

Intra- and Intermolecular Photochemical Properties of Poly(amidoamine) Dendrons with an Anthracene at Focal Point

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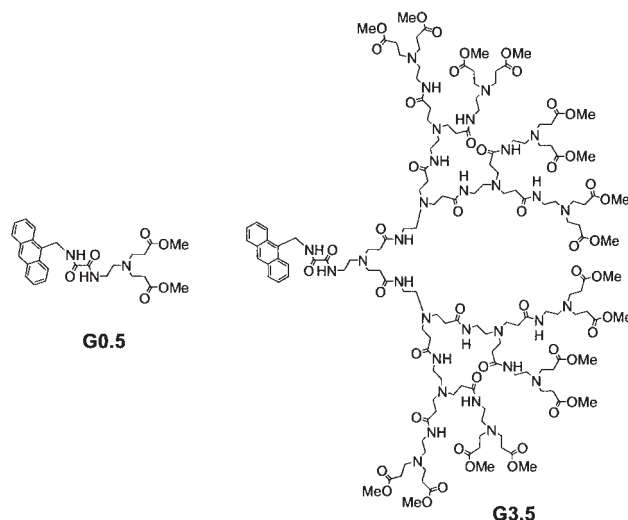
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Photophysical and photochemical properties of poly(amidoamine) dendrons containing an anthracene at the focal point have been studied by the steady-state and transient spectroscopic methods in solution. The fluorescence lifetime of the anthracene moiety in the higher generation dendron (G3.5) is slightly shorter than that of the lower generation homologue (G0.5). On the other hand, the triplet lifetime of G3.5 is longer than that of G0.5. The bimolecular rate constants for energy transfer from the triplet states of the anthracene moiety to O₂ (k_{O_2}) and for T–T annihilation (k_{TT}) were almost the same for the anthryl dendrons, G3.5 and G0.5, suggesting that the dendron groups do not hinder the approach of O₂ or the anthracene moiety. Photodimerization of G3.5 took place at a similar rate to G0.5, while the photodissociation rates of these anthracene dimers increase in the order of anthracene > G0.5 > G3.5, suggesting the presence of some attractive forces between dendron wedges.

New kinds of well-defined regularly branched macromolecules, dendrimers, have attracted much scientific attention in the past two decades.^{1–7} In particular, photoreactive moieties incorporated in dendritic architecture are of current interest from the viewpoint of photoresponsive dendrimers whose structures and properties can be switched under photoirradiation. In this regard, several groups have reported the covalent fixation of a highly photoreactive unit with a dendritic macromolecule as an intramolecular photo-switch.^{8–17} For example, Archut et al. reported the syntheses of dendrimers containing azobenzene units in the periphery toward photoswitchable dendritic hosts.⁸ Mizutani et al. have reported the photochemical *trans-cis* isomerization of stilbene dendrimers.¹⁴ Tominaga et al. have reported that the polyuracil dendrimers can be intramolecularly locked via photoinduced dimerization of the uracil units.¹⁵ Recently, we have reported the dechalcogenation reaction of dendrimer dichalcogenides upon light irradiation.¹⁶ Although photoreactions of dendrimers via intramolecular processes have been extensively reported, much less is known about the intermolecular photoreaction of dendrimer or dendron.^{18–22} Our group and Cao and Meier have recently reported on photo-switching by intermolecular [4+4] photocycloaddition of anthracene moieties at focal points of the dendrons.^{18,19} It is quite curious that the intermolecular photoreactions smoothly proceed in spite of the steric hindrance of bulky dendritic substituents. In order to understand fully the photoreaction process, we performed laser experiments employing anthryl dendrons.¹⁸

In the present study, we investigated photophysical and photochemical properties of poly(amidoamine) dendrons, G0.5 and G3.5, containing an anthracene at the focal point as shown in Scheme 1. After getting the information about intramolecular photophysical and photochemical properties, information about



Scheme 1. Molecular structures employed in the present study.

intermolecular ones is gathered using steady- and transient fluorescence and absorption spectra.

Experimental

Materials. Syntheses and purifications of poly(amidoamine) dendrons, G0.5 and G3.5, were carried out according to our published method.¹⁸ Highest grade methanol was used as a solvent for spectroscopic measurements.

