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Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 429–436

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photophysical and photochemical studies on bis(Dendron) poly(aryl ether) dendrimers: Intramolecular triplet energy transfer in poly(aryl ether) dendrimers via a folded conformation

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Received 9 November 2005; received in revised form 19 December 2005; accepted 10 January 2006

Available online 14 February 2006

Abstract

A series of Fréchet-type bis(dendron) poly(aryl ether) dendrimers ([BP-G*n*]$_2$-NBD, $n = 1$–3) with the benzophenone (BP) chromophores and the norbornadiene (NBD) group attached to the periphery and the core, respectively, were synthesized, and their photophysical and photochemical properties were investigated by using steady-state and time-resolved techniques. Intramolecular triplet energy transfer from the peripheral BP chromophores to the core NBD group in [BP-G*n*]$_2$-NBD occurs with the efficiency of ca. 84%, 56% and 48%, and with the rate constant of 1.9×10^7, 1.2×10^7, $1.1 \times 10^7\ \mathrm{s}^{-1}$ at room temperature for generations 1–3, respectively. Selective excitation of the BP groups resulted in the isomerization of NBD to the quadricyclane (QC). The quantum yields of the intramolecular photosensitized isomerization for [BP-G*n*]$_2$-NBD are measured to be ca. 0.147, 0.098 and 0.087 for generations 1–3, respectively. The light-harvesting ability of these molecules increases with increasing the number of peripheral chromophores. The rate constant of the triplet–triplet energy transfer decreases inconspicuously with increasing generation, which validates that the intramolecular triplet energy transfer mainly takes place via a through space mechanism involving the closest donor and the acceptor groups by folding of the dendrimer structure, and the bis(dendron) system takes more congested conformation than the corresponding monodendron system.

Keywords: Dendrimer; Light-harvesting; Triplet–triplet energy transfer; Photosensitized isomerization

1. Introduction

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 the dendrimer makes it as a mimic light-harvesting system, where the antenna chromophores surround the central reaction center [1–3].

The energy transfer in dendrimers has been extensively examined by several groups [4–9]. Most of the studies [10] on the intramolecular energy transfer between the periphery chromophores and the core in dendrimers are related to the singlet states only, and the energy transfer proceeds efficiently via Förster mechanism [11]. As we know, the triplet–triplet energy transfer is the most common and important type of energy transfer involved in chemical and biochemical processes [12,13]. Dendrimers capable of light harvesting through the triplet–triplet energy transfer mechanism have rarely been demonstrated [14]. Furthermore, the majority of the studies for intramolecular energy transfer of dendrimers concern photophysical processes. There are only a few examples of application of intramolecular energy transfer dealing with photochemical process [7]. Recently, our study shows that the intramolecular triplet energy transfer from the periphery chromophores to the core group in monodendron poly(aryl ether) dendrimers can occur efficiently, and we propose that the energy transfer proceeds via a through space mechanism involving the closest donor (D) and acceptor (A) groups [15]. Continuing our studies on the intramolecular triplet energy transfer in poly(aryl ether) dendrimer, we design and synthesize a series of bis(dendron) poly(aryl ether)

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doi:10.1016/j.jphotochem.2006.01.002

