

Valence isomerization in dendrimers by photo-induced electron transfer and energy transfer from the dendrimer backbone to the core

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Abstract

A series of poly(aryl ether) dendrimers with a norbornadiene (NBD) group attaching to the core (*Gn*-NBD), generations 1–4, were synthesized and characterized, and their photophysical and photochemical properties were examined. The fluorescence of the dendrimer backbone is quenched by the norbornadiene group as a result of the electron transfer and energy transfer from the dendrimer backbone to the norbornadiene group in *Gn*-NBD. Selective excitation of the dendrimer backbone results in an isomerization of the norbornadiene group to the quadricyclane (QC) group. The intramolecular electron transfer and energy transfer efficiencies are ca. 0.93, 0.73, 0.54, 0.30 in dichloromethane, and ca. 0.90, 0.70, 0.55, 0.34 in tetrahydrofuran for generations 1–4, respectively, with the rate constant ca. 10^{10} s^{-1} . The light-harvesting ability of these dendritic molecules is demonstrated by the enhanced valence isomerization rate of NBD to QC with increasing generation.

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1. Introduction

Photoinduced electron transfer (PET) plays a central role in most natural photosynthetic systems. The photosynthesis involves light-harvesting by an antenna system followed by a series of electron transfers to a precisely positioned reaction center. 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 [1]. Dendrimers are regularly and hierarchically branched macromolecules with numerous chain ends all emanating from a single core. The structure of the dendrimer, including the placement of functional groups, can be achieved by a controlled synthesis. The specific structure of the dendrimer makes it a mimic of a light-harvesting system, where the antenna chromophores surround the central reaction center [2].

Dendrimer chemistry expanded rapidly because its significance both in basic research and applications [3]. The particular attention has been paid to the photoactive dendrimers [4], which are useful as light-harvesting antennae, fluorescent chemosensors, and organic light-emitting diodes. Light-harvesting ability is one of the most specific characters of dendrimers. The electron transfer and energy transfer in dendrimers have been extensively examined. The dendrimer backbone can simply act as a spacer that holds the donor and acceptor chromophores, and also can be used as the energy and/or electron donor/acceptor. Several types of dendrimer backbone, such as poly(aryl ether) [5], poly(phenylacetylene) [6] and polyphenylene [7], have been used to absorb light, and then the energy was efficiently transferred to the core acceptor.

Comparing with photophysical studies [8], there are only a few examples of application of electron transfer and energy transfer activating the core acceptor group for chemical reaction within a dendrimer matrix [9]. Recently, our studies on benzophenone- and norbornadiene-labeled poly(aryl ether) dendrimers have shown that the periphery benzophenone chromophores capture photons and transfer their triplet energy to the norbornadiene (NBD) core group, resulting in

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the isomerization of the latter into the quadricyclane (QC) group [10]. The photosensitized valence isomerization of the NBD group to the QC group has been the subject of intense experimental and theoretical investigations [11] in view of the solar energy storage [12] and its mechanism interests [13]. It has been proved that the isomerization of the NBD group to the QC group can proceed either in the presence of a triplet energy donor sensitizer or an electron donor sensitizer [14]. In the present work, we synthesized a series of poly(aryl ether) dendrimers (*Gn*-NBD) with a norbornadiene group attached to the core. The photophysical studies and the photoisomerization results revealed that the intramolecular electron transfer and energy transfer from the dendrimer backbone to the NBD group accelerated the valence isomerization of the NBD group to QC.

2. Experimental

2.1. Materials

Reagents were purchased from Aldrich, Acros or Beijing Chemical Work and were used without further purification, unless otherwise noted. Acetone was dried with anhydrous K_2CO_3 and distilled. Spectral-grade tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were used for absorption and emission spectra, and steady-state photoirradiation measurements.

2.2. Instrumentation

1H NMR spectra were recorded on a Varian Gemini 300 MHz or a Bruker 400 MHz spectrometer. Infrared spectra were obtained with Bio-Rad Win IR spectrometer. MALDI-TOF mass spectrometry was performed on a Bruker BIFLEX spectrometer. Analytical TLC was performed on commercial plates coated with silica gel GF₂₅₄. Silica for chromatography was 400 meshes. HPLC was recorded at a Hitachi system with a Diamonsil C₁₈ column (5 μ m, 250 mm \times 4.6 mm) and an UV-vis detector. The mobile phase consisted of THF/ CH_3CN = 1/10 for generation 1–3 and 1/3 for generation 4, respectively. The flow rate was 0.5 ml/min for all of the compounds. Steady-state absorption spectra and emission spectra were measured by a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Fluorescence decay processes were recorded with single photon counting technique on an Edinburgh FLS920 fluorescence lifetime system.

2.3. Fluorescence and phosphorescence measurements

Fluorescence studies were performed in THF and CH_2Cl_2 at room temperature and phosphorescence measurements were proceeded in 2-methyltetrahydrofuran (MTHF) at 77 K. The excitation wavelength was 280 nm. For comparison of the fluorescence emission efficiency of *Gn*-NBD with *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.

2.4. Redox potentials of G1-OH and dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD)

The redox potentials of G1-OH and MNBD were determined by cyclic voltammetry in THF and CH_2Cl_2 , 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.

