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Photophysical Investigation of Similarities between Starburst Dendrimers and Anionic Micelles

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Abstract: The dynamics of the electron-transfer quenching of photoexcited Ru(phen)$_3^{2+}$ by methyl viologen in solutions containing various anionic micelles and anionic starburst dendrimers were investigated by the single-photon-counting technique by monitoring the luminescence decay of the excited complex. Analysis of the kinetics of luminescence quenching revealed that the quenching process in higher generation ($G > 3.5$ and higher) starburst dendrimer solutions obeys a general kinetic model previously employed for micellar solutions. In these cases the intramicellar or intrastarburst quenching rate constants (k_q) were found to be unimolecular and decreased with increasing the size of the host. In the case of lower generation starburst dendrimers ($G = 2.5$ and lower) as with smaller micelles (C-7 and C-8 alkyl sodium sulfates), the quenching reaction was found to be bimolecular in nature. This bimolecular quenching is attributed to the rapid exit of the probe from these macromolecules into the aqueous phase during its life time. Quenching studies using an anionic quencher such as K$_4$[Fe(CN)$_6$] substantiates this conclusion. Thus, in spite of the obvious structural differences between micellar aggregates and dendrimer molecules, some striking similarities exist in the ability of both types of restricted spaces to mediate and control electron-transfer processes conducted on their surfaces.

Introduction

Starburst dendrimers are a novel class of macromolecules having a definite molecular composition and constitution.[1] The poly(amidoamine) family of starburst dendrimers (PAMAMs) was the first to be synthesized and characterized in detail.[1a] These macromolecules consist of a central nitrogen initiator core to which radially branching amidoamine units are grafted in a symmetrical fashion (see Figures 1 and 2 for a schematic representation. Figure 2 also gives the approximate dimensions of these molecules). The branches at the external surface of the macromolecules may be terminated at either an ester stage (in which case the dendrimer is called a half-generation or $G = n.5$) or an amine stage (in which case they are called full generation or $G = n$ dendrimers). Although these macromolecules have a well-defined composition and constitution, their shapes, morphologies, and surface properties have not yet been directly characterized by spectroscopic techniques. However, molecular simulation[2] of the PAMAM dendrimers revealed that the morphology of the dendrimers changes dramatically after the second generation. For example, the $G = 0$, 1, and 2 dendrimers were found to possess a highly asymmetric disklike shape, whereas the $G = 4$ and later generations possess a nearly spherical shape. Also, the early generations (below $G = 2$) were found to possess average structures, which were very open, whereas the later generations were closed, densely packed structures, the transition from the open to closed structure occurring at generation 3. It is of interest to seek direct experimental information to support these simulations.

The carboxylic salts of the half-generation ($n.5$) PAMAM dendrimers represent a new class of *covalent anionic polyelectrolytes*,[1a] whose structures may be compared to those of anionic micelle systems.[1c,i] For example, the topological aspects of the dendrimer structures have considerable resemblance to the surface of the noncolvalent micellar aggregates formed from anionic surfactants. Thus, both dendrimer and micelles may be characterized as objects equivalent to a topological sphere; i.e., they possess an inside, a boundary, and an outside. Analogies also exist at the chemical level; i.e., the number of head groups as a function of generation can be compared to micellar aggregation numbers as a function of surfactant chain length. However, obvious differences exist between the two types of structures. A micellar aggregate is a dynamic object whose monomeric surfactant components exchange rapidly with its environment and which can be viewed as possessing two concentric spherical regions, an inner core consisting of close-packed, solvent-incompatible hydrophobic components and an outer layer of solvent-compatible swollen moieties. The starburst dendrimers, on the other hand, possess a covalent structure which, although it may also be viewed as possessing two concentric spherical regions, possesses an inner core that is hydrophilic and is relatively open to solvent. Furthermore, although the dendrimer dimensions for the earlier generations are in a range similar to those of micelles near their critical micelle concentration (cmc), the spatial extent of the later generations are an order of magnitude larger than typical micellar aggregates near the cmc.

The structural resemblance of the *surfaces* of anionic micelles to anionic dendrimers suggests an investigation of the ability of these two families of polyions to organize, assemble, and control the chemical reactivity of small positively charged molecules adsorbed on their anionic surfaces. In earlier reports from this laboratory, we have attempted to define some of the details of the morphology of the starburst dendrimers using photophysical and photochemical techniques.[3,4] For example, we have probed the surface of these dendrimers using the electron-transfer *steady-state* quenching of the luminescence of aqueous solutions of the dichloride of tris(2,2′-bipyridyl)ruthenium(II) (Ru(bpy)$_3^{2+}$).[3] The probe luminescence intensity and lifetimes were considerably enhanced in the presence of the later generation ($G > 2.5$) dendrimers. It was also found that the probe luminescence

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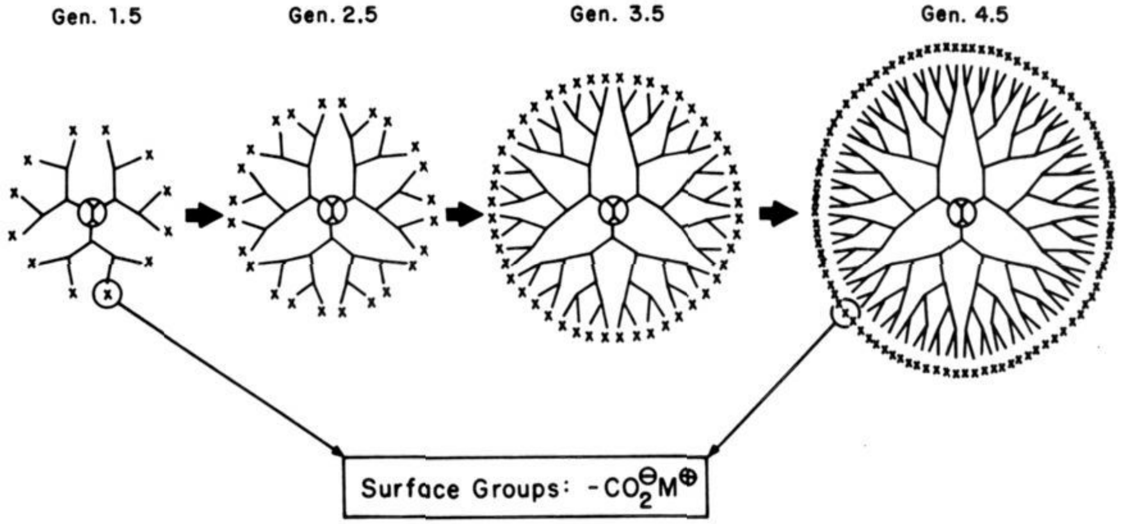
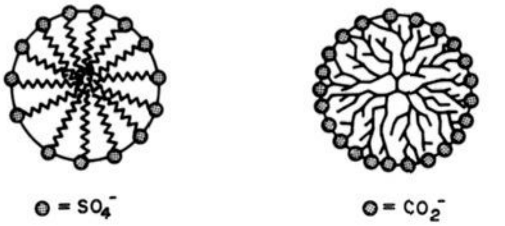


Figure 1. Two-dimensional projections of starburst dendrimers (Ne = 3; Nb = 2) generations 1.5–4.5.



