energy transfer mechanism have rarely been demonstrated. As we know, the triplet−triplet energy transfer is the most common and most important type of energy transfer involved in chemical and biochemical processes.[11] The mechanism for triplet energy transfer is usually described by Dexter electron-exchange interaction[12] and may be visualized in terms of two electron transfer processes or one electron transfer and one hole transfer processes.[11] Generally, this electron exchange requires strong D−A orbital overlap, and therefore the energy transfer rate constant in this case decreases exponentially with increasing D−A distance. Thus, one might expect that the rate constant of triplet energy transfer will become negligibly small as the D−A distance increases beyond 10 Å,[11] except the energy transfer occurs via a "through-bond mechanism" in a conjugated or rigid system. Furthermore, most of the studies of intramolecular energy transfer of dendrimer concern photophysical processes. There are only a few examples of application of intramolecular energy transfer dealing with photochemical process.[7]

In the present work, we create a dendritic system in which the energy transfer between the peripheral chromophores and the core is suitable for Dexter triplet state energy transfer, and a photochemical reaction of the core is used as the probe to detect the energy transfer occurrence. Benzophenone (BP) chromophores and norbornadiene (NBD) group are attached to the periphery and the core of the poly(aryl ether) dendrimer,[13] respectively, and the dendritic backbone acts as a scaffold that holds D and A in a desired spatial arrangement and does not play an antenna role in the energy transfer. The dendrimers are synthesized up to the fourth generation, as shown in Figure 1.

In these molecules, the BP chromophore can be selectively excited. After intersystem crossing with 100% efficiency, the triplet energy of BP is transferred to NBD, resulting in the isomerization of the latter to the quadricyclane (QC) group. The efficiency and the absolute rate constant of intramolecular triplet energy transfer were examined by steady-state and time-resolved spectroscopy. The rate constant decreases inconspicuously as the generation increases. These findings provide a new example of the use of the dendrimer for light harvesting; the periphery "antenna" chromophores "harvest" photon energy which is then utilized to activate the core group via the Dexter energy transfer mechanism.

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 an argon atmosphere. Acetone was dried with anhydrous K_2CO_3 and distilled. Spectral-grade 2-methyltetrahydrofuran and dichloromethane (CH_2Cl_2) were used for absorption and emission spectra, flash photolysis, and steady-state photoirradiation measurements.

Instrumentation. ^{1}H 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 spectrometer. Elemental analyses were carried out on a Flash EA1112 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 ID, 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, and the sample solutions were degassed by at least three freeze−pump−thaw cycles at a pressure of 5×10^{-5} Torr. The excitation wavelength was 343 nm. For comparison of the emission efficiency of G*n*-NBD with G*n*-QC, the spectra were run using solutions with identical optical density at the excitation wavelength. The relative emission efficiencies were measured from the peak areas of the emission spectra.

Redox Potentials of BP and MNBD. The redox potentials of BP and MNBD were determined by cyclic voltammetry in dichloromethane, using a 10 μm 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.

Laser Flash Photolysis. 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); the probe light source was a pulse-xenon lamp. The signals were detected by Edinburgh analytical instruments (LP900) and recorded on a Tektronix TDS 3012B oscilloscope and computer.

Results and Discussion

Synthesis and Stability of the Dendrimers. The synthesis and characterization of the compounds are described in Supporting Information. All of the compounds have been purified by column chromatography. The target compounds, G*n*-NBD ($n = 1-4$), were characterized by ^{1}H NMR, elemental analysis, IR, mass spectrometry (MALDI-TOF or EI), and HPLC (see

