

Dendrimers with a Photoactive and Redox-Active [Ru(bpy)₃]²⁺-Type Core: Photophysical Properties, Electrochemical Behavior, and Excited-State Electron-Transfer Reactions

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Received February 10, 1999. Revised Manuscript Received April 30, 1999

Abstract: We report the synthesis of six new dendrimers built around a [Ru(bpy)₃]²⁺-type core (bpy = 2,2'-bipyridine) and bearing up to 24 4'-tert-butylphenoxy or 48 benzyl units in the periphery. The metallodendrimers were obtained by complexation of ruthenium trichloride or Ru(bpy)₂Cl₂ with bipyridine ligands carrying dendritic wedges in the 4,4'-positions. The absorption spectra and luminescence properties (spectra and lifetimes at 77 and 298 K; quantum yields at 298 K) of the six novel compounds are reported. All of them show the characteristic luminescence of the [Ru(bpy)₃]²⁺-type core unit. The dendritic branches protect the luminescent excited state of the core by dioxygen quenching. For the three compounds containing the 4'-tert-butylphenoxy peripheral units, the electrochemical behavior and the excited-state quenching via electron transfer were also studied. The electrochemical experiments have evidenced an oxidation and three reduction one-electron processes centered in the [Ru(bpy)₃]²⁺-type core and two multielectron oxidation processes involving the dioxybenzene- and oxybenzene-type units of the dendritic branches. The core of the largest dendrimer shows an electrochemical behavior typical of encapsulated electroactive units. The reaction of the luminescent excited state of the [Ru(bpy)₃]²⁺-type core with three electron-transfer quenchers (namely, methyl viologen dication, tetrathiafulvalene, and anthraquinone-2,6-disulfonate anion) was found to take place by a dynamic mechanism in all cases. The quenching rate constants, obtained by Stern–Volmer kinetic analysis, are compared with those found for the simple [Ru(bpy)₃]²⁺ complex. The results show that, for each quencher, the value of the rate constant decreases with increasing number and size of the dendritic branches. For the second-generation dendrimer containing 24 4'-tert-butylphenoxy units at the periphery, the rate constant of the reaction with methyl viologen is more than 1 order of magnitude smaller than that of the "naked" [Ru(bpy)₃]²⁺ complex. All the experiments were performed in acetonitrile solution, except for luminescence experiments at 77 K where butyronitrile was used.

Introduction

Dendrimers¹ are well-defined macromolecules exhibiting a tree-like structure, first derived by the "cascade molecule" approach.² Dendrimer chemistry is a rapidly expanding field for both basic and applicative reasons.¹ Such compounds are particularly interesting when they carry units capable of performing specific function (e.g., redox reactions and photo-induced processes). Transition-metal complexes, especially Ru(II) complexes of polypyridine-type ligands,³ are useful components for constructing dendrimers because of their outstanding photochemical, photophysical, and electrochemical properties.^{4,5} In dendrimers, transition-metal units may be incorporated as a core, as components of the branches, and/or as peripheral units.^{4–9} When a dendrimer contains a photo- and/or electroactive unit as a core, the dendritic branches may modify the

photochemical and electrochemical properties of such a unit.^{5–8,10,11} This effect may be exploited, for example, to improve the luminescence properties of the core or to decrease the rate of electron-transfer processes.

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Continuing our investigations in the field of photoactive,^{4,10fi,12} metal-containing^{4,10fi} dendrimers, we report here (i) the synthesis of five 2,2'-bipyridine (bpy) ligands carrying dendritic wedges in the 4,4'-positions (Figure 1), (ii) the synthesis of six new dendrimers built around a [Ru(bpy)₃]²⁺-type core and bearing up to 24 4'-tert-butylphenoxy or 48 benzyl units in the periphery (Figure 2), (iii) the absorption spectra and luminescence properties (spectra and lifetimes at 77 and 298 K; quantum yields at 298 K) of the six novel metal-based dendrimers, and (iv) the electrochemical behavior and the excited-state quenching via bimolecular electron transfer of the three metal-based dendrimers containing the 4'-tert-butylphenoxy peripheral units.

Results and Discussion

Synthesis. The synthesis of the new dendritic ligands **1–5** (Figure 1) was performed with use of 4,4'-dimethyl-2,2'-bipyridine units as starting material, which were substituted with dendritic wedges of different generations and different peripheral groups.

(a) Dendritic Benzyl Bromides. The dendritic benzyl bromides **6–8** (Figure 1) have been prepared by the convergent procedure indicated by Fréchet.¹³ The same procedure was used to prepare the benzylic bromides **9** and **10** containing more flexible end groups with 4'-tert-butylphenoxy peripheral units. In the first step (Figure 3), the reaction of 3,5-dihydroxybenzyl

alcohol **11** with 2 equiv of 1-bromo-3-(4'-tert-butylphenoxy)propane (**12**)¹⁴ gives the benzylic alcohol of the first generation **13**. The reaction was carried out in boiling acetone in the presence of potassium carbonate and a catalytical amount of [18]crown-6. After purification the benzylic alcohol was obtained as colorless solid. The conversion to the benzylic bromide **9** was achieved with phosphorus tribromide¹⁵ in dry toluene at 0 °C. A colorless solid compound was obtained. Reaction of the first generation benzylic bromide with **11** under the same conditions described above gave the second generation alcohol **14**, which was again treated with PBr₃ to give the corresponding dendritic benzylic bromide **10**.