2.5. Photoirradiation and product analysis

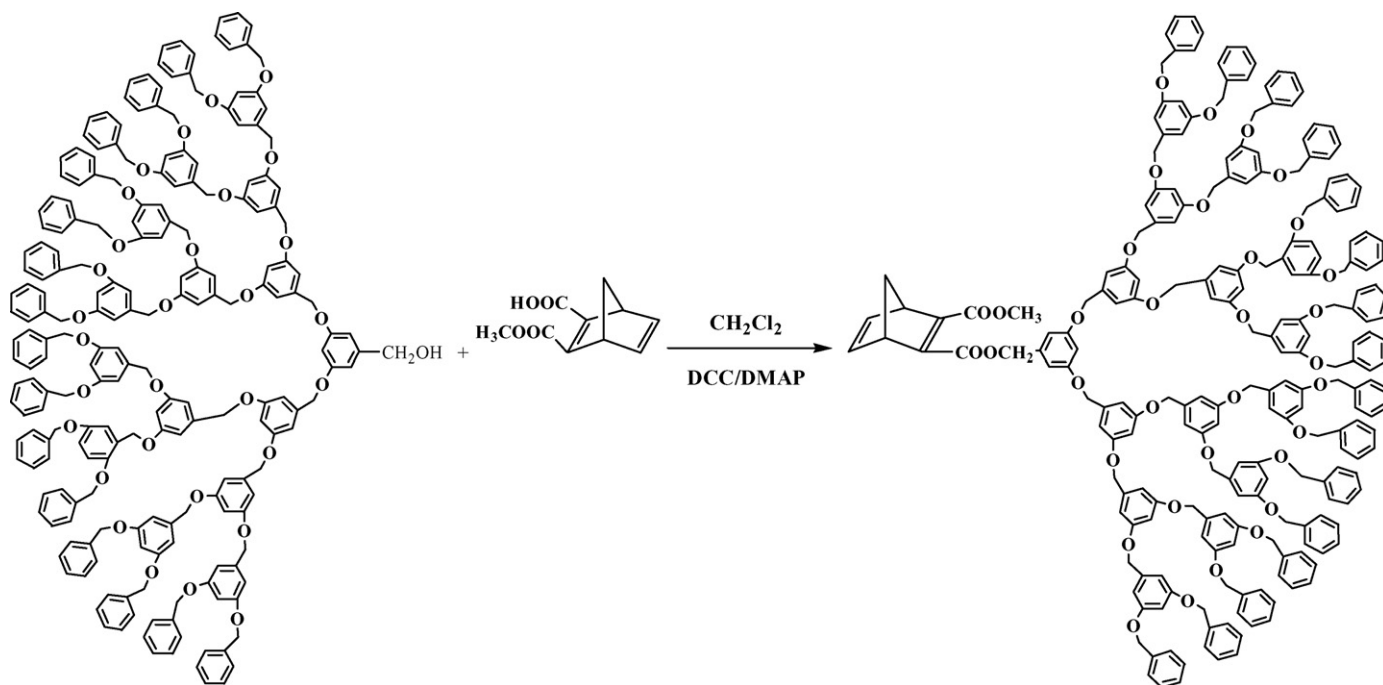
Photoirradiation was carried out in a quartz reactor, and the samples were purged with argon. A 500-W middle-high pressure mercury lamp was used as the excitation light source and the wavelength was controlled by solution filter combinations. After irradiation the solvent was evaporated from the sample under a reduced pressure. The product was characterized by 1H NMR spectroscopy. The conversions of *Gn*-NBD to *Gn*-QC were determined by the analysis of the fluorescence change before and after the irradiation.

2.6. General procedure for the synthesis of *Gn*-NBD system

These reactions were carried out on scales of about 500 mg as shown in Scheme 1. A mixture of the appropriate dendritic benzyl alcohol (*Gn*-OH, 1.00 equiv.), 2-(methoxycarbonyl)-bicyclo[2.2.1]hepta-2,5-diene-3-carboxylic acid (NBD-COOH, 3.00 equiv.), 1,3-dicyclohexylcarbodiimide (DCC, 3.00 equiv.) and 4-dimethylaminopyridine (0.1 equiv.) in dry CH_2Cl_2 was stirred under nitrogen for 24 h. For generations 3 and 4, larger excesses of NBD-COOH and DCC were required to force the reaction completion. The mixture was diluted with CH_2Cl_2 and partitioned into the water and the CH_2Cl_2 phases, and the aqueous layer was extracted with CH_2Cl_2 (3 \times). The combined organic layers were dried with $MgSO_4$ and evaporated to dryness. The crude product was purified as outlining in the following text.

G1-NBD (**1**) was prepared from G1-OH and NBD-COOH, purified by column chromatography eluting with 1/30 ethyl ether/ CH_2Cl_2 to give (**1**) as a colorless oil (95%). Retention time: t_R = 8.53 min in HPLC (acetonitrile/THF = 10/1). 1H NMR (300 MHz, $CDCl_3$) δ 2.12–2.29 (m, 2H), 3.65 (s, 3H), 3.95–3.97 (m, 2H), 5.05 (s, 4H), 5.15 (s, 2H), 6.58 (s, 1H), 6.64 (s, 2H), 6.93 (s, 2H), 7.33–7.42 (m, 10H). IR (KBr) ν (cm^{-1}) 1712, 1597, 1453, 1376, 1321, 1292, 1264, 1152, 1054. MS (EI) for $C_{31}H_{28}O_6$: m/z 496 [M^+], calcd m/z 496.56.

