

Conversion of Intramolecular Singlet Electron Transfer at Room Temperature into Triplet Energy Transfer at 77 K: Photoisomerization in Norbornadiene- and Carbazole-Labeled Poly(aryl ether) Dendrimers

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A series of Fréchet-type poly(aryl ether) dendrimers (CZ-Gn-NBD, $n = 1-3$) with carbazole (CZ) chromophores and a norbornadiene (NBD) group attached to the periphery and the core, respectively, were synthesized, and their photophysical and photochemical properties were investigated. Selective excitation of the carbazole units in CZ-Gn-NBD resulted in a singlet electron transfer from CZ to NBD at room temperature, and an intersystem crossing followed a triplet–triplet energy transfer from CZ to NBD in glassy 2-methyltetrahydrofuran at 77 K. Both singlet electron transfer and triplet energy transfer processes lead to the isomerization of the norbornadiene group into the quadricyclane (CZ-Gn-QC). The efficiencies and the rate constants for singlet electron transfer are approximately 88, 80, and 74% and 1.8×10^9 , 6.1×10^8 , and $4.0 \times 10^8 \text{ s}^{-1}$ for generations 1–3, respectively. The quantum yields of the intramolecular photosensitized isomerization are measured to be approximately 0.013, 0.012, and 0.011, and the efficiencies of triplet norbornadiene formation via singlet electron transfer are approximately 0.070, 0.065, and 0.059 for generations 1–3, respectively. The light-harvesting ability of CZ-Gn-NBD increases with the generation due to an increase of the number of peripheral chromophores. In glassy 2-methyltetrahydrofuran at 77 K, the triplet–triplet energy transfer proceeds with efficiencies of approximately 0.86, 0.64, and 0.36 and rate constants of 0.96, 0.25, and 0.08 s^{-1} for generations 1–3, respectively. The intramolecular singlet electron transfer and triplet energy transfer in CZ-Gn-NBD proceed mainly via a through-space mechanism involving the proximate donor (folding back conformation) and acceptor groups.

Introduction

Dendrimers¹ 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.²

Dendrimer chemistry expanded rapidly because of its significance both in basic research and in applications.³ 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 the energy transfer in dendrimers have been extensively examined by means of spectroscopic⁵ and electrochemical methods.⁶ Up to now, most of the studies on intramolecular electron transfer and energy transfer between the periphery chromophores and the core in poly(aryl ether) dendrimers have been related to the singlet states only and the

energy transfer has proceeded mainly via the Förster mechanism.⁷ Furthermore, 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.^{5c,8} Recently, our study on benzophenone and norbornadiene-labeled poly(aryl ether) dendrimers has shown that the periphery benzophenone chromophores capture photons and transfer their triplet energy to the norbornadiene core group, resulting in an isomerization of the latter into the quadricyclane (QC) group.^{5c} In the present work, we synthesized a series of poly(aryl ether) dendrimers (CZ-Gn-NBD) with carbazole (CZ) chromophores and a norbornadiene (NBD) group attached to the periphery and the core, respectively. Emission quenching, laser flash photolysis, and photochemical reaction of the core results suggest that the singlet electron transfer and triplet energy transfer can occur efficiently at room temperature and 77 K, respectively. These findings provide a new example of using dendrimers for light harvesting: the periphery “antenna” chromophores “harvest” photon energy which is then utilized to activate the core group for chemical reaction via electron transfer and triplet energy transfer. The dendrimers are synthesized up to third generation, as shown in Figure 1.

Experimental Section

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.

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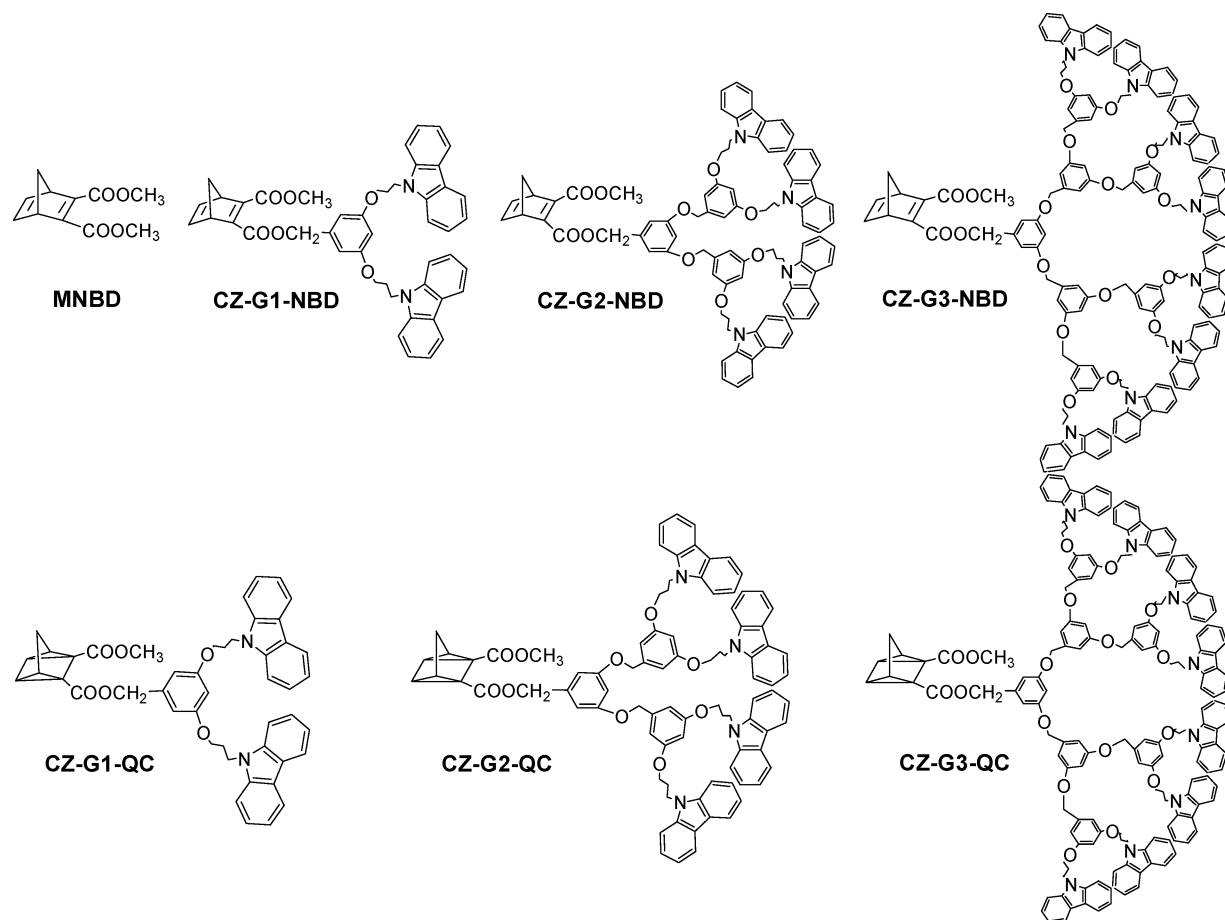


Figure 1. Structures of MNBD, CZ-*Gn*-NBD, and CZ-*Gn*-QC compounds.