(b) Dendritic Bipyridine Ligands. For the preparation of the dendritic bipyridine ligands **1–5** (Figure 1), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) was treated with an excess of LDA in dry THF at -10 °C to give the orange dilithio derivative. After 45 min the dendritic benzyl bromides, dissolved in a minimum amount of dry THF, were added to the reaction mixture and gave the desired symmetrical 4,4'-disubstituted dendritic bipyridine ligands (Figure 1). The crude products have been purified by column chromatography on silica gel. In all cases the product yield amounts to 50–60%. The structures of the new bipyridine ligands could be readily deduced from ¹H and ¹³C NMR spectra as well as from MALDI-TOF mass spectrometric analysis.

We were also able to get a single-crystal X-ray analysis of the second-generation bipyridine ligand **2**. As can be seen from Figure 4, the structure shows a trans configuration, which is typical for 2,2'-bipyridine derivatives. The whole structure is substantially planar and symmetrical with respect to the center of the pyridine–pyridine bond.

(c) Dendritic Bipyridine Complexes. The procedures used to obtain the metalodendrimers shown in Figure 2 followed those described in the literature for other Ru-bpy type complexes.^{3,10fi,16} The dendritic bipyridine ligands **1**, **2**, and **3** and a corresponding amount of ruthenium trichloride were dissolved in a mixture of chloroform and ethanol (2:1 (v/v)) and gently refluxed for 5 days. The reaction mixture turned from dark violet to bright orange, which indicates the formation of the trisbipyridine-type ruthenium complexes [Ru(**1**)₃]²⁺, [Ru(**2**)₃]²⁺, and [Ru(**3**)₃]²⁺. Contrary to what happens for the ligands with phenyl peripheral groups, the ligand with 4'-tert-butylphenylpropyl end groups **5** is soluble in more polar solvents so that the reaction was carried out in pure ethanol and was completed after 2 days, yielding the [Ru(**5**)₃]²⁺ compound. The mixed-ligand compounds [Ru(bpy)₂(**4**)]²⁺ and [Ru(bpy)₂(**5**)]²⁺ were obtained by refluxing the dendritic bipyridine ligands **4** and **5** and a stoichiometric amount of [Ru(bpy)₂Cl₂]²⁺·2H₂O in ethanol for 3 days.

The dendritic ruthenium complexes have been purified by column chromatography. Independently from the dendritic generation and the nature of the peripheral groups, all the ruthenium-based dendrimers are obtained as orange, highly viscous, oily compounds. Except for [Ru(bpy)₂(**4**)]²⁺, which was obtained as a chloride salt, the counterions were exchanged with hexafluorophosphate ions to facilitate purification.

Because of their highly branched dendritic wedges, the ruthenium complexes have almost lost any salt-like character, and are soluble in a wide spectrum of organic solvents. With increasing generation and depending on the end groups, they

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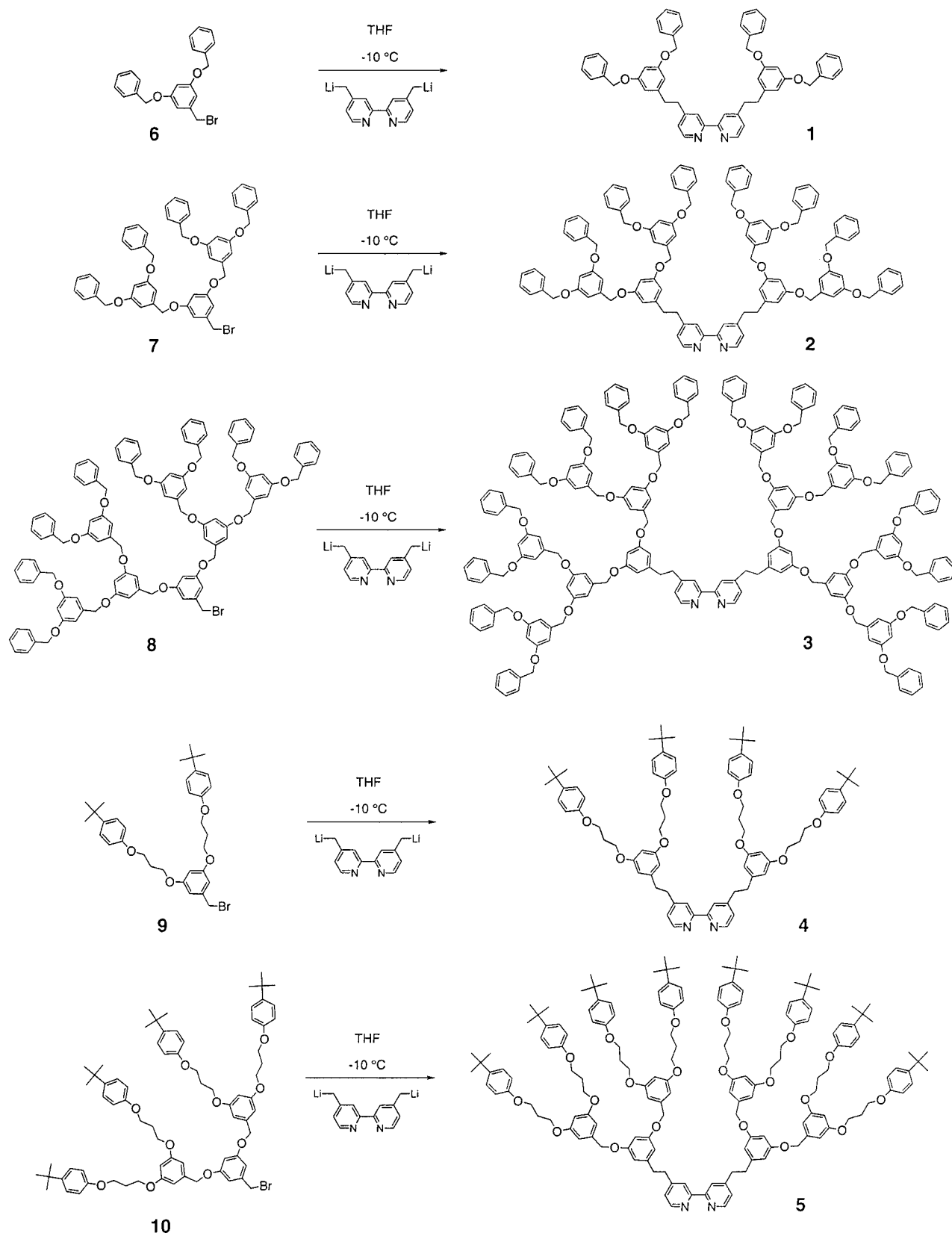


