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Aggregation-Controlled Excimer Emission from Anthracene-Containing Polyamidoamine Dendrimers

P. K. Lekha and Edamana Prasad*[a]

Abstract: Lower generations of polyamidoamine (PAMAM) dendrimers were peripherally modified with anthracene moieties, and excimer emission from anthracene chromophores was investigated in an acetonitrile–water mixture at acidic and basic pH values. Results from fluorescence spectroscopic experiments suggest that 1) the propensity of anthracene-modified PAMAM dendrimers to aggregate in acetonitrile is substantial in the presence of 15–20 vol% of water, and 2) aggregate formation in anthracene-modified PAMAM dendrimers leads to unique morphologies in the ground state, where the anthracene units are pre-arranged to form stable excimers upon photoexcitation. Three types of anthracene excimers are generated in the system, with face-to-face, angular, and T-shaped geometry. The formation of different types of anthracene excimers was confirmed by steady-state and time-resolved fluorescence spectroscopic experiments. Experimental results further suggest that it is feasible to alter the type of excimer formed by anthracene units attached to the PAMAM dendrimers through altering the propensity for ground-state aggregation. Most excitingly, increased π conjugation in the molecular framework of anthracene-substituted PAMAM dendrimers leads to intense and exclusive excimer emission from anthracene at room temperature.

Keywords: aggregation · anthracene · dendrimers · excimers · fluorescence

Introduction

Dendrimers are hyperbranched macromolecules that have potential applications in both fundamental and applied fields of physics,[1] chemistry[2] and biology.[3] While the notion of synthesizing structurally well-defined and aesthetically appealing dendritic structures originated from the initial work by Vögtle's and Tomalia's groups about three decades back, a plethora of subsequent studies resulted in versatile synthetic strategies for dendrimers with different structural scaffolds.[4] Since dendrimers provide unique structures with flexible molecular frameworks, recent research in this field has paid more attention towards utilizing these macromolecules for practical applications such as energy harvesting,[5] controlled guest release,[6] and catalysis.[7] Thus, it is important to know the basic rules which govern the structure–property relations in dendrimers.

Peripheral modification by suitable functional moieties has been an attractive strategy to control the functional properties of dendrimers.[8] In recent years, many reactions have been reported for peripheral modification of polyamidoamine (PAMAM) dendrimers. For example, functional groups such as azobenzene,[6a] dansyl,[8a] sulfonate,[8b] glucose,[8c] carbohydrates,[8d] cyanobiphenyl mesogens,[8e] stilbenes,[8f] and coumarin[8g,h] have been utilized to modify PAMAM dendrimers to obtain functional materials with unique applications. One of the interesting properties of the peripherally substituted PAMAM dendrimers is their enhanced propensity to aggregate in solution phase. Wang and co-workers reported the synthesis, aggregation, and luminescence properties of naphthyl-, phenyl-, pyrenyl-, and dansyl-substituted PAMAM dendrimers in water.[9] Intriguingly, the aggregation and its impact on the luminescence properties of PAMAM dendrimers with anthracene units attached to the periphery have not been studied in detail despite the fact that anthracene derivatives play a vital role in the design of luminescent materials, with wide applications in lasers, phosphors, and light-emitting devices.[10,11]

We have now investigated the aggregation propensity of lower generation anthracene-substituted PAMAM dendrimers as a function of solvent composition, excitation wavelength, and pH. The experimental results suggest that an-

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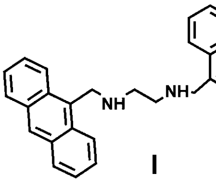
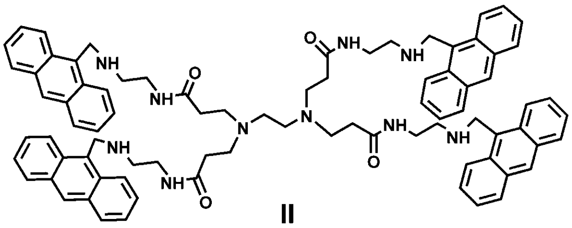
thracene-modified PAMAM (PAMAM-An) dendrimers in acetonitrile are extremely sensitive towards water. The presence of water (20 vol %) induces unique aggregation morphologies in PAMAM-An dendrimers and generate anthracene excimers with blue-to-green emission maxima on photoexcitation. Most excitingly, by means of detailed spectroscopic and photophysical analysis, we observed for the first time exclusive excimer emission from PAMAM-An dendrimers at room temperature, through increased π conjugation in the molecular framework, .