Tetrahydrofuran (THF) was distilled over Na/benzophenone under an argon atmosphere. Spectral-grade 2-methyltetrahydrofuran (MTHF) and dichloromethane (CH_2Cl_2) were used for absorption and emission spectra, flash photolysis, and steady state photoirradiation measurements.

Instrumentation. IR spectra were recorded on a Bio-Rad Win IR spectrometer. ^1H NMR spectra were performed on either a Varian Gemini 300 MHz or Bruker 400 MHz spectrometer. MALDI-TOF mass spectrometry was run on a Bruker BIFLEX III spectrometer. Elemental analyses were determined on a Flash EA 1112 spectrometer. Steady state absorption spectra and emission spectra were measured by a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively.

Emission Measurements. Fluorescence spectra were measured in CH_2Cl_2 and MTHF using a 1 cm quartz cuvette at room temperature (RT) and 77 K, and phosphorescence measurements were performed in MTHF at 77 K. The excitation wavelength was 330 nm. To compare the emission efficiency of CZ-*Gn*-NBD and CZ-*Gn*-QC, solutions at the excitation wavelength have the same optical density. The relative emission efficiencies were obtained from the peak areas of emission spectra.

Time-Resolved Spectroscopic Measurements. Fluorescence decay processes were recorded with a single photon counting technique on an Edinburgh FLS920 fluorescence lifetime system, and the equipment resolution is ~ 0.1 ns. Phosphorescence decay was detected by a 0.3 m spectrometer and a photomultiplier tube (PMT) coupled to a 32-bit microprocessor based data acquisition and spectrometer controller module (NCL Electronics Interface, Acton Research Corporation) and computer with a CW He-Cd laser (325 nm, Omnicrom) as the excitation source. The decay process was recorded after the laser

was cut off, and the accuracy of measurement is 10 ms. Nanosecond transient absorption spectra were performed on a LP-920 pump-probe spectroscopic setup (Edinburgh). The excited source was the unfocused third harmonic (355 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum surelite II), and the probe light source was a pulse-xenon lamp. The signals were detected by an Edinburgh analytical instruments (LP900) and recorded on a Tektronix TDS 3012B oscilloscope and computer.

Redox Potentials of *N*-Methylcarbazole (MCZ) and Dimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD). The redox potentials of MCZ and MNBD were carried out by cyclic voltammetry in dichloromethane and tetrahydrofuran, respectively, using a $10\ \mu\text{m}$ 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.

Results and Discussion

Synthesis and Stability of the Dendrimers. The synthesis and the characterization of the compounds are described in the Supporting Information. Dendritic benzyl alcohols and dendritic benzyl bromides were synthesized by Fréchet's method.⁹ Dendrimers (CZ-*Gn*-NBD) with carbazole chromophores and a norbornadiene group attached to the periphery and the core, respectively, were synthesized with dendritic benzyl alcohols (CZ-*Gn*-OH) and 2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-carboxylic acid (NBD-COOH). All of the compounds were purified by column chromatography. The compounds, CZ-*Gn*-NBD ($n = 1-3$), were characterized by analytical techniques

TABLE 1: Absorption and Emission Data of CZ-Gn-NBD and CZ-Gn-QC

compd	$\epsilon_{330\text{ nm}}^a \times 10^4$ ($\text{cm}^{-1}\text{ M}^{-1}$)	fluorescence ^a						phosphorescence ^b				
		$\lambda_{\text{max}}^{a,b}$ (nm)	Φ_{F}^a	$\tau^{\text{Fa},c}$ (ns)	$\chi^{2a,c}$	$\tau^{\text{Fb},c}$ (ns)	$\chi^{2b,c}$	λ_{max}^b (nm)	$\tau^{\text{Pb},c}$ (s)	$\chi^{2b,c}$	$\tau^{\text{Pa},d}$ (μs)	$\chi^{2a,d}$
CZ-G1-NBD	0.73	352 368	0.02	0.5	0.954	12.4	1.116	413 441	0.9	0.994		
CZ-G2-NBD	1.45	352 368	0.06	1.3	0.955	12.4	0.954	413 441	2.6	0.999		
CZ-G3-NBD	2.91	352 368	0.08	1.8	1.196	12.7	0.892	413 441	4.7	0.999		
CZ-G1-QC	0.71	352 368	0.29	6.1	1.175	12.7	1.014	413 441	6.6	0.999	3.5	0.983
CZ-G2-QC	1.43	352 368	0.30	6.2	1.035	12.7	1.089	413 441	7.2	0.999	3.6	0.992
CZ-G3-QC	2.87	352 368	0.31	6.3	1.049	12.8	0.892	413 441	7.3	0.999	3.3	0.990

^a In CH_2Cl_2 at RT. ^b In MTHF at 77 K. ^c Determined by time-resolved emission. ^d Determined by T-T transient absorption.

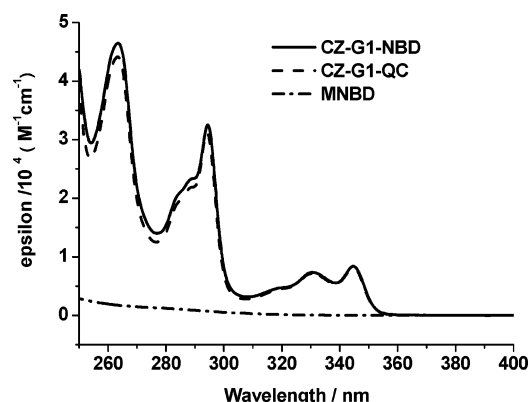


Figure 2. Absorption spectra for donor model compound CZ-G1-QC, acceptor model compound MNBD, and target compound CZ-G1-NBD in CH_2Cl_2 .

involving IR, ^1H NMR, mass spectrometry (MALDI-TOF or EI), and elemental analysis. The model compounds, CZ-Gn-QC ($n = 1-3$), the valence isomers with a structure similar to that of CZ-Gn-NBD, were synthesized by the photosensitized isomerization of CZ-Gn-NBD and characterized by IR, ^1H NMR, and mass spectrometry (MALDI-TOF or EI). Since the bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate group is a good electron and energy acceptor, the compound dimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (MNBD) is used as a suitable acceptor model. CZ-Gn-NBD must be stored in the dark because they are very sensitive to light, which can induce the isomerization of CZ-Gn-NBD to CZ-Gn-QC in solution even with room light, especially for the higher generation.