G2-NBD (**2**) was prepared from G2-OH and NBD-COOH, purified by column chromatography eluting with 1/30 ethyl ether/ CH_2Cl_2 to give (**2**) as a colorless oil (90%). Retention time t_R = 10.30 min in HPLC (acetonitrile/THF = 10/1). 1H NMR (300 MHz, $CDCl_3$) δ 2.09–2.30 (m, 2H), 3.64 (s, 3H), 3.95–3.96 (m, 2H), 4.99 (s, 4H), 5.04 (s, 8H), 5.15 (s, 2H), 6.56–6.69 (m, 9H), 6.92 (s, 2H), 7.31–7.42 (m, 20H). IR (KBr) ν (cm^{-1}) 1712, 1596, 1451, 1375, 1321, 1292, 1268, 1153, 1052. MS (MALDI-TOF) for $C_{59}H_{52}O_{10}$: m/z 943.4 [$M + Na^+$], 959.4 [$M + K^+$], calcd m/z 921.05.



Scheme 1. Synthesis of G4-NBD.

G3-NBD (**3**) was prepared from G3-OH and NBD-COOH, purified by column chromatography eluting with 1/20 ethyl ether/CH₂Cl₂ to give (**3**) as a colorless glass (80%). Retention time $t_R = 16.39$ min in HPLC (acetonitrile/THF = 10/1). ¹H NMR (300 MHz, CDCl₃) δ 2.06–2.28 (m, 2H), 3.64 (s, 3H), 3.92–3.95 (m, 2H), 4.97 (s, 12H), 5.02 (s, 16H), 5.13 (s, 2H), 6.55–6.68 (m, 21H), 6.90 (s, 2H), 7.29–7.42 (m, 40H). IR (KBr) ν (cm⁻¹) 1711, 1595, 1449, 1374, 1319, 1292, 1152, 1048. MS (MALDI-TOF) for C₁₁₅H₁₀₀O₁₈: m/z 1791.9 [M + Na⁺], 1807.9 [M + K⁺], calcd m/z 1770.04.

G4-NBD (**4**) was prepared from G4-OH and NBD-COOH, purified by column chromatography eluting with 1/20 ethyl ether/CH₂Cl₂ to give (**4**) as a colorless glass (60%). Retention time $t_R = 13.17$ min in HPLC (acetonitrile/THF = 3/1). ¹H NMR (400 MHz, CDCl₃) δ = 2.02–2.25 (m, 2H), 3.61 (s, 3H), 3.88–3.92 (m, 2H), 4.92 (s, 28H), 4.99 (s, 32H), 5.07 (s, 2H), 6.55–6.65 (m, 45H), 6.87 (s, 2H), 7.29–7.37 (m, 80H). IR (KBr) ν (cm⁻¹) 1712, 1595, 1449, 1373, 1320, 1293, 1152, 1046. MS (MALDI-TOF) for C₂₂₇H₁₉₆O₃₄: m/z 3490.1 [M + Na⁺], 3506.0 [M + K⁺], calcd m/z 3468.01.

3. Results and discussion

3.1. Synthesis of dendrimers

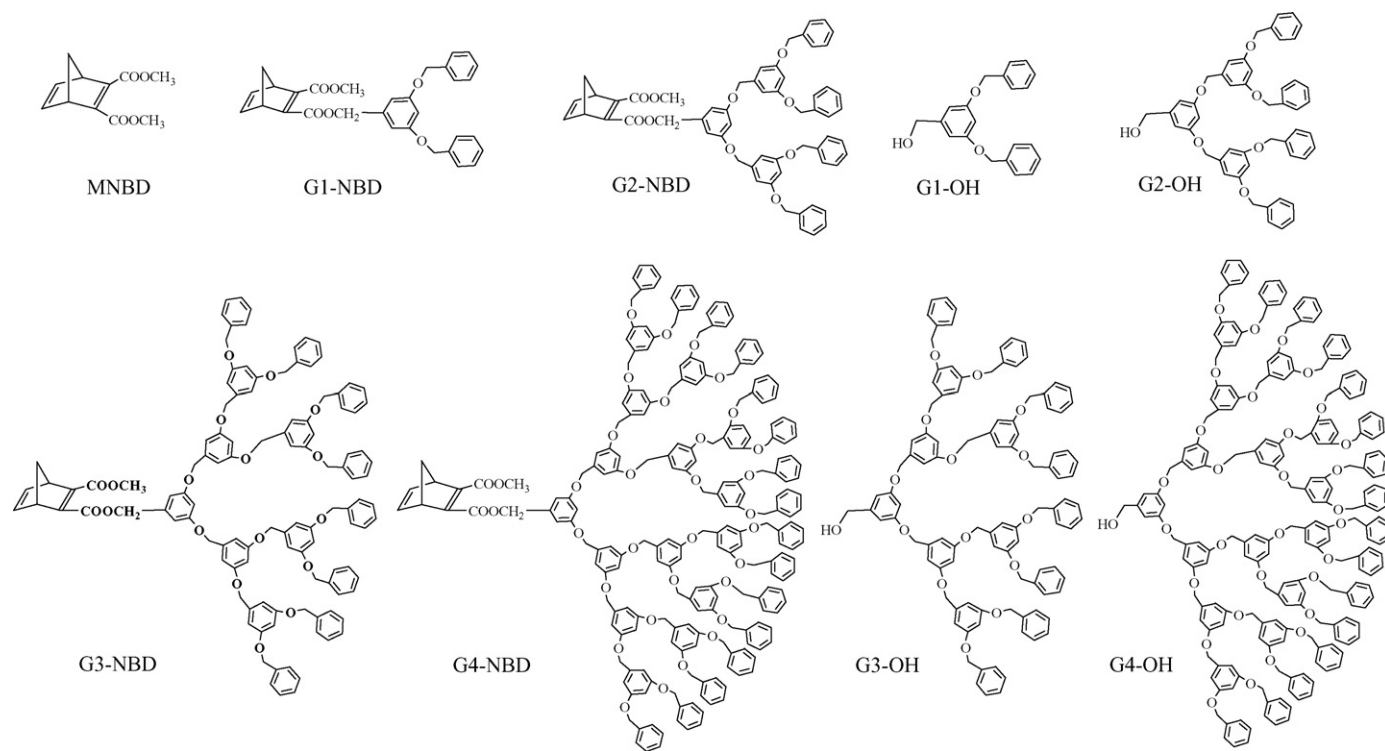
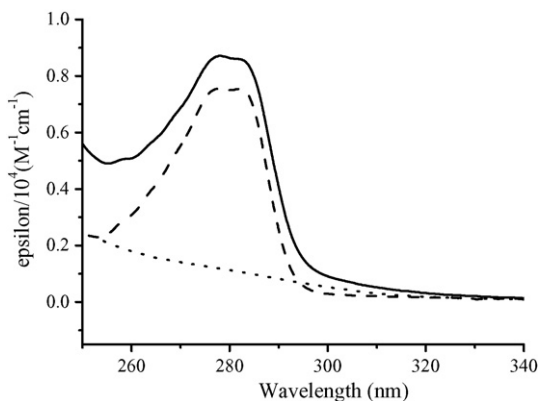
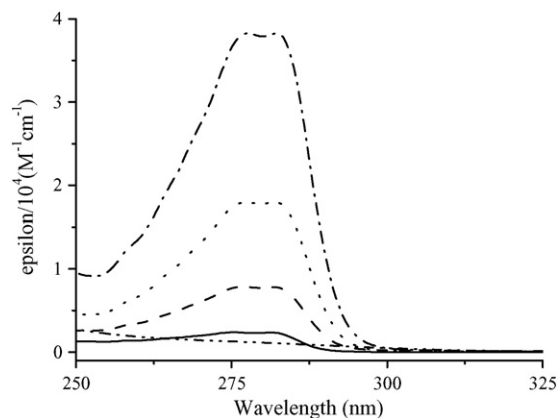
Dendritic benzyl alcohols, G_n-OH ($n = 1-4$), were synthesized with Fréchet's method [15], and were used as donor model compounds. Dendrimers with a norbornadiene group at the core, G_n-NBD ($n = 1-4$), were synthesized with G_n-OH and 2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-carboxylic acid (NBD-COOH). G_n-NBD and G_n-OH ($n = 1-4$) were characterized by ¹H NMR, IR, mass spectrometry (MALDI-TOF or EI), and HPLC. The structures of G_n-