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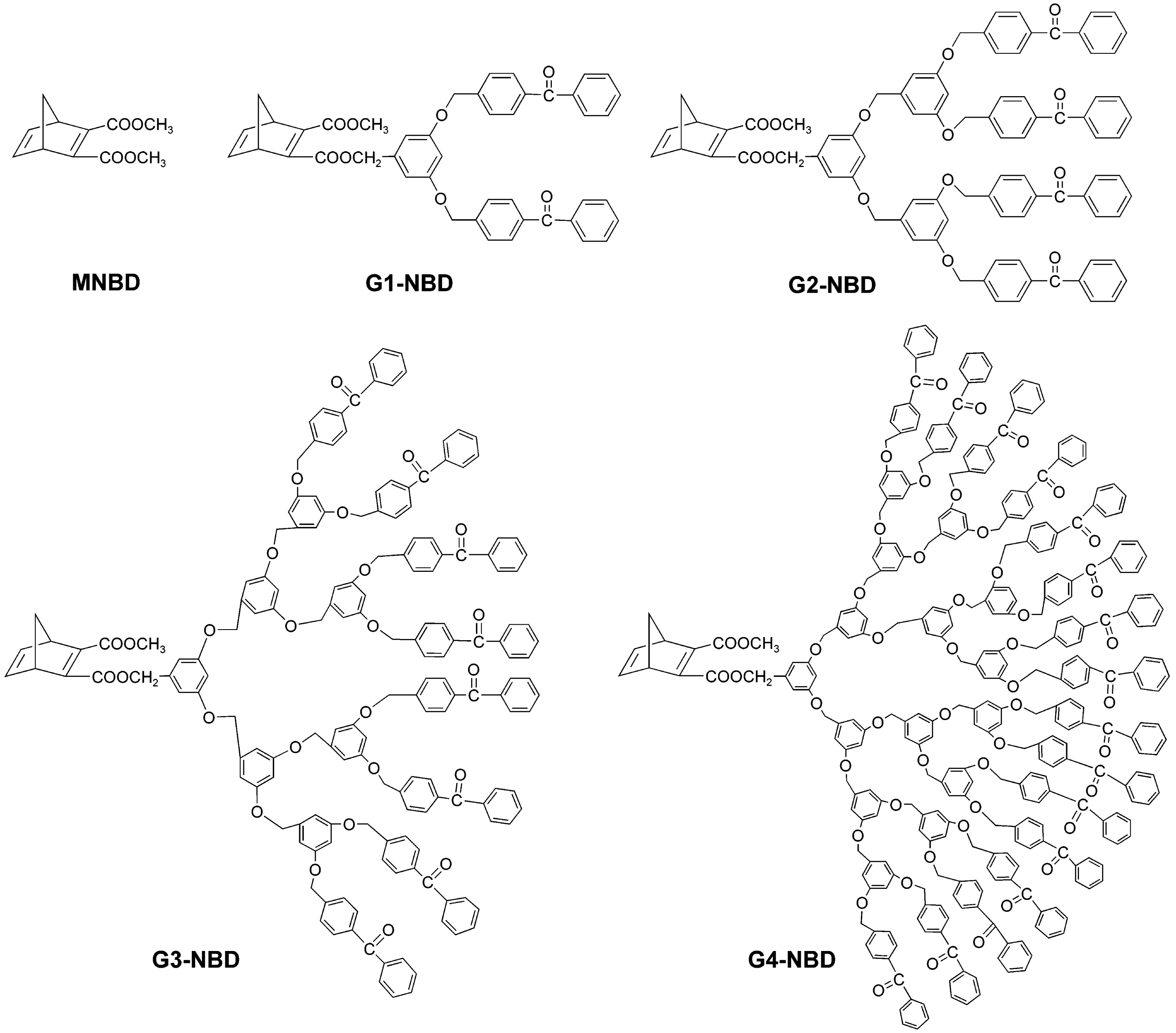

Figure 1. Structure of MNBD and G*n*-NBD compounds.

Supporting Information). For G*n*-QC (n = 1−4), the valence isomers with structure similar to that of G*n*-NBD were used as the model compounds. They were also characterized by ^{1}H NMR and mass spectrometry (MALDI-TOF or EI). G*n*-NBD (n = 1−4) must be stored in the dark because they are very sensitive to the light, which can induce the isomerization of G*n*-NBD to G*n*-QC in solution even with room light, especially for the higher generation.