I



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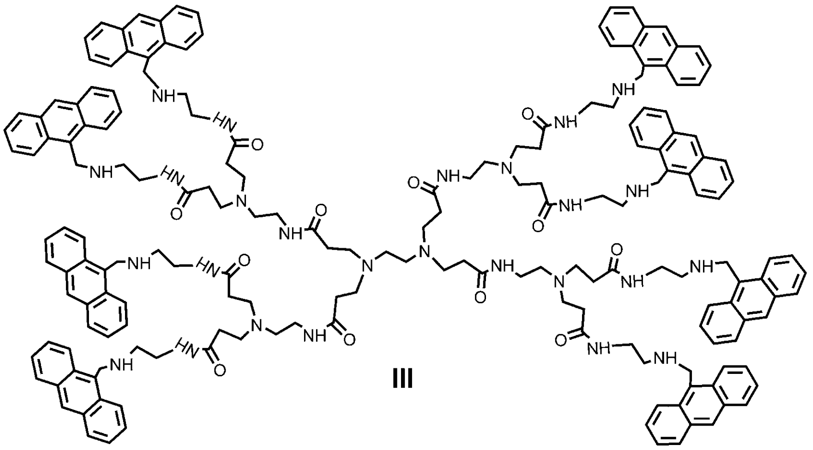

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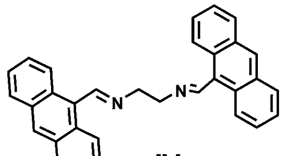

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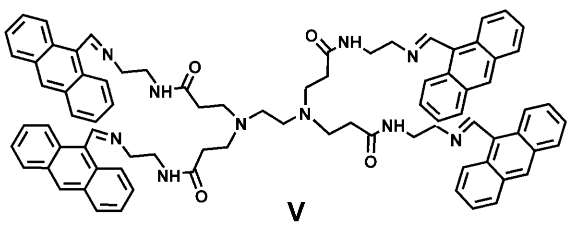

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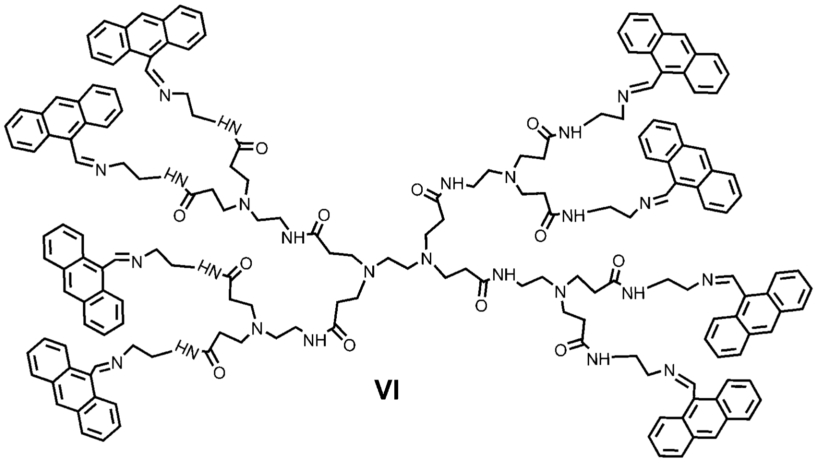
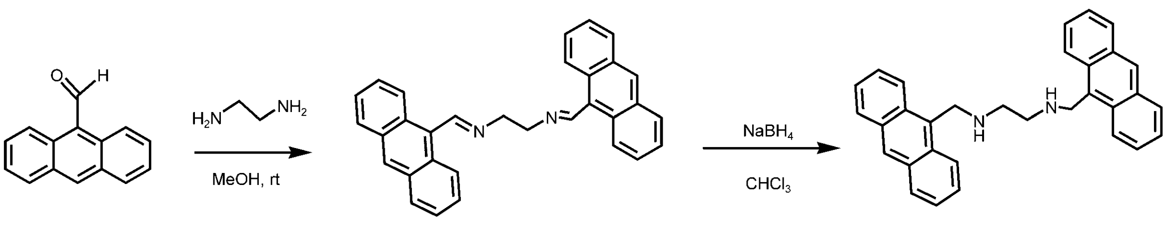


VI

Results and Discussion

Compounds used for the present study: In compounds **I** to **III**, each anthracene unit is attached to the PAMAM dendrimer through a methylene bridge, whereas in compounds **IV** to **VI**, anthracene is connected via imine bonds (−N=CH−). Compounds **I** and **IV** are the model compounds for the present study. The amino anthracene derivatives were efficiently synthesized by condensation of 9-anthraldehyde and appropriate amine-terminated dendrimers, followed by in situ reduction with an excess of $NaBH_4$ (Scheme 1).[12]

The corresponding imino anthracene derivatives **IV** to **VI** are precursors for compounds **I** to **III** and can be isolated



Scheme 1. Synthetic scheme to prepare anthracene derivatives of PAMAM dendrimers.

prior to reduction with $NaBH_4$. The solubility of compounds **I** to **VI** was checked in hexane, toluene, chloroform, and acetonitrile. All compounds are soluble in the above solvents, except in hexane, in which the solubility is marginal. The UV/Vis absorption spectra of the compound showed the well-characterized structured absorption bands of anthracene. They also exhibit emission from anthracene monomers on UV excitation in the above solvents, but excimer emission was not observed even at concentration as high as 10^{-3} M. Surprisingly, addition of as little as 20 μL of water to 10 mL of a solution of the PAMAM-An dendrimers in acetonitrile (10^{-6} M) led to dramatic changes in their absorption and emission properties.