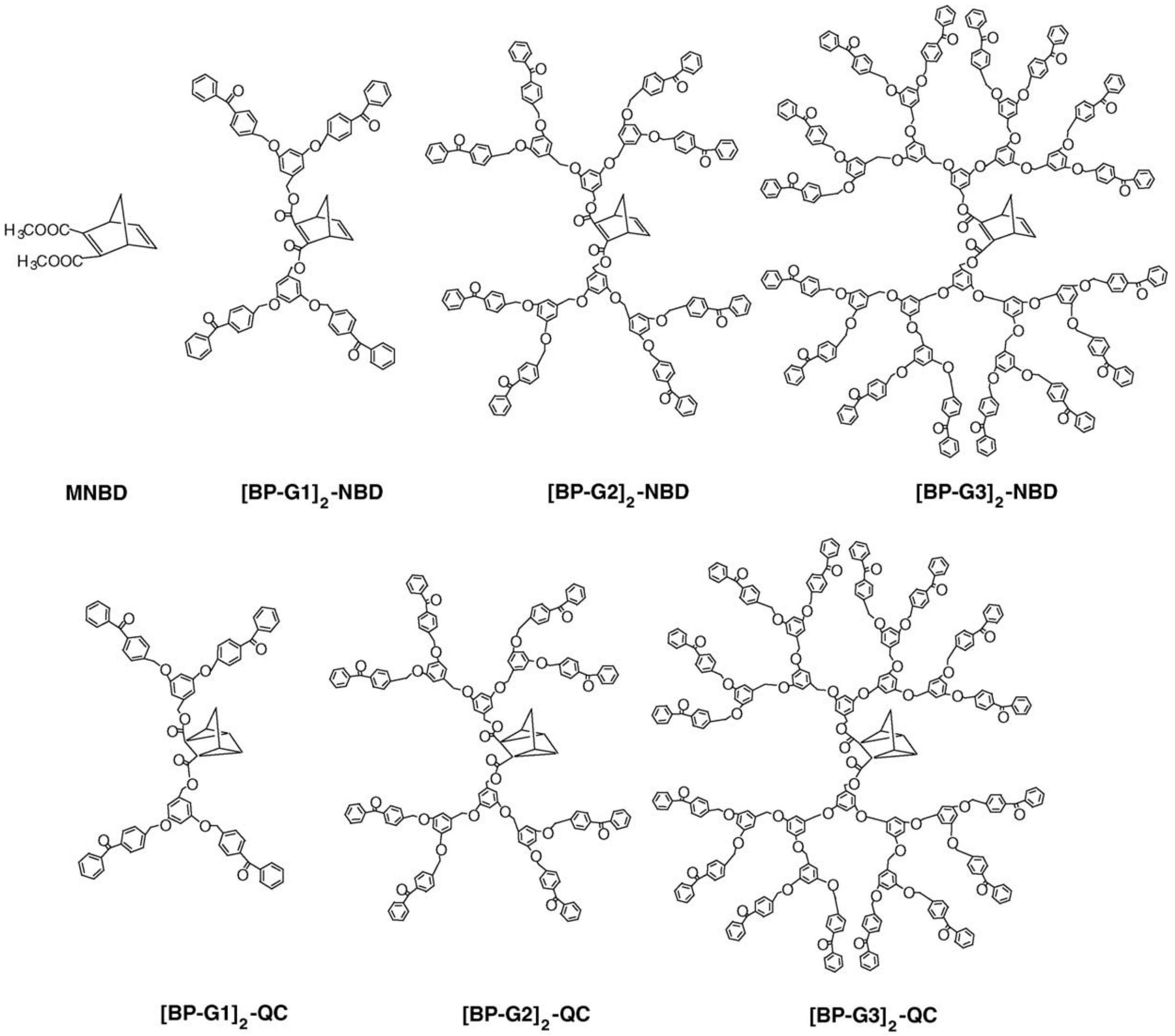


Fig. 1. Structures of MNBD, [BP-Gn]$_2$-NBD and [BP-Gn]$_2$-QC compounds.

dendrimers ([BP-Gn]$_2$-NBD) with the benzophenone (BP) chromophores and the norbornadiene (NBD) group attaching to the periphery and the core, respectively. The dendritic system we create is suitable for the Dexter triplet energy transfer, and a photochemical reaction of the core is used as the probe to detect the energy transfer occurrence. Emission quenching, laser flash photolysis and photochemical reaction of the core results suggest that the triplet energy transfer can occur efficiently. This study validates that the triplet energy transfer takes place by folding of the dendrimer structure. The dendrimers are synthesized up to third generation, as shown in Fig. 1.

2. Experimental

2.1. Materials

Reagents were purchased from Aldrich or Acros and were used without further purification, unless otherwise noted. Acetone was dried with anhydrous K_2CO_3 and distilled. Spectral-grade dichloromethane (CH_2Cl_2) and 2-methyltetrahydrofuran (MTHF) were used for absorption and emission spectra, flash photolysis, and steady-state photoirradiation measurements.

2.2. 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. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker BIFLEX spectrometer. High-performance liquid chromatography (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.

2.3. Phosphorescence measurements

Phosphorescence studies were performed in MTHF at 77 K. The excitation wavelength was 355 nm. For comparison of the emission efficiency of [BP-Gn]$_2$-NBD with the donor model compounds ([BP-Gn]$_2$-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.

2.4. 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 a computer.

2.5. General procedure for the synthesis of [BP-Gn]$_2$-NBD system

These reactions were carried out on scales of about 300 mg. A mixture of the appropriate dendritic benzyl alcohol (BP-Gn-OH) (2.00 equiv.), bicyclo[2.2.1]hepta-2,5-diene-2,3-bicarboxylic acid (NBD-[COOH]$_2$) (1.00 equiv.), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (2.00 equiv.), and 4-dimethylaminopyridine (0.2 equiv.) in dry CH_2Cl_2 was stirred under nitrogen and in dark for 24 h. For the generation 3, large excesses amount of DCC were required to complete the reaction. The reaction mixture was diluted by CH_2Cl_2 and washed by water. The aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

[BP-G1]$_2$-NBD: It was prepared from BP-G1-OH and NBD-[COOH]$_2$, purified by column chromatography eluting with CH_2Cl_2, gradually increasing to 1/30 ethyl ether/CH_2Cl_2 to give [BP-G1]$_2$-NBD as white amorphous solid: yield 86%; retention time $t_R = 11.7$ min in HPLC (acetonitrile/THF = 10/1); IR ν (cm^{-1}) 1711, 1658, 1597, 1448, 1374, 1316, 1278, 1149, 1051, 1017, 937, 923, 836, 786, 733, 700; ^{1}H NMR ($CDCl_3$) δ 2.11–2.31 (m, 2H, NBD bridge H), 3.97 (s, 2H, NBD bridgehead H), 5.07 (s, 8H, –CO-Ph-CH_2–), 5.12 (s, 4H, –$COOCH_2$–), 6.53 (m, 2H, ArH), 6.60 (m, 4H, ArH), 6.93 (s, 2H, NBD olefinic H), 7.45–7.61 (m, 20H, Ph-CO–), 7.77–7.81 (t, 16H, $J = 8$ Hz, –CO-Ph-); MS (MALDI-TOF): *m*/*z* 1223.6 ($M + Na^+$), 1239.5 ($M + K^+$), calcd. *m*/*z* 1201.31.