Micelle	Radius, Å	Starburst	Radius, Å
C-7	16.0	3.5 G	33.1
C-8	17.1	4.5 G	43.9
C-9	19.2	5.5 G	56.0
C-10	21.3	6.5 G	63.4
C-11	23.5	7.5 G	73.7
C-12	25.6	8.5 G	87.1
		9.5 G	105.2

Figure 2. Schematic representation of anionic micelles and starburst dendrimers with their respective radii. The micelles radii are calculated values and the dendrimer radii were determined by size-exclusion chromatography (SEC) in water.

is efficiently quenched by methyl viologen cations in the presence of later generation dendrimers (Stern Volmer constants (K_{SV}) in excess of 25 000 M^{-1}) whereas normal quenching rates ($K_{SV} \approx$ 150 M^{-1}) similar to those in aqueous solution were observed when starbursts below $G = 2.5$ were used. Strikingly, a plot of the values of K_{SV} against dendrimer generation resembled the cmc plots for micelles (i.e., an abrupt jump in K_{SV} occurred when the generation size increased from 2.5 to 3.5). These results suggested a *cooperative association of surface groups* on the dendrimer occurring at generation 3.5, similar to that observed in surfactant solutions above their cmc.

The observed enhancement of the probe luminescence and the resemblance of the K_{SV} vs dendrimer generation plot to a cmc plot provoked several questions. (1) How do the surface characteristics of dynamic noncovalently bound molecular aggregate such as micelle compare to a covalently bound starburst structure? (2) Does the distribution of solute molecules adsorbed on the surface of starburst dendrimers follow a Poissonian model as is observed in the case of micelles? (3) What are the solubilization sites and what are the restrictions to probe mobility offered by these two classes of compounds?

In order to elucidate these and other aspects of anionic micellar and starburst dendrimer surfaces, we have undertaken a detailed investigation of the dynamics of photoinduced electron transfer between positively charged species in the presence of anionic starburst dendrimers of varying sizes and also in the presence of anionic micelles of varying chain lengths using the time-resolved fluorescence probe method.[5] In the present paper, we examine the quenching of tris(1,10-phenanthroline)ruthenium(II) (Ru(phen)$_3^{2+}$) dichloride by methyl viologen (MV^{2+}) in the presence of sodium carboxylate terminated starburst dendrimers (G = 0.5–9.5) and also in the presence of a variety of sodium alkyl sulfate micelles (C-7–C-12). A schematic representation of these systems and their approximate dimensions are given in Figure 2. We have observed two types of quenching behavior. One for earlier generation ($G \leq 2.5$) dendrimers and smaller micelles where quenching is "bimolecular" and another for later generation ($G \geq 3.5$) dendrimers and larger micelles where quenching is "intramicellar" or "intrastarburst". Thus, our studies support the classification of the dendrimers into "earlier" and "later" generations, thereby supporting the findings of a molecular simulation study, which predicted a change in the morphology of the dendrimer at generation 3. Where intramicellar (intrastarburst) behavior was observed, we find that the previously demonstrated kinetic model for quenching of luminescent probes in sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) micelles[6-9] adequately describes the quenching behavior. These quenching rate constants were found to decrease with increasing size of the host macromolecule. Our results suggest a close packing of surface groups on the dendrimer surface that is similar to that in micelles. We shall demonstrate that the later generation dendrimers possess an anionic surface similar to that of the larger anionic micelles and that both adsorb cations on their surface according to Poissonian statistics.

Experimental Section

Synthesis of starburst dendrimers (SBD) has been described in previous papers.[1] Sodium salts obtained by the hydrolysis of methyl ester terminated generations with stoichiometric amounts of sodium hydroxide in methanol (termed *n*.5 generation SBD or abbreviated as *n*.5 SBD) were used for all experiments. Sodium octyl sulfate (OSS, C-8), sodium decyl sulfate (DSS, C-10), sodium dodecyl sulfate (SDS, C-12), and sodium dodecanoate (SD) were obtained from Eastman Kodak. Sodium heptyl sulfate (HSS, C-7), sodium nonyl sulfate (NSS, C-9), and sodium undecyl sulfate (UDS, C-11) were from Lancaster Synthesis. All surfactants were recrystallized from methanol/ether or ethanol/ether mixtures. Tris(1,10-phenanthroline)ruthenium(II) (Ru(phen)$_3^{2+}$) dichloride, methyl viologen dichloride (MV^{2+}), and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were purchased from Aldrich and used as received. All

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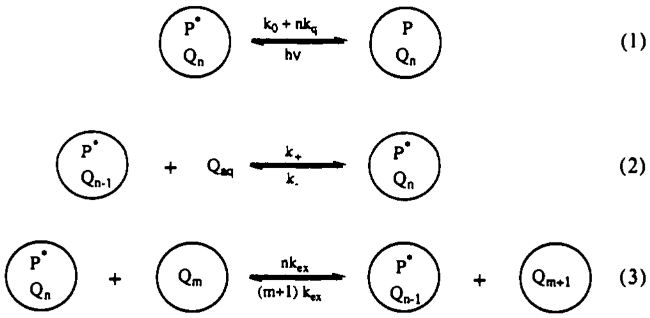
Scheme I



experiments were performed with air-equilibrated solutions in either distilled or deionized water.

Time-resolved emission measurements were conducted at 20.0 ± 0.2 °C, using a single-photon-counting unit equipped with a Edinborough 199F nanosecond flash lamp, Ortec electronics, and a Tracor-Northern TN-1710 multichannel analyzer interfaced to a IBM PS/2 Model 70 computer. The decay traces were analyzed by use of a computer program generously provided by Professor F. C. De Schryver of the University of Leuven, Leuven, Belgium. Laser flash photolysis experiments were performed using a DCR 2 Nd-YAG laser (355 nm, 2 mJ/pulse). The emission signals were fed to a Tektronix 7912 AD transient digitizer interfaced to a PDP 11/23 computer and analyzed by custom-developed software.

Results and Discussion

General Kinetic Equations. Quenching of the luminescence decays of emission probes in micellar solutions has given valuable information regarding the aggregation number of micelles, the solubilization processes of quenchers/probes, and diffusion of these particles on micellar surfaces.[5-26] Several kinetic models have been proposed for intramicellar quenching process.[6-9] One of the most general, which is given in Scheme I for micelles, can be readily extended to starburst dendrimers.