Singlet–Singlet Electron Transfer from the Carbazole to the Norbornadiene Chromophores in CZ-Gn-NBD at Room Temperature. The UV–vis absorption spectra of the target compounds (CZ-Gn-NBD) and the models for the donor (CZ-Gn-QC) and the acceptor (MNBD) were measured in CH_2Cl_2 . The absorption spectra of CZ-G1-NBD, CZ-G1-QC, and MNBD are shown in Figure 2. No measurable interaction between the norbornadiene and the carbazole chromophores of CZ-Gn-NBD in the ground state can be observed from the absorption spectra. Significantly, the absorption of the carbazole group extends to a wavelength longer than that of the norbornadiene group. The energy of the singlet excited state of the carbazole chromophore (~ 83 kcal/mol) is lower than that of MNBD (> 92 kcal/mol), as estimated from the absorption spectra. Thus, the singlet–singlet energy transfer from the excited carbazole chromophore to the norbornadiene group is impossible. Furthermore, this factor permits selective excitation of the carbazole moieties in

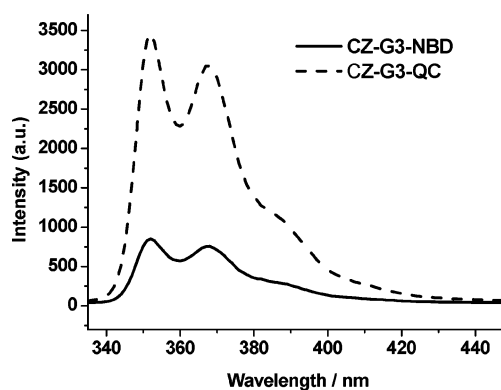


Figure 3. Fluorescence spectra of CZ-G3-NBD and CZ-G3-QC in CH_2Cl_2 at room temperature, $\lambda_{\text{ex}} = 330$ nm. $[\text{CZ-G3-NBD}] = [\text{CZ-G3-QC}] = 1.0 \times 10^{-5}$ M.

CZ-Gn-NBD. The parameters of the absorption spectra together with those of the fluorescence spectra and phosphorescence spectra for CZ-Gn-NBD and CZ-Gn-QC are given in Table 1. The molar extinction coefficient of carbazole chromophore doubles with each generation increase, which means that the light-harvesting capability of the molecules can be enhanced by increasing generation.

The fluorescence spectra of CZ-Gn-NBD and CZ-Gn-QC were measured in CH_2Cl_2 at room temperature. An example of the emission spectra of CZ-G3-NBD and CZ-G3-QC is given in Figure 3. Both compounds exhibit the structured fluorescence characteristic of the carbazole chromophore with maxima at 352 and 368 nm. The shape and peak positions of these two fluorescence spectra are essentially identical. However, the fluorescence efficiency of the carbazole chromophore in CZ-G3-NBD is $\sim 74\%$ less than that in the model compound, CZ-G3-QC. Generations 1 and 2 show similar results but various degrees of decrease in fluorescence efficiency, 88 and 80% for the first and second generations, respectively. The fluorescence quantum yields of CZ-Gn-NBD and CZ-Gn-QC were also measured, and the data are listed in Table 1. This observation indicates that the fluorescence of the carbazole chromophore is quenched by the norbornadiene group in CZ-Gn-NBD. Measurements at different concentrations indicate that the quenching is intramolecular.

The fluorescence lifetimes for CZ-Gn-NBD and CZ-Gn-QC were determined in CH_2Cl_2 at room temperature. The excitation wavelength was 330 nm, and the fluorescence decay was monitored at the emission maximum 352 nm for all compounds. All of the compounds we investigated exhibit monoexponential profiles, and the lifetimes are summarized in Table 1. The rate

TABLE 2: Electron Transfer and Energy Transfer Efficiencies and Rate Constants for CZ-Gn-NBD

compd	singlet electron transfer			triplet energy transfer		
	$k_{\text{SET}}^{a,c}$ (s^{-1})	$\Phi_{\text{SET}}^{a,c}$	$\Phi_{\text{SET}}^{a,b}$	$k_{\text{TT}}^{c,d}$ (s^{-1})	$\Phi_{\text{TT}}^{c,d}$	$\Phi_{\text{TT}}^{b,d}$
CZ-G1-NBD	1.8×10^9	0.92	0.88	0.96	0.86	0.90
CZ-G2-NBD	6.1×10^8	0.79	0.80	0.25	0.64	0.62
CZ-G3-NBD	4.0×10^8	0.71	0.74	0.08	0.36	0.36

^a In dichloromethane at RT. ^b By emission spectra measurement. ^c Determined by time-resolved emission. ^d In 2-methyltetrahydrofuran at 77 K.

constant (k_{SET}) and the quantum yield (Φ_{SET}) of the quenching can be calculated from the lifetimes of CZ-Gn-NBD and CZ-Gn-QC according to eqs 1 and 2, respectively. The quenching rate constants are 1.8×10^9 , 6.1×10^8 , and $4.0 \times 10^8 \text{ s}^{-1}$ for generations 1–3, respectively, which is consistent with those in polymer linked carbazole and norbornadiene systems.¹⁰ The rate constant only decreases moderately with the generation increase. The reason for this result is discussed in the mechanism section below. The quenching efficiencies are 0.92, 0.79, and 0.71 for generations 1–3, respectively, which are comparable with those obtained from the fluorescence efficiency measurements (Table 2).

$$k_{\text{SET(TT)}} = 1/\tau_{\text{NBD}} - 1/\tau_{\text{QC}} \quad (1)$$

$$\Phi_{\text{SET(TT)}} = 1 - \tau_{\text{NBD}}/\tau_{\text{QC}} \quad (2)$$

Since the possibility of singlet–singlet energy transfer being responsible for the intramolecular carbazole fluorescence quenching by the norbornadiene group in CZ-Gn-NBD is excluded on thermodynamic grounds, as mentioned above, we analyzed the reality of electron transfer between the carbazole chromophore and the norbornadiene group as the cause of the fluorescence quenching. We measured the redox potentials of model compounds, MCZ and MNBD. The redox potentials of MCZ ($E(\text{CZ}^{\bullet+}/\text{CZ})$) and MNBD ($E(\text{NBD}/\text{NBD}^{\bullet-})$) were determined to be +1.28 and −1.78 V in CH_2Cl_2 , respectively, with respect to Ag/Ag^+ . The free-energy change involved in an electron transfer process in CZ-Gn-NBD can be calculated by the Rehm–Weller equation:¹¹

$$\Delta G \text{ (kcal/mol)} = 23.06[E(\text{CZ}^{\bullet+}/\text{CZ}) - E(\text{NBD}/\text{NBD}^{\bullet-}) - e^2/r\epsilon] - E_{00} \text{ (kcal/mol)} \quad (3)$$

where E_{00} is the excited state energy, and in this case represents the singlet excited energy of the carbazole group, which is 83 kcal/mol. $e^2/r\epsilon$ is the Coulombic interaction in the ion pair state whose magnitude depends on the distance between the donor and acceptor (r) and the dielectric constant (ϵ) of the medium separating the charges. The distance between the donor and the acceptor is 6–7 Å for generations 1–3 (see the section on the mechanism below). Calculation according to eq 3 reveals that the electron transfer from the singlet state of the carbazole chromophore to the norbornadiene group in CZ-Gn-NBD is exothermic by ~18 kcal/mol in CH_2Cl_2 ($\epsilon = 9.08$ D). Therefore, we attributed the fluorescence quenching of the carbazole chromophores in CZ-Gn-NBD to the intramolecular electron transfer from the singlet excited carbazole chromophore to the norbornadiene group.