[BP-G2]$_2$-NBD: It was prepared from BP-G2-OH and NBD-[COOH]$_2$, purified by column chromatography eluting with CH_2Cl_2, gradually increasing to 1/20 ethyl ether/CH_2Cl_2 to give [BP-G2]$_2$-NBD as white amorphous solid: yield 73%; retention time $t_R = 9.8$ min in HPLC (acetonitrile/THF = 4/1); IR ν (cm^{-1}) 1711, 1658, 1597, 1448, 1372, 1316, 1278, 1156, 1052, 1018, 938, 924, 836, 788, 732, 701; ^{1}H NMR ($CDCl_3$) δ 2.13–2.38 (m, 2H, NBD bridge H), 3.99 (s, 2H, NBD bridgehead H), 4.92 (s, 8H, $ArCH_2$–), 5.09 (s, 16H, –CO-Ph-CH_2–), 5.14 (s, 4H, –$COOCH_2$–), 6.52–6.77 (m, 21H, ArH), 6.95 (s, 2H, NBD olefinic H), 7.48–7.62 (m, 40H, Ph-CO–), 7.80–7.87 (t, 32H, $J = 8$ Hz, –CO-Ph-); MS (MALDI-TOF): *m*/*z* 2488.1($M + Na^+$), 2504.0 ($M + K^+$), calcd. *m*/*z* 2466.71.

[BP-G3]$_2$-NBD: It was prepared from BP-G3-OH and NBD-[COOH]$_2$, purified by column chromatography eluting with CH_2Cl_2, gradually increasing to 1/10 ethyl ether/CH_2Cl_2 to give [BP-G3]$_2$-NBD as white amorphous solid: yield 60%; retention time $t_R = 14.2$ min in HPLC (acetonitrile/THF = 2.5/1); IR ν (cm^{-1}) 1710, 1658, 1596, 1447, 1371, 1315, 1278, 1155, 1050, 1017, 937, 924, 835, 787, 732, 701; ^{1}H NMR ($CDCl_3$) δ 2.02–2.25 (m, 2H, NBD bridge H), 3.91 (s, 2H, NBD bridgehead H), 4.78 (s, 8H, $ArCH_2$–), 4.82 (s, 16H, $Ar'CH_2$–), 5.00 (s, 36H, –$COOCH_2$– and –CO-Ph-CH_2–), 6.41–6.64 (m, 42H, ArH), 6.86 (s, 2H, NBD olefinic H), 7.41–7.56 (m, 80H, Ph-CO–), 7.72–7.75 (t, 64H, $J = 8$ Hz, –CO-Ph-); MS (MALDI-TOF): *m*/*z* 5038 ($M + K^+$), calcd. *m*/*z* 4997.51.

2.6. General procedure for the synthesis of [BP-Gn]$_2$-QC and the determination of quantum yields for the photosensitized isomerization of [BP-Gn]$_2$-NBD

The valence isomers ([BP-Gn]$_2$-QC, $n = 1$–3) were prepared from [BP-Gn]$_2$-NBD and the reactions were carried out on scales of about 20 mg. Photoirradiation was carried out in a Pyrex reactor, and the samples were purged with nitrogen. A 500 W middle-high-pressure mercury lamp was used as the excitation source. A WB-350 glass filter was used to cut off the light with $\lambda < 350$ nm. The concentrations of the sample (computed with benzonphenone) were ca. 10^{-3} M in CH_2Cl_2. The irradiation time was determined by TLC monitoring. After irradiation, the crude products were purified as outlined in the following text. For the determination of quantum yields for the intramolecular photosensitization isomerization of [BP-Gn]$_2$-NBD, same light source and filter were used as the photoirradiation. The number of photons (Np) absorbed by [BP-Gn]$_2$-NBD was measured by using a benzophenone/benzohydrol system for actinometry ($\Phi = 0.74$ in benzene) [16]. The phosphorescence changes before and after irradiation were used to measure the conversion of the isomerization, which was controlled below 10%.

[BP-G1]$_2$-QC: It was prepared from [BP-G1]$_2$-NBD and purified by column chromatography eluting with 1/20 ethyl ether/CH_2Cl_2 to give [BP-G1]$_2$-QC: yield 92%; ^{1}H NMR ($CDCl_3$) δ 2.14–2.54 (m, 6H, QC H), 5.06 (s, 4H, –$COOCH_2$–), 5.10 (s, 8H, –CO-Ph-CH_2–), 6.54 (s, 2H, ArH), 6.62 (s, 4H, ArH), 7.45–7.61 (m, 20H, Ph-CO–), 7.77–7.81 (t, 16H, $J = 8$ Hz, –CO-Ph-).