Absorption studies on I–VI in an acetonitrile–water mixture: To determine the role of water in altering the absorption properties of the system, the concentration of water was varied from 0 to 30 vol %. A clear shoulder absorption band with $\lambda_{max} \approx 400$ nm was observed in the presence of water, and its intensity increases with increasing amount of water in the system. The maximum absorption for the shoulder was observed in an acetonitrile–water (4:1 v/v) mixture. Figure 1 shows the UV/Vis absorption spectra of **II** and **III** in acetonitrile and an acetonitrile–water (4:1 v/v) mixture; the shoulder band is clearly evident in the latter case. To further confirm the role of water in generating long-wavelength absorption in PAMAM-An dendrimer systems, the following control experiments were performed: 1) The UV/Vis absorption spectrum of a saturated solution of **II** in acetonitrile was compared to that of a dilute solution (10^{-6} M) of **II** in an acetonitrile–water (4:1 v/v) mixture, and the shoulder appeared only in the latter case. 2) The UV/Vis absorption spectrum of **II** was recorded under very dilute conditions (10^{-6} M, 10 mL) in acetonitrile, and when as little as 20 μL of water was added to the system the shoulder was again generated. These remarkable observations clearly suggest that the shoulder originates from a water-induced solution-state structure. Identical behavior was observed for compound **I**.

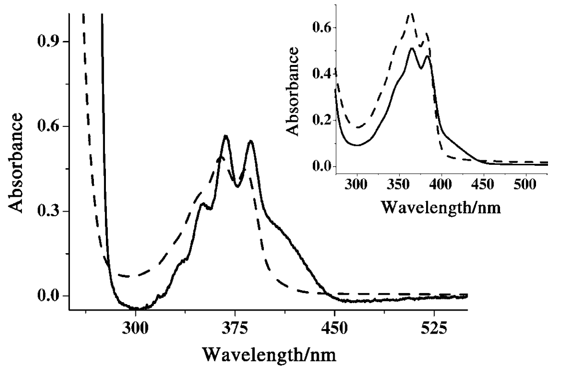


Figure 1. UV/Vis absorption spectra of **III** (1×10^{-6} M) in acetonitrile in the presence (solid) and absence (dotted) of water. The inset shows the corresponding spectra of **II**.

Surprisingly, the broad band around 400 nm becomes strongly prominent in compounds **IV**–**VI** in an acetonitrile–water mixture. The absorption spectrum of **V** in an acetonitrile–water mixture (Figure 2) shows an intense, broad absorption with $\lambda_{max} = 400$ nm and negligible absorption corresponding to anthracene monomer. The similarity in λ_{max} of the broad absorption bands in compounds **I**–**III** and **IV**–**VI** suggests that identical solution-state structures are formed in the ground state in both cases.

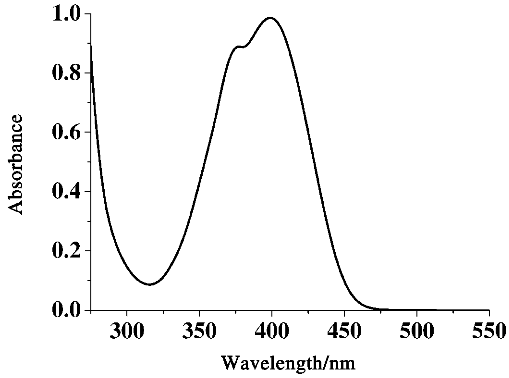


Figure 2. UV/Vis absorption spectrum of **V** (1×10^{-6} M) in an acetonitrile–water (4:1 v/v) mixture.

As compounds **I** to **VI** are insoluble in water, it is likely that the hydrophobic aromatic moieties in the molecules tend to aggregate in presence of water.[13] The broad absorption band generated only in presence of water is thus attributed to aggregation of the compounds. The intensity of the broad band is higher in **IV**–**VI** than in **I**–**III** at the same concentration, and this suggests that conjugation introduced through the imine double bonds in **IV**–**VI** significantly enhances the propensity to form aggregates.

The possibility that charge transfer complexes between amino and anthracene moieties gives rise to the shoulder cannot be excluded in the present case.[14]To determine whether any relationship between the shoulder and charge transfer exists, the UV/Vis spectrum was examined at pH 2, where charge-transfer probability can be neglected. Interestingly, the absorption band at about 400 nm appears with identical intensity to the earlier cases, which rules out the possibility of formation of charge-transfer complex in the present case (see Figure S1 in the Supporting Information).