The efficiency of the singlet electron transfer is 0.92, 0.79, and 0.71 for generations 1–3, respectively, which decreases with the generation increase in CZ-Gn-NBD. Usually, the decreased ratio of acceptor to donors (and hence the effective

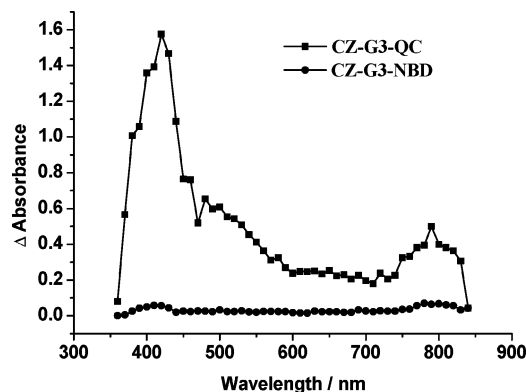


Figure 4. Transient absorption spectra observed upon photolysis of CZ-G3-QC and CZ-G3-NBD in CH_2Cl_2 at the peak of the laser pulse. Concentrations computed with the carbazole group are $1 \times 10^{-3} \text{ M}$.

local quencher concentration) and the increased separation of the acceptor and donors on electron transfer in the dendritic system are considered as the reason of the diminished quenching in higher generations.^{5e} In this work, the former factor could be the main cause of the decreased electron transfer efficiency due to the moderate change of the electron transfer rate constant with the generation.

Is there any photophysical process occurring from the triplet state of the carbazole chromophore to the norbornadiene group at room temperature? We estimated the triplet energy of the carbazole chromophore from the phosphorescence spectra to be ~69 kcal/mol. The triplet energy of the norbornadiene group was reported to be 53 kcal/mol,^{10,12} which is much lower than that of the carbazole chromophore. The energy transfer from the triplet state of the carbazole chromophore to the norbornadiene group in CZ-Gn-NBD is thermodynamically possible. The flash photolysis studies of CZ-Gn-QC were performed in deaerated CH_2Cl_2 by using 355 nm excitation light, which gave rise to a strong transient absorption spectrum with a maximum at 420 nm, as shown in Figure 4. This absorption can be assigned to the lowest triplet state of the carbazole chromophore by reference to the transient absorption of the triplet state of *N*-ethylcarbazole.¹³ Furthermore, this absorption is readily quenched by O_2 . In addition to the lowest triplet state absorption, Figure 4 also shows a transient absorption spectrum in the region of 750–830 nm, which is assigned to the radical cation of the carbazole chromophore by reference to the transient absorption of the radical cation of *N*-ethylcarbazole.¹³ This radical cation was considered to be produced by a two-photon ionization process.^{13a} Pulsed laser photolysis of CZ-Gn-NBD under identical conditions only leads to a very weak transient absorption of the carbazole chromophore. The absorbance of CZ-Gn-NBD at 420 nm is less than 5% of that from the corresponding CZ-Gn-QC, which means that the intersystem crossing from the singlet state of the carbazole chromophore to its triplet state in CZ-Gn-NBD is very inefficient. Therefore, the photophysical process occurring from the triplet state of the carbazole chromophore in CZ-Gn-NBD can be ignored; even the triplet–triplet energy transfer from the carbazole chromophore to the norbornadiene group is thermodynamically possible. This is also validated by the photochemical studies (see the details in the section on photosensitized isomerization below). Furthermore, we found that the transient absorption spectra of CZ-Gn-QC at 420 nm decayed monoexponentially with a lifetime of ~3.5 μs for generations 1–3. This result indicates that there is no intramolecular triplet–triplet annihilation between carbazole chromophores.

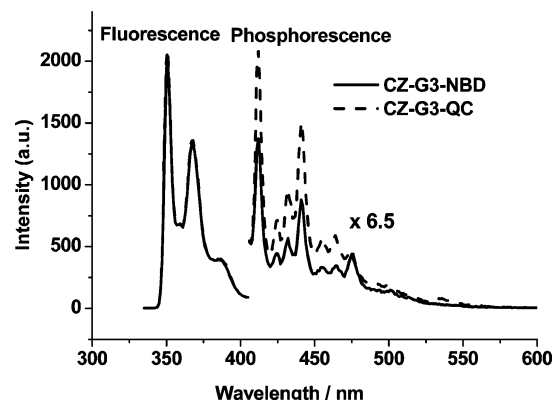


Figure 5. Emission spectra of CZ-G3-NBD and CZ-G3-QC in MTHF at 77 K. $\lambda_{\text{ex}} = 330$ nm. $[\text{CZ-G3-NBD}] = [\text{CZ-G3-QC}] = 1.0 \times 10^{-5}$ M.

Triplet–Triplet Energy Transfer from the Carbazole Chromophore to the Norbornadiene Group in CZ-Gn-NBD at 77 K. The emission spectra of CZ-Gn-NBD and CZ-Gn-QC were also studied in glassy 2-methyltetrahydrofuran at 77 K. An example of the emission spectra of CZ-G3-NBD and CZ-G3-QC, which is with the fluorescence and phosphorescence characters of the carbazole derivatives, is presented in Figure 5. In contrast to the results at room temperature, the fluorescence efficiency of the carbazole chromophore in CZ-Gn-NBD is only 1–2% less than that of the corresponding model compound, CZ-Gn-QC, which agrees with the results obtained by the time-resolved fluorescence measurements at 77 K (Table 1). This observation suggests that the photophysical process occurring from the singlet state of the carbazole chromophore can be disregarded in glassy 2-methyltetrahydrofuran at 77 K.