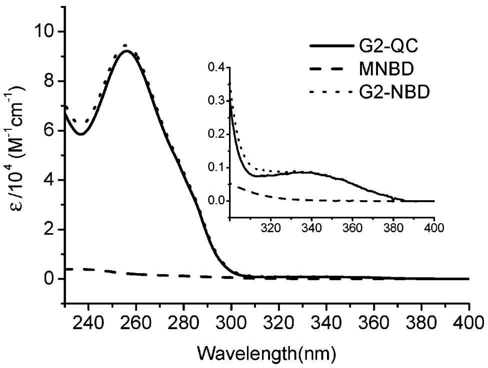

Figure 2. Absorption spectra for acceptor model compound MNBD, donor model compound G2-QC, and target compound G2-NBD.

Steady-State Absorption and Phosphorescence Spectroscopy. The absorption spectra of dendrimers (G*n*-NBD), the models for the donor (G*n*-QC) (see the structure in Supporting Information), and the model for the acceptor (dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD)) were measured in dichloromethane. Figure 2 illustrates the absorption spectra of G2-NBD, G2-QC, and MNBD in dichloromethane. There is no measurable interaction between the NBD, and BP chromophores of G*n*-NBD in the ground state can be observed from the absorption spectra. Significantly, the absorption of the BP group extends to a wavelength longer than that of the NBD group, which suggests that singlet−singlet energy transfer from the excited BP chromophore to the NBD group is endothermic and, consequently, unlikely. Furthermore, this fact permits selective excitation of the BP moiety in the G*n*-NBD system.

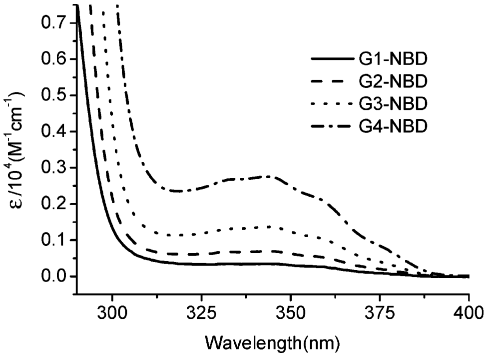

Figure 3. Absorption spectra of G*n*-NBD in CH_2Cl_2.

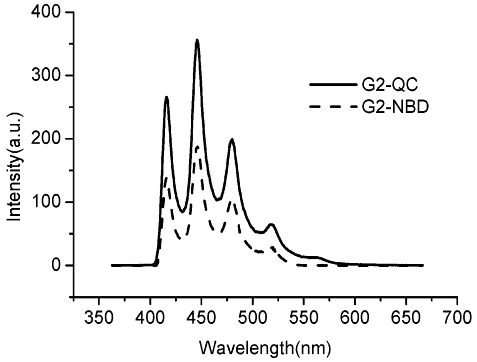

Figure 4. Phosphorescence spectra of G2-NBD and G2-QC in 2-methyltetrahydrofuran at 77 K ($\lambda_{ex} = 343$ nm). Concentrations computed with benzophenone are 2×10^{-5} M.

Figure 3 shows the absorption spectra of the G*n*-NBD series indichloromethane at the same concentration. Within experimental error, the absorption due to BP is proportional to the number of peripheral chromophores, which means that the light-harvesting capability of the molecules can be enhanced by increasing the generation number.