Apparatus. Steady-state UV-visible absorption spectra were measured with a JASCO/V-570 spectrophotometer. Steady-state fluorescence spectra were measured using a Shimadzu RF-5300 PC spectrofluorophotometer. The picosecond time-resolved fluorescence spectra and time profiles were measured using a THG (273 nm)

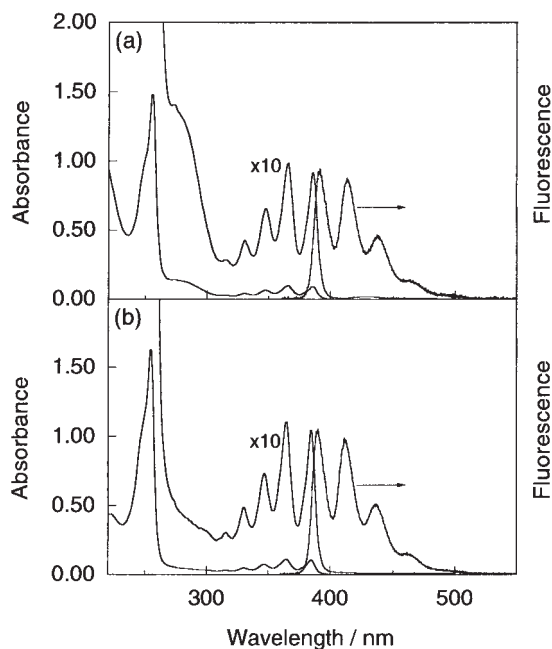


Fig. 1. Steady-state absorption and fluorescence spectra of (a) G3.5 and (b) G0.5 in methanol.

of a Ti:sapphire laser (Spectra Physics, Tsunami) and a streak scope (Hamamatsu Photonics) as an excitation source and a detector, respectively. Nanosecond transient absorption spectra in the UV and visible regions were measured by means of laser flash photolysis. A THG (355 nm) light from a Nd:YAG laser was used as an excitation source. A Si-PIN photodiode was used for detection of the monitoring light from a pulsed Xe-lamp. Long time-scale measurements ($>2 \mu\text{s}$) were performed using a photomultiplier tube and a continuous Xe-lamp as a detector and a probe light, respectively. Details are described in our previous report.²²

Results and Discussion

Steady-State Absorption and Fluorescence Spectra.

Absorption and fluorescence spectra of higher generation anthryl dendron G3.5 and its lower generation homologue G0.5 are shown in Fig. 1. Both G3.5 and G0.5 show the absorption band with vibronic peaks in the 320–400 nm region. These vibronic bands are assigned to the 1L_a (p)-band of the anthracene moiety.^{23–25} The intense single band at 250 nm was attributed to the 1B_b (β)-band of the anthracene moiety.^{23–25} No shift of the absorption peaks of the anthracene moiety was evident in the comparison of G3.5 with G0.5. The absorption band of G3.5 in

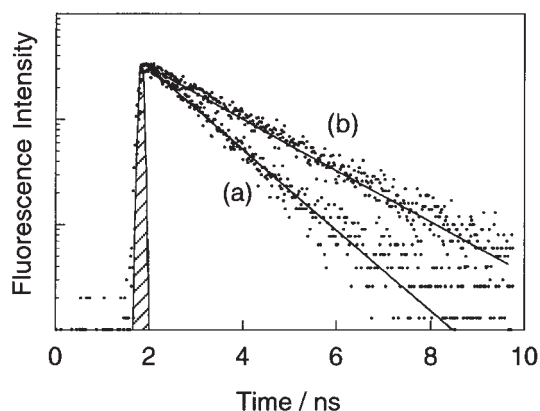


Fig. 2. Logarithm plots of fluorescence decays of (a) G3.5 and (b) G0.5 in methanol.

270–300 nm region may be attributed to the absorption of the dendron wedge, poly(amidoamine) moiety.

The fluorescence spectra of G3.5 and G0.5 are also shown in Fig. 1, in which the fluorescence intensities are normalized to the absorption peaks at the longest wavelength. The fluorescence peak positions of the dendron G3.5 were almost the same as those of G0.5. The observed fluorescence intensity of G3.5 is lower than that of G0.5, suggesting the low fluorescence quantum yield (Φ_f). Using unsubstituted anthracene as a reference ($\Phi_f = 0.30$),²⁵ the Φ_f value of G3.5 was evaluated to be 0.07, which is smaller than that of G0.5 ($\Phi_f = 0.13$). This suggests that the radiationless relaxation of the dendron G3.5 is more efficient than that of G0.5.