In Scheme I the circles represent micelles, P is the probe (P* is the excited probe), and Q is the quencher (in the scheme, the particles are shown inside the micelle, but this is not a necessary condition. They can be on the surface as well or associated with the micelle in any manner of binding). This model assumes that a micelle contains a maximum of one excited probe, which does not exit the micelle during its excited-state lifetime, and that the occupation of micelles by the particles (probe or quencher) follows Poisson statistics. Q_{aq} is a quencher in the aqueous phase and *n* and *m* represent the number of quencher molecules present in a given micelle. k_0 is the rate constant for the natural decay of the excited probe under a standard set of conditions and k_q is the unimolecular rate constant for intramicellar quenching. It is further assumed that for a given micelle the quenching probability is proportional to the number of cohabitating quencher molecules. Under our experimental conditions, the number of quenchers per micelle is kept low (zero, one, or two per micelle).

Equation 2 is any process that exchanges a quencher directly between the micellar and aqueous phase. The parameters k_+ (units in $M^{-1}\ s^{-1}$) and k_- (units s^{-1}) are the association and dissociation rate constants, respectively, of the quencher with the micelle ($K_{eq} = k_+/k_-$). Equation 3 is a quencher exchange process between two "colliding" micelles and k_{ex} is the rate constant for the transfer of the quencher between micelles.

On the basis of this scheme, the general equation for the decay of an emission probe after a δ pulse excitation in the presence of quencher molecules is given by 4, where $A_1 = i(0)$ is the emission

$$i(t) = A_1 \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \qquad (4)$$

$$A_2 = k_0 + \frac{k_q(k_+ + k_{ex}K_{eq}[M])[Q]}{(1 + K_{eq}[M])(k_q + k_{ex}[M] + k_-)} \qquad (5)$$

$$A_3 = \frac{k_q^2[Q]}{(k_q + k_{ex}[M] + k_-)^2(1 + K_{eq}[M])(k_- + k_{ex}[M])} \qquad (6)$$

$$A_4 = k_q + k_{ex}[M] + k_- \qquad (7)$$

intensity at zero time, and A_2–A_4 are given in eqs 5–7, respectively, where [Q] is the total quencher concentration and [M] is the concentration of the micelle. If we make the assumption that $k_q \gg k_- + k_{ex}[M]$, then the simplified eqs 8–10 result. Experimentally, the concentration of micelles [M] and the concentration of the quencher [Q] are variables, A_1–A_4 are observable parameters, and the rate constants of Scheme I are mechanistic parameters. According to eqs 8 and 9 a plot of A_2 vs [Q] yields a slope of S_2, and a plot of A_3 vs [Q] yields a slope of S_3. Algebraic manipulation of eqs 8 and 9 yields eqs 11 and 12. These show

$$A_2 = k_0 + \frac{(k_+ + k_{ex}K_{eq}[M])}{(1 + K_{eq}[M])}[Q] = k_0 + S_2[Q] \qquad (8)$$

$$A_3 = \frac{1}{1/K_{eq} + [M]}[Q] = S_3[Q] \qquad (9)$$

$$A_4 = k_q \qquad (10)$$

$$1/S_3 = 1/K_{eq} + [M] \qquad (11)$$

$$S_2/S_3 = k_- + k_{ex}[M] \qquad (12)$$

how the equilibrium constant K_{eq} as well as the exit and exchange rate constants can be extracted from variations in the micellar concentration, [M]. Thus, additional tests of the quenching model of Scheme I are available in plots of S_2/S_3 and $1/S_3$ against micelle concentration. This model treats micelles as a stable substrate that confines reactants to a small area by binding interactions. Clearly, the starburst dendrimers also act in this manner and quenching kinetics in their presence may also be described by the model.

Experimental Tests of the Kinetic Scheme. In order to evaluate the applicability of the kinetic scheme described above and to establish values for experimental parameters to be compared to the starburst systems, we have undertaken a systematic study of the quenching of $^*Ru(phen)_3^{2+}$ by MV^{2+} in SDS micelles. The quenching experiments were performed at different quencher and SDS concentrations. Note that in eqs 8–12 it is the concentration of micelles that is pertinent. The concentration of the micelle, in terms of the measured surfactant concentration, is given by $[M] = \{[SDS] - cmc\}/N$, where N is the aggregation number of the micelle (for SDS micelle cmc $= 8.2 \times 10^{-3}$ M and $N = 64$).[27] The

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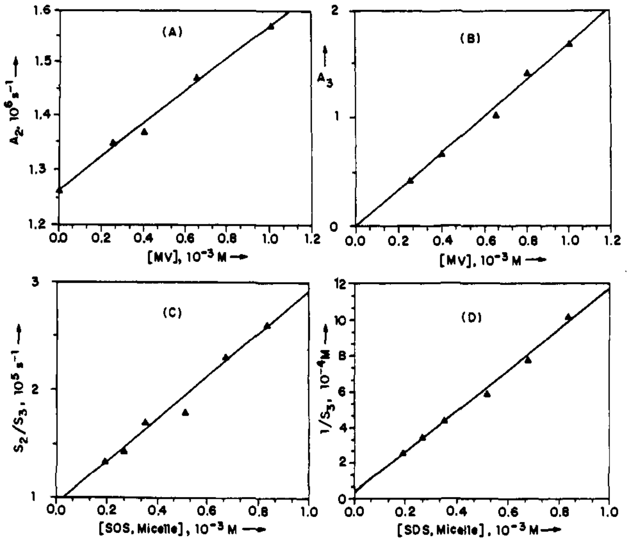

Figure 3. Illustration of eqs 8–12 in the quenching of $Ru(phen)_3^{2+}$ by MV^{2+} on SDS micelles. (A) Plot of A_2 in eq 8 against quencher concentration (0.04 M SDS); (B) plot of A_3 in eq 9 against quencher concentration (0.04 M SDS); (C) plot of S_2/S_3 in eq 11 against micelle concentration; (D) plot of $1/S_3$ in eq 12 against micelle concentration.

aggregation number N, however, is known to vary with the surfactant concentration. Since in our experiments the surfactant concentration is varied only over a narrow range, it is expected that any variation of aggregation number is negligible.[28] In all cases, the ratio of probe/micelle is kept low (≤0.1) in order to avoid multiple occupancy of the micelle by the probe.