[BP-G2]$_2$-QC: It was prepared from [BP-G2]$_2$-NBD and purified by column chromatography eluting with 1/15 ethyl ether/CH_2Cl_2 to give [BP-G2]$_2$-QC: yield 88%; ^{1}H NMR ($CDCl_3$) δ 1.94–2.44 (m, 6H, QC H), 4.84 (s, 8H, $ArCH_2$–), 4.95 (s, 4H, –$COOCH_2$–), 4.99 (s, 16H, –CO-Ph-CH_2–), 6.41–6.59 (m, 21H, ArH), 7.36–7.51 (m, 40H, Ph-CO–), 7.68–7.72 (t, 32H, $J = 8$ Hz, –CO-Ph-).

[BP-G3]$_2$-QC: It was prepared from [BP-G3]$_2$-NBD and purified by column chromatography eluting with 1/10 ethyl ether/CH_2Cl_2 to give [BP-G3]$_2$-QC: yield 81%; ^{1}H NMR ($CDCl_3$) δ 1.99–2.41 (m, 6H, QC H), 4.76 (s, 8H, $ArCH_2$–), 4.78 (s, 16H, $Ar'CH_2$–), 4.95 (d, 36H, –$COOCH_2$– and –CO-Ph-

CH_2–), 6.41–6.58 (m, 42H, ArH), 7.34–7.50 (m, 80H, Ph-CO–), 7.66–7.69 (t, 64H, $J = 8$ Hz, –CO-Ph-).

3. Results and discussion

3.1. Synthesis and stability of the dendrimers

Benzophenone functionalized dendritic benzyl alcohols (BP-G*n*-OH, $n = 1$–3) were synthesized with Fréchet's method [17], and were described elsewhere [15]. The target compounds, [BP-G*n*]$_2$-NBD ($n = 1$–3), were synthesized with BP-G*n*-OH and bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid (NBD-[COOH]$_2$). Synthesis of the fourth generation compound ([BP-G4]$_2$-NBD) was failed. Even more excessive amount of BP-G4-OH was used, we could only obtained a monodendron substituent product. The details of the synthesis and purification of [BP-G*n*]$_2$-NBD ($n = 1$–3), are described in Section 2. [BP-G*n*]$_2$-NBD ($n = 1$–3), were characterized by ^{1}H NMR, IR, mass spectrometry (MALDI-TOF), and HPLC. [BP-G*n*]$_2$-QC ($n = 1$–3), the valence isomers with the structure similar to that of (BP-G*n*)$_2$-NBD were used as the model compounds, which were prepared from the isomerization of [BP-G*n*]$_2$-NBD by irradiation with $\lambda > 350$ nm light. They were characterized by ^{1}H NMR. The structures of [BP-G*n*]$_2$-QC and the acceptor model compound, dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD), are also shown in Fig. 1. [BP-G*n*]$_2$-NBD ($n = 1$–3) must be stored in the dark because they are very sensitive to the light, which can induce the isomerization of [BP-G*n*]$_2$-NBD to [BP-G*n*]$_2$-QC in solution even with room light, especially for the higher generations.

3.2. Photophysical studies on the intramolecular triplet energy transfer from the benzophenone chromophores to the norbornadiene group in [BP-Gn]$_2$-NBD

To search for the evidence of ground state interactions between the donor benzophenone and the acceptor norbornadiene groups in [BP-G*n*]$_2$-NBD, the absorption spectra of dendrimers ([BP-G*n*]$_2$-NBD), models for the donor ([BP-G*n*]$_2$-QC) and the acceptor (MNBD), were measured in CH_2Cl_2. Table 1 gives the parameters of the absorption spectra for [BP-G*n*]$_2$-NBD, [BP-G*n*]$_2$-QC, and MNBD. No measurable interaction between the NBD and the BP chromophores of [BP-G*n*]$_2$-NBD in the ground state can be observed from the absorption spectra. Significantly, the absorption of BP extends to a wavelength longer than that of NBD, which suggests that the singlet–singlet energy transfer from the excited BP chromophore to the NBD group is impossible. Furthermore, this fact permits selective excitation of the BP moiety in the [BP-G*n*]$_2$-NBD system. Within experimental error, the molar extinction coefficient of benzophenone chromophore doubles with each generation increase, which means that the light-harvesting capability of the molecules can be enhanced by increasing the generation number.

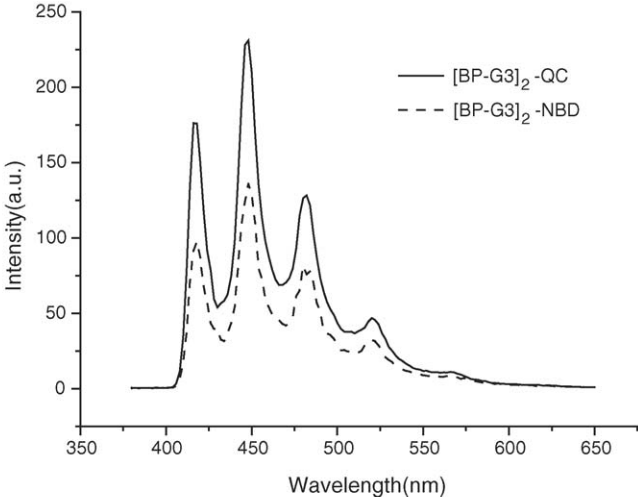


Fig. 2. Phosphorescence spectra of [BP-G3]$_2$-NBD and [BP-G3]$_2$-QC in MTHF at 77 K. $\lambda_{ex} = 355$ nm. Concentrations computed with benzophenone are both 6×10^{-5} M.