NBD, G_n-OH and the acceptor model compound, dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD), are shown in Fig. 1.

3.2. Intramolecular electron transfer and energy transfer from the singlet excited state of the dendrimer backbone to the norbornadiene chromophore in G_n-NBD

The absorption spectra of dendrimers (G_n-NBD), the models for the donor dendrimers (G_n-OH), and the model for the acceptor (MNBD), were measured in tetrahydrofuran and dichloromethane, and they were similar in two different solvents. Fig. 2 illustrates the absorption spectra of G2-NBD, G2-OH, and MNBD in CH₂Cl₂. From the absorption spectra, no measurable interaction between the NBD group and the dendrimer backbone of G_n-NBD in the ground state can be observed. Significantly, the absorption of the dendrimer backbone is much more intense than that of the NBD group at the wavelength of 280 nm, especially in higher generations, which can be seen clearly in Fig. 3. Fig. 3 shows the absorption spectra of the G_n-OH series in CH₂Cl₂. The absorption due to the dendrimer backbone ($\pi-\pi^*$ transition of the aromatic units) increased as the generation increasing, which means that the light-harvesting capability of the molecules can be enhanced by increasing the generation number. We also noticed that the absorption was not proportional to the number of aromatic units, especially for generation 1. This can be ascribed to the high molar extinction absorption of the aryl ether group than that of the benzyl [16].

To ascertain the absorption percentage of the dendrimer backbone and the NBD group at 280 nm, the molar extinction coefficients of G_n-OH and MNBD were examined, and are given in Table 1. For generations 3–4, more than 94% light is absorbed by the dendrimer backbone at 280 nm in G_n-NBD and we consider

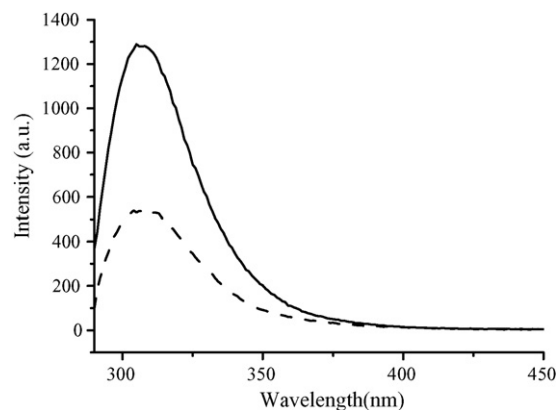
Fig. 1. Structures of MNBD, *Gn*-OH and -NBD.Fig. 2. Absorption spectra for the acceptor model compound MNBD (···), the donor model compound G2-OH (---) and the target compound G2-NBD (—) in CH_2Cl_2 .Fig. 3. Absorption spectra of G1-OH (—), G2-OH (---), G3-OH (···), G4-OH (— · — · —) and MNBD (·····) in CH_2Cl_2 .

that the dendrimer backbone can be selectively excited. For *Gn*-NBD ($n = 1-2$), the dendrimer backbone can only be partially selectively excited at this wavelength.