The emission spectra of G*n*-NBD and G*n*-QC were studied in glassy 2-methyltetrahydrofuran at 77 K. An example of the emission spectra of G2-NBD and G2-QC is presented in Figure 4. No fluorescence from these two compounds was observed with excitation at the maximal absorption of BP (343 nm), while a phosphorescence characteristic of the benzophenone with maxima at 416, 445, 480, and 519 nm was detected for both G2-NBD and G2-QC. The shape and peak positions of these two phosphorescence spectra are essentially identical, but the overall intensities are different. The phosphorescence efficiency of G2-NBD is ca. 52% less than that of model compound G2-QC. The other generations show similar results but various degrees of decreasing in phosphorescence efficiency, G1 with 95%, G3 with 38%, and G4 with 36%. This finding indicates that the phosphorescence of BP is quenched by the NBD group in G*n*-NBD. Measurements at different concentrations reveal that the quenching is intramolecular.

To clarify the reason for the intramolecular quenching of BP phosphorescence by the NBD group in G*n*-NBD, we measured the redox potentials of BP and the model compound, MNBD. The reduction potentials of MNBD, $E(\mathrm{NBD}^{\bullet+}/\mathrm{NBD})$, and BP, $E(\mathrm{BP}/\mathrm{BP}^{\bullet-})$, were determined in dichloromethane to be +1.50 and −2.40 V, respectively, with respect to $\mathrm{Ag}/\mathrm{Ag}^+$. The free energy change involved in an electron-transfer process can be calculated by the Rehm−Weller equation:[14]

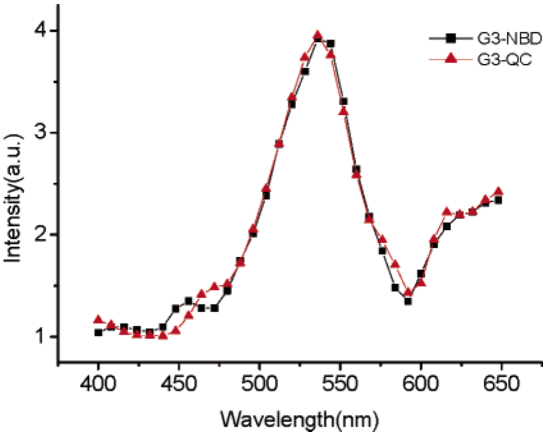

Figure 5. Transient absorption spectra of the benzophenone triplet state formed upon laser photolysis of G3-NBD and G3-QC in CH_2Cl_2.

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

E_{00} is the excited-state energy and in this study represents the triplet state energy of the 4-substituent benzophenone group, which is 69 kcal/mol.[15] The $e^2/r\epsilon$ represents the Columbic energy associated with bringing separated radical ions at a distance r in a solvent of dielectric constant ϵ ($r = 9.2$ Å in G1-NBD, 11.7 Å in G2-NBD, 14.4 Å in G3-NBD, and 16.5 Å in G4-NBD; see below). Calculation according to eq 1 shows that $\Delta G = 20.1-20.5$ kcal/mol from G1-NBD to G4-NBD, suggesting that electron transfer from NBD to the triplet state BP group would be very inefficient if any did occur. Furthermore, in the flash photolysis study, we could not detect any transient absorption attributable to a BP anion radical (see below). On the other hand, the triplet energy of NBD (53 kcal/mol)[16] is much lower than that of the BP group (69 kcal/mol). Thus, triplet−triplet energy transfer from the triplet excited BP chromophore to the NBD group is thermodynamically possible. Therefore, we infer that the quenching of the BP phosphorescence in G*n*-NBD is due to the intramolecular triplet−triplet energy transfer to the NBD group.

Flash Photolysis. The evidence for the intramolecular triplet−triplet energy transfer in G*n*-NBD based on phosphorescence efficiency is further strengthened by flash photolysis study. Pulsed-laser photolysis of the model compounds, G*n*-QC, and the target compounds, G*n*-NBD, was performed in degassed CH_2Cl_2 by using 355 nm excitation light, which gives rise to a strong transient absorption spectra with a maximum at 536 nm. The typical transient absorption spectra for G3-NBD and G3-QC are given in Figure 5.