The phosphorescence spectra of CZ-Gn-NBD and CZ-Gn-QC show distinct vibronic transitions. The phosphorescence efficiencies of CZ-Gn-NBD are 90, 62, and 36% less than that of CZ-Gn-QC for generations 1–3, respectively, suggesting that the triplet state of the carbazole chromophore in CZ-Gn-NBD is quenched by the norbornadiene group. To clarify the reason for the intramolecular quenching of CZ phosphorescence by the NBD group, we calculate the free-energy change involved in an electron transfer process by eq 4.^{11,14}

$$\Delta G \text{ (kcal/mol)} = 23.06[E(\text{CZ}^{\bullet+}/\text{CZ}) - E(\text{NBD}/\text{NBD}^{\bullet-})] - E_{00} - e^2/r_{\epsilon} - e^2/2(1/r_{+} + 1/r_{-})(1/\epsilon' - 1/\epsilon) \text{ (kcal/mol)} \quad (4)$$

E_{00} represents the triplet-excited energy of the carbazole group (69 kcal/mol) here. $E(\text{CZ}^{\bullet+}/\text{CZ})$ and $E(\text{NBD}/\text{NBD}^{\bullet-})$ are determined to be +1.25 and −1.83 V in tetrahydrofuran solution ($\epsilon' = 7.58$ D). The distance between the donor and the acceptor (r) is 6–7 Å. The last term in eq 4 is the Born correction to the solvation energy which depends on the radius of the donor cation (r_{+}) and the acceptor anion (r_{-}). To estimate the Born correction to the solvation energy, we set r_{+} and r_{-} equal to 3.7 and 3.6 Å, respectively, by assuming that both donor and acceptor are spherical. Calculation according to eq 4 reveals that the electron transfer from the triplet-excited carbazole portion of CZ-Gn-NBD to the norbornadiene group in glassy 2-methyltetrahydrofuran ($\epsilon = 2.6$ D)¹⁵ is endothermic by ~4–7 kcal/mol for generations 1–3. Therefore, we attributed the phosphorescence quenching of the carbazole chromophore in CZ-Gn-NBD to the intramolecular triplet–triplet energy transfer to the norbornadiene group.

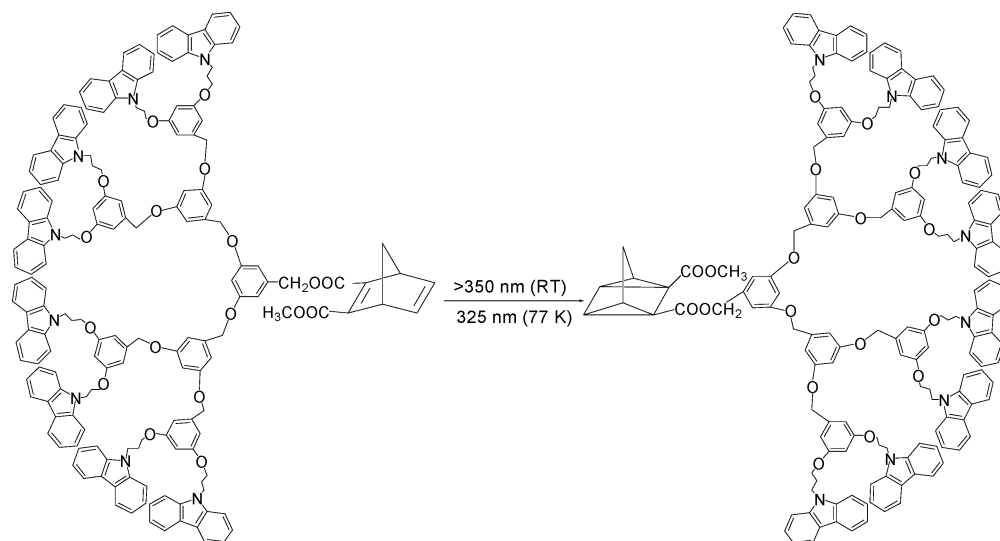
The phosphorescence lifetimes for CZ-G3-NBD and CZ-G3-QC in glassy 2-methyltetrahydrofuran were also examined. The

excitation wavelength was 325 nm, and the phosphorescence decay was monitored at the emission maximum 441 nm for all compounds. The compounds, CZ-Gn-QC ($n = 1-3$), exhibit monoexponential profiles, but the decay curves of CZ-Gn-NBD can only be fitted double-exponentially. The longer lifetime component with the same lifetime of the corresponding model compound, CZ-Gn-QC, is assigned to CZ-Gn-QC, which is converted from CZ-Gn-NBD under excitation, and the short lifetime species is assigned to CZ-Gn-NBD. The repetitious lifetime measurements on same sample validate our presumption. The proportion of the short lifetime component is getting less, and the portion of the longer lifetime component increases with each circle of the lifetime measurements. The conversion of CZ-Gn-NBD into CZ-Gn-QC was also confirmed by the characterization of the sample after the lifetime measurements. All of the phosphorescence lifetime data are listed in Table 1. These data allow the rate constant (k_{TT}) and the quantum yield (Φ_{TT}) for the triplet–triplet energy transfer to be calculated by using eqs 1 and 2. The rate constants are found to be 0.96, 0.25, and 0.08 s^{-1} and the quantum yields are 0.86, 0.64, and 0.36 for generations 1–3, respectively, which are compatible with the results obtained by the phosphorescence measurements (Table 2). The reason for the decrease of the energy transfer efficiency is thought to be the same as that of the electron transfer efficiency at room temperature.

Photosensitized Isomerization of the Norbornadiene to the Quadricyclane Group in CZ-Gn-NBD. The photosensitized valence isomerization of the norbornadiene to the quadricyclane has been the subject of intense experimental and theoretical investigations¹⁶ in view of its significance in solar energy storage¹⁷ and mechanism interests.¹⁸ The isomerization mechanism involving the triplet energy transfer is well understood.^{5c,19} Furthermore, the norbornadiene derivative is a good electron acceptor and can also undergo isomerization in the presence of an electron donor sensitizer.^{19c,d} On the basis of the observation of chemical induced dynamic nuclear polarization (CIDNP) effects, it has been proposed that this photosensitized isomerization involves an electron transfer from the sensitizer to the norbornadiene to generate a singlet state radical-ion pair, intersystem crossing of the resultant singlet radical-ion pair to its triplet state, and the recombination of the triplet radical-ion pair to give the triplet norbornadiene followed by a rearrangement to the quadricyclane. Thus, the study of intramolecular photosensitized isomerization of the norbornadiene group in CZ-Gn-NBD may provide the evidence of electron transfer and energy transfer in a dendritic system.

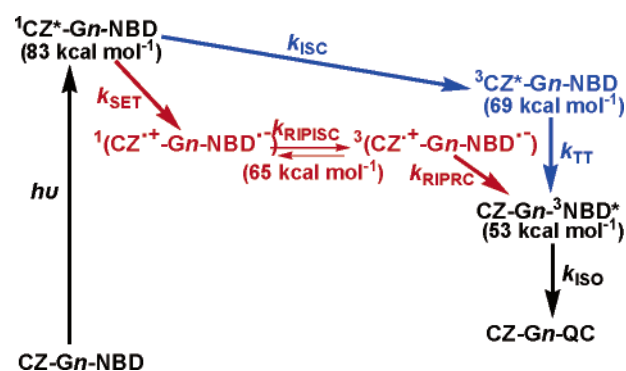
For CZ-Gn-NBD compounds, the energy of the radical-ion pair, $\text{CZ}^{\bullet+}\text{-Gn-NBD}^{\bullet-}$, in CH_2Cl_2 was calculated according to eq 3 to be about 65 kcal/mol. This energy is higher than the triplet energy of the norbornadiene group (53 kcal/mol). Thus, we infer that the triplet radical-ion pair $^3(\text{CZ}^{\bullet+}\text{-Gn-NBD}^{\bullet-})$ may undergo recombination to generate the triplet norbornadiene group CZ-Gn-³NBD*. From the flash photolysis studies, we know that the photophysical process occurring from the triplet state of the carbazole group in CZ-Gn-NBD can be ignored at room temperature. Therefore, the isomerization of the norbornadiene group in CZ-Gn-NBD might mainly proceed via a radical-ion pair recombination mechanism. Photoirradiation with $\lambda > 350$ nm of a 1.0×10^{-5} M solution of CZ-Gn-NBD in deaerated CH_2Cl_2 at room temperature results in the valence isomerization of the norbornadiene group to the quadricyclane group (CZ-Gn-QC), as shown in Scheme 1. Under this condition, only carbazole chromophores absorb light. Therefore, the isomerization of the norbornadiene to the quadricyclane group