Figure 1. Synthesis of the 2,2'-bipyridine (bpy) ligands carrying dendritic wedges.

have the tendency to become more and more insoluble in polar organic solvents. For example, the third generation compound $[\text{Ru}(\mathbf{3})_3]^{2+}$ is only poorly soluble in acetonitrile at room temperature. It is noteworthy that $[\text{Ru}(\mathbf{5})_3]^{2+}$, thanks to its 4'-*tert*-butylphenoxy end groups, is soluble even in ether and THF. The structures of the dendritic ruthenium complexes could

be readily deduced from ^1H and ^{13}C NMR spectra and, except for $[\text{Ru}(\mathbf{3})_3]^{2+}$, also from MALDI-TOF mass spectrometry.

Spectroscopic and Photophysical Properties. The absorption and emission spectra for the six metal-based dendrimers are shown in Figures 5 and 6, and the most relevant spectroscopic and photophysical data of the six compounds are gathered

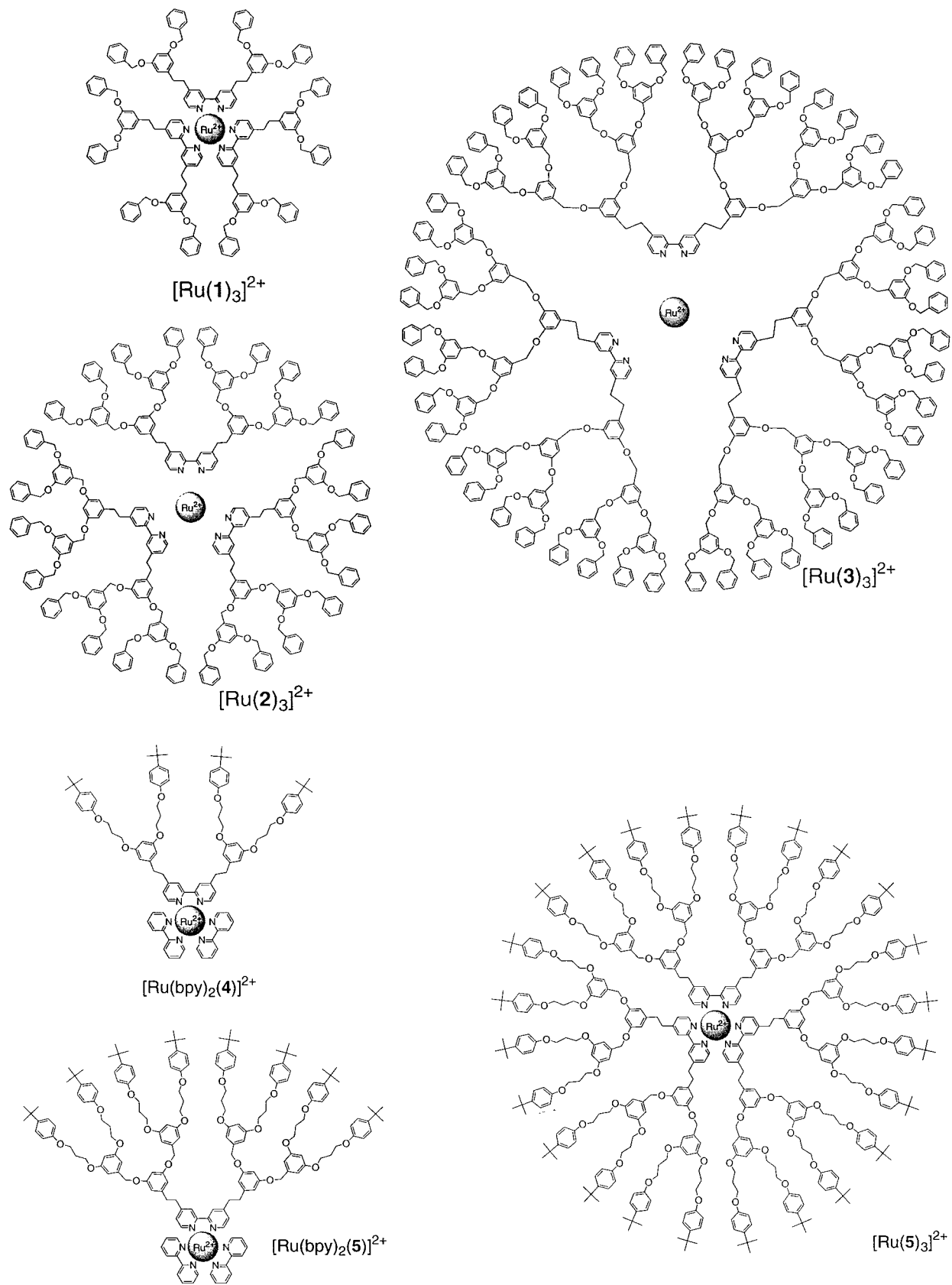


Figure 2. Dendritic metal complexes.