This absorption is assigned to the lowest triplet state of the BP chromophore on the basis of the following observations. First, this absorption is essentially identical to that of the alkyl benzophenone-4-carboxylate triplet state independently gener-

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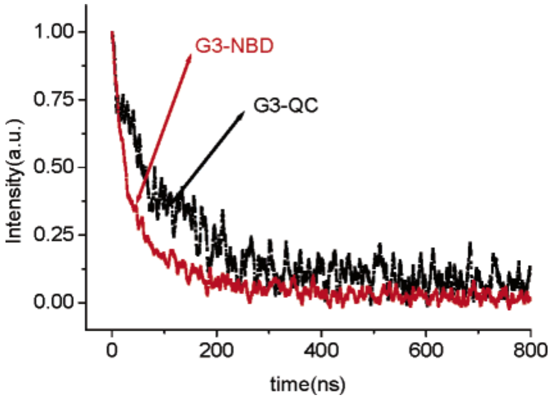

Figure 6. Decay traces for G3-NBD and G3-QC.

Table 1. Triplet State Lifetime for Dendrimers G*n*-NBD and G*n*-QC, All Measured in CH_2Cl_2 by Flash Photolysis

compound	τ1 (ns)	a1	τ2 (ns)	a2	τ(av) (ns)
G1-NBD	14	0.90	269	0.10	40
G2-NBD	21	0.70	206	0.30	77
G3-NBD	25	0.72	160	0.28	63
G4-NBD	23	0.80	214	0.20	61
G1-QC	633	0.82	9348	0.18	2202
G2-QC	139	0.82	333	0.18	174
G3-QC	57	0.72	314	0.28	129
G4-QC	37	0.76	290	0.24	98

ated.[17] Second, the 536 nm species is rapidly quenchable by O_2. The transient absorption of the model compounds G*n*-QC is identical with that of G*n*-NBD. Taking the transient spectra of G*n*-NBD and G*n*-QC at 536 nm as a function of time gives the decay curves of the compounds. Figure 6 shows the decay traces of G3-NBD and G3-QC, and the entire set of acquired data is summarized in Table 1.

None of the compounds investigated exhibit monoexponential decay profiles. This result is quite compatible with the data reported for laser-dye-labeled poly(aryl ether) dendrimers by Fréchet and co-workers.[8] They propose that the flexible nature of the dendrimers is responsible for the nonmonoexponential behavior. The conformational freedom of the dendritic backbone creates a variety of local microenvironments for the individual dyes. In our system, the flexible poly(aryl ether) dendritic backbone is also used. Since the photophysical properties of BP are not very sensitive to the environments, the changes of the local microenvironment induced by the dendrimer conformations would not affect the triplet state lifetimes of the individual BP dramatically. The molecule modeling (calculated by HyperChem 6.0) shows that the BP groups are close to each other, especially in higher generations (G2−G4). Molecular modeling suggests that 4 Å is the shortest distance between the BP chromophores for generations 2−4, and triplet−triplet annihilation could easily occur within that space.[11,18] So, we propose that nonmonoexponential behavior is mainly due to the intramolecular triplet−triplet annihilation. Phosphorescence measurement and the laser power dependence of the transient data support this supposition. All acquired data could be well fitted by double-exponentials with acceptable χ^2 value. However, it should be noted that the number of exponentials used is not intended to signify the exact number of distinct processes being observed.

