

resulting from the indirect determination of  $\Delta H_f^\circ$  of the latter is one possibility.

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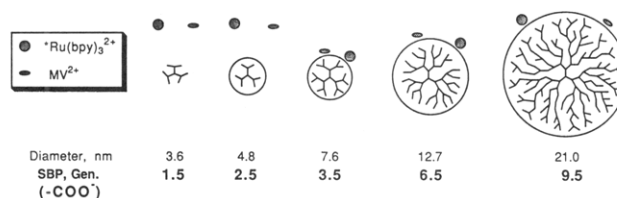
## Photoinduced Electron-Transfer Reactions To Probe the Structure of Starburst Dendrimers

The so-called *starburst dendrimers*, a new class of compounds possessing unique structural and topological features, have recently been introduced by Tomalia and co-workers.<sup>1</sup> Controlled branching reactions from an initiator core allow for the synthesis of particles with various types of surface groups that might be successfully compared to micellar structures (schematic two-dimensional cross sections of the 1.5, 2.5, 3.5, 6.5, and 9.5 generations are shown in Figure 1) without their dynamic structure. For example, an increase in the ionic strength of the medium will change the aggregation number and size of micelles but not of the starburst particles. The measured hydrodynamic diameter increases from 2.8 to 21.0 nm (e.g., Figure 1) as the dendrimer generation (number of synthetic steps,  $G$ ) rises from 0.5 to 9.5.<sup>2</sup> Recent molecular dynamics calculations have pointed out that a shape transition from a starfishlike to a more congested structure is brought about the generation 3.<sup>3</sup> This paper describes the use of photoinduced electron-transfer reactions to probe the structure of the starburst dendrimers as a function of their generation and opens the exciting possibility of studying this kind of reaction in microenvironments of well-defined geometry.<sup>4</sup>

The luminescence from the triplet metal-to-ligand charge-transfer (MLCT) excited state of tris(2,2'-bipyridine)ruthenium(II) (abbreviated  $\text{Ru}(\text{bpy})_3^{2+}$ ) is quenched by electron transfer to the 1,1'-dimethyl-4,4'-bipyridinium ion (methyl viologen,  $\text{MV}^{2+}$ ).<sup>5</sup> In homogeneous solution, the rate constant of this process is slightly below diffusion control (ca.  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and follows a normal Debye-Hückel behavior as a function of the ionic strength.<sup>6</sup> Several authors have also investigated this photoreaction (and related complex/viologen couples) in microheterogeneous media (micelles,<sup>7</sup> vesicles,<sup>8</sup> polyelectrolytes<sup>9</sup>), particularly in connection to light-induced water-splitting research.

In recent years, our interest has focused on the study of photoinduced electron-transfer quenching of ruthenium(II) polypyridyls to provide information about the structure of different microenvironments such as micelles,<sup>10</sup> anionic polyelectrolytes,<sup>11</sup> polynucleotides,<sup>12</sup> and clays.<sup>13</sup> The carboxylate-terminated starburst dendrimers are very suitable candidates for the employment of this type of cationic probes, and a systematic relationship between the external features of the former and the quenching constants of the latter is expected.

The decrease of the emission intensity of  $\text{Ru}(\text{bpy})_3^{2+}$  as a function of added  $\text{MV}^{2+}$  has been monitored with a Perkin-Elmer LS-5 spectrofluorometer at  $25^\circ\text{C}$  in water, in the presence of different generation dendrimers (sodium carboxylate terminated). The  $I_0/I$  ratio initially



**Figure 1.** Schematic drawing of the carboxylate-terminated starburst dendrimers and the  $\text{Ru}(\text{II})$ /quencher system selected to probe their structure. The hydrodynamic diameters have been determined by size-exclusion chromatography.

follows a linear dependence with the concentration of  $\text{MV}^{2+}$ , but upward curvature of the plot is always observed above a certain amount of quencher. The slopes of the linear portion of the plots (Stern-Volmer constants,  $K_{\text{SV}}$ ), as well as the linear ranges exhibited, are collected in Table I.

The lowest generation dendrimers (0.5 and 1.5) show  $K_{\text{SV}}$  values very similar to those obtained in homogeneous solution and are in agreement with previously reported values.<sup>5</sup> In the presence of the 2.5-G dendrimer a borderline behavior is observed: more efficient quenching occurs at low  $\text{MV}^{2+}$  concentration whereas a rate comparable to that for the aqueous phase occurs for high quencher conditions. A plateau is observed between both regimes. This fact indicates that the 2.5-G starburst already possesses certain polymeric features and is capable of attracting simultaneously some amount of probe and quencher into its electrostatic field. However, some of the probe is displaced from the dendrimer surface when the concentration of quencher is raised. The enhancement of the quenching rate due to a simple ionic strength effect has to be ruled out: control experiments in the presence of sodium chloride or sodium acetate (Table I) show only a 2.5-fold increase of  $K_{\text{SV}}$ .