in Table 1, where the literature data of the [Ru(bpy)₃]²⁺ model compound¹⁷ are also shown for comparison purposes. For the fully dendritic [Ru(1)₃]²⁺, [Ru(2)₃]²⁺, [Ru(3)₃]²⁺, and [Ru(5)₃]²⁺ compounds the absorption spectra in the visible region are quite similar, showing that the shape and chemical nature of the

dendritic branches do not substantially affect the [Ru(bpy)₃]²⁺-based chromophoric core. The absorption spectra of the [Ru(bpy)₂(4)]²⁺ and [Ru(bpy)₂(5)]²⁺ compounds are slightly different from the spectra of the other compounds, as expected because of their mixed-ligand nature. As far as emission is

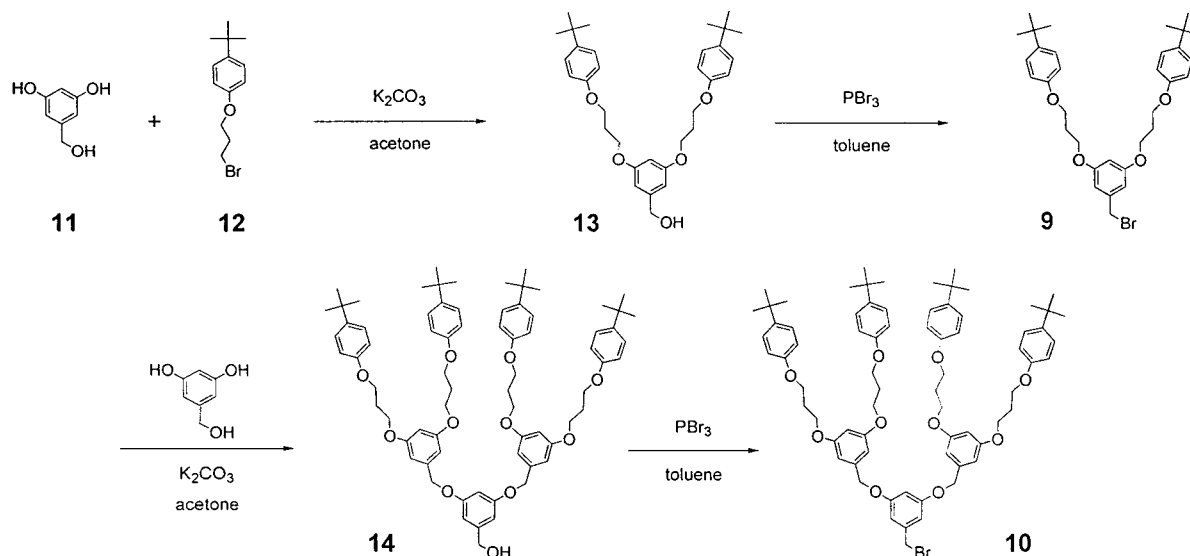


Figure 3. Synthesis of dendritic benzyl bromides.

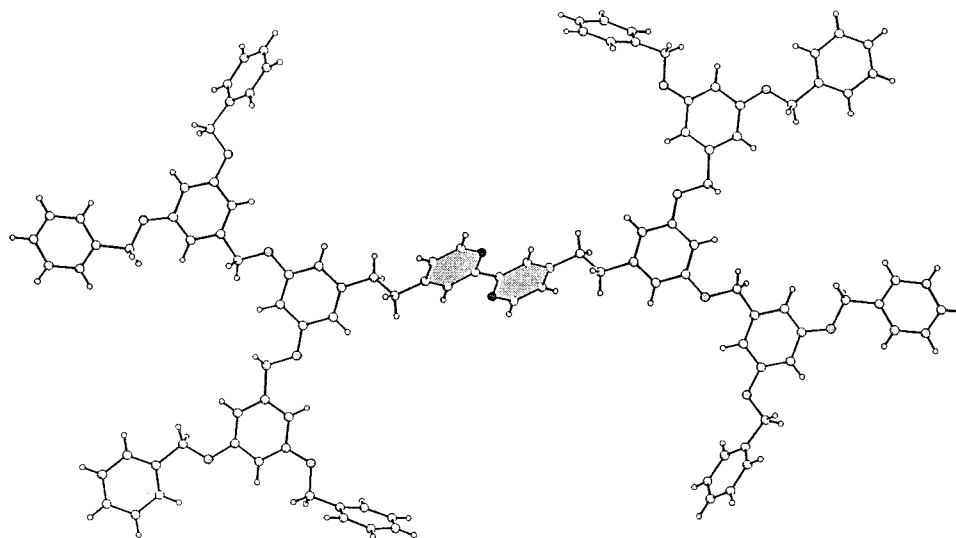


Figure 4. X-ray structure of the second-generation bipyrindine ligand 2.

concerned, all compounds exhibit the characteristic luminescence of triplet metal-to-ligand charge-transfer (MLCT) excited states of Ru-bpy type compounds,³ i.e., of their metal-based cores. However, several differences can be noted, related to different overall chemical composition.

(i) A slight red shift can be observed in the case of the $[\text{Ru}(\text{bpy})_2(\mathbf{4})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\mathbf{5})]^{2+}$ compounds, most likely because of their mixed-ligand nature.³

(ii) In the homogeneous $[\text{Ru}(\mathbf{1})_3]^{2+}$, $[\text{Ru}(\mathbf{2})_3]^{2+}$, and $[\text{Ru}(\mathbf{3})_3]^{2+}$ family, the emission maximum moves slightly to higher energy with increasing size of the branches, both at 293 and 77 K. This can be accounted for by a decrease in the number of (polar) solvent molecules surrounding the core, with consequent destabilization of the CT excited state.