The emission spectra of [BP-G*n*]$_2$-NBD and [BP-G*n*]$_2$-QC were studied in glassy 2-methyltetrahydrofuran at 77 K. An example of the emission spectra of [BP-G3]$_2$-NBD and [BP-G3]$_2$-QC is presented in Fig. 2. [BP-G*n*]$_2$-NBD and [BP-G*n*]$_2$-QC both show the structured phosphorescence characteristic of the benzophenone chromophore with maxima at 416, 445, 480, and 519 nm. The shape and peak positions of these two phosphorescence spectra are essentially identical, but the overall intensities are different. The phosphorescence efficiency of [BP-G*n*]$_2$-NBD is ca. 84%, 37%, and 38% less than that of the model compound, [BP-G*n*]$_2$-QC, for generations 1–3, respectively. This finding indicates that the phosphorescence of BP is quenched by the NBD group in [BP-G*n*]$_2$-NBD.

To clarify the reason for the intramolecular quenching of BP phosphorescence by the NBD group in [BP-G*n*]$_2$-NBD, we estimated the free energy change involved in an electron transfer process, which can be calculated by the Rehm–Weller equation [18]:

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

Table 1
Absorption data of [BP-G*n*]$_2$-NBD, [BP-G*n*]$_2$-QC and MNBD

	[BP-G*n*]$_2$-NBD			[BP-G*n*]$_2$-QC			MNBD
	G1	G2	G3	G1	G2	G3	
λ_{max} (nm)	255, 343	255, 343	255, 343	255, 343	255, 343	255, 343	–
ε_{343} ($\times 10^{-3}$ M^{-1} cm^{-1})	0.85	1.72	3.40	0.88	1.73	3.48	0

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 [19]. The redox potentials of BP, $E(\text{BP}/\text{BP}^{\bullet -})$, and the acceptor model compound (MNBD), $E(\text{NBD}^{\bullet +}/\text{NBD})$, in dichloromethane are −2.40 and +1.50 V, respectively, with respect to Ag/Ag$^+$ [15]. The $e^2/r\varepsilon$ represents the Coulombic energy associated with bringing separated radical ions at a distance r (r = 5–6 Å in [BP-Gn]$_2$-NBD, n = 1–3; see Section 3.4) in a solvent of dielectric constant ε ($\varepsilon = 9.08D$). Calculation according to Eq. (1) shows that ΔG = 14–15 kcal/mol for [BP-Gn]$_2$-NBD (n = 1–3), suggesting that the 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) [20] is much lower than that of the BP group (69 kcal/mol). Thus, the 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 [BP-Gn]$_2$-NBD is due to the intramolecular triplet–triplet energy transfer to the NBD group.

The evidence for the intramolecular triplet–triplet energy transfer in [BP-Gn]$_2$-NBD based on phosphorescence efficiency is further strengthened by the flash photolysis study. Pulsed-laser photolysis of the model compounds, [BP-Gn]$_2$-QC, and the target compounds, [BP-Gn]$_2$-NBD, was performed in deaerated CH_2Cl_2 by using 355 nm excitation light, which gives rise to a strong transient absorption spectrum with a maximum at 536 nm. The typical transient absorption spectra for [BP-G3]$_2$-NBD and [BP-G3]$_2$-QC are given in Fig. 3. This absorption is assigned to the lowest triplet state of the BP chromophore by reference to the transient absorption of the triplet state of alkyl benzophenone-4-carboxylate [15,21]. Furthermore, the 536 nm species is rapidly quenched by O_2. The transient absorption of the model compounds [BP-Gn]$_2$-QC is identical with that of [BP-Gn]$_2$-NBD.

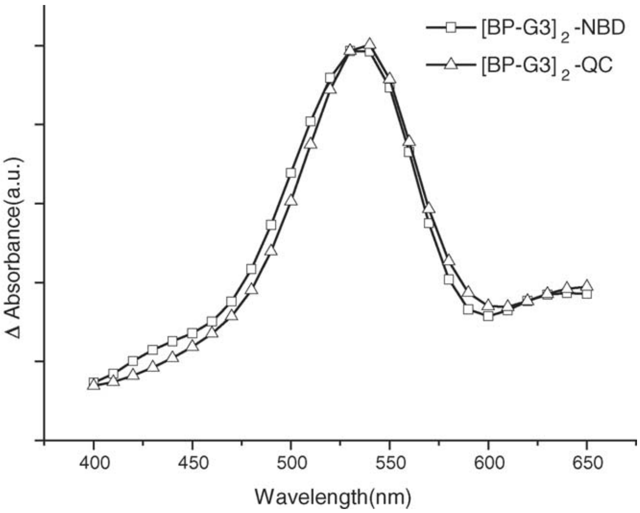


Fig. 3. Transient absorption spectra of benzophenone triplet state formed upon laser photolysis of [BP-G3]$_2$-NBD and [BP-G3]$_2$-QC in CH_2Cl_2 190 ns after the laser pulse (λ_{ex} = 355 nm, concentrations computed with benzophenone are both 8×10^{-4} M).