Critical aggregation concentration for compounds I–VI: Next, the effect of concentration on the aggregate absorption peak was examined over a range of concentrations (10^{-7} to 10^{-3} M). The intensity ratio between monomer and aggregate absorption peaks of anthracene remains identical throughout the concentration range (see Figure S4 in the Supporting Information). This suggests that a constant fraction of PAMAM-An remains in the aggregated form in the ground state. Photoexcitation of the system at $\lambda_{max} \approx 430$ nm, where the aggregates absorb, leads to anthracene excimer emission ranging from 470 to 560 nm, depending on concentration and pH. Interestingly, excimer formation in the system was found to be strongly dependent on the concentration of the substrate, that is, excimer formation involves "inter-type" molecular interaction between anthracene units. The plot of excimer emission intensity versus substrate concentration shows a clear inflection point, from which the critical aggregation concentrations (CAC) for PAMAM-An systems were determined. The CACs of **I–III** and **IV–VI** are 10^{-5} and 10^{-6} M, respectively (see Figures S5 and S6 in the Supporting Information).

Steady-state and time-resolved experiments on I–III below the CAC: Compounds **I–III** show strong blue luminescence with characteristic emission peaks of anthracene monomer in an acetonitrile–water mixture on irradiation with UV light at concentrations lower than 10^{-4} M. However, excitation above 400 nm leads to structureless emission from anthracene excimer. This substantiates the hypothesis that the shoulder around 400 nm for **I–III** is due to ground-state aggregation of the monomers. The aggregation may lead to a prearranged geometry which is favorable for formation of the anthracene excimer on excitation. Compounds **I–III** exhibit pH-dependent emission intensity from anthracene monomer and excimer at concentrations below the CAC. The steady-state emission spectra of **II** with excitation at 360 nm and pH 2 and 8 are shown in Figure 3 A. Figure 3 B shows the steady-state emission spectra of **II** at pH 2 and 8 when the excitation wavelength was 430 nm. Luminescence quenching of the monomer and excimer peaks of **II** under basic pH conditions could be due to photoinduced electron transfer (PET) from the amino groups to anthracene residues.[15]

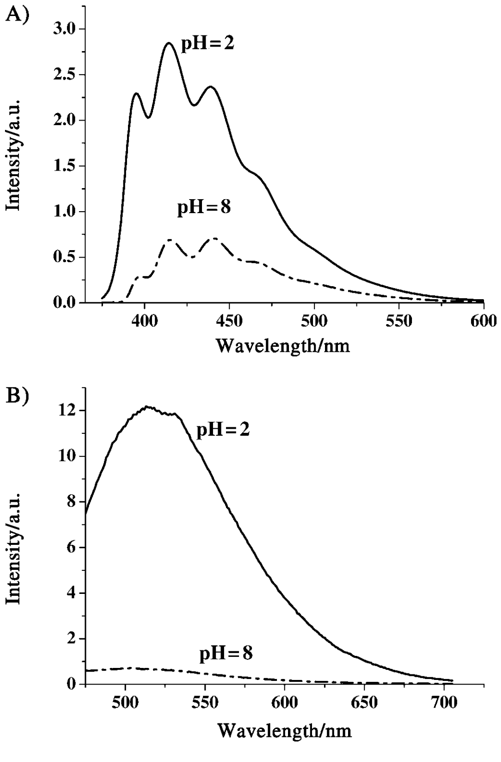


Figure 3. A) Steady-state fluorescence spectra of **II** in an acetonitrile–water (4:1 v/v) mixture at pH 2 (solid) and pH 8 (dash-dot); λ_{exc}= 360 nm. B) Steady-state fluorescence spectra of **II** in an acetonitrile–water (4:1 v/v) mixture at pH 2 (dash-dot) and pH 8 (solid); λ_{exc}= 430 nm. For both A) and B), [**II**]$=10^{-5}$ M.

Excited-state lifetime data for UV excitation of the system results in multi-exponential decays, corresponding to monomer and a mixture of excimers of anthracene. The monomer anthracene lifetime ($\tau \approx 5$ ns) was found to be quenched through either PET (in basic medium) or collisions (in acidic medium), to 2.3 ns for **I** and about 1.5 ns for **II** and **III**. The anthracene excimer emission from **I–III** exhibited lifetimes in the range of 7 to 10 ns, which correspond to formation of anthracene excimer with an angle of 55° between monomers.[16] Excitation of the system at 430 nm also resulted in multi-exponential decays for **I–III**, corresponding to different types of anthracene excimers. From the lifetime data of **II** and **III**, it is evident that anthracene excimers with lifetimes in the range of 9–10, 2.7–3.2, and 0.21–0.43 ns were formed, among which that with a lifetime in the range of 9–10 ns existed with relative amplitude greater than 40 %. For model compound **I**, the decays remain double-exponential for $\lambda_{exc}=430$ nm at pH 2 and 8, that is, only two types of anthracene excimers are formed in this case. Interestingly, the long-lifetime component (9–10 ns) was absent for the model compound when excited at 430 nm. This could presumably be due to lesser steric hindrance in the model compound, in which lateral overlapping is more feasible than angular overlapping. The lifetime studies are summarized in Table 1.

