

Interactions between positively charged starburst dendrimers and $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$

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Abstract

The emission intensity and emissive lifetimes of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ in solutions containing various cationic starburst dendrimers (SBD) in the presence and absence of potential quenchers were investigated. The binding constants of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ to SBD were determined using changes in the probe's excited state lifetime as a function of the SBD concentration and generation. An observed increase in the probe's lifetime in the presence of SBD is attributed to a lower O_2 concentration at the dendrimer's surface than in water. The quenching constants between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and methylviologen (MV^{2+}) and $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ were determined by laser flash-photolysis in the presence of various generations of SBD. © 1998 Elsevier Science S.A.

Keywords: Starburst dendrimers; Methylviologen; Photolysis

1. Introduction

During the past decades considerable research has been devoted to systems involving the catalytic action of certain macromolecular hosts which enhance reaction rates of bound substrates. The binding between the reactants and the interior or surface of the host creates a supramolecular system leading to unimolecular reactions possessing high selectivity and whose dynamics differ from those displayed by the random bimolecular diffusion steps between the reactants. Understanding the nature of reactant/host interaction and how reactions are influenced by the microheterogeneous environment is crucial for the design of more effective catalytic systems. Macromolecular hosts, such as micelles [1–9], vesicles [10–13], polyelectrolytes [13–17] and DNA [18–23] are capable of binding both ionic and hydrophobic reactants and, therefore, provide an environment for supramolecular reactions. In this paper, we focus on starburst dendrimers (SBD) as the supramolecular host environment for electron transfer reactions between a guest Ruthenium(II) complex and different quenchers. The poly-(amidoamine) family of SBD represents a novel class of covalent polyelectrolytes whose structures may be compared to those of micelle systems (see Fig. 1) [24–26]. The macromolecules in the present study consist of an ethylenediamine initiator core with radially pro-

jecting amidoamine units grafted in a symmetrical fashion [26]. The branches at the external surface are terminated at an amine stage (in which case they are called full generation or $G=n$ dendrimers) which are protonated in an aqueous environment to provide a cationic surface. It has been established from molecular simulations that the 'earlier' generations ($G < 4$) possess an open, highly asymmetric shape, whereas the later generations ($G > 4$) are more closed and nearly spherical [25]. In this report, the emission decay of the triplet metal-to-ligand charge transfer (MLCT) excited state of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ bound to the ammonium salts of full-generation SBD was analyzed in the presence and absence of quencher. The increase in lifetime and emission intensity in the presence of different SBD generations and concentrations was utilized to determine the binding between the probe and the macromolecules. The quenching studies provide a means of characterizing the type of quenching kinetics operative in these systems.

2. Experimental

The synthesis and characterization of the SBD has been previously reported in detail [8,9]. The polypyridine ligand, RuCl_3 and methylviologen were purchased from Aldrich and used without further purification. Synthesis of the Ru(II) complex is described elsewhere [27]. The purity of Ru(4,7-

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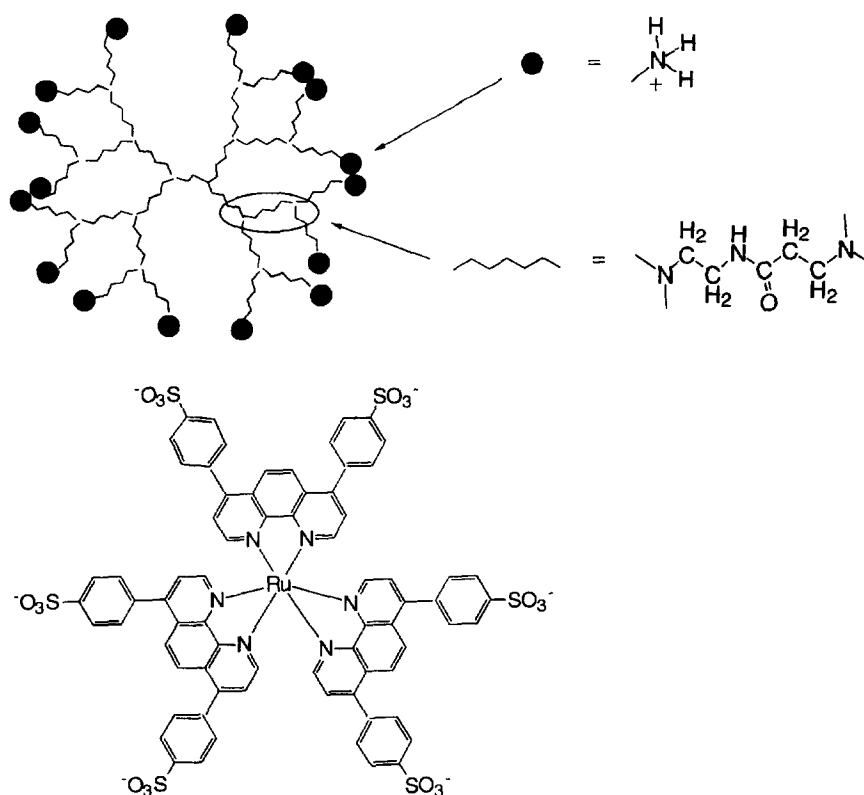