(iii) In deaerated solution the lifetime of the luminescent excited state is only slightly different for the various dendrimers and also very close to that of the $[\text{Ru}(\text{bpy})_3]^{2+}$ model compound. In aerated solution, however, the lifetimes (and quantum yields) are very different. The $[\text{Ru}(\text{bpy})_2(\mathbf{4})]^{2+}$ compound exhibits

almost the same lifetime as $[\text{Ru}(\text{bpy})_3]^{2+}$, whereas $[\text{Ru}(\text{bpy})_2(\mathbf{5})]^{2+}$ and the fully dendritic $[\text{Ru}(\mathbf{1})_3]^{2+}$, $[\text{Ru}(\mathbf{2})_3]^{2+}$, $[\text{Ru}(\mathbf{3})_3]^{2+}$, and $[\text{Ru}(\mathbf{5})_3]^{2+}$ compounds exhibit considerably longer lifetimes. It can also be noticed that in the homogeneous $[\text{Ru}(\mathbf{1})_3]^{2+}$, $[\text{Ru}(\mathbf{2})_3]^{2+}$, and $[\text{Ru}(\mathbf{3})_3]^{2+}$ family the lifetime in aerated solution increases with increasing size of the branches. The lifetime of the largest compound is three times longer than that of the smallest one. An increase in lifetime with increasing size or number of the dendritic branches occurs also for the $[\text{Ru}(\text{bpy})_2(\mathbf{4})]^{2+}$, $[\text{Ru}(\text{bpy})_2(\mathbf{5})]^{2+}$, and $[\text{Ru}(\mathbf{5})_3]^{2+}$ family. These results show that the dendrimer branches protect the $[\text{Ru}(\text{bpy})_3]^{2+}$ -based core from dioxygen quenching, as has been previously observed for other similar compounds.^{10fi} A more detailed discussion of dioxygen quenching will be given below. A long lifetime of the luminescent excited state in aerated solutions is important for immunoassay applications since the signal of the label can be read after the decay of the background fluorescence of the sample, whose lifetime usually is in the nanosecond time scale.¹⁸

Electrochemical Behavior. The amount of compound needed for electrochemical investigations is much larger than that

(17) Slightly closer model compounds for the dendrimer cores would have been $[\text{Ru}(\text{Me}_2\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{Me}_2\text{bpy})]^{2+}$. For such compounds, however, full spectroscopic and photophysical data under our experimental conditions are not available.³

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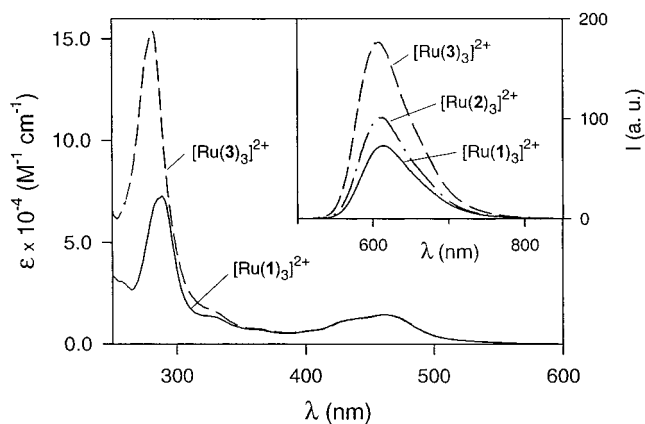


Figure 5. Absorption and (inset) emission spectra of the [Ru(1)₃]²⁺, [Ru(2)₃]²⁺, and [Ru(3)₃]²⁺ compounds in deaerated acetonitrile solution at 298 K ($\lambda_{\text{exc}} = 450$ nm). The absorption spectrum of [Ru(2)₃]²⁺, not shown for the sake of clarity, is identical with that of the other two compounds for $\lambda > 380$ nm.

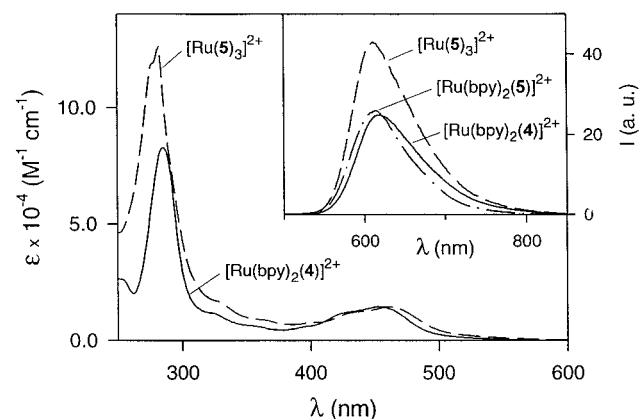


Figure 6. Absorption and (inset) emission spectra of the [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ compounds in deaerated acetonitrile solution at 298 K ($\lambda_{\text{exc}} = 450$ nm). The absorption spectrum of [Ru(bpy)₂(5)]²⁺, not shown for the sake of clarity, is identical with that of [Ru(bpy)₂(4)]²⁺ for $\lambda > 380$ nm.

