

Inhibition of the Formation and Decay of Stilbene Core Radical Cations by the Dendron during the Photoinduced Electron Transfer

Michihiro Hara,[†] Shingo Samori,[†] Xichen Cai,[†] Sachiko Tojo,[†] Tatsuo Arai,[‡] Atsuya Momotake,[‡] Junpei Hayakawa,[‡] Mayuko Uda,[‡] Kiyohiko Kawai,[†] Masayuki Endo,[†] Mamoru Fujitsuka,[†] and Tetsuro Majima^{*,†}

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan, and Graduate School for Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Received: September 16, 2004; In Final Form: October 28, 2004

Formation and decay processes of stilbene core radical cation ($\text{ST}^{\bullet+}$) during the photoinduced electron transfer have been studied for a series of stilbene bearing benzyl ether-type dendrons (**D**). $\text{ST}^{\bullet+}$ and the radical cation of peripheral dendron ($\text{D}^{\bullet+}$) were generated by intermolecular hole transfer from biphenyl radical cation, which was generated from photoinduced electron transfer from biphenyl to the singlet-excited 9,10-dicyanoanthracene in a mixture of acetonitrile and 1,2-dichloroethane (3:1). An intramolecular dimer radical cation of benzyl groups at the terminal of stilbene dendrimer was indicated as a hole trapping site. Subsequent hole transfer from the trapping site to the core **ST** generated $\text{ST}^{\bullet+}$. The shielding effects of **D** depending on the dendrimer generation on the growth and decay of $\text{ST}^{\bullet+}$ were observed. It was revealed for the first time that **D** acts as the hole trapping site and the hole conductor on the way of the exothermic hole transfer from the terminal of **D** to the central core **ST**. We also found that **D** inhibits the charge recombination with 9,10-dicyanoanthracene radical anion because of the steric hindrance.

Introduction

Recently, dendrimers have received quite wide attention. Their three-dimensional and site-isolated structures are interesting from the fundamental viewpoint. Furthermore, they are useful intelligent materials for light-harvesting antennas, fluorescent chemosensor, organic light-emitting diode, and drug delivering molecules.^{1–10} The functionalization of the dendron with photo- and redox-active units will realize various novel properties. Recently, we reported that the benzyl ether-type dendrons can act as hole-harvesting antennas during the two-photon ionization and an effective shield against the neutralization of stilbene core radical cations with chloride ion.¹¹ The ability to create specific site-isolated nano-environments is one of the most interesting characters of dendrimers. Therefore, the previous work demonstrated that both electric conduction and isolation are also available functions of the dendrimers.

Behavior of the electric carrier generated during the electron transfer can be elucidated in detail by various methods. Electron transfer of dendrimers have been investigated by means of spectroscopic^{12–17} and electrochemical methods.^{18–20} Although these studies often emphasized the steric effects of the dendrimers, carrier migration in the dendron unit has been scarcely discussed.¹⁷

In the present study, photoinduced electron-transfer reactions of a series of stilbene bearing benzyl ether-type dendrons (**G0–4**, Scheme 1) were examined to elucidate the intermolecular photoinduced hole transfer and the subsequent processes

depending on the dendrimer generation during the laser flash photolysis in the presence of 9,10-dicyanoanthracene (DCA) and biphenyl (Bp). Here, we first report intermolecular hole transfer from Bp radical cation ($\text{Bp}^{\bullet+}$), which is generated by the photoinduced electron transfer between DCA in the singlet excited state ($^1\text{DCA}^*$) and Bp, to the dendrimers giving **ST** radical cation ($\text{ST}^{\bullet+}$) and peripheral radical cation ($\text{D}^{\bullet+}$) and the subsequent hole transfer process from $\text{D}^{\bullet+}$ to the core **ST** giving $\text{ST}^{\bullet+}$. In addition, various “dendrimer effects” on the growth and decay of $\text{ST}^{\bullet+}$ is described.

Experimental Section

Materials. **G0–4** (Scheme 1) were prepared according to the procedure previously described in the literature.²¹ Acetonitrile (AN) and 1,2-dichloroethane (DCE) (Wako, spectroscopic grade) were used without further purification. DCA was purchased from Aldrich and purified by recrystallization from benzene before use. Bp was purchased from Wako and purified by recrystallization from ethanol before use.