Time-Resolved Measurements. Time profiles of fluorescence intensity after the picosecond-laser excitation of the anthracene moiety are shown in Fig. 2. The decay time profiles are fitted with a single exponential function, giving fluorescence lifetimes (τ_f) as listed in Table 1. The τ_f value for the dendron G3.5 (1.1 ns) is shorter than that of G0.5 (1.8 ns) and anthracene (5.5 ns). Although the observed difference between G0.5 and anthracene is attributed to a substituent effect, the difference between G3.5 and G0.5 is to the dendron effect, probably because the dendron surrounding the anthracene moiety enhances the radiationless relaxation process of the singlet excited state of the anthracene moiety to the ground state.

A more quantitative treatment was possible using a relationship between Φ_f and relaxation rate constants such as k_f (radiative relaxation rate constant) and k_{nr} (non-radiative relaxation rate constant) (Eq. 1):²⁶

Table 1. Rate Parameters of the Excited States of Anthryl Dendrons and Anthracene in Methanol

Compounds	τ_f/ns ($\lambda_{\text{fluor}}/\text{nm}$)	Φ_f	Φ_{isc}	$\tau_T/\mu\text{s}$ (λ_T/nm)	k_{O_2} $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	k_{TT} $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
G3.5	1.1 (393)	0.070	0.23	170 (430)	1.8×10^9	$3.7 \times 10^{9a)}$
G0.5	1.8 (391)	0.13	0.70	77 (430)	2.1×10^9	$4.2 \times 10^{9a)}$
Anthracene	5.5 (380)	0.30	0.71 ^{b)}	77 (430)	2.4×10^9	$4.1 \times 10^{9a)}$

a) Molar extinction coefficients at 430 nm; $43000 \text{ mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ for methylanthracene in alcohol was employed as a model of dendrons,²⁸ $52000 \text{ mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ for anthracene in alcohol.²⁸ b) From Ref. 25.

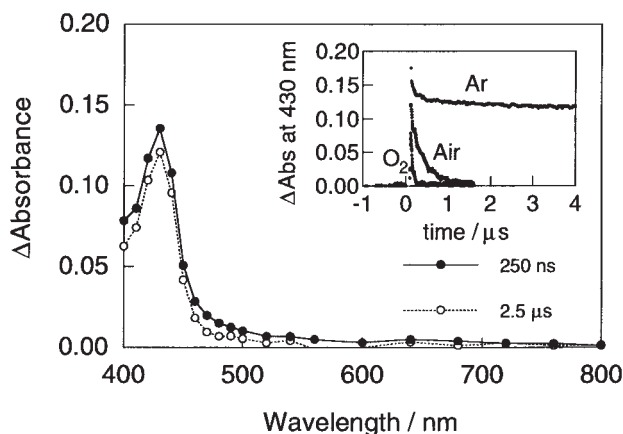


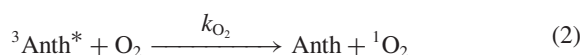
Fig. 3. Nanosecond transient absorption spectra observed by the laser light (355 nm) excitation of G3.5 in deaerated methanol. Inset: Time profiles at 430 nm in the presence and absence of O_2 .

$$\Phi_f = k_f / (k_f + k_{nr}) \quad (1)$$

Using the Φ_f and $\tau_f (= 1/(k_f + k_{nr}))$ values, the k_f and k_{nr} values were evaluated to be 0.73×10^8 and $4.9 \times 10^8 \text{ s}^{-1}$ for G0.5 and 0.65×10^8 and $8.7 \times 10^8 \text{ s}^{-1}$ for G3.5, respectively. A prominent difference was found in the k_{nr} values rather than in the k_f values.

Nanosecond transient absorption spectra observed by the laser excitation of the anthracene moiety of the G3.5 dendron are shown in Fig. 3. An absorption peak that appeared at 430 nm was attributed to the triplet-triplet absorption band of the anthracene moiety.^{25,27,28} Similar transient spectra with a peak at 430 nm were observed for G0.5 and anthracene.