The luminescence decays of $^*Ru(phen)_3^{2+}$ were analyzed by using the general eq 4, and the experimental parameters A_1–A_4 were obtained from the data employing the De Schryver computer fitting program.[29] The goodness of fit of the decay curves is judged by (1) the reduced χ^2 value, (2) the Durbin–Watson test statistics, (3) plots of residuals of the data to the fit, and (4) plots of the autocorrelation function of the residuals.[30] The parameters (A_1–A_4) were obtained from fitting the luminescence decay to eq 4 and were then plotted as per eqs 8–12 (see Figure 3) to determine values of the various rate constants described in Scheme I. The values thus obtained for the quenching in SDS micelles are $k_{eq} = 1.7 \times 10^4$ M^{-1}, $k_- = 9.3 \times 10^4$ s^{-1}, and $k_{ex} = 1.98 \times 10^8$ M^{-1} s^{-1}. From the values of K_{eq} and k_- we obtained the association rate constant $k_+ = 1.6 \times 10^9$ M^{-1} s^{-1}. These values are in very good agreement with values reported in the literature[5a,9] for quenching of luminescent probes in SDS micelles by divalent cations.

In a series of reports, Miyashita et al.[24-26] have studied the quenching of ruthenium complexes by viologen derivatives in SDS micelles. These authors observed nonexponential decays that they were able to fit to a more simplified model than the one described in Scheme I. Their model assumes a stronger binding of the quencher with the micelle such that any quencher exchange process is negligible during the lifetime of the excited probe. Under these conditions eqs 5 and 6 becomes eqs 13 and 14 respectively, even

$$A_2 = k_0 \qquad (13)$$

$$A_3 = [Q]/[M] \qquad (14)$$

though the luminescence decay has the same functional form as eq 4. Thus, upon plotting, A_2 should not vary with [Q] and A_3 should vary linearly with [Q] with a slope of 1/[M]. However, in our studies, we have observed that a plot of A_2 vs [MV^{2+}] was linear (see Figure 3) with a slope that varied with the concentration of the micelle. Substituting the values of the various rate constants (vide supra) in 8 we obtain

$$A_2 = 1.2 \times 10^6 \text{ s}^{-1} + 3.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \times [Q]$$

at 0.04 M SDS concentration. This clearly demonstrates that A_2 varies linearly with [Q] in the range of quencher concentrations used in our experiments. This proves beyond doubt that the simplified model considered by Miyashita et al. is not adequate to describe the quenching reaction at hand. Nevertheless, it should be mentioned that the quenching rate constant obtained by Miyashita et al. for the $Ru(phen)_3^{2+}/MV^{2+}$ system on SDS micelles was very similar to the value we obtained (8.4×10^5 s^{-1} against 9.4×10^5 s^{-1} in our work). This is because the data were analyzed by eq 4 in both cases and $k_q = A_4$ in both cases. Given these considerations, we suggest that eqs 8–12 describe the probe quenching in SDS micelles and now turn our attention to the reaction in starburst dendrimers.

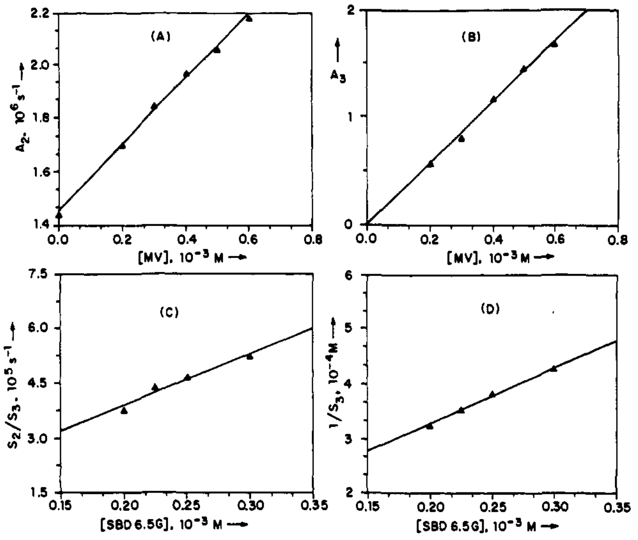

Figure 4. Illustration of eqs 8–12 in the quenching of $Ru(phen)_3^{2+}$ by MV^{2+} on starburst $G = 6.5$ dendrimer. (A) Plot of A_2 in eq 8 against quencher concentration (0.2 mM SBD); (B) plot of A_3 in eq 9 against quencher concentration (0.2 mM SBD); (C) plot of S_2/S_3 in eq 11 against starburst concentration; (d) plot of $1/S_3$ in eq 12 against starburst concentration.

Although steady-state quenching studies of a ruthenium complex by methyl viologen adsorbed on starburst dendrimers have been reported,[3] dynamic quenching behavior studies in starburst dendrimers by time-resolved methods have not been attempted previously. We have observed that luminescence decays of $Ru(phen)_3^{2+}$ in the presence of quencher (MV^{2+}) and later generation dendrimers ($G \geq 3.5$) are satisfactorily described by eq 4. We have focused on the starburst $G = 6.5$ dendrimer and performed the quenching experiments at different quencher (0–1.2 mM) and SBD (0.2–0.3 mM) concentrations. In all cases, to avoid mutliple occupancy of the SBD by the probe, the ratio of [$Ru(phen)_3^{2+}$] to [SBD] is kept low (≤0.1). The decay profiles were analyzed with use of the computer program to obtain the parameters A_1–A_4. Satisfactory plots for all parameters as required by eqs 8–12 were obtained for this system (see Figure 4). The values of the rate constants extracted from these plots are $k_q = 2.3 \times 10^6$ s^{-1}, $k_{eq} = 8.0 \times 10^3$ M^{-1}, $k_+ = 8.7 \times 10^8$ M^{-1} s^{-1}, $k_- = 1.1 \times 10^5$ s^{-1}, and $k_{ex} = 1.4 \times 10^9$ M^{-1} s^{-1}. All these values are in the range of values reported for quenching in micelles in the literature.[5a,9] Thus, we believe that the kinetic model outlined in Scheme I for micelles is applicable to starburst dendrimers as well. *This supports the idea that for ionic particles having charges opposite to that of the surface groups, quenching reactions occur mainly on the surface of the dendrimers, not in the aqueous phase, and that the distribution of the particles among the SBD is Poissonian in nature.*

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Table I. Quenching Rate Constants for Luminescence Quenching of $Ru(phen)_3^{2+}$ in Various Micelles

micelle	cmc, M[a]	N[a]	k_q
C-7	0.22	22	4.3×10^9 M^{-1} s^{-1}
C-8	0.13	27	3.1×10^9 M^{-1} s^{-1}
C-9	6.0×10^{-2}	33	$3.8 \pm 0.2 \times 10^6$ s^{-1}
C-10	3.3×10^{-2}	41	$2.3 \pm 0.3 \times 10^6$ s^{-1}
C-11	1.6×10^{-2}	52	$1.5 \pm 0.2 \times 10^6$ s^{-1}
C-12	8.2×10^{-3}	64	$9.4 \pm 0.3 \times 10^5$ s^{-1}
sodium laurate	2.4×10^{-2}	56	$2.2 \pm 0.4 \times 10^6$ s^{-1}

[a] For the alkyl sodium sulfate micelles the cmc values and aggregation numbers (N) are taken from ref 27. For sodium laurate these values are taken from ref 3.