Nanosecond Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were carried out using the third harmonic oscillation (355 nm) of a Nd^{3+} :YAG laser (Quantel, Brilliant Q-switch laser; pulse width of 5-ns fwhm) as an excitation source. The monitor light was obtained from a 450-W Xe lamp (Osram, XBO-450) synchronized with the laser flash and monitored using a photomultiplier (Hamamatsu Photonics, R928) or a silicon photodetector (Hamamatsu Photonics, S5343). The signal from the detector was digitized with an oscilloscope and transmitted to a personal computer via the GPIB interface. The dendrimer samples in a rectangular quartz cell (0.5 × 1.0

* To whom correspondence should be addressed. Telephone: +6-6879-8495. Fax: +6-6879-8499. E-mail: majima@sanken.osaka-u.ac.jp.

[†] Osaka University.

[‡] University of Tsukuba.

SCHEME 1. Stilbene Dendrimers

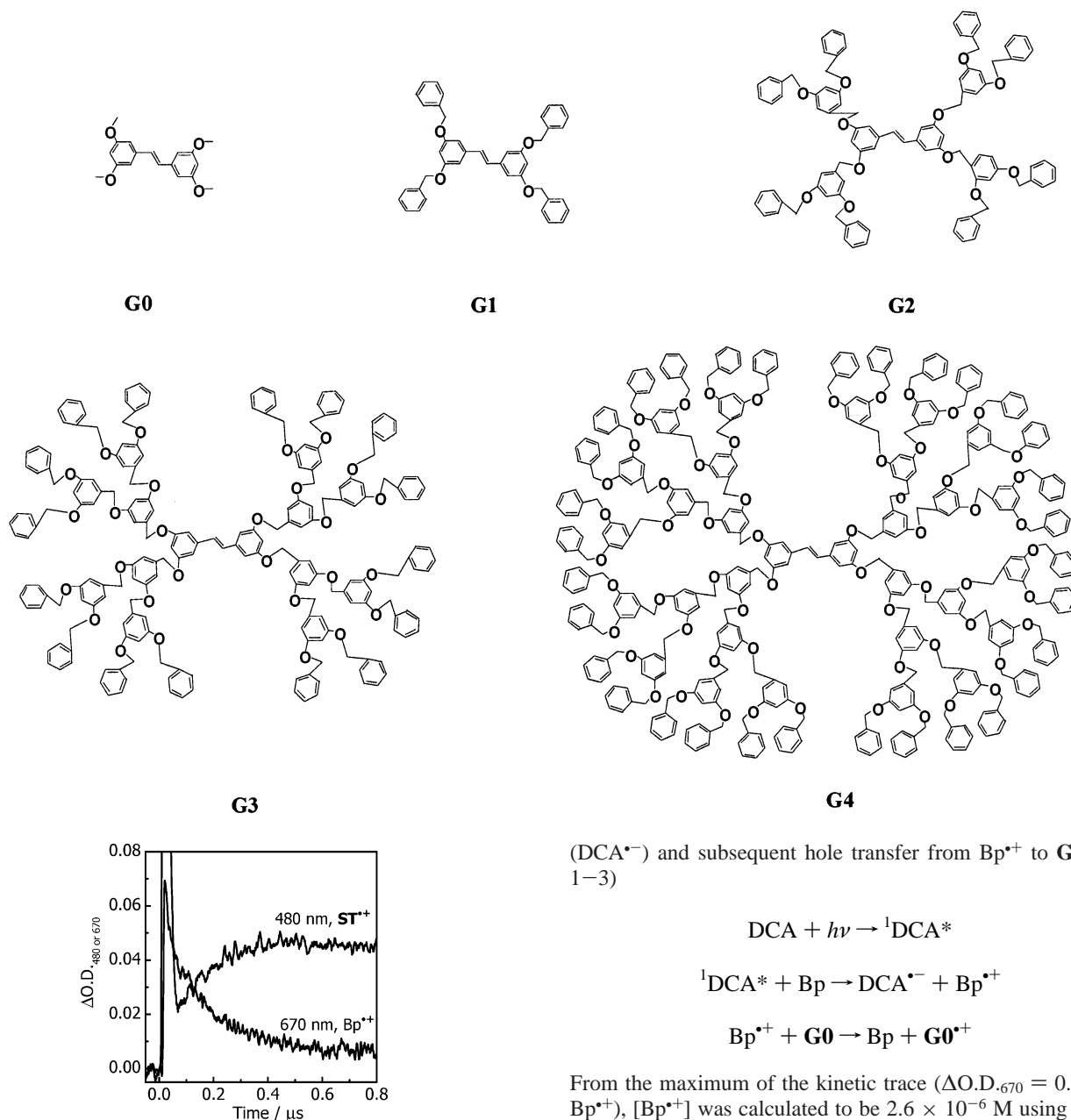


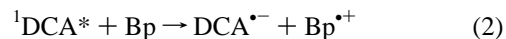
Figure 1. Time profiles of the transient absorption at 480 and 670 nm assigned to $\text{ST}^{\bullet+}$ and $\text{Bp}^{\bullet+}$, respectively. $[\text{ST}^{\bullet+}]$ of **G0** during the 355-nm 5-ns laser flash photolysis of a mixture of DCA (0.1 mM), Bp (100 mM), and **G0** (0.3 mM) in 3:1 AN-DCE. The initial spike was caused by laser light scattering.

$\times 4.0$ cm, optical path length of 1.0 cm) were prepared in a mixture of AN and DCE (3:1) at room temperature.

Results and Discussion

The transient absorption band of Bp radical cation ($\text{Bp}^{\bullet+}$) was observed at 670 nm immediately after the laser flash (355-nm, 5-ns fwhm) during the laser flash photolysis of DCA (0.1 mM), Bp (100 mM), and **G0** (0.3 mM) in a mixture of AN and DCE (3:1) (Figure 1). The $\text{Bp}^{\bullet+}$ absorption decayed concomitantly with the formation of new peaks at 480 and 510 nm of $\text{G0}^{\bullet+}$. These spectral changes are attributable to electron transfer from Bp to $^1\text{DCA}^*$ to form $\text{Bp}^{\bullet+}$ and DCA radical anion

($\text{DCA}^{\bullet-}$) and subsequent hole transfer from $\text{Bp}^{\bullet+}$ to **G0** (eqs 1–3)