Fig. 1. Schematic representation of SBD ($G=2$) with protonated end groups and the structure of the examined complex $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$.

$(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ was determined by ^1H NMR and mass spectroscopy (FAB or electrospray). Solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ were freshly prepared for each experiment. A millipore water purification system was used. All experiments were performed with air equilibrated solutions in water at room temperature. Steady-state fluorescence was measured on a LS-5 fluorescence spectrometer (Perkin-Elmer). Time-resolved emission measurements were conducted with a frequency-doubled Nd-YAG laser ($\lambda_{\text{ex}} = 532$ nm; flash duration, ca. 15 ns).

3. Results and discussion

3.1. Photophysical properties of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ with SBD

By the absorption of light, the singlet MLCT excited state of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ (Fig. 1) is produced, followed by fast inter-system crossing to the nominal triplet $^3\text{MLCT}$ with a reported lifetime of 3860 ns in deaerated aqueous solutions [28]. The emission maxima, intensities and lifetimes of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ in aerated water and in aqueous solutions containing various generations of cationic SBD are listed in Table 1.

The emission maxima are only slightly shifted by the presence of SBD, however, the lifetimes are significantly enhanced. The lifetime enhancement is attributed to binding between the probe molecules and SBD. The monoexponential

decay of the observed lifetime τ_{obs} can be attributed to a weighted fraction of the bound and unbound rate constants by Eq. (1).

$$\tau_{\text{obs}}^{-1} = f_{\text{F}}\tau_{\text{F}}^{-1} + f_{\text{B}}\tau_{\text{B}}^{-1} \quad (1)$$

The factors f_{F} and f_{B} represent the fractions of free and bound probe molecules; τ_{F} and τ_{B} are the corresponding lifetimes [29]. According to Snyder et al. [29] the dependence of τ_{obs} on the host concentration can be utilized to determine the binding constants between cationic Ru(II) complexes and anionic and neutral micelles.

We have used a similar approach to determine the binding constants between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and cationic SBD of generation 1, 4 and 7. By increasing the SBD concentration, the observed lifetime τ_{obs} increases and reaches a plateau in which all probe molecules are assumed to be bound on the SBD surface. Thus, the lifetime in the

Table 1
Lifetimes, emission maxima and relative emission intensities of $10 \mu\text{M}$ $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ in water and in the presence of $100 \mu\text{M}$ SBD of varying generations

Medium	Lifetime (ns)	λ_{em} (nm)	Relative intensity
Water	897	614	1
$G=1$	2150	615	1.21
$G=4$	2710	616	1.90
$G=7$	3290	614	2.35

plateau region can be considered as the bound lifetime of the complex τ_B . Fig. 2 shows the observed lifetime, τ_{obs} , vs. the SBD concentration for the generations $G=1, 4$ and 7 . Eq. (1) may be rearranged to Eq. (2).

$$\tau_{\text{obs}}^{-1} = (\tau_F^{-1}) + (K_B[\text{SBD}]\tau_B^{-1}) / (1 + K_B[\text{SBD}]) \quad (2)$$

with K_B the binding constant and $[\text{SBD}]$ the respective SBD concentration [29]. The solid lines in Fig. 2 are the best fits of the experimental data to Eq. (2). From fits of Eq. (2) to the $[\text{SBD}]$ concentration dependencies of the observed lifetime, the binding constant K_B for the bound complex were determined and are collected in Table 2 for $G=1, 4$ and 7 .