Table 1. Luminescence Data^a

	298 K ^b			77 K ^c	
	λ_{max} , nm	τ , μs	$10^{-2}\Phi$	λ_{max} , nm	τ , μs
[Ru(bpy) ₃] ²⁺ ^d	611	0.172 0.990 ^e	1.6	582	4.8
[Ru(1) ₃] ²⁺	614	0.191 1.16 ^e	1.9	586	5.3
[Ru(2) ₃] ²⁺	611	0.316 0.990 ^e	2.9	584	5.4
[Ru(3) ₃] ²⁺	609	0.562 1.04 ^e	4.8	579	5.6
[Ru(bpy) ₂ (4)] ²⁺	620	0.170 1.08 ^e	1.8	588	5.2
[Ru(bpy) ₂ (5)] ²⁺	616	0.193 1.05 ^e	1.9	586	5.6
[Ru(5) ₃] ²⁺	611	0.415 0.992 ^e	3.5	581	5.5

^a Aerated solution, except otherwise noted. ^b Acetonitrile solution. ^c Butyronitrile solution. ^d From ref 10f. ^e Deaerated solution.

needed for photophysical experiments. With the available samples, we could study the electrochemical behavior only for the compounds of the [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ series. The electrochemical data are gathered in Table 2.

In the examined compounds, besides the electroactive [Ru(bpy)₃]²⁺-type core,³ there are several oxybenzene- and dioxy-

benzene-type units that are known to undergo oxidation at moderately positive potentials.¹⁹ More specifically, the oxybenzene- and dioxybenzene-type units are 4 and 2 for [Ru(bpy)₂(4)]²⁺, 8 and 6 for [Ru(bpy)₂(5)]²⁺, and 24 and 18 for [Ru(5)₃]²⁺, respectively. To assign the observed electrochemical processes, we have taken as model compounds of the cores the [Ru(bpy)₂(Me₂bpy)]²⁺ and [Ru(Me₂bpy)₃]²⁺ complexes, whose electrochemical behavior, also displayed in Table 2, is known from literature.²⁰ They show three reversible one-electron reduction processes involving the three ligands and a reversible one-electron oxidation process localized on the metal ion. Methoxybenzene and 1,3-dimethoxybenzene, which are reported¹⁹ to undergo a one-electron oxidation process at +1.76 and +1.50 V (vs SCE, acetonitrile solution), respectively, are close model compounds of the electroactive groups present in the branches.

The small [Ru(bpy)₂(4)]²⁺ dendrimer shows six redox processes (Table 2).²¹ By comparison with the behavior of [Ru(bpy)₂(Me₂bpy)]²⁺, the three reduction processes and the oxidation process at less positive potential, all reversible and mono-electronic, can be straightforwardly assigned to the metal-complex moiety. The two oxidation processes observed at more positive potentials can be assigned to the oxidation of the dioxybenzene- and oxybenzene-type units of the branches, respectively. Since these processes are not fully reversible, it is difficult to establish whether the number of exchanged electrons corresponds to that of the involved units.

The first oxidation (metal-centered) and reduction (ligand-centered) processes of [Ru(bpy)₂(5)]²⁺ occur at the same potentials as those of the smaller [Ru(bpy)₂(4)]²⁺ compound. The potential values for the second and third reduction processes, however, cannot be determined since the third wave in the cathodic scan and the wave corresponding to the second process in the anodic scan are covered by a stripping peak. This suggests that the uptake of two or three electrons by [Ru(bpy)₂(5)]²⁺ causes adsorption on the electrode surface. Since such a phenomenon is not present in the fully dendritic [Ru(5)₃]²⁺ (vide infra), it cannot be attributed to the peripheral units of the wedge and is likely related to the particular "comet shape" of [Ru(bpy)₂(5)]²⁺. On the oxidation side, the two not fully reversible multielectron processes involving the electroactive units of the wedge are also present. The area of the DPV peaks corresponding to these processes is larger than that observed in the case of [Ru(bpy)₂(4)]²⁺, in agreement with the larger number of electroactive units present in the wedge of [Ru(bpy)₂(5)]²⁺.

The closest model compound for the core of the fully dendritic [Ru(5)₃]²⁺ compound is the [Ru(Me₂bpy)₃]²⁺ complex (Table 2). The assignment of the observed processes is again straightforward, taking into account that the two multielectron oxidation processes related to the numerous dioxybenzene- and oxybenzene-type units of the branches merge into a high and very broad DPV peak. In CV experiments, such oxidation processes result in a huge wave that does not permit a detailed investigation of the core-based oxidation process. The potential value for this process can be obtained from DPV, where the corresponding peak seems to involve less than one electron. Comparison with the behavior of the [Ru(Me₂bpy)₃]²⁺ model compound shows that (i) oxidation occurs at a more positive potential, (ii) reduction takes place at less negative potential, and (iii) the

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(21) Since [Ru(bpy)₂(4)]²⁺ was available as Cl⁻ salt, oxidation of the anion was also present at ca. +1.0 V vs SCE, but it did not interfere with the other processes.

Table 2. Electrochemical Data^a

compd	oxidation ^b		reduction ^b		
	branch-centered	Ru-centered	bpy-centered		
[Ru(bpy) ₂ (Me ₂ bpy)] ²⁺ ^c		+1.25 (1)	-1.36 (1)	-1.56 (1)	-1.81 (1)
[Ru(Me ₂ bpy) ₃] ²⁺ ^c		+1.13 (1)	-1.44 (1)	-1.62 (1)	-1.86 (1)
[Ru(bpy) ₂ (4)] ²⁺ ^d	+1.68 ^e	+1.54 ^e	+1.27 (1)	-1.35 (1)	-1.81 (1)
[Ru(bpy) ₂ (5)] ²⁺	+1.80 ^e	+1.56 ^e	+1.27 (1)	-1.35 (1)	<i>f</i>
[Ru(5) ₃] ²⁺	+1.57 ^{e,g}	+1.26 ^h	-1.33 ^h	-1.52 ^h	<i>i</i>