SCHEME 1



must be attributed to the sensitization via electron transfer from the carbazole chromophore to the norbornadiene group. The yield of the 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.^{5c,10} The mass spectroscopy shows that the product and the starting material have the same molecular weight. Measurements of product formation at different concentrations reveal that the isomerization is induced by intramolecular photosensitization. The quantum yields of the intramolecular photosensitized isomerization ($\Phi_{\text{ISO}}(\text{CZ-Gn-NBD})$) were measured to be approximately 0.013, 0.012, and 0.011 for generations 1–3, respectively, by using a benzophenone/benzohydrol system as actinometry.²⁰

Formation of the triplet state of the norbornadiene group via recombination of the triplet radical-ion pair was further supported by the determination of the quantum yield for the isomerization of the norbornadiene group in CZ-Gn-NBD in the presence of *cis*-piperylene. The triplet state energy of the *cis*-piperylene is ~ 57 kcal/mol,²¹ which lies below the triplet state of the carbazole chromophore (69 kcal/mol) but above the triplet state of the norbornadiene group (53 kcal/mol). Thus, the *cis*-piperylene may selectively quench the triplet carbazole in the presence of the triplet norbornadiene. In the presence of *cis*-piperylene, the intermolecular quenching of the carbazole triplet state by *cis*-piperylene would compete with the intramolecular quenching by NBD, if the triplet energy transfer from CZ to NBD in CZ-Gn-NBD could occur. Therefore, the intramolecular photosensitized isomerization of the norbornadiene group in CZ-Gn-NBD in the presence of a sufficient amount of the *cis*-piperylene should exclusively originate from the singlet electron transfer path. Photoirradiation of a solution of CZ-Gn-NBD (the concentration computed with the carbazole group is 2.0×10^{-5} M) with 2.0×10^{-2} M *cis*-piperylene gave the quantum yield of the isomerization to be the same as that in the absence of *cis*-piperylene within the experiment error ($\pm 3\%$). This indicates that the triplet state of the norbornadiene group in CZ-Gn-NBD at room temperature is exclusively formed via the singlet electron transfer process. By using $\Phi_{\text{ISO}}(\text{NBD})$, which represents the quantum yield of the isomerization reaction of the NBD triplet state and is ~ 0.185 ,^{19b} the quantum yield of the triplet norbornadiene formation via the singlet electron

SCHEME 2^a

^a The data in parentheses represent the energies of the corresponding states relative to the ground state. Red color represents the processes that occur at room temperature. Blue color indicates the processes proceeded in glassy MTHF at 77 K. Black color means that the processes can occur both at room temperature and at 77 K.

transfer is calculated to be 0.070, 0.065, and 0.059 for generations 1–3, respectively.

At room temperature, the quantum yield of the triplet norbornadiene formation via the singlet electron transfer pathway (0.070 for G1, 0.065 for G2, and 0.059 for G3) is a product of Φ_{SET} , the efficiency of the intersystem crossing (Φ_{RIPISC}) from $^1(\text{CZ}^{*+}\text{-Gn-NBD}^{\bullet-})$ to $^3(\text{CZ}^{*+}\text{-Gn-NBD}^{\bullet-})$, and the efficiency of the recombination of the resultant $^3(\text{CZ}^{*+}\text{-Gn-NBD}^{\bullet-})$ (Φ_{RIPRC}). Since Φ_{SET} (0.92 for G1, 0.79 for G2, and 0.71 for G3) is known, $\Phi_{\text{RIPISC}} \cdot \Phi_{\text{RIPRC}}$, the efficiency of the triplet norbornadiene formation from $^1(\text{CZ}^{*+}\text{-Gn-NBD}^{\bullet-})$ via intersystem crossing and the subsequent recombination, is calculated to be approximately 0.080, 0.082, and 0.084 for generations 1–3, respectively. The isomerization of NBD to QC in CZ-Gn-NBD could occur efficiently via the intramolecular triplet–triplet energy transfer from the carbazole chromophore to the norbornadiene group at 77 K, which has been demonstrated in the time-resolved phosphorescence measurements. On the basis of the experimental results mentioned above, the primary photophysical and photochemical processes in CZ-Gn-NBD can be expressed by Scheme 2.

To determine the light-harvesting ability of CZ-Gn-NBD, further intramolecular photosensitized isomerization experiments of CZ-Gn-NBD in CH_2Cl_2 were done. The same concentration (1.0×10^{-5} M) was used in the experiments for CZ-Gn-NBD.

After irradiation for 5 min with a 500 W middle-high-pressure mercury lamp in a merry-go-round apparatus, the conversions of CZ-*Gn*-NBD to CZ-*Gn*-QC were 5, 12, and 22% ($\pm 3\%$) for generations 1–3, respectively. The observed rates of the isomerization for CZ-G1-NBD to CZ-G3-NBD were 1.0×10^{-7} , 2.4×10^{-7} , and 4.4×10^{-7} M min $^{-1}$, respectively. Obviously, the higher isomerization rate for higher generation is attributed to the increase of light-harvesting ability in CZ-*Gn*-NBD, referring to the larger molar absorption coefficient of the higher generation.

Mechanism of Intramolecular Singlet–Singlet Electron Transfer and Triplet–Triplet Energy Transfer from the Carbazole Chromophore to the Norbornadiene Group in CZ-*Gn*-NBD. The steady state and transient spectroscopy studies and photosensitized reaction experiments reveal that the excitation of the carbazole chromophore in CZ-*Gn*-NBD results in an intramolecular electron transfer at room temperature and an intramolecular triplet–triplet energy transfer at 77 K to the norbornadiene group, subsequently leading to an isomerization of the latter to the quadricyclane (Scheme 2). The efficiencies and rate constants of singlet–singlet electron transfer at room temperature and those of triplet–triplet energy transfer at 77 K are summarized in Table 2. Because the rate constant of the singlet electron transfer (k_{SET} is $\sim 10^8$ – 10^9 s $^{-1}$) is 1–2 orders of magnitude higher than that of the intersystem crossing process of the carbazole group (k_{ISC} is $\sim 10^7$ s $^{-1}$ for *N*-alkyl carbazole),²² the photophysical process from the triplet state of the carbazole chromophore can be neglected at room temperature. It has been demonstrated that the electron transfer is classically forbidden in a solid environment or at cryogenic temperatures.²³ In glassy 2-methyltetrahydrofuran at 77 K, there is no sufficient thermal energy to overcome the free-energy barrier; therefore, the electron transfer process cannot occur efficiently. Most of the photophysical processes proceed via the triplet–triplet energy transfer at 77 K.