Fluorescence with the maximum at 310 nm was detected for both *Gn*-NBD and *Gn*-OH with the excitation at 280 nm. An example of the emission spectra of G3-NBD and G3-OH is presented in Fig. 4. The intensity of the fluorescence is normalized

Table 1
Absorption data of MNBD and dendrimer backbones in CH_2Cl_2

| | MNBD | G1-OH | G2-OH | G3-OH | G4-OH |
|---|------|-------|-------|-------|-------|
| λ_{max} (nm) | 236 | 280 | 280 | 281 | 281 |
| $\epsilon_{280\text{nm}}/10^3$ ($\text{M}^{-1} \text{cm}^{-1}$) | 1.13 | 2.44 | 7.50 | 17.9 | 38.9 |

Fig. 4. Fluorescence spectra of G3-NBD (---) and G3-OH (—) in THF. ($[\text{G3-NBD}] = [\text{G3-OH}] = 2 \times 10^{-5} \text{ M}$, $\lambda_{\text{ex}} = 280 \text{ nm}$).

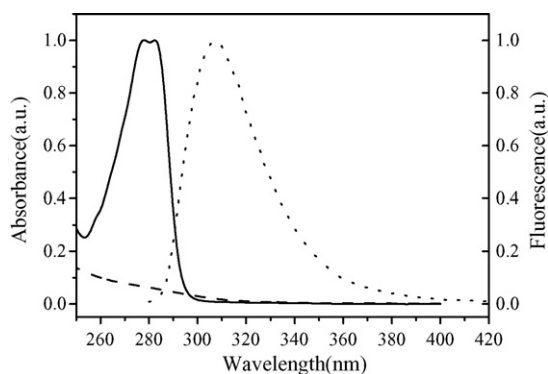


Fig. 5. Normalized emission for G3-OH (···) and absorption for G3-OH (—) and MNBD (---) in CH_2Cl_2 .

to the part of the dendrimer backbone absorption in G_n -NBD at 280 nm. The shape and the peak position of these two fluorescence spectra are essentially identical, but the overall intensities are very different. The fluorescence quenching efficiencies of G_n -NBD are ca. 93, 73, 54, 30% in CH_2Cl_2 and ca. 90, 70, 55, 34% in THF as compared with the corresponding model compound, G_n -OH, for generations 1–4, respectively. This finding indicates that the fluorescence of the dendrimer backbone 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 the dendrimer backbone fluorescence by the NBD group in G_n -NBD, a comparison of the absorption and emission spectra of the model donor compound, G3-OH, and the absorption of the model acceptor compound, MNBD, is presented in Fig. 5. The relative absorption intensity of MNBD and G3-OH represents the absorption percentage of the NBD group and dendrimer backbone in G3-NBD. It can be seen that the overlap of the donor emission and the acceptor absorption is quite small, even the overlap of the donor emission with its own absorption is bigger than it. The small spectral overlap between the fluorescence of the dendrimer backbone and the absorption of the NBD group indicates that the singlet–singlet energy transfer from the dendrimer backbone to the NBD group should not be very efficient, which is not consistent with the fluorescence quenching results. Therefore, we infer that the intramolecular singlet–singlet electron transfer should also be responsible for the fluorescence quenching.

Calculation of the free energy change in G_n -NBD confirmed the reality of the electron transfer between the dendrimer backbone and the NBD group as the cause of the fluorescence quenching. We measured the redox potentials of G1-OH and the model compound, MNBD, in CH_2Cl_2 and THF. The redox potentials of MNBD, $E(\text{NBD}/\text{NBD}^{\bullet-})$, and G1-OH, $E(\text{G1-OH}^{\bullet+}/\text{G1-OH})$, were determined to be -1.78 and $+1.14$ V in CH_2Cl_2 , -1.82 and $+1.36$ V in THF, respectively, with respect to Ag/Ag^+ . The free energy change involved in an electron transfer process can be calculated by the Rehm–Weller equation [17]:

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

E_{00} is the excited state energy, in this case represents the singlet-state energy of the dendrimer backbone, which is 92 kcal/mol (estimated from the emission spectra). $E(\text{D}^{\bullet+}/\text{D})$ and $E(\text{A}/\text{A}^{\bullet-})$ are the redox potentials of the donor and the acceptor, respectively. The $e^2/r\epsilon$ represents the Coulombic energy associated with bringing separated radical-ions at a distance r in a solvent of dielectric constant ϵ . Since the poly(aryl ether) dendrimer is not rigid, it is difficult to determine the distance between the dendrimer backbone and the NBD group within each generation. We estimated this distance from the computation lowest-energy conformation, which is calculated by using MM+, the Polak-Ribiere algorithm (HyperChem 6.0 program). While optimizing the conformation, the solvent effect could not be taken into account due to the limitation of the HyperChem program. All of the aryl ether moieties in dendrimer backbone are considered for electron transfer and the distance between the donor and acceptor groups is defined as the average distance between the carbon atom of the vinyl closely connected to the dendrimer backbone and every saturated carbon atom in the dendrimer backbone. They are estimated to be 5.8, 7.9, 9.0, and 12.0 Å for generations 1–4, respectively. Analysis of Eq. (1) shows that the change of r will result in only a minor impact on ΔG in this distance range. Calculation according to Eq. (1) reveals that the electron transfer from the dendrimer backbone to the norbornadiene group in CH_2Cl_2 ($\epsilon = 9.08D$) is exothermic by 31, 29, 29, and 28 kcal/mol, and 26, 24, 24, and 22 kcal/mol in THF ($\epsilon = 7.58D$) for generation 1–4, respectively, which means that the intramolecular electron transfer from the singlet excited dendrimer backbone to the NBD group in G_n -NBD could occur efficiently. The previous studies have demonstrated that the poly(aryl ether) dendrimer are provided with the folding back conformation [10,8b,18]. It is difficult to ascertain whether the electron transfer from the dendrimer backbone to NBD occurs in one hop or through a multi-step hopping pathway.