Table II. Quenching Rate Constants for the Luminescence Quenching of $Ru(phen)_3^{2+}$ in Various Starburst Dendrimers

G	k_q	G	k_q
0.5	5.6×10^9 M^{-1} s^{-1}	5.5	$5.1 \pm 0.4 \times 10^6$ s^{-1}
1.5	4.1×10^9 M^{-1} s^{-1}	6.5	$2.3 \pm 0.3 \times 10^6$ s^{-1}
2.5	4.9×10^9 M^{-1} s^{-1}	7.5	$1.8 \pm 0.3 \times 10^6$ s^{-1}
3.5	$1.2 \pm 0.6 \times 10^7$ s^{-1}	8.5	$7.7 \pm 0.4 \times 10^5$ s^{-1}
4.5	$7.4 \pm 0.5 \times 10^6$ s^{-1}	9.5	$6.4 \pm 0.4 \times 10^5$ s^{-1}

Quenching as a Function of the Variation in the Surface Size of Micelles and Starburst Dendrimers. In the second part of our study we investigated the quenching reaction in starburst dendrimers, which we compared to similar studies in micelles. Starburst dendrimers of $G = 0.5$–9.5 and alkyl sodium sulfate micelles with chains of 7–12 carbon atoms were examined in these studies. We also compared our results to ones obtained with sodium dodecanoate micelles, which have carboxylate head groups.

In each case, the quenching rate constant k_q was obtained by fitting the probe decay to eq 4. In the case of alkyl sodium sulfate micelles the cmc decreases 0.5 times for every CH_2 group added to the alkyl chain.[27] The cmc values and aggregation numbers of all these micelles are given in Table I. In order to eliminate any influence of detergent concentration on the quenching rate constant, the experiments were done both at fixed surfactant monomer concentration (0.1 M) and at fixed micelle concentration (0.3–1.0 mM) for C-9–C-12 alkyl sodium sulfate micelles. In the case of starburst dendrimers, quenching experiments were performed at fixed surface group (CO_2^-) concentration (0.01 M) and also at fixed starburst concentration (0.5–0.6 mM). In all cases, the ratio of probe to macromolecule is kept very low. We have observed that, in the range of concentrations studied, the intramicellar quenching rate constants were independent of the surfactant concentration in the case of larger micelles (C-9 and higher). The quenching rate constants obtained in the case of later generation ($G \geq 3.5$) dendrimers also did not depend on the concentration of the dendrimers.

The quenching rate constants obtained in the case of alkyl sodium sulfate micelles are given in Table 1. Similar data for the starburst dendrimers are given in Table II. In the case of anionic micelles, n-nonyl (C-9) sodium sulfate served as a lower limit where efficient quenching on the surface of the micelles was observed. In n-octyl (C-8) and n-heptyl (C-7) sodium sulfate micelles, the luminescence decay was found to be monoexponential at all quencher concentrations, so that the normal Stern–Volmer treatment for quenching in homogeneous solutions is appropriate. Accordingly, the rate constants for C-7 and C-8 alkyl sulfates are given in units of M^{-1} s^{-1}. Similar "homogeneous" behavior was also noted for the quenching reaction in SBD of $G = 2.5$, 1.5, and 0.5 whereas eq 4 fits for starburst of $G \geq 3.5$. As for the micellar systems, the bimolecular quenching rate constants (M^{-1} s^{-1}) for SBD < 3.5 G were obtained from the Stern–Volmer plots and the data are gathered in Table II. Thus, in our studies we have encountered two types of quenching behavior, one for earlier generation dendrimers and smaller micelles where quenching is homogeneous and "bimolecular" in nature and another for later generation dendrimers and larger micelles where quenching is heterogeneous and "intramicellar" or "intrastarburst". Figures 5 and 6 show the variation of the intramicellar (intrastarburst) quenching rate constants with number of carbon atoms of the alkyl chain of micelle and starburst generation, respectively. It can be noted from Figures 5 and 6 that the intramicellar quenching rate constants decrease with an increase in the size of the micelle or dendrimer.

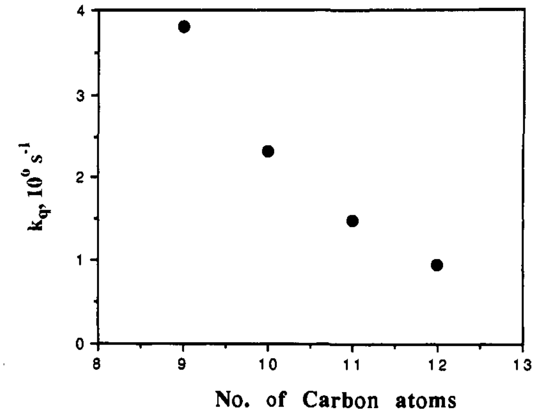


Figure 5. Plot of intramicellar quenching rate constant as a function of the number of carbon atoms in the alkyl chain for sodium alkyl sulfate micelles.

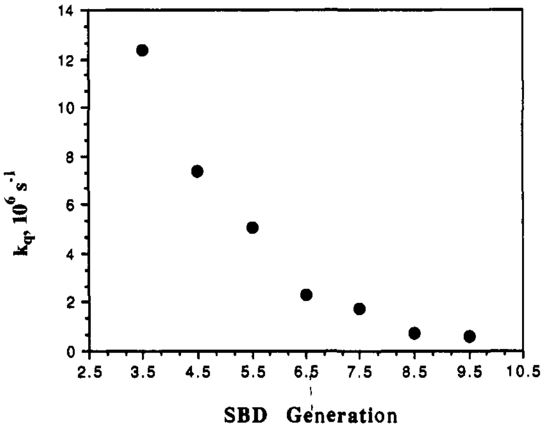
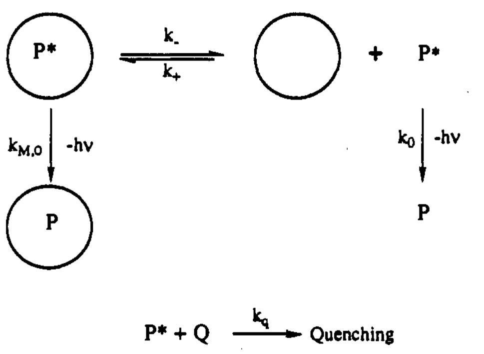


Figure 6. Plot of intrastarburst quenching rate constant as a function of starburst generation.