Steady-state and time-resolved experiments on I–III above the CAC: On increasing the solution concentration above 10^{-4} M, excitation with UV light leads to an intense, structureless emission at 470 nm for **I–III** at pH 2. When the excitation wavelength was changed to 430 nm, the luminescence changed dramatically, and two new emission bands appeared at approximately 520 and 560 nm. Figure 4 shows the dependence of excitation wavelength on the emission maxima for **II** at pH 2.

This indicates that two different types of anthracene excimers are formed upon excitation at $\lambda_{exc}=430$, with almost equal concentrations. Under acidic conditions, PAMAM-An will be in an extended conformation due to the presence of large number of protonated nitrogen atoms, which brings great constraints to the aggregates to form exclusively a single type of excimers. Model compound **I**, however, exhibited only one emission peak for $\lambda_{exc}=430$ at pH 2, which suggests formation of a single type of anthracene excimer. This could presumably be due to the decreased repulsion between the protonated nitrogen atoms and reduced steric repulsion in the model compound. Photoexcitation of the system at 430 nm and pH 8 always results in excimer emission with lower intensity.

The lifetime data for **I–III** above the CAC is listed in Table 1 along with the relative amplitude of the species. It is clear from the data that UV excitation for **I** to **III** provides

Table 1. Photophysical emission properties of compounds **I** to **III** in an acetonitrile–water (4:1 v/v) mixture below and above the CAC.

c [M]	λ_{exc} [nm]	Anthracene-modified ethylenediamine **I**				PAMAM-An (G0, NH_2) **II**				PAMAM-An (G1, NH_2) **III**			
		pH 2		pH 8		pH 2		pH 8		pH 2		pH 8	
		λ_{max} [nm]	T [ns] (rel. ampl. [%])	λ_{max} [nm]	τ [ns] (rel. ampl. [%])	λ_{max} [nm]	τ [ns] (rel. ampl. [%])	λ_{max} [nm]	τ [ns] (rel. ampl. [%])	λ_{max} [nm]	τ [ns] (rel. ampl. [%])	λ_{max} [nm]	τ [ns] (rel. ampl. [%])
$c < 10^{-4}$	360	397	2.3 (36.3)	395	2.3 (33.0)	415	1.9 (79.8)	415	1.5 (76.3)	415	1.7 (82.81)	415	1.4 (81.0)
		417	9.1 (63.7)	415	7.8 (40.3)	445	7.8 (20.2)	445	7.0 (23.7)	445	6.08 (17.19	445	7.2 (19.0)
		441		440	4.8 (26.7)	465		465		465		465	
		470		465									
	430	530	0.85 (76.9)	520	0.21 (76.5)	520	2.8 (33.5)	520	2.7 (28.5)	520	2.9 (35.2)	525	3.17 (41.1)
			5.3 (23.1)		4.8 (23.5)		0.4 (19.7)		0.23 (11.8)	560	0.47 (23.4)		0.43 (10.5)
							10.5 (46.8)		9.96 (59.7)		10.2 (41.4)		9.40 (48.4)
$c > 10^{-4}$	360	470	7.2 (79.7)	397	2.3 (45.6)	470	1.7 (16.8)	415	5.04 (42.7)	470	1.5 (16.4)	415	1.7 (82.2)
			1.6 (20.3)	417	8.63 (33.3)		7.3 (83.2)	440	1.21 (17.6)		7.8 (83.6)	445	5.79 (17.8)
				445	0.54 (21.1)			467	9.88 (39.7)			465	
				465									
	430	520	0.27 (87.9)	525	0.27 (88)	515	2.6 (30.3)	520	3.2 (33.5)	515	2.7 (34.0)	520	2.9 (35.3)
			7.8 (12.1)		7.8 (12)	560	0.14 (25.1)		0.30 (12.2)	560	0.44 (22.6)		0.47 (23.5)
							9.4 (44.6)		10.8 (54.3)		9.92 (43.4)		10.3 (41.2)

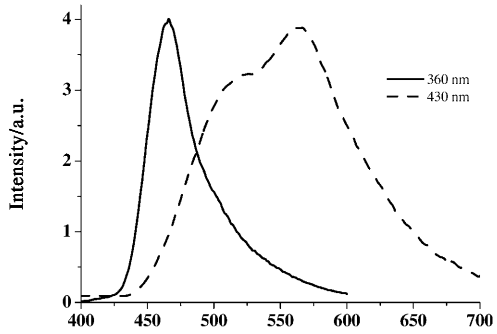


Figure 4. Different types of excimer emission from anthracene in **II** at pH 2 for two different excitation wavelengths as specified in the graph. [**II**] = 10^{-3} M.