Table 2
Triplet state lifetime for dendrimers [BP-Gn]$_2$-NBD and [BP-Gn]$_2$-QC, all measured in CH_2Cl_2 by flash photolysis

Compound	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_{av} (ns)
[BP-G1]$_2$-NBD	203	0.14	17	0.86	43
[BP-G2]$_2$-NBD	145	0.17	27	0.83	47
[BP-G3]$_2$-NBD	168	0.16	25	0.84	48
[BP-G1]$_2$-QC	421	0.17	230	0.83	262
[BP-G2]$_2$-QC	161	0.20	92	0.80	106
[BP-G3]$_2$-QC	318	0.19	48	0.81	99

Analysis of the transient spectra of [BP-Gn]$_2$-NBD and [BP-Gn]$_2$-QC at 536 nm as a function of time yields lifetimes of [BP-Gn]$_2$-NBD and [BP-Gn]$_2$-QC, and the entire set of acquired data is summarized in Table 2. None of the compounds investigated exhibits monoexponential decay profile. This result is quite compatible with the data reported for laser-dye-labeled poly(aryl ether) dendrimers by Fréchet et al. [8] and what we obtained in monodendron system [15]. The molecular modeling (calculated by HyperChem 6.0) shows that the BP groups are close to each other with ca. 4 Å shortest distance, and the triplet–triplet annihilation could easily occur within this space [12,22]. Thus, we propose that the non-monoexponential behavior is mainly due to the intramolecular triplet–triplet annihilation, which is supported by the phosphorescence measurement and the laser power dependence of the transient data. 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.

The average lifetime of the donor model compounds [BP-Gn]$_2$-QC decreases with the generation, which should be mainly induced by the triplet–triplet annihilation. The shorter average lifetime of the triplet state for [BP-Gn]$_2$-NBD in comparison with that of the corresponding [BP-Gn]$_2$-QC is consistent with the result of the phosphorescence experiments, and indicates that an intramolecular triplet–triplet energy transfer from the BP to the NBD chromophores in [BP-Gn]$_2$-NBD indeed occurs.

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

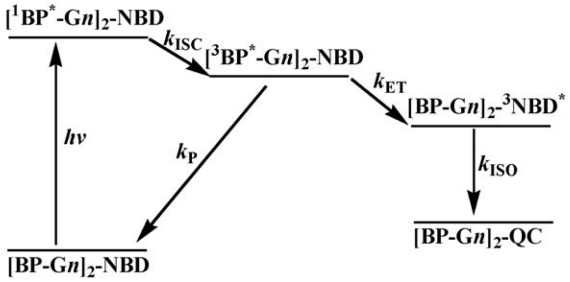
$$\Phi_{\text{ET}} = 1 - \tau_{\text{NBD}}/\tau_{\text{QC}} \tag{3}$$

The rate constant (k_{ET}) and the efficiency (Φ_{ET}) for the energy transfer can be calculated from the average lifetimes of [BP-Gn]$_2$-NBD (τ_{NBD}) and [BP-Gn]$_2$-QC (τ_{QC}) according to Eqs. (2) and (3), respectively. k_{ET} is 1.9×10^7, 1.2×10^7, and $1.1 \times 10^7\ \text{s}^{-1}$ for generations 1–3, respectively, which does not change conspicuously along with the generation increase and is at the same magnitude as that of the monodendron system [15]. These results validate the triplet energy transfer takes place by folding of the dendrimer structure (see more in Section 3.4). The energy transfer efficiency, Φ_{ET}, is 0.84, 0.56 and 0.48 for generations 1–3, respectively, which agrees with the trend obtained by the phosphorescence measurements ($\Phi_{\text{ET}}^{\text{P}}$). The difference of the energy transfer efficiencies between Φ_{ET} and $\Phi_{\text{ET}}^{\text{P}}$ for the same generation can be rationalized to the temperature effect. In our work, because the increase of the triplet–triplet annihilation of BP chromophores with generation cannot be ignored, we consider that besides the increase in donor–acceptor (D–A) separation that occurs as the dendrimer generation increases is as the main reason for the decrease in energy transfer efficiency, the triplet–triplet annihilation of BP chromophores also contributes some to the decrease of the energy transfer efficiency in our work.

3.3. *Photosensitized isomerization of the norbornadiene to the quadricyclane group in [BP-Gn]$_2$-NBD*

The photosensitized valence isomerization of NBD to QC has been the subject of intense experimental and theoretical investigations in view of its significance in solar energy storage [23] and mechanism interests [24]. Benzophenone and some other aromatic ketones are known to sensitize NBD to QC isomerization through triplet–triplet energy transfer [25]. Thus, the study of the intramolecular photosensitized isomerization of the NBD group in [BP-G*n*]$_2$-NBD may provide the evidence of triplet–triplet energy transfer in the dendritic system.