^a Argon-purged acetonitrile solution, room temperature, TBAPF₆ as supporting electrolyte, glassy carbon as working electrode. ^b Halfwave potential values in V vs SCE, unless otherwise noted; the number of exchanged electrons is indicated in parentheses. ^c Data from ref 20. ^d An irreversible oxidation process is observed at ca. +1.0 V, due to the chloride counterions of this complex. ^e Not fully reversible process; potential value estimated from DPV peaks. ^f The observation of this process is precluded by adsorption phenomena. ^g Very broad DPV peak. ^h Less than one electron is involved; see text for details. ⁱ A poorly defined process is observed at ca. -1.9 V.

observed processes are not fully reversible (as indicated by both CV and DPV for reduction, and from DPV for oxidation). This behavior, which has been observed for other dendrimers containing an electroactive core,¹¹ is that expected for encapsulated electroactive units.⁸

Quenching Reactions. It is well-known that electronically excited molecules can be quenched via energy or electron transfer by other molecules.²² In fluid solution a quenching reaction usually occurs during an encounter between the excited molecule and quencher. It follows that only the excited states that exhibit a reasonably long lifetime may undergo quenching processes. The lifetime of the ³MLCT luminescent excited state of Ru(II)-polypyridine complexes is long enough, even in aerated solutions,²³ to allow the occurrence of encounters when the quencher concentration is not extremely high.³

When a luminescent unit is buried into the core of a dendrimer, the rate of the quenching reactions is expected to be slower than for the free unit. Despite its potential interest for a variety of applications,⁸ this effect has been the object of only a few scattered investigations.^{10a-c,f-i} More attention has been paid to dendrimers as the supramolecular host environment for quenching reactions involving excited Ru-bpy type complexes and a variety of quenchers.²⁴

We have studied the quenching of the ³MLCT excited state of the [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ dendrimers by three compounds which were already known to quench the ³MLCT excited state of the [Ru(bpy)₃]²⁺ model compound:²⁵ methyl viologen dication (MV²⁺), tetrathiafulvalene (TTF), and anthraquinone-2,6-disulfonate anion (AQ²⁻). These three molecules do not possess excited states below the ³MLCT level of the [Ru(bpy)₃]²⁺ chromophoric unit, but are easy to reduce (MV²⁺ and AQ²⁻) or to oxidize (TTF). As a consequence, quenching can only take place by electron transfer. The experiments have been performed in acetonitrile solutions containing TBAPF₆ at 298 K.

Electron-transfer quenching reactions may involve the oxidation or the reduction of the excited state:



The thermodynamic driving force of the reaction can be estimated from the approximate equations:

$$\Delta G^\circ = -\Delta E^{\circ\circ} + E(A^+/A) - E(B/B^-) \quad (3)$$

$$\Delta G^\circ = -\Delta E^{\circ\circ} - E(A/A^-) + E(B^+/B) \quad (4)$$

where $\Delta E^{\circ\circ}$ is the excited-state spectroscopic energy (in eV) and $E(A^+/A)$, $E(B^+/B)$, $E(A/A^-)$, and $E(B/B^-)$ are the energies (in eV) of the respective one-electron reduction processes.²⁹ The [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ dendrimers and the [Ru(bpy)₃]²⁺ model compound have practically the same excited-state energy (about 2.12 eV),³⁰ and the same $E(A^+/A)$ and $E(A/A^-)$ potential values (Table 2 and ref 3). The values of $E(B/B^-)$ are -0.44²⁶ and -0.57 V²⁷ (vs SCE) for MV²⁺ and AQ²⁻, respectively, and the value of $E(B^+/B)$ is +0.33 V for TTF.²⁸ Insertion of these values in eqs 3 or 4 shows that (i) both oxidative quenching by MV²⁺ and AQ²⁻ and reductive quenching by TTF are thermodynamically allowed processes and (ii) the free energy change is practically the same for the quenching of the three dendrimers by the same quencher.

The rate constant k_q of a quenching process taking place by a dynamic mechanism can be calculated from the Stern-Volmer equation²²

$$\tau^\circ/\tau = I^\circ/I = 1 + k_q\tau^\circ[Q] \quad (5)$$

where τ° and I° are the excited-state lifetime and quantum yield in the absence of quencher, and τ and I are the same quantities measured in the presence of a quencher concentration [Q]. For each one of the [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ dendrimers, we have measured the luminescence lifetime ($\lambda_{\text{ex}} = 350$ nm; $\lambda_{\text{em}} > 500$ nm) and intensity ($\lambda_{\text{ex}} = 480$ nm; $\lambda_{\text{em}} = 610$ nm) for different concentrations of the three selected quenchers. In the case of TTF and AQ²⁻ the intensity measurements gave less precise results because of spectral overlap at high quencher concentration. When the interference by quencher absorption was not exceedingly high, the linear behavior

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(30) Approximately given^{29a} by the energy of the emission maximum at 77 K.

(22) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, 1978. (b) Gilbert, A.; Baggot, J. *Essentials of Molecular Photochemistry*; Blackwell: Oxford, 1991.

(23) Since in deaerated solution the excited-state lifetime is longer than in air-equilibrated solution (Table 1), it would appear that quenching can be more profitably investigated in the former condition. It should be noted, however, that the quenching constants are calculated from correlations of results obtained from sets of experiments. A not uniform deaeration of the various solutions is likely to introduce errors that are not present when the experiments are performed in air-equilibrated solution.