The measurements of the fluorescence lifetime for the dendrimer backbone, $\tau_{G_n\text{-OH}}$, have been done in CH_2Cl_2 and THF. The fluorescence lifetime of G_n -OH is ca. 0.2 ns for generation 1, and ca. 0.1 ns for generations 2–4 in two different solvents, which is consistent with the data reported in the literature [8b]. The effect of the hydroxyl group in G_n -OH on the fluorescence lifetime can be excluded by comparing the lifetimes of G1-OH and G1-OOCCH₃. The fluorescence lifetime of G_n -NBD, $\tau_{G_n\text{-NBD}}$, is shorter than the corresponding model compound for generations 3–4, and we could not obtain appropriate decay curves for generations 1–2 due to the weak emission. Because of the limitation of the equipment resolution (about 0.1 ns), we could not calculate the exact rate constant of the fluorescence quenching. The magnitude of the fluorescence quenching rate constant, $k_{\text{SET}} + k_{\text{ET}}$, is estimated from Eq. (2) by using the fluorescence quenching efficiencies of G_n -NBD (Φ_{F}), which were obtained by the fluorescence measurement. $k_{\text{SET}} + k_{\text{ET}}$ is estimated to be $\sim 10^{10} \text{ s}^{-1}$ for G_n -NBD:

$$k_{\text{SET}} + k_{\text{ET}} = \frac{\Phi_{\text{F}}}{(1 - \Phi_{\text{F}})\tau_{G_n\text{-OH}}} \quad (2)$$

We also measured the phosphorescence of G_n -OH and G_n -NBD in 2-methyltetrahydrofuran (MTHF) at 77 K. Very weak

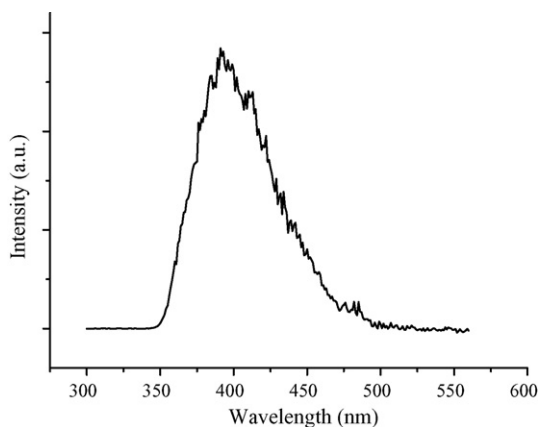


Fig. 6. Phosphorescence spectrum of G2-OH in MTHF at 77 K ($c = 5.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 280$ nm).

phosphorescence from G_n -OH was observed with maximal at 390 nm after the excitation at the maximal absorption of the dendrimer backbone (280 nm) [19], but no phosphorescence from G_n -NBD was detected. An example of the phosphorescence spectrum for G2-OH is presented in Fig. 6. Although the triplet–triplet energy transfer from the dendrimer backbone ($E_T = 73$ kcal/mol, estimated from the phosphorescence spectra) to the NBD group ($E_T = 53$ kcal/mol) [20] is thermodynamically possible, the intramolecular triplet energy transfer can still be neglected because the inefficient intersystem crossing process ($k_{\text{ISC}} \sim 10^7 \text{ s}^{-1}$) [21] cannot compete with the intramolecular singlet electron transfer and energy transfer in G_n -NBD ($k_{\text{SET}} + k_{\text{ET}} = 10^{10} \text{ s}^{-1}$). The triplet state of the dendrimer back-