Large values of  $K_{\text{SV}}$  (2 or 3 orders of magnitude when compared to the experiments in homogeneous media) are obtained for dendrimers of the 3.5 generation and higher (Table I; Figure 2). A strong interaction between the starburst dendrimers and the ruthenium complex is also evident from the enhanced luminescence of the latter as the dendrimer is added to the solution. Nevertheless, no changes in the intensity or position of the metal-to-ligand charge-transfer absorption band of the  $\text{Ru}(\text{bpy})_3^{2+}$  are detected. Time-resolved emission measurements (vide infra) also confirm this interaction and stress the polyelectrolyte behavior of the larger dendrimers (Figure 2). The highly efficient quenching observed should be related to the effect of the reaction occurring in a reduced space, namely, the polymer surface.<sup>9</sup> Additional observations corroborate the fact that the excited complex is quenched on the surface of the starburst: (a)

**Table I**  
**Stern-Volmer Constants for the Quenching of**  
**\*[Ru(bpy)<sub>3</sub>]<sup>2+</sup> by Methylviologen (MV<sup>2+</sup>) in the Presence**  
**of Starburst Polymers (SBP)<sup>a</sup>**

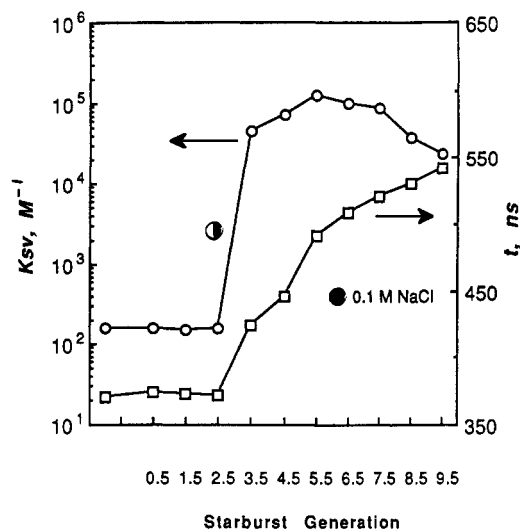
SBP, G	medium	$K_{SV}^b$ M <sup>-1</sup>	$c_{MV^{2+}}^c$ M	$K_{SV}^d$ M <sup>-1</sup>	$c_{MV^{2+}}^e$ M
	NaCl (0.1 M)	156	$4 \times 10^{-3}$	163	$4 \times 10^{-3}$
	NaAc (0.03 M)	411 <sup>e</sup>	$>7 \times 10^{-3}$		
0.5		159	$4 \times 10^{-3}$	272	$8 \times 10^{-3}$
1.5		149 <sup>e</sup>	$4 \times 10^{-3}$	159	$6 \times 10^{-3}$
2.5		161	$4 \times 10^{-3}$	2600 <sup>f</sup>	$8 \times 10^{-5}$
3.5		46 000	$5 \times 10^{-6}$	29200	$2 \times 10^{-5}$
4.5		71 200	$6 \times 10^{-6}$	38200	$2 \times 10^{-5}$
5.5		12 8000	$6 \times 10^{-6}$	38000	$3 \times 10^{-5}$
6.5		99 400	$2 \times 10^{-5}$	27600	$4 \times 10^{-5}$
6.5	NaCl (0.001 M)	88 400	$2 \times 10^{-5}$		
6.5	NaCl (0.1 M)	414 <sup>e</sup>	$5 \times 10^{-3}$		
7.5		87 600	$3 \times 10^{-5}$		
8.5		38 600	$4 \times 10^{-5}$		
9.5		24 400	$4 \times 10^{-5}$	5900	$1 \times 10^{-4}$

<sup>a</sup> In air-equilibrated aqueous solution at  $25.0 \pm 0.5$  °C. <sup>b</sup> Excitation wavelength 490 nm; [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and SBP concentrations, 5  $\mu$ M; estimated error  $\pm 5\%$ . <sup>c</sup> Upper limit of the linear Stern-Volmer plot. <sup>d</sup> Excitation wavelength 452 nm; [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and SBP concentrations, 20  $\mu$ M; estimated error  $\pm 5\%$ . <sup>e</sup> A similar value is obtained by plotting  $\tau_0/\tau$  vs the quencher concentration. <sup>f</sup> A different regime ( $K_{SV}$  179 M<sup>-1</sup>) was observed above  $3 \times 10^{-3}$  M of MV<sup>2+</sup>.