Table 2 also shows the binding constants between the probe and the SBD of generation $G=4$ and 7 in a 0.23 M and 0.47 M NaCl solution. As expected for electrostatic interactions, the binding constant decreases as the salt concentration increases.

In the presence of excess dendrimer the emission lifetime and intensities are enhanced while no shift in the emission maximum of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ could be observed. The lifetime enhancement relative to that in pure water is only apparent in aerated solutions and is not seen when the sample is bubbled with argon prior to the experiment. Therefore, it may be concluded that SBD surface bound complexes are quenched less effectively by oxygen than those in the bulk solution. In deaerated solutions the measured lifetime for $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ remains the same in the presence and absence of SBD and was determined to

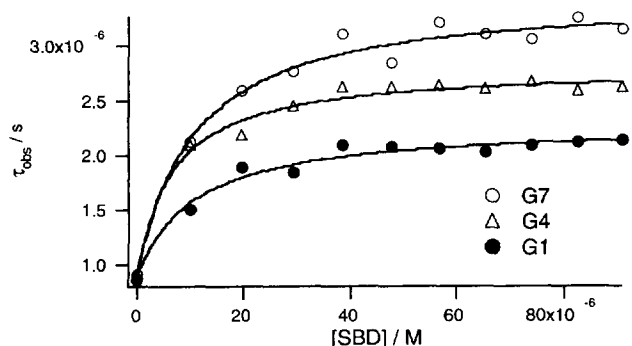


Fig. 2. Plot of the emissive lifetime of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ ($1 \times 10^5 \text{ M}$) in the presence of SBD generation 1 (\bullet), generation 4 (Δ) and generation 7 (\circ) at varying concentrations. The solid curves are computer fits using Eq. (2) and the parameters given in the text.

Table 2

Lifetime of bound complex τ_B and binding constants K_B ($\pm 15\%$) in water, in 0.23 M NaCl and 0.47 M NaCl solutions in the presence of SBD generation $G=1, 4$ and 7 . The lifetime of the free complex τ_F is 897 ns

Generation	τ_B (μs)	K_B (water) \times 10^6 M^{-1}	K_B (0.23 M) \times 10^6 M^{-1}	K_B (0.47 M) \times 10^6 M^{-1}
$G=1$	2.15	2.4	—	—
$G=4$	2.71	4.7	0.36	0.18
$G=7$	3.29	5.0	0.84	0.60

be $3.79 \mu\text{s}$ which is close to the reported value of $3.86 \mu\text{s}$ [28]. Using the Stern–Volmer relation and a concentration of O_2 in pure water at room temperature of $2.6 \times 10^{-4} \text{ M}$ [30], we calculate the bimolecular quenching rate constant of $3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Due to the decreasing solubility of oxygen with an increasing electrolyte concentration in aqueous solution [31], the SBD surface concentration of O_2 in the presence of different SBD generations can be calculated. With a SBD concentration of $9 \times 10^{-5} \text{ M}$, the bound lifetime in the presence of O_2 is 2290 ns ($G=1$), 2720 ns ($G=4$) and 3290 ns ($G=7$). Utilizing the Stern–Volmer treatment, we calculated the corresponding local O_2 concentrations on the SBD surfaces to $5.03 \times 10^{-5} \text{ M}$, $3.03 \times 10^{-5} \text{ M}$ and $1.17 \times 10^{-5} \text{ M}$, respectively. The increase in lifetime of the complex with rising SBD generation is consistent with a greater charge density on the surface of the larger SBD so that the oxygen concentration is expected to decrease near the surface of the SBD as the generation increases.