The mechanism of the triplet–triplet energy transfer is usually described by the Dexter electron-exchange interaction²⁴ and may be visualized in terms of two electron transfer processes or one electron transfer process and one hole transfer process.²⁵ Generally, the electron transfer requires strong donor–acceptor orbital overlap, and therefore, the electron transfer and triplet energy transfer rate constants should decrease exponentially with increasing donor–acceptor distance. Thus, one might expect that the rate constants for the electron transfer or the triplet energy transfer will become negligibly small as the donor–acceptor distance increases beyond the sum of their van der Waals radii (5–10 Å) except it occurs via a “through-bond mechanism” in a conjugated or a rigid system. In this study, we can exclude the through-bond mechanism because the rate constants (k_{SET} and k_{TT}) do not decrease exponentially with the generation increase. Since dendrimers are not crystalline, it is difficult to determine the distance between donor and acceptor in each generation. Although the detailed three-dimensional structures of dendrimers are not well-understood, recent theoretical²⁶ and experimental results^{5c,7c,d,27} suggest that dendrimers with a flexible backbone will take the folded conformation, especially at higher generations, which gives a probable closest donor–acceptor distance of ~ 6 Å. In the present work, since the flexible poly(aryl ether) dendrimer backbone is used, and a soft linker, $-(\text{CH}_2\text{CH}_2\text{CH}_2)-$, connects the carbazole chromophore with the dendrimer backbone, CZ-*Gn*-NBD should take the folding back conformation. Computation by the Polak–Ribiere algorithm (HyperChem 6.0 program) shows that the lowest-energy conformation of CZ-*Gn*-NBD is folded. While

optimizing the conformation, the solvent effect could not be taken into account due to the limitation of the program. The distance between the carbazole and norbornadiene groups is defined as the distance between the nitrogen atom of the carbazole chromophore and the carbon atom of the vinyl group closely connected to the dendrimer backbone. Estimation from the molecular modeling gives a similar shortest donor–acceptor distance in CZ-*Gn*-NBD of 6–7 Å for generations 1–3, which is in good accord with the theoretical results.^{26d} At these distances, the electron transfer and the triplet–triplet energy transfer could occur efficiently, which was accordant with the experiment results. Because the rate constant of electron transfer is at the same magnitude, we infer that the electron transfer mainly happens between the closest terminal donor chromophore and the acceptor core group. On the basis of the experimental results and the interpretation, we infer that a through-space mechanism operates the intramolecular electron transfer at room temperature and the triplet energy transfer at 77 K in CZ-*Gn*-NBD. When the excitation happens on the CZ chromophore in proximity to the NBD group, the electron transfer and energy transfer occur directly. If the distance between the excited CZ chromophore and NBD is out of the range of effective electron transfer and energy transfer, the dynamic motion of the excited CZ toward NBD within the lifetime and the energy migration to the closest CZ can make the electron transfer occur at room temperature, but only the latter operates the triplet energy transfer at 77 K.

Conclusions

Photochemical reaction and photophysical studies reveal that CZ-*Gn*-NBD undergoes the singlet electron transfer process at room temperature with an efficiency of 88, 80, and 74% and a rate constant of 1.8×10^9 , 6.1×10^8 , and 4.0×10^8 s $^{-1}$ for generations 1–3, respectively. In glassy 2-methyltetrahydrofuran at 77 K, the triplet energy transfer dominates the photophysical process in CZ-*Gn*-NBD with an efficiency of 0.86, 0.64, and 0.36 and a rate constant of 0.96, 0.25, and 0.08 s $^{-1}$ for generations 1–3, respectively. Both electron transfer and triplet energy transfer processes lead to a valence isomerization of NBD to QC. The quantum yields of the intramolecular photosensitized isomerization are approximately 0.013, 0.012, and 0.011 for generations 1–3, respectively. The higher observed isomerization rate at higher generations indicates that the light-harvesting ability of CZ-*Gn*-NBD increases with generation due to the number of peripheral chromophores that doubles from one dendrimer generation to the next, although the electron transfer efficiency decreases some with increasing generation. The through-bond mechanism is excluded because the rate constants of electron transfer and triplet energy transfer do not decrease exponentially with the increase in generation number. A through-space mechanism involving the closest donor (folding back conformation) and acceptor groups is proposed to operate the intramolecular singlet electron transfer and triplet energy transfer in CZ-*Gn*-NBD. These findings provide a new example of using dendrimers for light harvesting: the periphery antenna chromophores harvest photon energy which is then utilized to activate the core group for chemical reaction via electron transfer and triplet energy transfer.

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Supporting Information Available: Experimental procedures for the synthesis of all dendritic compounds, including