The decay time-profiles of the triplet state of the anthracene moiety are shown in the inset of Fig. 3. In the absence of O_2 , after an initial fast decay, the absorbance shows a slow decay. The initial fast decay may be attributed to the decay tail of the singlet excited state of the anthracene moiety. When the solution was saturated by O_2 ($[O_2] = 1.02 \times 10^{-2} \text{ mol dm}^{-3}$ in methanol),²⁵ the decay rate of the triplet state increased. This finding can be attributed to the triplet energy transfer from anthracene to O_2 (Eq. 2):



Acceleration of the decay of the triplet state was also observed in air-saturated solution ($[O_2] = 2.1 \times 10^{-3} \text{ mol dm}^{-3}$). Each decay obeys first-order kinetics giving the first-order rate constant (k_{1st}). From the slope of the plots of the k_{1st} values against O_2 concentrations, the second-order rate constant (k_{O_2}) was evaluated to be $1.8 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for G3.5, which is almost the same as those of G0.5 ($2.1 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) and anthracene ($2.2 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). Since small O_2 molecule can approach to the focal anthracene by sneaking through the space between the dendron branches, no appreciable slow-down was observed in the second-order rate constant, k_{O_2} , of the higher generation of the dendron.

In the absence of molecular oxygen, the decay time-profiles in the longer time-scale measurements show the laser power

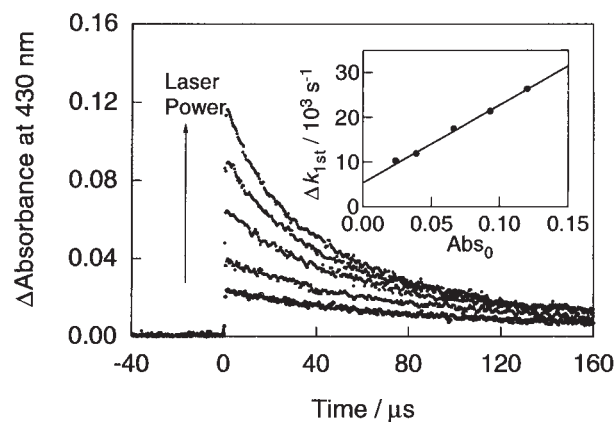
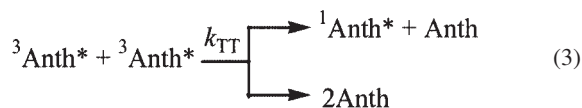


Fig. 4. Laser power dependence of the decay at 430 nm of G3.5 in long time scale in deaerated methanol. Inset: Plots of Eq. 4.

dependence as shown in Fig. 4. At higher laser power, the decay can be fitted with mixed order kinetics of first- and second-order. The second-order kinetics can be attributed to the T-T annihilation process (Eq. 3), which is prominent at the high concentration of the triplet state under the high laser power.



where k_{TT} is a rate constant of the T-T annihilation process. In the first-order plots of the decay curve, the slope of the initial part, which is referred to Δk_{1st} , increases with the initial absorbance (ΔA_0) according to Eq. 4:

$$-d[\ln(\Delta A_{\text{initial}})]/dt = \Delta k_{1st} = k_0^T + (2k_{TT}/\epsilon)\Delta A_0 \quad (4)$$

where $\Delta A_{\text{initial}}$, k_0^T , and ϵ are the absorbance change in the initial part, the intrinsic rate constant for the triplet state, and the molar extinction coefficient of the triplet absorption band of the anthracene moiety, respectively. The k_0^T value can be evaluated from the intercept of the plot of Eq. 4, as shown in the inset of Fig. 4. The triplet lifetimes (τ_T) were evaluated from the relation, $\tau_T = 1/k_0^T$. The k_{TT} values are evaluated from the slope of the plots ($2k_{TT}/\epsilon$), employing the ϵ values of 9-methylanthracene ($43000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$),²⁸ which is slightly smaller than the unsubstituted anthracene ($52000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).²⁸ These estimated parameters are listed in Table 1. The τ_T value of G3.5 is longer than that of G0.5 by a factor of 2, which is the opposite tendency of the τ_f values. In the case of the triplet state, a solvent effect may control the lifetimes; thus, the dendron of higher generation abrogates methanol solvent from the proximity of anthracene, which causes deceleration of relaxation of the anthracene triplet state in G3.5 compared with relaxations of triplet states of G0.5 and anthracene.