3.2. Quenching of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ by MV^{2+} in the presence of positively charged SBD

The bimolecular quenching rate constant, k_q , for the electron transfer reaction between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and Methylviologen MV^{2+} has been measured using the Stern–Volmer treatment, where from the slope of plots τ_0/τ vs. $[\text{Q}]_0$, the initial quencher concentrations, a value of $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for k_q was obtained. This quenching rate constant is close to the diffusion limit for two small ions with opposite charges ($4-$ and $2+$) in water in the absence of electrolyte [32]. For instance, Harriman et al. [33] and Richoux and Harriman [34] found, for a series of Zn porphyrins with different peripheral water solubilizing groups, quenching rate constants k_q in the range of 1.0 – $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ between the $4-$ charged metal complexes and methylviologen in water.

In the case of negatively charged SBD and micelles, it was found that quenching of the luminescence of $\text{Ru}(\text{phen})_3^{2+}$ by $[\text{Fe}(\text{CN})_6]^{4-}$ is diffusion-controlled and dependent on the size of the micelles and the generation of the dendrimers, respectively [35]. Ferrocyanide ions, being negatively charged, are expected to be strongly repelled from the macromolecules by electrostatic forces. Therefore, effective quenching only takes place when the probe molecules are capable of exit from the host molecules during their lifetime and are quenched in the bulk aqueous phase.

The same scheme is applicable for the reaction between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and MV^{2+} in the presence of positively charged SBD. Due to the electrostatic repulsion between similar charges, the quencher is repelled by the external surface of the starburst molecule and only those probe molecules that exit the dendrimer during their lifetime are quenched. Since the quenching rate constant k_q between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and MV^{2+} in the bulk aqueous phase is not affected by the presence of SBD, the different quenching rate constants measured for different dendrimer

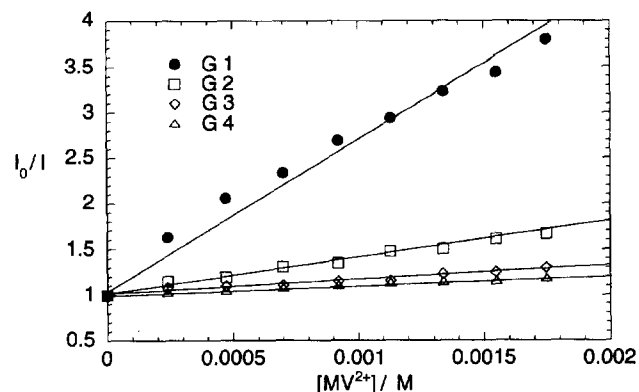


Fig. 3. Fluorescence quenching of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ at different MV^{2+} concentrations and with different SBD generations.

generations mirror the capability of the probe molecules to exit from the macromolecules and in this way they are proportional to the dissociation rate constant k_- .

We have measured the quenching rate constants k_q for $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ (1×10^{-5} M) with MV^{2+} in the presence of starburst $G=1-4$ dendrimers (1×10^{-5} M SBD, see Fig. 3).

The bimolecular quenching rate constant k_q decreases from $9.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $G=1$ to $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($G=2$) to $6.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ($G=3$) to $4.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for SBD generation 4. This result clearly indicates that the exit rate decreases with an increasing size of the macromolecule. If we consider the exit rate and the dissociation rate constant k_- as inversely proportional to the interaction that holds the probe on the surface of the SBD, then the quenching reaction with MV^{2+} indicates that the interaction of the probe increases with the size and the surface charge density of the host molecule.

3.3. Quenching of $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ by $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ in the presence of positively charged SBD

We have measured the bimolecular quenching rate constant for the reaction between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and $\text{Fe}(\text{CN})_6^{4-}$ in pure water to be $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This is likely to be near the diffusion limit for two small highly negatively charged ions in the absence of electrolyte. According to Brown and Sutin [36], a theoretical approach to estimate the quenching constant k_q can be derived from Eq. (3).

$$k_q = K_0 k_{\text{et}} \quad (3)$$

where k_{et} is the unimolecular rate constant for the electron transfer step. K_0 represents the ion-pair equilibrium constant and can be calculated from Eq. (4).

$$K_0 = 4\pi N r / 3000 \exp[-w r / RT] \quad (4)$$

In the above expression, N is Avogadro's number, r is the sum of radii of the two reactants, and w is the work term required to bring the two reactants together. Furthermore, the

diffusion controlled nature of this quenching reaction is evident when it is performed in the presence of electrolyte, since k_q increases in value to $k_q = 6.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in a 0.47 M NaCl solution. Such an increase in the value of the quenching rate constant reflects the decrease in repulsion between two like-charged ions as the ionic strength increases and the electrostatic repulsion of like-charges are screened from one another.