Scheme II



Quenching of $Ru(phen)_3^{2+}$ Luminescence with Ferrocyanide. In the case of starburst dendrimers ($G \leq 2.5$), as in the case of C-7 and C-8 micelles, we observed that quenching of the luminescence of $Ru(phen)_3^{2+}$ by MV^{2+} is bimolecular in nature. This indicates that quenching in these cases is not intramicellar (or intrastarburst) and most probably occurs outside the micelle (starburst) surface in the bulk aqueous phase. This conclusion requires that the probe exit the micelle (starburst) during its lifetime and be quenched by a quencher present in the aqueous phase. In order to evaluate this hypothesis we have studied the quenching of the luminescence of $Ru(phen)_3^{2+}$ by an anionic quencher such as ferrocyanide ions ($[Fe(CN)_6]^{4-}$). Ferrocyanide ions, being strongly negatively charged, are expected to be repelled from the macroanions by electrostatic forces and only those probe molecules that exit the

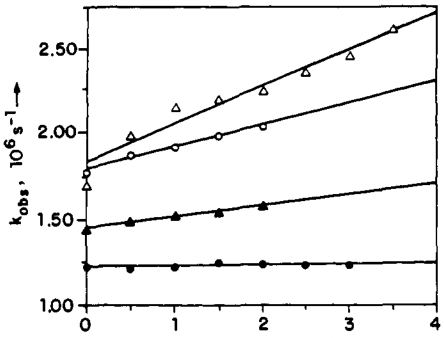


Figure 7. Observed rate constant for the decay of Ru(phen)$_3^{2+}$ by K$_4$[Fe(CN)$_6$]$^{4-}$ in various micelles as a function of ferrocyanide concentration: (△) in HSS, (○) in OSS, (▲) in NSS, and (●) in SDS.

micelle or starburst will be quenched by these ions. The kinetic model for the partitioning of the probe between the aqueous and micellar phases is given in Scheme II. From this scheme, eq 15

$$k_{\text{obsd}} = \frac{1}{\tau_{\text{obsd}}} = k_- + k_{\text{M,0}} - \frac{k_-k_+[\text{M}]}{k_q[\text{Q}] + k_0 + k_+[\text{M}]} \quad (15)$$

may be derived for the observed rate constant.[15,31] In eq 15, k_- and k_+ are the association and dissociation rate constants between the probe and the macromolecules, k_0 and $k_{\text{M,0}}$ are the rates of deactivation of the excited probe in aqueous and in micellar (or starburst) phases, respectively, and k_q is the rate of quenching in the aqueous phase. If conditions are chosen such that $k_+[\text{M}]$ is much greater than $k_q[\text{Q}] + k_0$, and assuming that k_- is greater than $k_{\text{M,0}}$, then eq 15 can be further reduced to

$$k_{\text{obsd}} = k_-k_q[\text{Q}]/k_+[\text{M}] + \alpha \quad (16)$$

where

$$\alpha = \frac{k_0k_- + k_{\text{M,0}}k_0 + k_{\text{M,0}}k_+[\text{M}]}{k_+[\text{M}]} \quad (17)$$

Thus the exit rate constant k_- can be obtaned from the slope of k_{obsd} vs [Q] plot provided that k_q, k_+, and [M] are known.

It should be noted that the conditions mentioned above are not strictly applicable for the systems we are considering (e.g., the assumption that $k_- > k_{\text{M,0}}$ is valid, perhaps, only in the case of sodium heptyl sulfate micelle), and we recognize that the k_- values obtained from the slopes would be in error. What is intended here is only a *qualitative comparison of the quenching reaction between excited Ru(phen)$_3^{2+}$ and [Fe(CN)$_6$]$^{4-}$* in the presence of various anionic starburst dendrimers and micelles. For the series of anionic micelles (or SBD) the rate of binding (k_+) with the cationic probe is expected to be diffusion controlled. If we assume that k_+ is constant in a series of micelles or starburst dendrimers, then the slope of a plot of k_{obsd} vs [Q] (eq 16) is proportional to the exit rate of the probe at a given micelle (or SBD) concentration. Thus a *qualitative estimate* of the exit rates of the probe from these macromolecules can be obtained from the slopes of the k_{obsd} vs [Q] plot.

We have carried out the quenching reaction of *Ru(phen)$_3^{2+}$ by [Fe(CN)$_6$]$^{4-}$ in the presence of alkyl sodium sulfate micelles of varying chain length by monitoring the luminescence decay of the probe. The luminescence decays in the presence of the quencher were all exponential and were analyzed to obtain k_{obsd}. Plots of k_{obsd} vs [Fe(CN)$_6$]$^{4-}$ concentration for C-7, C-8, C-9, and C-12 alkyl sodium sulfate micelles are given in Figure 7. It can be seen from Figure 7 that the slopes of these plots decrease as the size of the micelle increases, indicating that the rate of exit of the probe decreases with increasing micelle size. It can also be noted *from Figure 7 that there is no observable quenching in the C-12 micelle case, indicating that the exit of the probe is negligible in this case during the lifetime of the probe.*

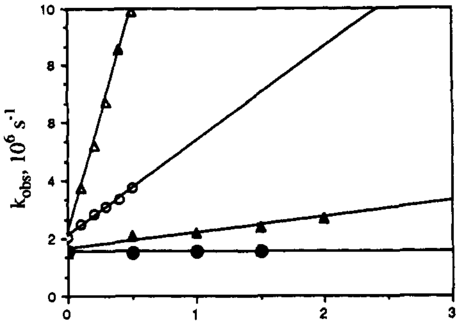


Figure 8. Observed rate constant for the decay of Ru(phen)$_3^{2+}$ by K$_4$[Fe(CN)$_6$]$^{4-}$ in various starburst dendrimer solutions as a function of quencher concentration: (△) G = 0.5, (○) G = 1.5, G = 3.5, (▲), and (●) G = 6.5.

We have also carried out the luminescence quenching reaction of *Ru(phen)$_3^{2+}$ by [Fe(CN)$_6$]$^{4-}$ in the presence of starburst dendrimers (G = 6.5 and lower). In the presence of earlier generation dendrimers we observed that the luminescence decay profiles changed with time and so the quenching experiments were done by laser flash photolysis. In other cases single-photon-counting technique was used. Luminescence decays in the presence of the quencher were exponential in all cases. Plots of k_{obsd} vs [Fe(CN)$_6$]$^{4-}$ concentration are given in Figure 8 for a few cases. It can be noted from Figure 8 that the slope decreases with increasing size of the dendrimer. In the case of SBD of G = 6.5 practically no quenching is observed. These results indicate that in the case of earlier generation dendrimers the probe exits the dendrimer during its lifetime whereas in the case of later generation dendrimers this process is too slow to be observed.