From the maximum of the kinetic trace ($\Delta\text{O.D.}_{670} = 0.036$ of $\text{Bp}^{\bullet+}$), $[\text{Bp}^{\bullet+}]$ was calculated to be 2.6×10^{-6} M using $\epsilon_{670} = 1.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.²² Assuming $[\text{Bp}^{\bullet+}] = [\text{G0}^{\bullet+}]$, ϵ at 480 nm of $\text{G0}^{\bullet+}$ was estimated to be $\epsilon_{480} = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Because the spectral shape and intensity of transient absorption spectra of radical cation of **G0–4** were independent of the generation of dendrimer under the same two-photon ionization condition, all ϵ values of the core $\text{ST}^{\bullet+}$ are regarded as identical for **G0–4**.¹¹

The decay profiles of $\text{Bp}^{\bullet+}$ as a hole donor were analyzed with the pseudo-first-order kinetics, from which the rate constants of $(2.0 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ were obtained for **G0–4** (Table 1). Therefore, it is indicated that the hole transfer occurs from $\text{Bp}^{\bullet+}$ to the dendrimers **G0–4** at the same rate constant. However, $\text{ST}^{\bullet+}$ showed both fast and much slower growth components in the time range of a few microseconds (Figure 2). The fast growth component can be attributed to the direct hole transfer from $\text{Bp}^{\bullet+}$ to the central ST core. The slower component indicates the indirect generation of $\text{ST}^{\bullet+}$ via an intermediate state.

The present **D** is composed of methoxybenzene, methoxymethylbenzene, and 1,3-dimethoxybenzene moieties. Since the

TABLE 1: Rate Constants of Intermolecular Hole-Transfer with Bp^+ (k_{BP^+}) and Intramolecular Hole Transfer (k_{IH}), Charge Recombination Rates between Dendron $^+$ and DCA^- (k_{CR}) and between ST^+ and DCA^- (k_{CR}'), and Quantum Yields of Hole Transfer (Φ_{H}) from Dendron to ST and G1–4 in AN-DCE Mixture

<i>G</i>	$k_{\text{BP}^+}/10^9 \text{ M}^{-1}\text{s}^{-1}$	$k_{\text{IH}}/\text{s}^{-1}$	$k_{\text{CR}}/\text{s}^{-1}$	$k_{\text{CR}}'/\text{s}^{-1}$	Φ_{H} ^b
G1	2.1	4.2×10^6	0.31×10^6	2.2×10^5	0.93
G2	1.7	3.3×10^6	2.4×10^6	1.7×10^5	0.57
G3	2.2	2.3×10^6	2.5×10^6	1.6×10^5	0.48
G4	1.8	1.6×10^6	3.1×10^6	1.3×10^5	0.34

^a Estimated from eq 4. ^b Calculated from eq 5.