mostly (relative amplitude ca. 80 %) a single excimer at pH 2, with lifetimes in the range 7–10 ns, which is consistent with the single emission maximum in the steady-state spectra (Figure 4, solid line). Conversely, excitation at 430 nm leads to a mixture of excimers under identical conditions, consistent with the steady-state fluorescence spectroscopic analysis. Figure 5 shows the excited-state decay traces for **I** to **III** in an acetonitrile–water mixture for concentrations above the CAC at acidic pH values and excitation below and above 400 nm. Comparison between corresponding figures in the first ($\lambda_{exc} = 430$) and second ($\lambda_{exc} = 430$) rows in Figure 5 clearly suggests that multi-exponential character is more pronounced in the second row.

Different types of anthracene excimers for I–III: The results discussed above suggest that, in solution, compounds **I–III** form aggregates in which the anthracene conformation is compatible with the formation of different types of excimer as a function of concentration, wavelength, and pH. It has been reported in the literature that anthracene can form mainly two types of excimers based on the geometry that the individual anthracene units adopt in the excited state.[16–19] The first is relatively stable and has two anthracene units overlapping at an angle of 55° to each other, a short excited-state lifetime (< 10 ns), and emission close to 470 nm.[20] The second is a sandwich-type excimer in which the two anthracene units are symmetrically π-stacked with a longer lifetime at lower temperatures and emission maximum at 560 nm.[20] A recent report suggests emission from a third type of anthracene excimer (T-shaped excimer) at 510 nm with an excited-state lifetime of about 20 ns.[13] Compounds **I–III** form all three different types of anthracene excimers, as is evident from the "tunable" (470, 515, and 560 nm) emission wavelength observed for the system. While the steady-state emission maxima of the anthracene excimers of the present study match with the above discussed three cases, the excited-state lifetimes vary for lateral overlap and for the T-shaped excimer. The excited-state lifetime quenching could be presumably due to 1) the presence of water in the system, 2) higher temperatures than in the reported cases, and 3) quenching due to PET and collision.

Thus, in compounds **I–III**, excitation below and above 400 nm leads to emission from monomer and excimer anthracene, respectively, if the concentration is below the CAC. Conversely, above the CAC, excitation below and above 400 nm results in emission from anthracene excimers, and the type of anthracene excimer formed is heavily dependent on the pH of the medium.

Emission characteristics of compounds IV–VI: Intrigued by the initial results from anthracene substituted amine compounds **I** to **III**, further experiments were performed with compounds **IV** to **VI** in an acetonitrile–water (4:1 v/v) mixture to verify the effect of extended π bonds in the molecular framework on excimer formation. As mentioned before, the absorption spectra of compounds **IV** to **VI** show an intense peak at 400 nm, due to enhanced ground-state aggregate formation in an acetonitrile–water mixture. Three-di-