Discussion

Molecular simulation studies on the starburst dendrimers predict that the earlier generation dendrimers have an open disklike structure.[2] In an earlier study,[3] no evidence was found for the binding of Ru(bpy)$_3^{2+}$ to the earlier generation dendrimers ($G \leq 2.5$). Neither the lifetime of this probe nor the quenching by MV^{2+} was affected by the presence of earlier generation dendrimers. In this study, however, it was observed that both the lifetime of Ru(phen)$_3^{2+}$ and its quenching by MV^{2+} are enhanced in the presence of earlier generation dendrimers. Similarly, the bimolecular quenching rate constants were enhanced in the presence of n-heptyl and n-octyl sodium sulfate micelles compared to aqueous solutions of similar ionic strength. The fact that the lifetime of the probe is enhanced in the presence of these macromolecules suggests that there is a *weak* electrostatic interaction between these cationically charged particles and the anionic macromolecules. Since exponential decays are observed at all quencher concentrations in the presence of earlier generation dendrimers and smaller micelles, it is to be assumed that the particles exchange with the aqueous phase very rapidly in these cases and spend most of their time near the dendrimers/micelles. This leads to an increase in the local concentration of the reactants at the micelle (starburst)/water interface, which in turn leads to an increase in the bimolecular quenching rate constant. We cannot, however, speculate exactly where or at what distance from the micellar (starburst) surface this quenching reaction occurs.

These conclusions are further supported by quenching experiments using a negatively charged quencher. In this case the quencher cannot enter the anionic micelle or starburst molecule due to electrostatic repulsion between similar charges and only those probe molecules that exit the micelle (starburst) during their lifetime are quenched. The fact that we have observed quenching of the luminescence of Ru(phen)$_3^{2+}$ by [Fe(CN)$_6$]$^{4-}$ for earlier generation dendrimers and smaller micelles indicates that the probes actually exit the host molecules during their lifetime. We have also noted that (Figure 7 and 8) the larger the size of the macromolecule, the lower the exit rate. If we consider the exit

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rate as inversely proportional to the interaction that holds the probe on the surface of the macromolecule, then the quenching reaction with ferrocyanide ions indicates that *the interaction of the probe with the macromolecule increases with the size of the macromolecule.*

The intramicellar quenching rate constants for quenching by MV^{2+} (k_q) presented in Tables I and II for larger micelles (C-9 and higher) and later generation dendrimers ($G \geq 3.5$) show that *k_q decreases as the size of the host molecule increases* (see also Figures 5 and 6). Furthermore, a change in the surface group from sulfate to carboxylate increases the quenching rate constant by a factor of 2 in the case of C-12 micelles (these micelles have comparable sizes and aggregation numbers. See Table I). Exothermic electron-transfer (in the normal region) and exothermic energy-transfer reactions are typical of processes in which the chemical event is very rapid when the participating molecules are in close proximity. In the usual terminology such reactions are termed diffusion-controlled reactions. The observed rate of such processes is usually dependent only upon the rate of encounter of the participating species. Given that a micelle contains one probe molecule and a few quenchers randomly distributed on the micelle surface, an increase in the surface area of the micelle leads to an increase in the average separation between these molecules. This in turn leads to a decrease in the encounter probability of the reacting particles, thereby leading to a decrease in the observed quenching rate constant. A few scattered reports on intramicellar quenching in SDS micelles substantiates this result.[28] For example, Croonen et al. studied the quenching of 1-methylpyrene in SDS micelle by *m*-dicyanobenzene as a function of total detergent concentration and ionic strength (in terms of added sodium chloride) of the medium.[28a] When the detergent concentration or ionic strength of the medium is increased, the aggregation number increases, leading to an increase in the size of the micelle. It was observed in these studies that the quenching rate constant decreased with increase in micellar size. It must be mentioned here that theoretical treatments of the diffusion-controlled reactions in micelles and restricted geometries by Sano and Tachiya[32] and others[33,34] predict lowering of k_q values with increase in micelle radius.

The quenching rate constants obtained for the $^*Ru(phen)_3^{2+}/MV^{2+}$ system on starburst dendrimers of varying sizes are given in Table II. The k_q's obtained are of the same order of magnitude (ca. 10^6 s^{-1}) as those obtained for the micellar systems. However, the starburst molecules are much larger in size as compared to the micelles (see Figure 2). For example, starburst $G = 3.5$ has a radius of 33 Å and the observed k_q was 1.24×10^7 s^{-1}. Use of the Sano–Tachiya[32] equation (theoretical treatment for diffusion on a micellar surface) for a micelle of this size give a value of 5.30×10^5 s^{-1} (assuming $D = 2.55 \times 10^{-7}$ cm^2 s^{-1}, where D is the sum of the diffusion coefficients for the probe and quencher) for k_q. This indicates that quenching on the surface of starburst dendrimers is ~20 times faster than that on an alkyl sodium sulfate micelle of comparable size. We speculate that these differences are mainly due to the differences in the nature of surface groups for these two systems (SO_4^- vs CO_2^-), their degree of ionization, and their interaction with the probe and quencher molecules. A similar explanation can also be given for the difference in the observed quenching rate constants on sodium laurate and sodium dodecyl sulfate.

Another factor contributing to the decrease in k_q is the diffusion rates of the probe and quencher on the surface of these species. These rates may vary depending on the nature of the interaction between the charged particles and the charged surface of the host macromolecule. If the interaction is weak, the particles will move from one binding site to another relatively quickly. If there is strong interaction, movement or diffusion on the surface is expected to be slower and may require an activation energy. Quenching studies with ferrocyanide indicate that the interaction of the probe increases with the size of the macromolecule. Thus, we would expect the rate of diffusion and hence the intramicellar quenching rate constant to decrease with increase in micellar size.