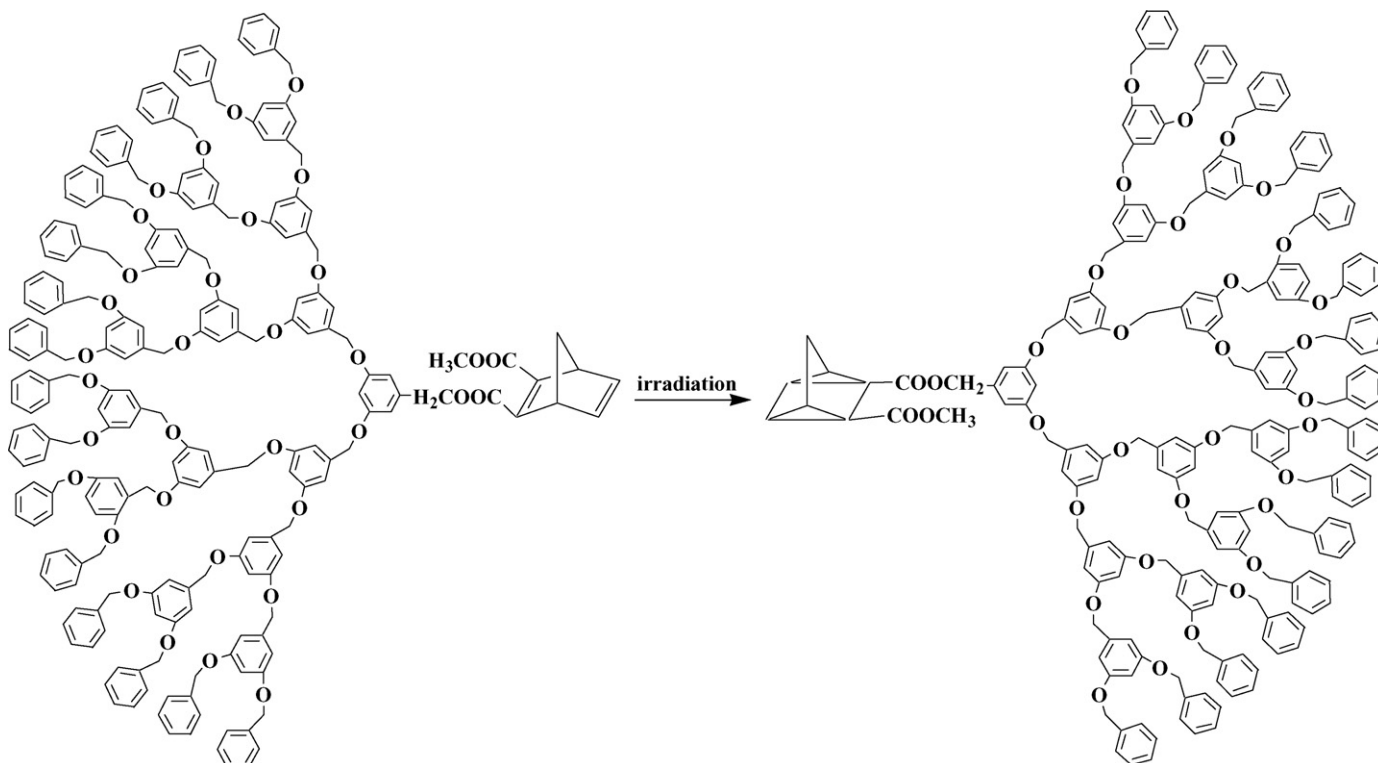
bone cannot be formed efficiently, and this also explains that there is no phosphorescence of the dendrimer backbone in G_n -NBD to be observed in our experiment.

The electron transfer and energy transfer efficiency, Φ_F , decreases with the generation increase. 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 or electron transfer efficiency. In our work, the nonirradiation decay may be also responsible for this [22], and the experiment results of the normalized fluorescence intensity in G_n -OH decreasing with the generation increase support this supposition.

3.3. Photosensitized isomerization of the norbornadiene to the quadricyclane group in G_n -NBD

The mechanism of photosensitized valence isomerization of norbornadiene to quadricyclane has been extensively studied. The isomerization mechanism involving the triplet energy transfer is well understood [23]. Furthermore, norbornadiene is a good electron acceptor and can also undergo isomerization in the presence of an electron donor sensitizer [24]. Thus the study of the intramolecular photosensitized isomerization of the NBD group in G_n -NBD may provide evidence of the intramolecular electron transfer and energy transfer from the dendrimer backbone to NBD.

Irradiation with $260 \text{ nm} < \lambda < 300 \text{ nm}$ [21a] of a 2.0×10^{-5} M solution of G_n -NBD in degassed THF at room temperature resulted in a valence isomerization of the NBD group to the QC group (G_n -QC), as shown in Scheme 2. The yield of the



Scheme 2. Isomerization of G4-NBD to G4-QC.

isomerization product was almost 100% on the basis of the consumption of the starting material. The assignment of the products as the quadricyclane derivatives relies mainly on their ^1H NMR spectra, which are in close agreement with those reported in the literature [10,20]. Two protons assignable to vinyl group with the chemical shift around 6.90 ppm and two bridgehead protons with chemical shift around 3.95 ppm in *Gn*-NBD disappeared, and there are new peaks assigned to QC appearing at 2.00–2.50 ppm. Meanwhile, the protons assignable to methoxy group in NBD shifted 0.03 ppm to the high field. The ^1H NMR spectral details and assignment for the products, *Gn*-QC, are given in Table 2. Former photophysical experiments demonstrated that there was only intramolecular electron transfer and energy transfer at this concentration.

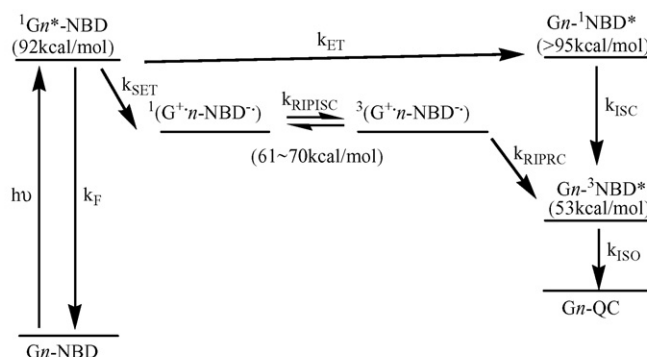
To ascertain the occurrence of the isomerization in *Gn*-NBD is induced by electron transfer and energy transfer from the dendrimer backbone to NBD, the kinetic studies of the valence isomerization of NBD to QC in *Gn*-NBD and MNBD were done. The same concentration (2.0×10^{-5} M) was used in the experiments for *Gn*-NBD and MNBD. After irradiation ($260 \text{ nm} < \lambda < 300 \text{ nm}$) for 5 min with a 500-W middle-high pressure mercury lamp in a merry-go-round apparatus, the conversion of the NBD group to the QC group was determined by the fluorescence change before and after irradiation for *Gn*-NBD, and by the absorption change for MNBD. The experiment results are listed in Table 3. There is a great contrast between *Gn*-NBD and MNBD. Under this condition ($260 \text{ nm} < \lambda < 300 \text{ nm}$), most of the light was absorbed by the dendrimer backbone, especially for generation 3–4. Thus, the difference between *Gn*-NBD and MNBD should be attributed to the photoinduced intramolecular singlet electron transfer and energy transfer processes from the dendrimer backbone to NBD. The observed rates of the isomerization for *Gn*-NBD are also given in Table 3. The higher isomerization rate for the higher generation can be ascribed to the light-harvesting ability of the dendrimer backbone of *Gn*-NBD, referring to the larger molar extinction coefficient of the higher generation.