A similar result was found for the reaction between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$. In the absence of any electrolyte, the quenching rate constant is $k_q = 4.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and, as expected, is slightly faster than in the case for $\text{Fe}(\text{CN})_6^{4-}$ as quencher. In a 0.47 M NaCl solution, we found a slight acceleration giving a value $k_q = 8.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ due to the diminished repulsion. In both cases, the increase of the rate constant k_q by adding sodium chloride is smaller than expected. In the case of $\text{Ru}(\text{phen})_3^{2+}$ and MV^{2+} as quenchers, the quenching constant k_q was determined to be $k_q = 4.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in water. In 0.5 M NaCl k_q increases in value to $k_q = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [37].

A similar influence of increasing ionic strength towards the quenching reaction between two ions with the same charge in the presence of oppositely charged macromolecules has been observed [35]. For a system containing $\text{Ru}(\text{phen})_3^{2+}$ as a probe and MV^{2+} as quencher it was found that the electron transfer reaction is bimolecular in the presence of negatively charged SBD ($G=0.5-2.5$) and unimolecular or 'intrastarburst' at higher SBD generations [35]. This supports the idea that quenching reactions in such systems occur mainly on the surface of the dendrimer and not in the aqueous phase, when the external surface is 'closed' as the result of close packing of the charged head-groups. Under these conditions, the excited probe does not exit the host during the complexes' excited state lifetime and the quenching probability is proportional to the number of quencher molecules which exist on the same dendrimer. However, it should be noted that in this case the ratio between the [probe] and [SBD] < 0.1 and in this way each probe molecule is bound to a host.

We have examined the influence of positively charged SBD on the quenching reaction between $\text{Ru}(4,7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and $\text{Fe}(\text{CN})_6^{4-}$. In contrast to the experimental conditions mentioned above, we have chosen a [probe] to [SBD] ratio of approximately one. In this case, we have to consider the fact that the average occupancy of the host vs. probe molecules is ≥ 1 and a certain fraction of probe molecules can exit from the SBD and be deactivated in solution. The reaction rates between probes and macrocations were estimated from reaction scheme I from which Eq. (5) may be derived [38,39].

$$\tau_{\text{obs}}^{-1} = k_- + k_p + k'_q [\text{Fe}(\text{CN})_6^{4-}] \quad (5)$$

$$-k_+ k_- [\text{SBD}] / (k_+ [\text{SBD}] + k_w + k_q [\text{Fe}(\text{CN})_6^{4-}])$$

In Eq. (5), k_+ and k_- are association and dissociation

Table 3
Kinetic parameters of quenching of $\text{Ru}(4,7\text{-(SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ (1×10^{-5} M) by $\text{Fe}(\text{CN})_6^{4-}$ in the presence of different SBD generations (1×10^{-5} M)

SBD	$10^4 k_-$ (s^{-1})	$10^5 k_p$ (s^{-1})	$10^9 k_q'$ ($\text{M}^{-1} \text{s}^{-1}$)	$10^9 k_+$ ($\text{M}^{-1} \text{s}^{-1}$)	$10^6 k_w$ (s^{-1})	$10^8 k_q$ ($\text{M}^{-1} \text{s}^{-1}$)
$G=2$	1.9	4.5	6.0	6.8	1.1	1.6
$G=3$	1.1	3.9	6.2	8.1	1.1	1.6
$G=4$	2.5	3.8	5.8	8.8	1.1	1.7
$G=5$	3.3	3.7	6.7	9.0	1.1	1.7
$G=6$	2.4	3.7	6.9	11	1.1	1.7
$G=7$	3.3	3.6	22	12	1.1	1.7

The estimated uncertainties are: $\pm 20\%$ (k_-) and $\pm 15\%$ (k_+).