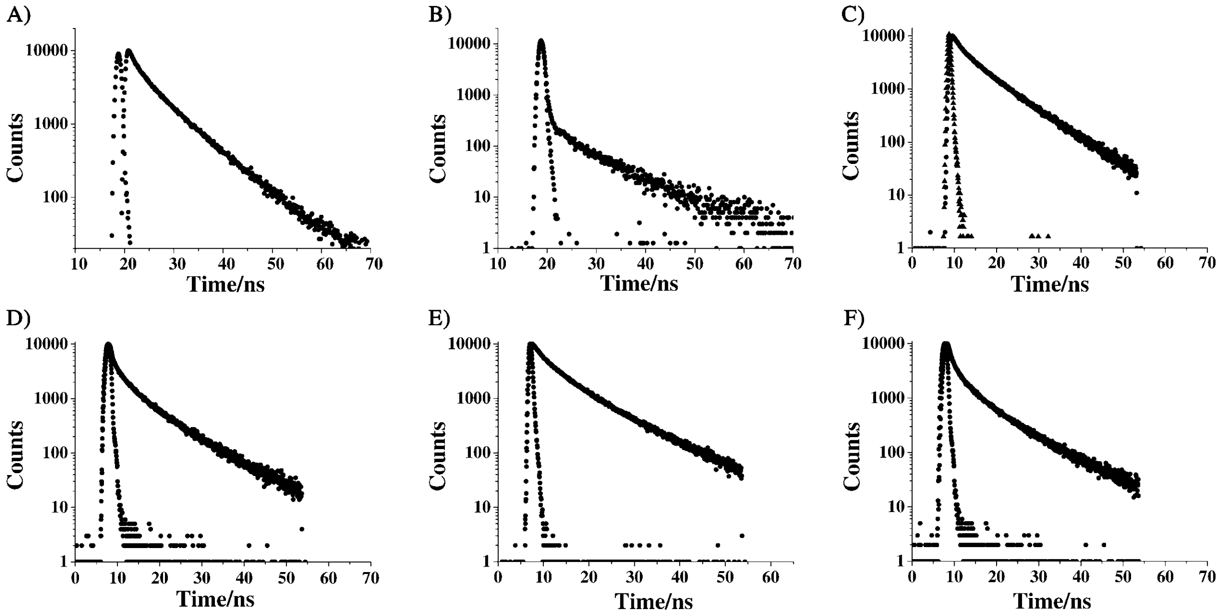


Figure 5. Time resolved spectra of **I** (A and B), **II** (C and D), and **III** (E and F) at pH 2 above the CAC. The excitation wavelengths were 360 nm (A, C, and E) and 430 nm (B, D, and F).

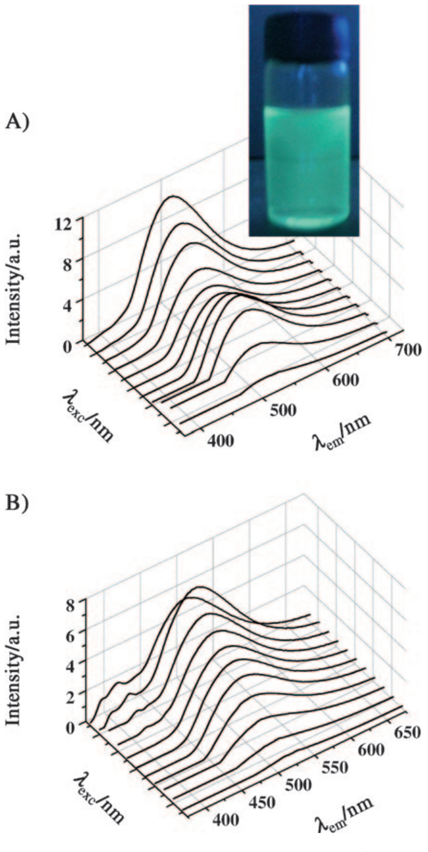


Figure 6. Steady-state fluorescence spectra of **V** (10^{-4} M) in acetonitrile–water (4:1) at pH 2 (A) and pH 8 (B) at different excitation wavelengths. The emission was collected between 400 to 600 nm. The λ_{max} of emission is 505 nm. The photograph shows the bright anthracene excimer emission from **V** at room temperature and pH 2.

mensional plots of the emission spectra of **V** at different pH (Figure 6) show unique excimer emission from the system at 505 nm, irrespective of the excitation wavelength and pH. The CAC of compounds **IV** to **VI**, as expected, was well below that of compounds **I** to **III** (the value obtained was ~10^{-6} M). A photograph of a UV-illuminated sample of **V** is shown in Figure 6, which clearly shows that the anthracene excimer emission is quite intense even at room temperature. As expected from the steady-state spectral analysis, the excited state decay from compounds **IV** to **VI** corresponds to emission from a single species with >90% relative amplitude for all possible combinations of pH, excitation wavelength, and concentration. This strongly suggests that extended π bonds in compounds **IV** to **VI** generate a unique ground-state aggregation morphology leading to the formation of exclusively T-shaped anthracene excimers, as indicated by the emission maximum. The excited-state decay trace of compound **V** is shown in Figure 7, and those of **IV** and **VI**

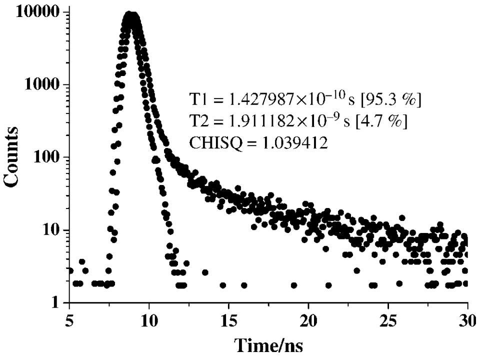


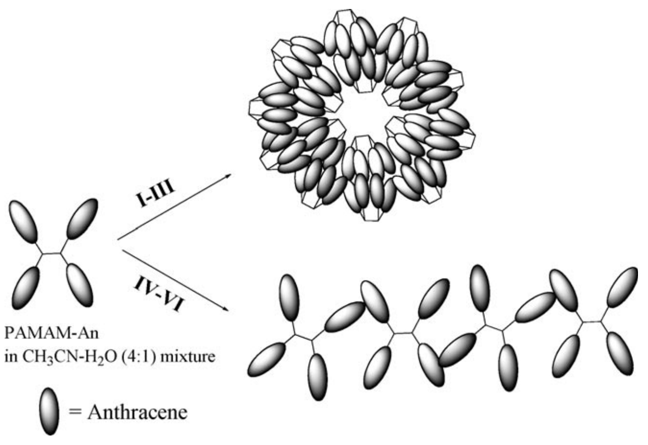
Figure 7. Time-resolved fluorescence decay of **V** (10^{-4} M) at pH 2. λ_{exc} = 340 nm and emission was collected at 505 nm.

are given in Figures S19 and S20 in the the Supporting Information. The excited-state decay value is 0.14 ns, which suggests that considerable quenching of the excited-state lifetime has occurred, either through PET or through collisional quenching by solvent.