Table 2
 ^1H NMR data of *Gn*-QC

| δ | Split | Intensity | Assignment ^a |
|--------------|-------|-----------|-------------------------|
| G1-QC | | | |
| 2.11–2.53 | m | 6 | QC |
| 3.62 | s | 3 | OCH ₃ |
| 5.06 | s | 4 | (P)ArCH ₂ |
| 5.15 | s | 2 | COOCH ₂ |
| 6.58–6.64 | m | 3 | (I)ArH |
| 7.36–7.44 | m | 10 | (P)ArH |
| G2-QC | | | |
| 2.09–2.52 | m | 6 | QC |
| 3.62 | s | 3 | OCH ₃ |
| 4.99 | s | 4 | (I)ArCH ₂ |
| 5.06 | s | 8 | (P)ArCH ₂ |
| 5.15 | s | 2 | COOCH ₂ |
| 6.56–6.70 | m | 9 | (I)ArH |
| 7.32–7.44 | m | 20 | (P)ArH |
| G3-QC | | | |
| 2.07–2.50 | m | 6 | QC |
| 3.61 | s | 3 | OCH ₃ |
| 4.98 | s | 12 | (I)ArCH ₂ |
| 5.04 | s | 16 | (P)ArCH ₂ |
| 5.14 | s | 2 | COOCH ₂ |
| 6.56–6.69 | m | 21 | (I)ArH |
| 7.32–7.43 | m | 40 | (P)ArH |
| G4-QC | | | |
| 2.06–2.46 | m | 6 | QC |
| 3.58 | s | 3 | OCH ₃ |
| 4.94 | s | 28 | (I)ArCH ₂ |
| 5.00 | s | 32 | (P)ArCH ₂ |
| 5.04 | s | 2 | COOCH ₂ |
| 6.54–6.67 | m | 45 | (I)ArH |
| 7.30–7.40 | m | 80 | (P)ArH |

^a (I)Ar, inner layer aromatic ring; (P)Ar, periphery aromatic ring.

According to the observation of chemical-induced dynamic nuclear polarization (CIDNP) effects [13,25], it has been proposed that this photosensitized isomerization involves electron transfer from the sensitizer to the norbornadiene to generate the



^a The data in parentheses represent the energies of the corresponding states relative to the ground state. The radical ion pair was obtained by calculation from eq 1, and the energies of $^1\text{Gn}^*\text{-NBD}$ and $\text{Gn-}^1\text{NBD}^*$ were determined by fluorescence and absorption spectra, respectively. The energy of $\text{Gn-}^3\text{NBD}^*$ is from ref 20.

Scheme 3. Primary photophysical and photochemical processes in *Gn*-NBD.

Table 3

Conversions and the isomerization rates of the valence isomerization of MNBD and *Gn*-NBD at ambient temperature after irradiation for 5 min with 260 nm < λ < 300 nm (2.0×10^{-5} M)

| | MNBD | G1-NBD | G2-NBD | G3-NBD | G4-NBD |
|--|---------|--------|--------|--------|--------|
| Conversion (%) | $\ll 1$ | 5 | 10 | 13 | 19 |
| Isomerization rate (10^{-7} Mmin $^{-1}$) | – | 2.0 | 4.0 | 5.2 | 7.6 |

singlet-state radical–ion pair, intersystem crossing to its triplet state (RIPISC), and the recombination of the triplet radical–ion pair to give the triplet norbornadiene (RIPRC), followed by a rearrangement to the quadricyclane. On the basis of the experimental results mentioned above and the electron transfer mechanism of the NBD isomerization, the isomerization of the norbornadiene group in *Gn*-NBD might proceed both via singlet energy transfer and via radical–ion pair recombination mechanisms. The primary photophysical and photochemical processes in *Gn*-NBD can be expressed by Scheme 3. Because the overlap of the donor emission and the acceptor absorption is very small, we infer that the electron transfer from the singlet excited state of the dendrimer backbone to the norbornadiene group in *Gn*-NBD plays a dominant role in the norbornadiene isomerization. We cannot exclude the existence of the singlet energy transfer from the dendrimer backbone to the norbornadiene group.

4. Conclusions

The photophysical and photochemical isomerization studies demonstrate that the poly(aryl ether) dendrimer backbone in *Gn*-NBD can act as an electron/energy donor to sensitize the norbornadiene group attaching to the core, leading to the valence isomerization of the NBD group to QC. The rate constant of the singlet electron transfer and energy transfer from the dendrimer backbone to the core NBD group is ca. 10^{10} s $^{-1}$ for *Gn*-NBD. The higher isomerization rate for higher generation indicates that the light-harvesting ability of *Gn*-NBD increases with the generation, referring to the larger molar extinction coefficient of the dendrimer backbone at the higher generation, although the electron transfer and energy transfer efficiencies decrease with increasing generation. These findings reveal that the poly(aryl ether) dendrimers can be antennae to harvest photons for electron transfer and energy transfer, which could be used for the photochemical energy conversion and information processing.

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