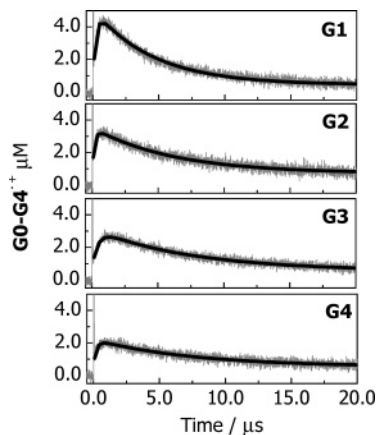


Figure 2. Time profiles of the transient absorption at 480 nm assigned to ST^+ of G1–G4 during the 355-nm 5-ns laser flash photolysis of a mixture of DCA (0.1 mM), Bp (100 mM), and G1–G4 (0.3 mM) in 3:1 AN-DCE. The initial spikes were caused by laser light scattering. Curves were calculated from eq 4.

oxidation potentials of methoxybenzene (1.62 V vs SCE), methoxymethylbenzene (1.55 V), and 1,3-dimethoxybenzene (1.49 V) are lower than 1.75 V of Bp,^{23,24} exothermic hole transfer from Bp^+ to **D** is possible. Furthermore, the oxidation potential of **ST** (1.27 V) is the lowest in the dendrimers. A hole can move from **D** to **ST**. Thus, ST^+ can be generated also by the indirect mechanism including the hole transfer from D^+ to **ST**. It has been reported that the hole transfer from D^+ to **ST** giving ST^+ occurs within the laser pulse duration of 5 ns.^{11,25} Therefore, a slow formation of ST^+ implies existence of a hole trapping state as an intermediate in **D** before hole transfer to **ST**. Since the hole transfer from Bp^+ to the terminal benzyl moiety (**Bz**) occurs initially to give Bz^+ , a dimer radical cation between Bz^+ and neutral **Bz**, $(\text{Bz})_2^+$, can be assumed to be the intermediate before the hole transfer to **ST**. The stabilization energy of 15.5 kcal mol⁻¹, which is reported for toluene dimer radical cation, seems to be sufficient to trap the hole before the migration.²⁶

Transient absorption spectra in the near-IR region of **G0** and **G1** during the two-photon ionization in the AN and DCE mixture (3:1) were shown in Figure 3, in which the absorption band of **G1** showed two times larger intensity and shifted to longer wavelength than that of **G0**, even though the absorbances of **G0** and **G1** were equivalent at the excitation wavelength. Since the near-IR band of **G0** is assigned to radical cation of stilbene core, the increase of the near-IR band of **G1** can be attributed to the Bz_2^+ . Figure 3 inset showed the difference transient spectrum of the near-IR band around 950 nm, which is well consistent with the reported one.²⁶ The above phenomena suggested that hole from Bp^+ is localized as Bz_2^+ in dendron before hole transfer to **ST**. The energy minimized structure of **G1** at MM2 level showed that **Bz** is located at close proximity

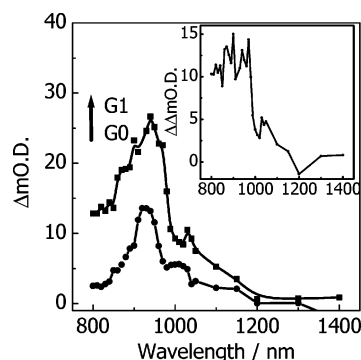
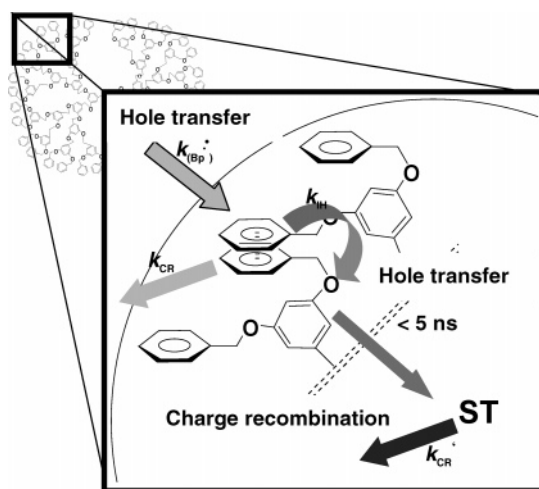


Figure 3. Transient absorption spectra assigned to G0^+ and G1^+ observed at 100 ns after a 266 nm laser flash (30 mJ pulse⁻¹) during the TPI of **G0** and **G1**, respectively, in an AN and DCE mixture (3:1). Inset is the difference transient absorption spectrum of **G0** and **G1**, and assigned to Bz_2^+ .