The parameters k_p , k_q' , k_w and k_q were directly derived from measurements with estimated uncertainties about $\pm 10\%$.

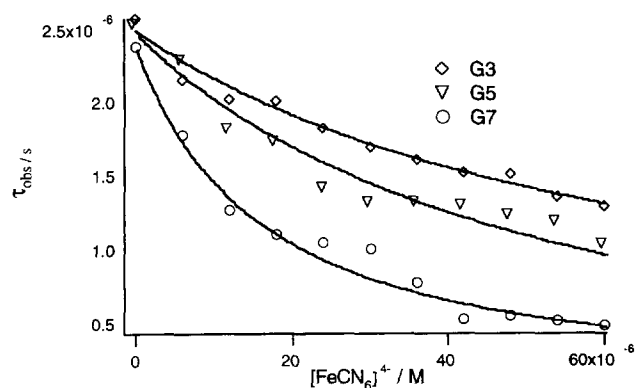


Fig. 4. τ_{obs} vs. $[\text{Fe}(\text{CN})_6^{4-}]$ plots in the presence of SBD generation 3 (\diamond), generation 5 (∇) and generation 7 (\circ); $[\text{Ru}(4,7\text{-(SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}] = 1 \times 10^{-5}$ M, $[\text{SBD}] = 1 \times 10^{-5}$ M. The solid curves are based on Eq. (5) and the parameters are given in Table 3.

rates between the SBD and the probe ions. k_w and k_p represent the probe's deactivation rate constants in the water phase and bound to the SBD, respectively, and can directly be derived from the measurement of the probe's lifetime in water and in the presence of the different SBD. Since the anionic quencher $\text{Fe}(\text{CN})_6^{4-}$ has a charge of $4-$, it is attracted by the cationic host surface in the same way as the probe molecules. Therefore, the $k_q[\text{Fe}(\text{CN})_6^{4-}]$ term in Eq. (5) is expected to be smaller than $k_q'[\text{Fe}(\text{CN})_6^{4-}]$ term if binding is significant [36]. This was proven by measuring the quenching rate constants k_q in water and k_q' , in the presence of the SBD (see Table 3). The remaining parameters k_- and k_+ of Eq. (5) were determined by computer simulation of experimental data. In Fig. 4, examples of such plots are given with the solid curves representing the results from Eq. (5). The kinetic parameters utilized for the computer fits are displayed in Table 3.

The k_+ values obtained for the bimolecular binding reaction from Eq. (5) are of the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ and close to that expected for diffusion-controlled reactions. They are slightly higher than the k_+ values reported for $\text{Ru}(\text{phen})_3^{2+}$ with negatively charged SBD [35] with the difference being attributed to the stronger electrostatic attraction between $\text{Ru}(4,7\text{-(SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ and the dendrimers based on a higher charge of the probe molecule. The data in Table 3 show that the quenching rate constants k_q' are bimolecular

for all SBD generations examined. This result is in contrast to the findings for the quenching reaction of $\text{Ru}(\text{phen})_3^{2+}$ with MV^{2+} or $\text{Co}(\text{phen})_3^{3+}$ in the presence of negatively charged SBD [35–37]. Here, the quenching rate constant is bimolecular for early generations ($0.5 \leq G \leq 3.5$) and turns unimolecular or 'intrastarburst' in the case of higher generations ($4.5 \leq G$). To explain these results we must focus on the different ratios between probe, quencher and SBD used for the experiments. In the case of $\text{Ru}(\text{phen})_3^{2+}$ with $\text{Co}(\text{phen})_3^{3+}$ as quencher, the ratio between $[\text{Ru}(\text{phen})_3^{2+}]/[\text{SBD}]$ and $[\text{Co}(\text{phen})_3^{3+}]/[\text{SBD}]$ was kept low (≤ 0.1) giving certain amounts of dendrimers containing only probe molecules $[\text{Ru-SBD}]$ and certain amounts containing both probe and quencher molecules $[\text{Ru-SBD-Co}]$ [37]. Therefore, the decay of the lifetime of the excited probe molecules is biexponential due to the different environments and can be expressed as:

$$I(t) = F_1 \exp(-t/\tau_L) + F_2 \exp(-t/\tau_S) \quad (6)$$

where

$$F_1 = [\text{Ru-SBD}] / ([\text{Ru-SBD}] + [\text{Ru-SBD-Co}]) \quad (7)$$

and

$$F_2 = [\text{Ru-SBD-Co}] / ([\text{Ru-SBD}] + [\text{Ru-SBD-Co}]) \quad (8)$$

In our case, the ratio $[\text{Ru}(4,7\text{-(SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}] / [\text{SBD}] \cong 1$ and $[\text{Fe}(\text{CN})_6^{4-}] / [\text{SBD}] \geq 1$. Based on these conditions, the decay of the lifetime is expected to be monoexponential, since in Eq. (6) the pre-exponential factor $F_1 \approx 0$. This was proven by measuring the lifetime of $^*\text{Ru}(4,7\text{-(SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ [1×10^{-5} M] in the presence of $\text{Fe}(\text{CN})_6^{4-}$ [1×10^{-5} M] and varying the SBD concentration. Increasing the concentration of SBD ($G=4$) from 1.3×10^{-6} M to 6.25×10^{-5} M, the measured lifetime increases from $1.72 \mu\text{s}$ to $2.43 \mu\text{s}$ but the decay remains monoexponential. Assuming that a quencher molecule binds similarly to a SBD containing a probe to one which does not, we can exclude dendrimers with only probe molecules attached when the quencher concentration increases. Therefore, the decay of the observed lifetime τ_{obs} is due to the quenching reaction on the surface of a SBD containing both probe and quencher molecules and can be expressed by Eq. (5), which describes

the dependence of the quenched lifetime from the quencher concentration.

4. Conclusion

The anionic Ru(4,7-(SO₃C₆H₅)₂-phen)₃⁴⁻ binds strongly to the positive surface of full generation SBD, in an electrostatic manner. When bound to SBD, the lifetime and emission intensity of the probe are enhanced due to the decreased O₂ concentration on the dendrimers surface, which reduces quenching of the triplet excited state. By quenching experiments with MV²⁺, which is strongly repelled from the similarly charged SBD, it could be shown that with an increasing size of the dendrimer the exit rate for an excited probe molecule from the surface of the host decreases. For like-charged probe and quencher molecules it was shown that the kind of quenching reaction depends on the SBD concentration. Using ratios ≥ 1 for [probe]/[SBD] and [quencher]/[SBD] the quenching rate constant, which is unimolecular at low ratios, remains bimolecular.