characterization data, and emission spectra and time-resolved fluorescence spectra of CZ-Gn-NBD and CZ-Gn-QC at room temperature and 77 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) *Topics in Current Chemistry: Dendrimers V*; Vögtle, F., Schalley, C., Eds.; Springer Verlag: Berlin, 2003. (b) *Dendrons and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley, New York, 2001. (c) Tully, D. C.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1229. (d) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, 40, 74. (e) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, 99, 1665. (f) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, 97, 1681.
- (2) (a) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701. (b) Hu, X.; Damjanovic, A.; Ritz, T.; Schulten, K. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, 95, 5935. (c) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, 374, 517. (d) Fréchet, J. M. J. *Science* **1994**, 263, 1710. (e) Tomalia, D. A.; Naylor, A.; Goddard, W. A. *Angew. Chem., Int. Ed.* **1990**, 29, 138.
- (3) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Synthesis, Application*; VCH: Weinheim, Germany, 2001. (b) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, 38, 884.
- (4) (a) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, 122, 1175. (b) Sakamoto, M.; Ueno, A.; Mihara, H. *Chem.—Eur. J.* **2001**, 7, 2449. (c) Balzani, V.; Vögtle, F. C. R. *Chim.* **2003**, 6, 867. (d) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Sereoni, S. *Coord. Chem. Rev.* **2001**, 219–221, 545.
- (5) (a) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, 10, 286. (b) Kawa, M.; Fréchet, J. M. J. *Thin Solid Films* **1998**, 331, 259. (c) Chen, J.; Li, S.; Zhang, L.; Liu, B.; Han, Y.; Yang, G.; Li, Y. *J. Am. Chem. Soc.* **2005**, 127, 2165. (d) Ghaddar, T. H.; Wishart, J. F.; Kirby, J. P.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, 123, 12832. (e) Stewart, G. M.; M. Fox, A. *J. Am. Chem. Soc.* **1996**, 118, 4354. (f) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, 118, 3978. (g) Gronheid, R.; Hofkens, J.; Köhn, F.; Weil, T.; Reuther, E.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2002**, 124, 2418.
- (6) (a) Chasse, T. L.; Sachdeva, R.; Li, Q.; Li, Z.; Petrie, R. J.; Gorman, C. B. *J. Am. Chem. Soc.* **2003**, 125, 8250. (b) Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **1999**, 38, 1422. (c) Pollak, K. W.; Leon, J. W.; Fréchet, J. M. J.; Maskus, M.; Abruña, H. D. *Chem. Mater.* **1998**, 10, 30. (d) Vögtle, F.; Plevoets, M.; Nieger, M.; Azzellini, G. C.; Credi, A.; De Cola, L.; De Marchis, V.; Venturi, M.; Balzani, V. *J. Am. Chem. Soc.* **1999**, 121, 6290. (e) Gorman, C. B.; Smith, J. C. *J. Am. Chem. Soc.* **2000**, 122, 9342.
- (7) (a) Hara, M.; Samori, S.; Cai, X.; Tojo, S.; Arai, T.; Momotake, A.; Hayakawa, J.; Uda, M.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, 126, 14217. (b) Ghaddar, T. H.; Wishart, J. F.; Thompson, D. W.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2002**, 124, 8285. (c) Capitost, G. J.; Cramer, S. J.; Rajesh, C. S.; Modarelli, D. A. *Org. Lett.* **2001**, 3, 1645. (d) Rajesh, C. S.; Capitost, G. J.; Cramer, S. J.; Modarelli, D. A. *J. Phys. Chem. B* **2001**, 105, 10175. (e) Ceroni, P.; Vicinelli, V.; Maestri, M.; Balzani, V.; Müller, W. M.; Müller, U.; Hahn, U.; Osswald, F.; Vögtle, F. *New J. Chem.* **2001**, 25, 989.
- (8) (a) Jiang, D.-L.; Aida, T.; Yashima, E.; Okamoto, Y. *Thin Solid Films* **1998**, 331, 254. (b) Jiang, D.-L.; Aida, T. *Nature* **1997**, 388, 454.
- (9) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, 112, 7638. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (c) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, 115, 11496.
- (10) Wu, Q. H.; Zhang, B. W.; Ming, Y. E.; Cao, Y. *J. Photochem. Photobiol., A* **1991**, 61, 53.
- (11) (a) Weller, A. *Z. Phys. Chem. N. F.* **1982**, 133, 93. (b) Rehn, D.; Weller, A. *Isr. J. Chem.* **1970**, 8, 259.
- (12) Schwarz, W.; Dangel, K. M.; Jones, G. II.; Bargan, J. *J. Am. Chem. Soc.* **1982**, 104, 5686.
- (13) (a) Masuhara, H.; Tamai, N.; Mataga, N.; De Schryver, F. C. Vandendriessche, J. *J. Am. Chem. Soc.* **1983**, 105, 7256. (b) Masuhara, H.; Shioyama, H.; Mataga, N.; Inoue, T.; Kitamura, N.; Tanabe, T.; Tazuke, S. *Macromolecules* **1981**, 14, 1738. (c) Masuhara, H.; Ohwada, S.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *J. Phys. Chem.* **1980**, 84, 2363.
- (14) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, 109, 3258. (b) Zhu, Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1993**, 115, 2190.
- (15) (a) Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, 113, 719. (b) Furutsuka, T.; Imura, T.; Kojima, T.; Kawabe, K. *Technol. Rep. Osaka Univ.* **1974**, 24, 367.
- (16) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, 86, 401.
- (17) (a) Harel, Y.; Adamson, A. W.; Kutal, C.; Gotsch, P. A.; Yasufuku, K. *J. Phys. Chem.* **1987**, 91, 901. (b) Basu, A.; Saple, A. R.; Sapre, N. Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1797. (c) Yashida, Z. I. *J. Photochem.* **1985**, 29, 27.
- (18) (a) Arai, T.; Oguchi, T.; Wakabayashi, T.; Tsuchiya, M.; Nishimura, Y.; Oishi, S.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1987**, 60, 2937. (b) Jones, G., II; Schwarz, W.; Malba, V. *J. Phys. Chem.* **1982**, 86, 2286. (c) Schwarz, W.; Dangel, K. M.; Jones, G., II; Bargan, J. *J. Am. Chem. Soc.* **1982**, 104, 5686.
- (19) (a) Helms, A. M.; Caldwell, R. A. *J. Am. Chem. Soc.* **1995**, 117, 358. (b) Tung, C.-H.; Zhang, L.-P.; Li, Y.; Cao, H.; Tanimoto, Y. *J. Phys. Chem.* **1996**, 100, 4480. (c) Tung, C.-H.; Zhang, L.-P.; Li, Y.; Cao, H.; Tanimoto, Y. *J. Am. Chem. Soc.* **1997**, 119, 5348. (d) Zhang, L.-P.; Chen, B.; Wu, L.-Z.; Tung, C.-H.; Cao, H.; Tanimoto, Y. *Chem.—Eur. J.* **2003**, 9, 2763. (e) Murov, S.; Hammond, G. S. *J. Phys. Chem.* **1968**, 72, 3797. (f) Hammond, G. S.; Wyatt, P.; Deboer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, 86, 2532. (g) Gorman, A. A.; Hamblett, I.; McNeeney, S. P. *Photochem. Photobiol.* **1990**, 51, 145.
- (20) Hammond, G. S.; Moore, W. M.; Eaker, W. P. *J. Am. Chem. Soc.* **1961**, 83, 2795.
- (21) (a) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. J. *Am. Chem. Soc.* **1964**, 86, 3197. (b) Kellogg, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, 87, 4230.
- (22) Bonesi, S. M.; Erra-Balsells, R. *J. Lumin.* **2001**, 93, 51.
- (23) Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH Publishers: New York, 1993.
- (24) (a) Dexter, D. L. *J. Chem. Phys.* **1953**, 21, 836. (b) Katz, J. L.; Jortner, J.; Chol, S. I.; Rice, S. A. *J. Chem. Phys.* **1963**, 39, 1897.
- (25) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 9.
- (26) (a) Murat, M.; Grest, G. S. *Macromolecules* **1996**, 29, 1278. (b) Cavallo, L.; Fraternali, F. *Chem.—Eur. J.* **1998**, 4, 927. (c) Mansfield, M. L. *Macromolecules* **2000**, 33, 8043. (d) Ortiz, W.; Roitberg, A. E.; Krause, J. L. *J. Phys. Chem. B* **2004**, 108, 8218.
- (27) (a) Wooley, K. L.; Klug, C. A.; Tasaki, K.; Schaefer, J. J. *Am. Chem. Soc.* **1997**, 119, 53. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, 115, 4375. (c) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, 25, 2401. (d) Gutierrez-Nava, M.; Accorsi, G.; Masson, P.; Armadori, N.; Nierengarten, J.-F. *Chem.—Eur. J.* **2004**, 10, 5076.