The k_{TT} value of G3.5 is almost the same as those of G0.5 and anthracene, suggesting that the rates of the bimolecular reactions are not so much affected by the steric crowding of the dendron groups. These k_{TT} values are almost 1/3 of the diffusion-controlled limit ($k_{\text{diff}} = 1.2 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in methanol).²⁹

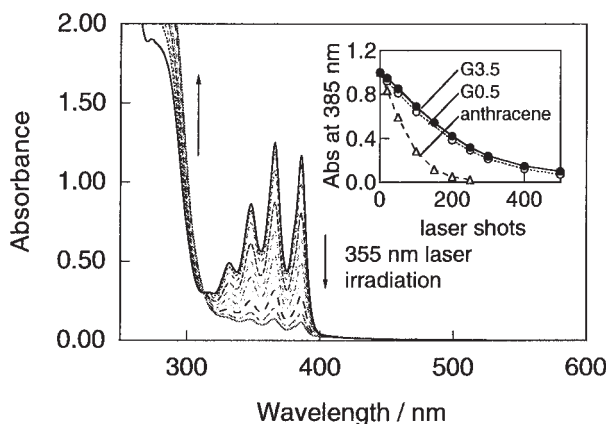


Fig. 5. Dimerization by the 355 nm laser light irradiation of G3.5 in deaerated methanol. Inset: Plots of decreases of the absorbance at longest wavelength for G3.5, G0.5, and anthracene in deaerated methanol.

Under the optical match condition, the initial absorbance observed under the low laser power is the relative measure of the quantum yields for the intersystem crossing (Φ_{isc}). The initial absorbance of G3.5 is 1/3 of those of G0.5 and anthracene. Thus, the Φ_{isc} value of G3.5 is 1/3 of those of G0.5 and anthracene.

Using these Φ_{isc} values, the k_{nr} value was further divided into the rate constants of internal conversion process (k_{ic}) and intersystem crossing process (k_{isc}) according to Eq. 5:²⁶

$$\Phi_{isc} = k_{isc} / (k_f + k_{ic} + k_{isc}) \quad (5)$$

The k_{ic} and k_{isc} values were evaluated to be 0.96×10^8 and 4.0×10^8 s⁻¹ for G0.5 and 6.5×10^8 and 2.2×10^8 s⁻¹ for G3.5, respectively. A prominent difference was found in the k_{ic} values rather than in the k_{isc} values. This indicates that the radiationless relaxation process of the singlet excited state of G3.5 is mainly attributed to the internal conversion to the ground singlet state, but not to the triplet state of the anthracene moiety. Above finding that the k_{ic} value of G3.5 is larger than that of G0.5 may be attributed to the higher generation dendron wedge, which probably stimulates the relaxation of the excited singlet state of the anthracene moiety via the vibronic interaction.

Photodimerization of Anthracenes. Upon the selective photoirradiation of anthracene chromophores with the 355 nm