In general, the interactions between the macromolecular host and the adsorbed particles are hydrophobic and electrostatic in nature. In a series of alkyl sodium sulfate micelles, we do not expect the hydrophobic interactions to change because the positively charged probe and quencher are solubilized in the Stern layer of the micelle, where hydrophilic and electrostatic interactions are dominant.[17,36] A certain degree of hydrophobic interaction is associated with the solubilization arising from the intercalation of the aromatic moities of the particles into the hydrocarbon domain of the micelle, but one would expect this to be similar for the larger micelles. The electrostatic interactions, on the other hand, depend on the number of ionic charges, their separation and their "mutual" interactions.[37] Thus, the aggregation number and the degree of ionization of the micelle are important parameters in determining binding of charged probes. As one goes from C-9 to C-12 alkyl sodium sulfate micelle, the aggregation number varies from 33 to 64 (see Table I). Thus, as the size of the micelle increases, one can expect the moving charged particles to interact with more oppositely charged head groups per unit distance, thereby decreasing the rate of diffusion. Similar considerations apply for the interaction of the probe/quencher with the starburst dendrimers. In this case, however, the interaction is mostly hydrophilic or electrostatic in nature. In an earlier study[4] we observed that the ratio of the vibrational band intensities I_3/I_1 of pyrene fluorescence in the presence of starburst dendrimers is close to its value in water (0.55–0.62 for SBD $G = 0.5$–9.5). This indicates that the starburst surface does not possess strong hydrophobic sites. The interaction with the particles in this case thus depends on the number of head groups and their close packing on the dendrimer surface. The distance between the head groups for the $G = 0.5$–3.5 SBDs are all 12.6 ± 0.2 Å, whereas at the $G = 4.5$ the distance abruptly drops to 11.5 Å and then linearly decreases with the starburst generation.[1i,4] This closer packing of the head groups for higher generation dendrimers leads to increased electrostatic interaction with the cationic probe/quencher, thereby leading to a decrease in the value of the intrastarburst quenching rate constant.

Conclusions

The fluorescence probe method reveals a definite structural dependence of starburst dendrimer morphology as a function of dendrimer generation. This is consistent with molecular simulations that predict a change in surface morphology occurring around generation 3.5. This behavior justifies the classification of the starburst dendrimers into "earlier" and "later" generations based on the difference in their observed properties.

In the presence of the earlier generation dendrimers ($G = 0.5$–2.5), the quenching of the luminescence of $Ru(phen)_3^{2+}$ by methyl viologen is "bimolecular" in nature. The probe molecules exit the dendrimers during their lifetime and are quenched in the vicinity of the dendrimers. This is corroborated by results obtained from quenching studies using ferrocyanide ion. These results can only be explained by considering a very open structure for these lower generation dendrimers, which may lead to a much weaker interaction with the probe molecules.

Smaller micelles (C-7 and C-8) compare very well with SBD of $G \leq 2.5$. Luminescence quenching by MV^{2+} was "bimolecular" and is due to exit of the probe from the micelles. This conclusion was supported by quenching due to ferrocyanide ions.

In the case of later generation dendrimers ($G = 3.5$–9.5) and larger micelles (C-9 and higher), the observed luminescence quenching was an "intramicellar" type, thereby indicating strong

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resemblance between these two classes of polymers. Both classes of macromolecules possess a negatively charged, solvent-compatible, congested outer surface into which postively charged molecules can be solubilized. Our results indicate that the occupation of the molecules among these macromolecules is Poissonian in nature and their distribution on the surface is random. The exact location of solubilization, however, is not well-known at this time. The solubilized molecules are capable of diffusion on the surface and the rate of diffusion and rate of exit from the surfaces depend on the size of the macromolecule. For example, we have noted that the intramicellar quenching rate constant decreased with increase in the size of the micelle or starburst dendrimer. Quenching studies with ferrocyanide indicated that the exit of the probe is significant only in the case of the smaller micelles or dendrimers.

In summary, the flourescence probe method can be profitably employed to investigate the morphology of the starburst dendrimers and to define similarities between these systems and anionic micelles. Our studies reveal a strong resemblance between these two classes of macromolecules and also support the results of the molecular simulation studies, which predict a change in the morphology of the dendrimers at generation 3.

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Registry No. OSS, 142-31-4; DSS, 142-87-0; SDS, 151-21-3; HSS, 18981-98-1; NSS, 1072-15-7; UDS, 1072-24-8; MV^{2+}, 1910-42-5; Ru(phen)$_3^{2+}$·2Cl$^-$, 23570-43-6; K$_4$[Fe(CN)$_6$], 13943-58-3.

Molecular Recognition at the Air–Water Interface. Specific Binding of Nitrogen Aromatics and Amino Acids by Monolayers of Long-Chain Derivatives of Kemp's Acid

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Contribution from the Molecular Architecture Project, JRDC, Kurume Research Park, Kurume 830, Japan. *Received March 11, 1991*

Abstract: Long-chain derivatives of Kemp's acid formed stable monolayers at the air–water interface, where the carboxylic acid groups produced the cyclic dimer species and served as a molecular cleft for specific binding of nitrogen aromatics and amino acids. The structure of the long-chain substituents was crucial for forming the cyclic dimer. Combinations of FT-IR, XPS, and UV spectroscopies of LB films and surface pressure–area isotherms revealed that substrates of complementary shape and functionality bound to the cleft mainly by hydrogen bonding. Phthalazine formed the 1:2 (substrate/amphiphile) complex, and enhanced binding of phthalazine (binding constant, 30 M^{-1}) compared to that of quinazoline, quinoxaline, and pyridazine was ascribable to the proper location of nitrogen atoms within the molecule as well as smaller solubility in water. A more basic substrate, benzimidazole, bound to the monolayer 5 times more strongly probably in a form of the 1:1 complex. It is remarkable that significant substrate binding was attained even when the host monolayer and the substrates remained in exposure to the aqueous microenvironment. The monolayer of octadecanoic acid was not an effective receptor, implying that the convergent carboxylic acids were the intrinsic element of the molecular recognition.

Introduction

Molecular recognition is a key concept in many areas of chemistry. The use of multiple hydrogen bonding as a means of specific recognition is especially popular in recent years. This interest is derived from its analogy to molecular recognition in the biological system. Rebek and co-workers took advantage of the rigid molecular skeleton of Kemp's triacid to develop a new class of host molecules in which two hydrogen-bonding groups converged to form molecular clefts.[1] Multiple, complementary hydrogen bonding is responsible also for structure-selective extraction of sugars by resorcinol cyclotetramers into CCl$_4$,[2a] complexation of thymine derivatives with diamidopyridine receptors,[2b,c] and efficient binding of proton acceptors to urea derivatives.[2d]

These host molecules are effective only in organic solvents, due to deteriorating influences of water against host–guest hydrogen bonding. However, sites of molecular recognition in the biological system are usually exposed to the aqueous phase. It is therefore desirable to develop artificial host systems that can recognize guest molecules in direct contact with bulk water.

Organized molecular assemblies on water are uniquely suited for this purpose. Their macroscopic and microscopic organizations are readily characterized by the conventional physicochemical method, and binding functional units can be placed in fixed spatial arrangements in exposure to the aqueous subphase. Specific binding of metal ions by surface monolayers has been reported for host functionalities such as crown ethers,[3] noncyclic crown ethers,[4] and calixarenes.[5] The hydrophobic and electrostatic interactions were mainly responsible for binding by cyclodextrin monolayers.[6] The complementary hydrogen bonding was implied

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