SCHEME 2



favorable to the Bz_2^+ formation (see the Supporting Information). Thus, the slow growth of ST^+ can be attributed to the hole transfer from Bz_2^+ to the other part of **D**, from which hole transfer to **ST** proceeds within 5 ns. This process is competitive with the charge recombination between Bz_2^+ and DCA^- . Furthermore, the decay of ST^+ in the time range of 100 μs can be attributed to the charge recombination between ST^+ and DCA^- (Scheme 2).

The rate constants of the hole transfer and charge recombination processes were evaluated according to eq 4

$$[\text{ST}^+] = (\text{Bz}_2^+)_0 / (k_{\text{IH}} - k_{\text{CR}} - k_{\text{CR}}') (\exp(-k_{\text{CR}}' t) - \exp(-k_{\text{IH}} - k_{\text{CR}}) t) \quad (4)$$

where $(\text{Bz}_2^+)_0$, k_{IH} , k_{CR} , and k_{CR}' are maximum concentration of Bz_2^+ formed, rate constant of the intramolecular hole transfer from Bz_2^+ to other part of **D**, rate constant of charge recombination between Bz_2^+ and DCA^- , and rate constant of charge recombination between ST^+ and DCA^- , respectively. Since the rate constants of the hole transfer from Bp^+ to **D** of G1–4 were identical, $(\text{Bz}_2^+)_0 = [\text{Bp}^+]$ can be assumed for G1–4. The hole transfer from D^+ to **ST** giving ST^+ occurs within the laser pulse duration of 5 ns for G1–4.¹¹ From these assumptions, the rate constants were estimated as listed in Table 1.

k_{IH} of G1, G2, G3, and G4 were determined to be 4.2×10^6 , 3.3×10^6 , 2.3×10^6 , and $1.6 \times 10^6 \text{ s}^{-1}$, respectively. The slower k_{IH} for larger dendrons indicates that Bz_2^+ is stabilized

in the larger dendrons, because of high density of **Bz** group in the larger dendrons, in which the distance between **Bzs** is shorter. Stabilization of **Bz₂^{•+}** indicates smaller driving force for the hole transfer from **Bz₂^{•+}** to **D** or **ST**. k_{CR} of **G1**, **G2**, **G3**, and **G4** were determined to be 0.31×10^6 , 2.4×10^6 , 2.5×10^6 , and 3.1×10^6 s⁻¹, respectively. The possible explanation of fast k_{CR} of larger dendrons will be increase of the interaction between **Bz₂^{•+}** and DCA. The quantum yields of the intramolecular hole transfer (Φ_H) were estimated from eq 5

$$\Phi_H = k_{IH} / (k_{IH} + k_{CR}) \quad (5)$$

The Φ_H values of **G1**, **G2**, **G3**, and **G4** were estimated to be 0.93, 0.57, 0.48, and 0.34, respectively. The lower Φ_H value for larger dendrons indicates the enhanced shielding effect on the direct hole transfer from **Bp^{•+}** to **ST** giving **ST^{•+}** as well as the results from smaller k_{IH} and larger k_{CR} values for larger dendrimers in the indirect mechanism.

k_{CR}' of **G1**, **G2**, **G3**, and **G4** were determined to be 2.2×10^5 , 1.7×10^5 , 1.6×10^5 , and 1.3×10^5 s⁻¹, respectively. The bimolecular rate constants were estimated to be 4.6×10^{10} , 3.4×10^{10} , 3.3×10^{10} , and 2.7×10^{10} M⁻¹ s⁻¹, respectively, based on $[DCA^{•-}] = [Bp^{•+}]$, suggesting the enhanced shielding effect of larger dendrimer on the charge recombination between **ST^{•+}** and **DCA^{•-}**. Similarly, the bimolecular rate constants between **Bz₂^{•+}** of **G1**, **G2**, **G3**, and **G4** and **DCA^{•-}** were estimated to be 6.5×10^{10} , 5.0×10^{11} , 5.2×10^{11} , and 6.3×10^{11} M⁻¹ s⁻¹, respectively. It is suggested that the charge recombination between **ST^{•+}** and **DCA^{•-}** occurs much more slowly than that between **Bz₂^{•+}** and **DCA^{•-}** because of steric hindrance of **D** for the approach of **DCA^{•-}** to **ST^{•+}**. Furthermore, slower k_{CR}' of larger dendrimer indicates that the large dendrons can maintain reactive intermediate for a long time which is important characteristics of site-isolated nano environment.