Table 2. Energy Transfer Efficiencies and Rate Constants for Compounds G*n*-NBD

compound	k_{ET} (s^{-1})	Φ_{ET}	Φ_{ET}^{P}
G1-NBD	2.49×10^7	0.98	0.95
G2-NBD	7.32×10^6	0.56	0.52
G3-NBD	8.16×10^6	0.51	0.38
G4-NBD	6.11×10^6	0.37	0.36

For the donor model compounds G*n*-QC, the average lifetime decreases as the generation increases. The generation-dependent trend for the target compounds G*n*-NBD is the same as that of the donor model compounds. These should be mainly induced by the triplet−triplet annihilation. Meanwhile, the shorter average lifetime of the triplet state for G*n*-NBD in comparison with that of corresponding G*n*-QC is consistent with the result of the phosphorescence experiments and indicates that an intramolecular triplet−triplet energy transfer from BP to NBD chromophores in G*n*-NBD indeed occurs. The rate constant (k_{ET}) and efficiency (Φ_{ET}) for the energy transfer can be calculated from the average lifetime of G*n*-NBD (τ_{NBD}) and G*n*-QC (τ_{QC}) according to eqs 2 and 3, respectively. The results are shown in Table 2. Along with the generation increase, the distance between donor and acceptor becomes larger, and we expected that k_{ET} should decrease dramatically. However, the experimental results show that k_{ET} for different generations is at the same magnitude. The reason for this unexpected result is discussed in the Mechanism of Energy Transfer section below.

$$k_{ET} = 1/\tau_{NBD} - 1/\tau_{QC} \tag{2}$$

$$\Phi_{ET} = 1 - \tau_{NBD}/\tau_{QC} \tag{3}$$

The energy transfer efficiency, Φ_{ET}, decreases with the generation increase, and this result agrees with the trend obtained by the phosphorescence measurements (Φ_{ET}^{P}). A little difference of the energy transfer efficiencies from the steady-state and time-resolved data for the same generation can be rationalized to the accuracy and the different experimental conditions. Usually, the increase in donor−acceptor separation that occurs as dendrimer generation increases is thought to be the reason for the decrease in energy transfer efficiency. In our work, the triplet−triplet annihilation of BP chromophores could be the main cause of the decrease of energy transfer efficiency because of the small change of the energy transfer rate constant with the generation. (See more in the Energy Transfer Mechanism part.)

Photosensitized Isomerization of the Norbornadiene to the Quadricyclane Group in G*n*-NBD. The photosensitized valence isomerization of NBD to QC has been the subject of intense experimental and theoretical investigations[19] in view of its significance in solar energy storage[20] and mechanism interests.[21] Benzophenone and some other aromatic ketones are known to sensitize NBD → QC isomerization through triplet−

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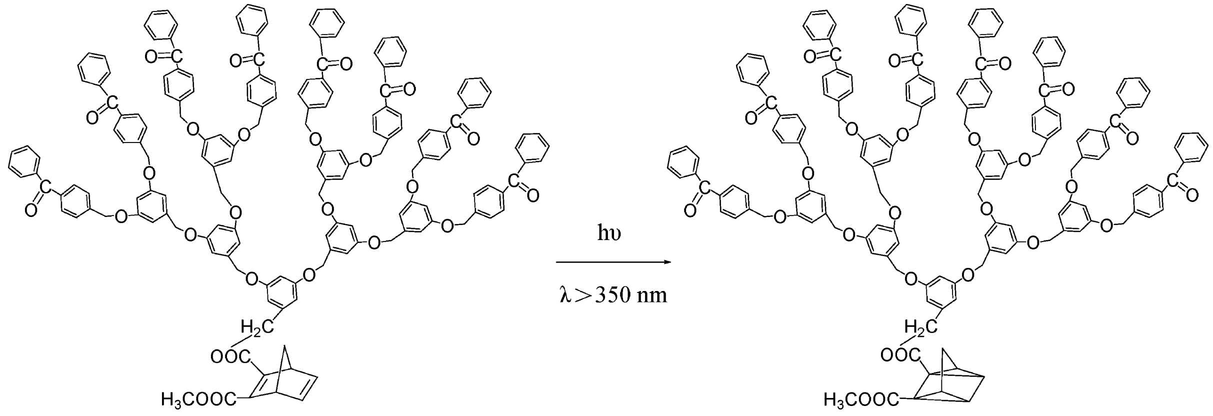
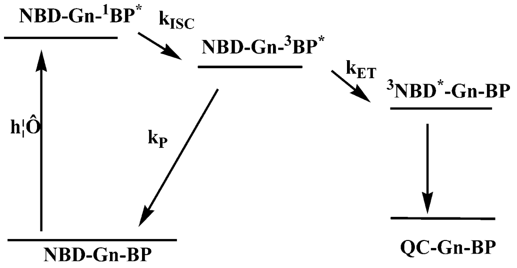
Scheme 1