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References

- [1] K. Kalyanasundaran, *Photochemistry in Microheterogeneous Systems*, Academic Press, New York, 1987.
- [2] R.H. Schmehl, D.G. Whitten, *J. Am. Chem. Soc.* 102 (1980) 1938.
- [3] R.H. Schmehl, L.G. Whitesell, D.G. Whitten, *J. Am. Chem. Soc.* 103 (1981) 3761.
- [4] J.K. Thomas, *Chem. Rev.* 80 (1980) 283.
- [5] J.K. Thomas, *J. Phys. Chem.* 91 (1987) 267.
- [6] J.H. Fendler, *Chem. Rev.* 87 (1987) 877.
- [7] M. Grätzel, *Heterogeneous Photochemical Electron Transfer*, CRC Press, Boca Raton, FL, 1989.
- [8] G.G. Warr, F.J. Grieser, *Chem. Soc., Faraday Trans.* 82 (1986) 1829.
- [9] F. Grieser, C.J. Drummond, *J. Phys. Chem.* 92 (1988) 5580.
- [10] W.E. Food, J.W. Otvos, M. Calvin, *Nature* 274 (1978) 504.
- [11] N. Takeyama, H. Sakaguchi, Y. Hashiguchi, M. Shiomura, H. Nakamura, T. Kunitake, T. Matsuo, *Chem. Lett.*, 1985, 1735.
- [12] S.V. Lymar, V.N. Parmon, K.I. Zamarev, *Topics Curr. Chem.* 159 (1991) 1.
- [13] T. Matsuo, K. Takuma, Y. Tsutsui, T. Nishijima, *Coord. Chem.* 10 (1980) 187.
- [14] G.L. Duveneck, C.V. Kumar, N.J. Turro, J.K. Barton, *J. Phys. Chem.* 92 (1988) 2028.
- [15] D. Meisel, M.S.J. Matheson, *J. Am. Chem. Soc.* 99 (1977) 6577.
- [16] A. Slama-Schwok, J. Rabani, *Macromolecules* 21 (1988) 764.
- [17] J.W. Park, M.H. Kim, S.H. Ko, Y.H. Paik, *J. Phys. Chem.* 97 (1993) 5424.
- [18] G. Caminati, N.J. Turro, D.A. Tomalia, *J. Am. Chem. Soc.* 112 (1990) 8515.
- [19] M.F. Ottaviani, N.D. Ghatlia, S.H. Bossmann, N.J. Turro, J.K. Barton, H. Dürr, *J. Am. Chem. Soc.* 114 (1992) 8946.
- [20] R.J. Fiel, J.C. Howard, E.H. Mark, N. Datta Gupta, *Nucleic Acids Res.* 6 (1979) 3093.
- [21] R.F. Pasternack, E.J. Gibbs, in: T. Tullius (Ed.), *Metal-DNA Chemistry*, ACS Symposium Series 402, American Chemical Society, Washington, DC, 1989, pp. 59–73.
- [22] F. Liu, K.A. Meadows, D.R. McMillin, *J. Am. Chem. Soc.* 115 (1993) 6699.
- [23] C. Hiort, P. Lincoln, B.J. Norden, *Am. Chem. Soc.* 115 (1993) 3448.
- [24] N.J. Turro, J.K. Barton, D.A. Tomalia, *Acc. Chem. Res.* 24 (1991) 332.
- [25] D.A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J. (Tokyo)* 17 (1985) 117.
- [26] A.M. Naylor, W.A. III Goddard, G.E. Kiefer, D.A. Tomalia, *J. Am. Chem. Soc.* 111 (1989) 2341.
- [27] B.L. Hauenstein, K. Mandal, J.N. Demas, B.A. DeGraff, *Inorg. Chem.* 23 (1984) 1101.
- [28] C. Creutz, M. Chou, T.L. Netzel, M. Okumura, N. Sutin, *J. Am. Chem. Soc.* 102 (1980) 1309.
- [29] S.W. Snyder, L.B. Scott, J.N. Demas, B.A. DeGraff, *J. Phys. Chem.*, 93 (1989) 5265.
- [30] S.L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, p. 89.
- [31] R. Battine (Ed.), *Solubility Data Series*, Vol. 7, Pergamon, New York, pp. 56–76.
- [32] G.J. Kavarnos, N.J. Turro, *Chem. Rev.* 86 (1986) 401.
- [33] A. Harriman, G. Porter, M.C.J. Richoux, *Chem. Soc., Faraday Trans.* 2 (78) (1982) 1955.
- [34] M.C. Richoux, A.J. Harriman, *Chem. Soc., Faraday Trans.* 2 (78) (1982) 1873.
- [35] K.R. Gopidas, A.R. Leheny, G. Caminati, N.J. Turro, D.A. Tomalia, *J. Am. Chem. Soc.* 113 (1991) 7335.
- [36] G.M. Brown, N. Sutin, *J. Am. Chem. Soc.* 101 (1979) 883.
- [37] C. Turro, S.H. Bossmann, S. Niu, D.A. Tomalia, N.J. Turro, *J. Phys. Chem.* 99 (1995) 5512.
- [38] T. Okubo, N.J. Turro, *J. Phys. Chem.* 85 (1981) 4034.
- [39] M. Almgren, F. Grieser, J.K. Thomas, *J. Am. Chem. Soc.* 101 (1979) 279.