Conclusions

We found that the terminal **Bz** moieties of **D** of **G1–4** act as the hole acceptor to **Bp^{•+}**. The generated hole was stabilized as the hole-trapping site, **Bz₂^{•+}**, before the hole transfer to **ST**. For larger dendron, highly dense **Bz** group, which stabilized **Bz₂^{•+}**, can be expected, as evidenced from the slower k_{IH} of the larger dendrons. This effect can be regarded as the “dendrimer effect” of hole-conductive dendrons. Although there are many examples for the inhibition effect of **D** on the reaction of the central core, this is the first example for the **D** as the hole trapping site and hole dispersion effect, on the way of the exothermic hole transfer from the terminal **Bz₂^{•+}** to the central core. We also found other type of “dendrimer effect” on electron-transfer that **D** inhibits the direct hole transfer from **Bp^{•+}** to **ST** and charge recombination between **ST^{•+}** and **DCA^{•-}** because of the steric hindrance.

Acknowledgment. This work has been partly supported by a Grant-in-Aid for Scientific Research on Priority Area (417), 21st Century COE Research, and others from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

Supporting Information Available: Energy minimized structure of **G1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.
- (2) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.
- (3) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991.
- (4) Adronov, A.; Frechet, J. M. J. *Chem. Commun.* **2000**, 1701.
- (5) Hecht, S.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74.
- (6) Liu, D.; De Feyter, S.; Cotlet, M.; Stefan, A.; Wiesler, U.-M.; Herrmann, A.; Grebel-Koehler, D.; Qu, J.; Muellen, K.; De Schryver, F. C. *Macromolecules* **2003**, *36*, 5918.
- (7) de Groot, F. M. H.; Albrecht, C.; Koekkoek, R.; Beusker, P. H.; Scheeren, H. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4490.
- (8) Amir, R. J.; Pessah, N.; Shamis, M.; Shabat, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 4494.
- (9) Li, S.; Szalai, M. L.; Kevitch, R. M.; McGrath, D. V. *J. Am. Chem. Soc.* **2003**, *125*, 10516.
- (10) Momotake, A.; Arai, T. *J. Photochem. Photobiol. C* **2004**, *5*, 1.
- (11) 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.
- (12) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978.
- (13) Kimura, M.; Nakada, K.; Yamaguchi, Y.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *Chem. Commun.* **1997**, 1215.
- (14) Devadoss, C.; Bharathi, P.; Moore, J. S. *Macromolecules* **1998**, *31*, 8091.
- (15) Kunieda, R.; Fujitsuka, M.; Ito, O.; Ito, M.; Murata, Y.; Komatsu, K. *J. Phys. Chem. B* **2002**, *106*, 7193.
- (16) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354.
- (17) Ghaddar, T. H.; Wishart, J. F.; Kirby, J. P.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 12832.
- (18) Chasse, T. L.; Sachdeva, R.; Li, Q.; Li, Z.; Petrie, R. J.; Gorman, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 8250.
- (19) Voegtle, F.; Plevvoets, 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.
- (20) Gorman, C. B.; Smith, J. C.; Hager, M. W.; Parkhurst, B. L.; Sierzputowska-Gracz, H.; Haney, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 9958.
- (21) Uda, M.; Mizutani, T.; Hayakawa, J.; Momotake, A.; Ikegami, M.; Nagahata, R.; Arai, T. *Photochem. Photobiol.* **2002**, *76*, 596.
- (22) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
- (23) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.
- (24) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. J. *J. Phys. Chem. Ref. Data* **1977**, *6*(Suppl. 1).
- (25) Miyasaka, H.; Khan, S. R.; Itaya, A. *J. Photochem. Photobiol. C* **2003**, *4*, 195.
- (26) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2576.