Aggregation morphology of compounds I–VI: It is noteworthy that photoexcitation of compounds **I**–**III** at 360 nm leads to anthracene monomer emission, while photoexcitation at 430 nm (the shoulder) leads to emission from anthracene excimers above the CAC. This suggests that the shoulder peak is due to pre-arranged anthracene units in the ground state (static-type excimer) which are in a favorable orientation to form dynamic excimers without diffusion or rearrangement of the anthracene units. The presence of static excimer was further confirmed by monitoring the shift in the excitation spectra of **I**–**III**, recorded at the anthracene excimer emission maximum (530 nm) and monomer emission maximum (445 nm). The excitation spectrum monitored at 530 nm was redshifted in comparison with that recorded at 445 nm, which is explicit evidence for static-excimer formation (see Figure S22 in the Supporting Information).[21] Since the excimer emission is observed between 530 and 560 nm for compounds **I**–**III**, the excimer formed would be of sandwich type, in which partial or complete π stacking occurs between the anthracene units (angular overlap between anthracene units normally leads to excimer emission at 470 nm). Since anthracene units are hydrophobic and the experiments are carried out in presence of water, it is likely that anthracene units aggregate together to form micelle- or vesicle-type structures in which excimer formation through partial or complete face-to-face overlap between anthracene units is feasible. Earlier works by Wang et al. pointed out that PAMAM dendrimers peripheral modified by polyaromatic units exist in vesicular morphology (twin type) with a bilayer thickness of about 2.5 nm.[9]

Experimental results from the present study also indicate that increased π conjugation in the system can alter the morphology of the static excimer. The excimer emission from compounds **IV**–**VI** lies in the range of 505–510 nm, which indicates a possible T-shaped geometry for anthracene excimer.[13] Thus, intuitively, aggregate formation would result in a chainlike structure in which the anthracene units overlap in an edge-to-face dimeric conformation. This notion is depicted in Scheme 2. Excited-state lifetime studies on **IV**–**VI** have clearly demonstrated the formation of single species (relative amplitude >95%), which also suggests that micelle- or vesicle-type aggregates are absent for **IV**–**VI**, since formation of exclusively one type of anthracene excimer is less likely in micelle- or vesicle-type topologies.

The results taken together suggest that lower generations of anthracene-substituted PAMAM dendrimersare capable of generating anthracene excimers very efficiently as a function of solvent composition, excitation wavelength, and pH. Furthermore, this is the first example of generating exclusively one type of anthracene excimer from anthracene-substituted PAMAM dendrimer by incorporating extended π bonds in the molecular framework.



Scheme 2. Possible model for the static-type anthracene excimers in PAMAM-An dendrimers **I**–**VI** in an acetonitrile–water (4:1 v/v) mixture.

Conclusions

Lower generation PAMAM dendrimers were peripherally modified by anthracene moieties and the effects of their aggregation behavior on the emission properties were investigated. In the presence of water, these molecules exhibit strong aggregation propensity, and the morphology of aggregation has an impact on the type of anthracene excimer formed in the system. Exclusive anthracene excimer emission is achieved by introducing anthracene chromophore units into PAMAM dendrimer through double bonds, which leads to a unique ground-state morphology in the system. Aggregation-controlled excimer formation in anthracene-containing PAMAM dendrimers leads to tunable, intense emission from anthracene excimers at room temperature.

Experimental Section

Materials: The PAMAM dendrimers were synthesized according to a reported procedure. 9-Anthraldehyde, sodium borohydride, and solvents were purchased from Ranchem Chemicals, India. 9-Anthraldehyde was purified by repeated recrystallization from a methanol–water mixture. Experiments were done with distilled water. All solvents were distilled twice and de-aerated under nitrogen atmosphere before use.

Instruments: UV/Vis experiments were performed on a Perkin-Elmer Lambda 25 UV/Vis Spectrophotometer. Luminescence experiments were carried out on a Horiba Jobin Yvon Fluoromax-4 fluorescence spectrophotometer. The fluorescence decay measurements were carried out by the time-correlated single-photon counting technique (TCSPC) with a microchannel plate photomultiplier tube (MCP-PMT) as detector and picosecond laser as excitation source (model 5000 U, IBH, UK).

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