Irradiation with $\lambda > 350$ nm of a 6.0×10^{-5} M (concentration is calibrated by BP chromophore) solution of [BP-G*n*]$_2$-NBD in deaerated CH_2Cl_2 at room temperature results in a valence isomerization of the norbornadiene group to the quadricyclane ([BP-G*n*]$_2$-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 triplet 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 [15]. Measurements of the product formation at different concentrations reveal that the isomerization is induced by the intramolecular photosensitization. The quantum yields of the intramolecular photosensitized isomerization (Φ_{iso}([BP-G*n*]$_2$-NBD)) were measured to be ca. 0.147, 0.098 and 0.087 for generations 1–3, respectively, by using a benzophenone/benzohydrol system as actinometry [25]. On the basis of the experimental results mentioned above, the primary photophysical and photochemical processes in [BP-G*n*]$_2$-NBD can be expressed by Scheme 2. According to Scheme 2, Φ_{iso}([BP-G*n*]$_2$-NBD) is a product of the efficiency of intersystem crossing from the singlet to the triplet excited state of the BP group (Φ_{isc}), the energy transfer efficiency (Φ_{ET}), and the quantum yield of the isomerization reaction of the NBD triplet state (Φ_{iso}(NBD)). Φ_{iso}(NBD) is determined to be 0.185 [21], and Φ_{isc} is assumed to be unity [12]. These in turn give Φ_{ET} as 0.79, 0.53, and 0.47 for generations 1–3, respectively, which agrees with the numbers obtained by the transient absorption measurements.

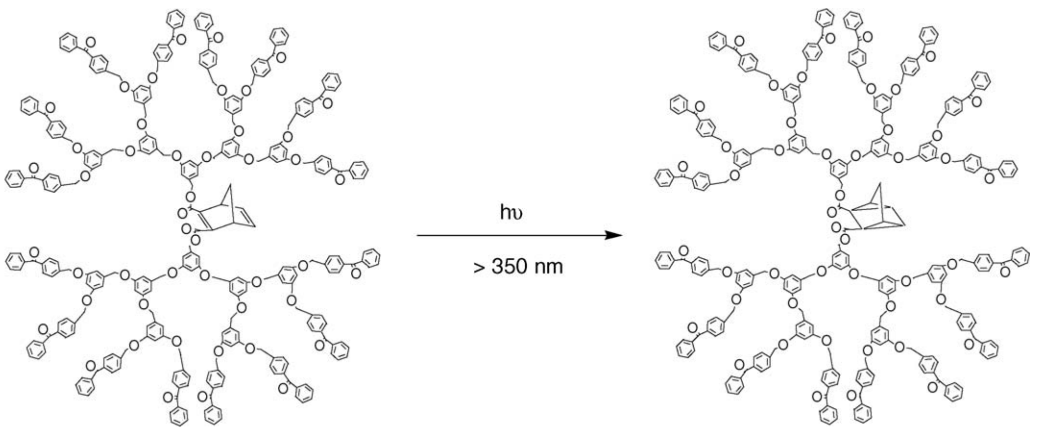


Scheme 2.

Further intramolecular photosensitized isomerization experiments of [BP-G*n*]$_2$-NBD in deaerated MTHF were done to determine the light harvesting ability of [BP-G*n*]$_2$-NBD. For comparison the isomerization of the monodendron system (BP-G*n*-NBD, see structure in the Supplementary data) was also done. The same concentration (1.5×10^{-5} M) was used in the experiments for [BP-G*n*]$_2$-NBD and BP-G*n*-NBD. The conversions of [BP-G*n*]$_2$-NBD to [BP-G*n*]$_2$-QC, and BP-G*n*-NBD to

Table 3
Conversions of [BP-G*n*]$_2$-NBD and BP-G*n*-NBD in CH_2Cl_2 at ambient temperature after irradiation for 5 min with $\lambda > 350$ nm at the same condition (1.5×10^{-5} M)

	Conversion (%)		Observed isomerization rate (M min^{-1})	
	[BP-G*n*]$_2$-NBD	BP-G*n*-NBD	[BP-G*n*]$_2$-NBD	BP-G*n*-NBD
G1	7	5	2.1×10^{-7}	1.5×10^{-7}
G2	16	11	4.8×10^{-7}	3.3×10^{-7}
G3	29	18	8.7×10^{-7}	5.4×10^{-7}



Scheme 1.

Table 4
Energy transfer efficiencies and rate constants for compounds [BP-G*n*]$_2$-NBD and BP-G*n*-NBD

	k_{ET} (s^{-1})		Φ_{ET}		Φ_{ET}^{P}	
	[BP-G*n*]$_2$-NBD	BP-G*n*-NBD[a]	[BP-G*n*]$_2$-NBD	BP-G*n*-NBD[a]	[BP-G*n*]$_2$-NBD	BP-G*n*-NBD[a]
G1	1.9×10^7	2.49×10^7	0.84	0.98	0.84	0.95
G2	1.2×10^7	7.32×10^6	0.56	0.56	0.37	0.52
G3	1.1×10^7	8.16×10^6	0.48	0.51	0.38	0.38

[a] Data from Ref. [15].

BP-G*n*-QC after irradiation for 5 min with a 500 W middle-high-pressure mercury lamp in a merry-go-round apparatus, were listed in Table 3, together with the observed rates of the isomerization. The conversions of isomerization are determined by the phosphorescence changes before and after irradiation with accuracy ca. ±3%. Obviously, the relative higher observed isomerization rate for bis(dendron) compounds is attributed to the higher light-harvesting ability of [BP-G*n*]$_2$-NBD, referring to their larger molar absorption coefficient. However, it should be pointed out that the increased observed rate of the isomerization with generation does not mean higher energy utilization.