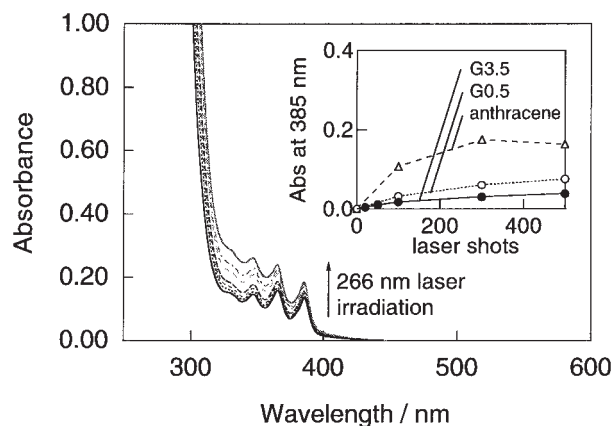
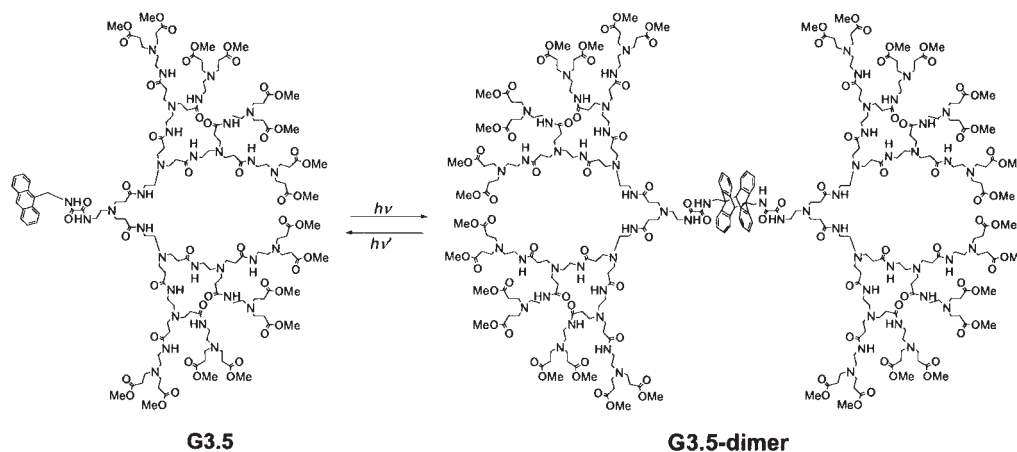


Fig. 6. Dissociation by the 266 nm laser light irradiation of G3.5-dimer in deaerated methanol. Inset: Plots of increase in the absorbance at longest wavelength for anthracene dimers in deaerated methanol.

laser light in the deaerated solution, the absorption of the anthracene decreases as shown in Fig. 5. From the absorption and MALDI-TOF MS spectra of the products,¹⁸ the dimerization reaction of the anthracene moieties in G3.5 was confirmed (Scheme 2). Almost complete consumption of the monomeric anthracene absorption under repeated irradiation of the laser light (Fig. 5) indicates that the reaction occurs quantitatively.

In the inset of Fig. 5, the absorption intensities due to the anthracene moieties were plotted against the number of the laser shots. Although anthracene shows the fastest decrease, the anthryl dendrons G3.5 and G0.5 show the almost the same dimerization rate. The difference between the anthracene and G0.5 can be attributed to the retardation effect of the substituent at the 9-position of anthracene, which will be the bridgehead position after the photodimerization. The similarity of the dimerization rates between the dendrons G3.5 and G0.5 indicates that the dendron group does not retard the dimerization rate, which is in good agreement with the similarity of the observed k_{TT} values, because dimerization of anthracene derivatives occurs via the triplet excited states.²⁶ This suggests that the fixation reaction of the anthracene moiety at focal points in the dendron takes place at a rate similar to that in anthracene in solution. The locking reaction of the dendrons seems to occur efficiently even in higher



Scheme 2. Photodimerization of G3.5.

generation.

Photodissociation of Anthracene Dimers. Under the photoirradiation of the anthracene dimers with the 266 nm laser light, the recovery of the absorption band of monomeric anthracene was observed as shown in Fig. 6. Since the 266 nm laser light excites predominantly the anthracene dimers under the low anthracene monomer concentrations, dissociation of the dimers occurs at the initial stage. But when the monomer was accumulated, the excitation of the monomer regenerates the dimer. Thus, the saturation of the reaction occurs as shown in the inset of Fig. 6. The dissociation of unsubstituted anthracene dimer is faster and produces a higher yield than the dimers with 9-substituents. Dendron G3.5 shows a further slower dissociation rate and a lower yield than G0.5, suggesting that the unlocking reaction is slightly dependent on the dendron generation. This implies that dendron wedges in the G3.5-dimer have attractive forces, probably due to mutual intertangles.

Summary

Intramolecular properties such as fluorescence lifetime, triplet state lifetime and quantum yield of the intersystem crossing of the anthracene moiety in the higher generation dendron are considerably different from those of lower generation dendron and pristine anthracene. On the other hand, bimolecular rate constants for the energy transfer with O₂ and T-T annihilation processes were similar between the G3.5 and G0.5. Similarity was also observed in the dimerization rates. On the other hand, the unlocking reaction of the anthracene dimers for higher dendron generation is less efficient than that for lower dendron generation.

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