the addition of a large amount of electrolyte (e.g., NaCl; Table I) produces a dramatic decrease of the quenching rate; (b) a plot of  $I_0/I$  vs the ratio of quenchers per dendrimer for the two different concentrations of 5.5, 6.5, and 9.5 G employed shows that the data fall on a single line independently of the dendrimer concentration; (c) the apparent decrease of the quenching rate as the starburst generation increases from 5.5 to 9.5 might be related to the quadratic growth<sup>2</sup> of the external surface of the polymer with the radius of the sphere; (d) a progressive extension in the linear range of the Stern-Volmer plot also parallels the size increase of the dendrimer and points out the ability of the largest polymers to accommodate simultaneously several quencher molecules.

Similar experiments were performed by using potassium hexacyanoferrate(II) as reductive quencher of the excited Ru(bpy)<sub>3</sub><sup>2+</sup> adsorbed onto the starburst dendrimers. In this case, an efficient quenching has been reported to occur in homogeneous solution,<sup>14</sup> mainly due to extensive ion pairing between the two ground-state species. Our measurements yield a  $K_{SV}$  of 19 000 M<sup>-1</sup> in aqueous solution and a slight decreased value in the presence of the 1.5- and 2.5-G dendrimers (17 600 and 13 400 M<sup>-1</sup>, respectively), which might be attributed to the ionic strength effect on the rate constants (electron-transfer reactions between oppositely charged species are decelerated in the presence of electrolytes). However, quenching of the excited ruthenium complex by the hexacyanoferrate(II) ion is strongly hindered when the 6.5-G dendrimer is added to the solution ( $K_{SV}$  66 M<sup>-1</sup> for 20  $\mu$ M Ru and 20  $\mu$ M dendrimer), due to the protection that the anionic polyelectrolyte provides to the probe. Similar results have been reported in the presence of other polyanions (PSS, NaPAA,<sup>11</sup> DNA<sup>12</sup>) and show that the excited complex does not leave the polymer surface during its lifetime. Again a normal quenching behavior is observed when 0.1 M sodium chloride is incorporated to the reaction medium.

Emission lifetimes of \*[Ru(bpy)<sub>3</sub>]<sup>2+</sup> have been measured by laser flash photolysis (452-nm excitation with ca. 15-ns 2-mJ pulses) as a function of the starburst dendrimer added to air-equilibrated solutions. From the



**Figure 2.** Stern-Volmer constants ( $K_{SV}$ , from steady-state emission intensity measurements) for the quenching of \*[Ru(bpy)<sub>3</sub>]<sup>2+</sup> (5  $\mu$ M) by MV<sup>2+</sup> and emission lifetimes ( $\tau$ , from single photon counting measurements) of \*[Ru(bpy)<sub>3</sub>]<sup>2+</sup> (20  $\mu$ M) at 25 °C, in air-equilibrated aqueous solution as a function of the starburst dendrimer generation ([dendrimer]/[Ru] = 1). Values of  $K_{SV}$  and  $\tau$  in the absence of dendrimers are listed at the extreme left of the figure. Values of  $K_{SV}$  (○) is in the presence of the 2.5-G dendrimer ([dendrimer] = [Ru] = 20  $\mu$ M), and  $K_{SV}$  (●) is in the presence of the 6.5-G dendrimer and 0.1 M NaCl.

results depicted in Figure 2, a steady increase of the lifetime is apparent above the 3.5 G, which reflects the progressively larger polymer-like features of the dendrimer particles. Thus, deactivation of the excited probe by oxygen or solvent quenching is partially prevented upon binding to the polyelectrolyte surface. Additional NMR experiments (data not shown) conducted with the 1.5- and 5.5-G dendrimers demonstrate that, whereas the proton resonances of Ru(bpy)<sub>3</sub><sup>2+</sup> are unaffected by increasing amounts of the former, the latter starburst generations cause deshielding of the NMR signals in a fashion similar to the SDS micelles.

In conclusion, the photoinduced electron transfers between species adsorbed on the carboxylate-terminated starburst dendrimers demonstrate that a change in dendrimer structural features occurs about generation 3.5, in agreement with the shape transition predicted on the basis of theoretical calculations.<sup>3</sup> Future studies will characterize further these electron-transfer reactions in a well-defined microenvironment of reduced dimensionality, through a systematic variation of the ruthenium probes and the cationic quenchers bound to the different starburst polymers.

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## CORRECTIONS

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The authors should have been listed as J. Runt,\* Lei Du, L. M. Martynowicz, M. E. Hancock, D. M. Brezny, and M. Mayo. M. E. Hancock's name was inadvertently left out.