Scheme 2



triplet energy transfer.[22] Thus, study of the intramolecular photosensitized isomerization of the NBD group in G*n*-NBD may provide evidence of triplet−triplet energy transfer in the dendritic system.

Irradiation with $\lambda > 350$ nm of a 2.0×10^{-5} M (concentration is calibrated by BP chromophore) solution of G*n*-NBD in degassed CH_2Cl_2 at room temperature results in valence isomerization of the norbornadiene group to the quadricyclane group (G*n*-QC), as shown in Scheme 1. Under this condition, only the BP chromophores absorb the light. Thus, the isomerization of NBD to QC must be attributed to the energy transfer. The yield of the isomerization product is almost 100% on the basis of the consumption of the starting material. The assignment of the product as the quadricyclane derivative relies mainly on its ^{1}H NMR spectrum, which is in close agreement with that reported in the literature.[16] The mass spectrometry shows that the product and the starting material have the same molecular weight. Measurements of the product formation at different concentrations revealed that the isomerization is induced by intramolecular photosensitization. On the basis of the experimental results mentioned above, the primary photophysical and photochemical processes in G*n*-NBD can be expressed by Scheme 2.

The quantum yield of this intramolecular photosensitization isomerization, Φ_{iso}(G*n*-NBD), can be calculated according to eq 4:

$$\Phi_{iso}(Gn\text{-}NBD) = \Phi_{isc}\Phi_{ET}\Phi_{iso}(NBD) \qquad (4)$$

where Φ_{isc} represents the quantum yield of the intersystem crossing from the singlet to the triplet excited state of the BP group and is assumed to be unity.[11] Φ_{ET} was obtained by phosphorescence and flash photolysis experiments mentioned above. Φ_{iso}(NBD) represents the quantum yield of the isomerization reaction of the NBD triplet state and is 0.185.[17] These in turn give Φ_{iso}(G*n*-NBD) as 0.18, 0.10, 0.082, and 0.068 for generations 1−4, respectively. The quantum yield of the isomerization of G*n*-NBD decreases with increasing generation due to the decrease of the energy transfer efficiency.

Further intramolecular photosensitized isomerization experiments of G*n*-NBD in degassed CH_2Cl_2 were done to determine the light-harvesting ability of G*n*-NBD. The same concentration (2.0×10^{-5} M) was used in the experiments for G*n*-NBD. After irradiation for 5 min with a 450 W high-pressure mercury lamp in a merry-go-round apparatus, the conversions of G*n*-NBD to G*n*-QC were 9, 15, 22, and 29% (the experiment accuracy is ±3%) for G1−G4, respectively. The observed rates of the isomerization for G1-NBD−G4-NBD were 3.6×10^{-7}, 6.0×10^{-7}, 8.8×10^{-7}, and 1.2×10^{-6} M min^{-1}, respectively. Obviously, the higher isomerization rate for higher generation is attributed to the light-harvesting ability of G*n*-NBD, referring to the larger molar absorption coefficient of higher generation.

Mechanism of BP to NBD Group Intramolecular Triplet−Triplet Energy Transfer. The flash photolysis and photosensitization reaction experiments reveal that the excitation of the BP chromophore in G*n*-NBD results in an intramolecular triplet−triplet energy transfer to the NBD group and subsequently leads to the isomerization of the latter group to QC (Scheme 2). The efficiencies of such triplet−triplet energy transfer are ca. 97, 54, 45, and 37% (average of steady-state and transient data), and the rate constants are ca. 2.5×10^7, 7.3×10^6, 8.2×10^6, and 6.1×10^6 s^{-1} for generations 1−4, respectively.