3.4. Mechanism of intramolecular triplet–triplet energy transfer

The flash photolysis and the photosensitization reaction experiments reveal that the excitation of the BP chromophores in [BP-G*n*]$_2$-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. The efficiencies and the rate constants of the triplet–triplet energy transfer for [BP-G*n*]$_2$-NBD, together with those of monodendron system BP-G*n*-NBD are summarized in Table 4.

The mechanism for the triplet energy transfer is usually described by Dexter electron exchange interaction [13] and may be visualized in terms of two electron transfer processes or one electron transfer and one hole transfer processes [12]. Generally, this electron exchange requires strong D–A orbital overlap, and therefore the energy transfer rate constant decreases exponentially with increasing D–A distance. The energy transfer is normally expected to become very inefficient as the D–A distance increases beyond 10 Å except the energy transfer occurs via a "through bond mechanism" in a conjugated or a rigid system. We can exclude the through bond mechanism in our study because there is only a moderate change for the rate constant with the generation increase. In the bis(dendron) system [BP-G*n*]$_2$-NBD, the BP and NBD chromophores are located at the periphery and the core of the poly(aryl ether) dendrimer. Since the poly(aryl ether) dendrimer is not rigid, it is difficult to determine the interchromophoric distances within each generation. Although the detailed three-dimensional structures of dendrimers are not well-understood, recent theoretical [26] and experimental results [15,27,28] suggest that dendrimers with flexible backbone will take a folded conformation, especially at higher generation. Our previous study on the monodendron system proposed that the triplet energy transfer from the periphery chromophores to the core took place via a through space mechanism involving the closest donor and acceptor groups by folding of the dendrimer structure. In the present study the rate constant of the triplet energy transfer from the periphery chromophore to the core changes inconspicuously with increasing generation, which means that the separation of the donor and the acceptor involved in the energy transfer in different generation is similar. Therefore, [BP-G*n*]$_2$-NBD must take a folded conformation to make the donor and the acceptor groups in an effective triplet energy transfer range.

The rate constants of the energy transfer for [BP-G*n*]$_2$-NBD are at the same magnitude, and a little bit higher than those of the monodendron system, BP-G*n*-NBD, for generations 2 and 3. The rate constant of the energy transfer for the electron exchange mechanism can be expressed by Eq. (4):

$$k_{ET} = KJ \exp(-2R_{DA}/L) \tag{4}$$

where *K* is related to the specific orbital interactions, *J* is a spectral overlap integral normalized for the extinction coefficient of the acceptor, and R_{DA} is the donor–acceptor separation relative to their van der Waals radii, *L*. Since same donor and acceptor are used in mono- and bis(dendron) system, taking R_{DA} of BP-G*n*-NBD as 6–7 Å [15] and setting *L* equal to 4.3 + 3.6 Å by assuming that both donor and acceptor are spherical, R_{DA} of [BP-G*n*]$_2$-NBD ($n = 2$–3) is estimated to be ca. 1–2 Å shorter than that of the corresponding generation BP-G*n*-NBD. This result demonstrates that the higher generation bis(dendron) system prefers to take more congested conformation.

On the basis of the calculation and experimental results mentioned above, we propose that the triplet energy transfer in [BP-G*n*]$_2$-NBD mainly proceeds via a through space mechanism. After the BP group is selectively excited, the intersystem crossing occurs with 100% efficiency. The triplet energy transfers to the NBD group mainly via the closest BP chromophore, which results in the isomerization of NBD to the QC group. Because the dynamic motion of the molecular moiety is prohibited at 77 K, the energy transfer efficiency at 77 K is lower than that at room temperature for [BP-G*n*]$_2$-NBD ($n = 2$ and 3). The high energy transfer efficiency for [BP-G1]$_2$-NBD at 77 K is due to the proximity of the donor and the acceptor.

4. Conclusions

Flash photolysis and photochemical reaction studies demonstrate that the triplet energy in [BP-G*n*]$_2$-NBD can be transferred from the peripheral BP groups to the core NBD group with 84%, 56%, and 48% efficiency for generations 1–3, respectively, leading to a valence isomerization of the NBD group to QC.

The triplet energy transfer rate constant is ca. $10^7\ s^{-1}$, which is almost independent of the generation. The quantum yields of the intramolecular photosensitized isomerization of $[BP\text{-}Gn]_2$-NBD to $[BP\text{-}Gn]_2$-QC are ca. 0.147, 0.098 and 0.087 for generations 1–3, respectively. The higher observed isomerization rates for bis(dendron) compounds indicate that the light-harvesting ability increases with the number of peripheral chromophores. The intramolecular triplet energy transfer proceeds mainly via a through space mechanism involving the proximate donor and acceptor groups by folding of the dendrimer structure. The bis(dendron) system takes more congested conformation than the corresponding monodendron system, which gives a relative higher energy transfer rate constant. These findings validate the existence of the folded conformation in poly(aryl ether) dendrimers.

Acknowledgements

Financial support for this work by National Science Foundation of China (Nos. 20273081 and 20574086) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.jphotochem.2006.01.002.

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