It has been well established that triplet−triplet energy transfer proceeds via the Dexter electron-exchange mechanism, and its rate constant decreases exponentially with an increasing of the distance between D and A.[11] The energy transfer is normally expected to become very inefficient as the D−A distance increases beyond 10 Å. In this study, the BP and NBD chromophores are located at the periphery and the core of the poly(aryl ether) dendrimer, G*n*-NBD ($n = 1{-}4$). Since the poly(aryl ether) dendrimer is not rigid, it is difficult to determine the interchromophoric distances within each generation. We used the HyperChem 6.0 program to calculate the lowest-energy conformation for each generation. While optimizing the conformation, the solvent effect could not be taken into account due to the limitation of the HyperChem program. The distance

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(22) (a) Murov, S.; Hammond, G. S. *J. Phys. Chem.* **1968**, *72*, 3797. (b) Hammond, G. S.; Wyatt, P.; Deboer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532.

Table 3. Distance between the BP and NBD

D–A distance (Å)	G1	G2	G3	G4
average	9.2	11.7	14.4	16.5
shortest	7.2	7.0	6.2	6.3

between the BP and NBD groups is defined as the distance between the C of the carbonyl in BP and the C of the vinyl closely connected to the dendrimer backbone. The average distances from our calculation are shown in Table 3, which are consistent with the data obtained by Fréchet et al.[8] The average distance between D and A increases with the generation and is 9.2 Å for generation 1. At such separation between the chromophores, triplet−triplet energy transfer via a through-space exchange process would be very inefficient and this is contrary to the experimental results. From the molecular modeling (shown in Supporting Information), we noticed that there is always a BP group folding back which is close to the acceptor at the core. Calculation of the shortest distance between the BP and NBD groups gave a similar number for generations 1−4, ca. 6−7 Å. In these distances, the triplet−triplet energy transfer could occur, which is accordant with the time-resolved results. One may argue that the energy transfer could proceed via a through-bond mechanism. However, if this energy transfer is via a through-bond mechanism, the rate constant will decrease with the generation increase. This is not consistent with the observation for the generation independence of the rate constants. On the basis of the calculation and experimental results mentioned above, we propose that the energy transfer mainly proceeds via a through-space mechanism. After the BP group is selectively excited, the intersystem crossing occurs with 100% efficiency. The triplet energy of BP migrates from one BP group to another rapidly and is transferred to the NBD group mainly via the closest BP group, which results in the isomerization of NBD to the QC group.

Conclusions

Flash photolysis and photochemical reaction studies demonstrate that triplet energy in G*n*-NBD can be transferred from the peripheral BP groups to the core NBD group with 97, 54, 45, and 37% efficiency for generations 1−4, respectively, leading to the valence isomerization of the NBD group to QC. The higher isomerization rate at higher generation indicates that the light-harvesting ability of G*n*-NBD increases with generation due to the number of peripheral chromophores that doubles from one dendrimer generation to the next, although the energy transfer efficiency decreases with increasing generation. The triplet energy transfer rate constant is ca. 10^6-10^7 s^{-1}, almost independent of the generation. The intramolecular triplet energy transfer proceeds mainly via a through-space mechanism involving the closest donor (folding back conformation) and acceptor groups. These findings reveal that one can use the peripheral antenna chromophore to harvest photon energy which is then utilized to initiate chemical reaction of a functional group at the core of the dendritic system.

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Supporting Information Available: Experimental procedures for the synthesis of all dendritic compounds, including analytical data. Structures of model compounds, phosphorescence spectra of G*n*-NBD and G*n*-QC, and molecular modeling for G*n*-NBD. This material is available free of charge via the Internet at http://pubs.acs.org.

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