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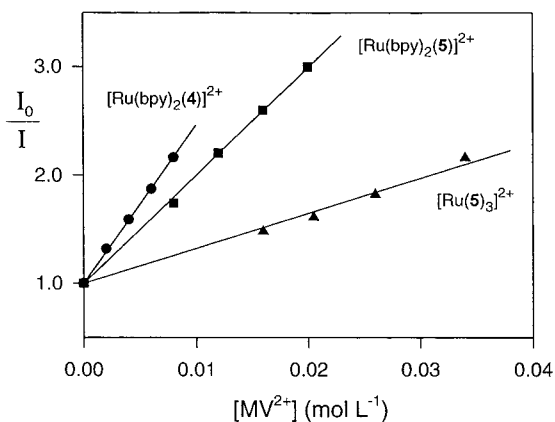


Figure 7. Stern–Volmer plots for the quenching of the [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ compounds by MV²⁺ in acetonitrile solutions containing 5 × 10^{−2} M TBAPF₆ at 298 K.

Table 3. Quenching Rate Constants *k_q* (M^{−1} s^{−1})

	MV ²⁺ ^a	TTF ^a	AQ ^{2−} ^a	O ₂ ^b
[Ru(bpy) ₃] ²⁺	1.4 × 10 ⁹	1.2 × 10 ¹⁰	1.2 × 10 ¹⁰	3 × 10 ⁹
[Ru(bpy) ₂ (4)] ²⁺	7.8 × 10 ⁸	9.9 × 10 ⁹	7.3 × 10 ⁹	3 × 10 ⁹
[Ru(bpy) ₂ (5)] ²⁺	5.8 × 10 ⁸	8.3 × 10 ⁹	8.6 × 10 ⁹	2 × 10 ⁹
[Ru(5) ₃] ²⁺	1.0 × 10 ⁸	5.4 × 10 ⁹	2.7 × 10 ⁹	7 × 10 ⁸

^a Acetonitrile solution containing 5 × 10^{−2} M TBAPF₆; *k_q* values obtained from eq 5 by using lifetimes from at least five different quencher concentrations; λ_{ex} = 350 nm, λ_{em} > 500 nm. ^b Acetonitrile solution; *k_q* values obtained from eq 5 by using the lifetimes of deaerated and air-equilibrated solutions.

predicted by eq 5 was obtained from intensity measurements, yielding the same *k_q* values obtained from lifetime measurements.³¹ Figure 7 shows the Stern–Volmer plots for the quenching of [Ru(bpy)₂(4)]²⁺, [Ru(bpy)₂(5)]²⁺, and [Ru(5)₃]²⁺ by MV²⁺. The values of the quenching constants are gathered in Table 3, where approximate *k_q* values for dioxygen quenching, obtained from eq 5 by using the lifetimes of deaerated and air-equilibrated solutions, are also shown.³² As one can see, there is an almost generalized decrease of the quenching constant with increasing number and size of the organic branches appended to the [Ru(bpy)₃]²⁺-type core. This effect, however, is not the same in all cases. For the positively charged MV²⁺ quencher, the rate constant decreases by more than 1 order of magnitude in going from [Ru(bpy)₃]²⁺ to the fully dendritic [Ru(5)₃]²⁺ compound, whereas the effect is smaller for the negatively charged AQ^{2−} quencher and very small (only a factor of 2) for the neutral TTF quencher. In going from [Ru(bpy)₃]²⁺ to [Ru(bpy)₂(4)]²⁺, a comparable decrease is observed for MV²⁺ and AQ^{2−}, and practically no effect for TTF and O₂. On increasing the length of the dendritic wedge in the Ru(bpy)₂-type species, a small decrease is observed for MV²⁺, TTF, and O₂, whereas for AQ^{2−} the rate constant increases slightly. Finally, replacement of the two unsubstituted bpy ligands of [Ru(bpy)₂(5)]²⁺ with dendritic ligands has a much larger effect for AQ^{2−} than for TTF. These results are difficult to rationalize, presumably because the rate constant of the quenching process is affected by several, sometimes contrasting, factors including the following: (i) dependence of the diffusion rate constant on the

(31) In the case of [Ru(5)₃]²⁺, when very high concentrations of quencher had to be used, the luminescence decay was not strictly monoexponential, and the τ⁰/τ plot showed some upward curvature. In such conditions, the very weak luminescence intensity, along with strong spectral interference of the quencher, prevented a more accurate analysis.

(32) The O₂ concentration in air-equilibrated acetonitrile solution is 1.9 × 10^{−3} M at 297 K: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993.

radius of the compound; (ii) protection of the dendritic branches toward diffusion of the quencher within the dendrimer volume; (iii) competition between solvent and dendritic branches for the solvation of the core; (iv) Coulombic attraction/repulsion between the positively charged core and the charged quenchers; and (v) folding of the dendritic branches of [Ru(bpy)₂(4)]²⁺ and [Ru(bpy)₂(5)]²⁺ around the unsubstituted bpy ligands. Clearly, the dynamic quenching of an excited state situated in the core of a dendrimer is a very complex process that needs further investigations. Anyway, a protection effect by the dendritic branches is certainly present and can perhaps be exploited for practical applications requiring an increase in the excited-state lifetime under particular experimental conditions.⁸

Conclusions

We have synthesized six new dendrimers built around a [Ru(bpy)₃]²⁺-type core and bearing up to 24 4'-*tert*-butylphenoxy or 48 benzyl units in the periphery. All compounds exhibit the characteristic ³MLCT luminescence of their [Ru(bpy)₃]²⁺-type core. However, several differences can be noted in the photo-physical parameters (particularly in the emission lifetime in aerated solution), related to different overall chemical composition of the compounds. For the three compounds containing the 4'-*tert*-butylphenoxy peripheral units, the electrochemical behavior and the excited-state electron-transfer quenching by cationic (MV²⁺), neutral (TTF), and anionic (AQ^{2−}) quenchers have been investigated. The core of the largest dendrimer shows an electrochemical behavior typical of encapsulated electroactive units. Oxidation of the electroactive units contained in the dendritic branches has also been observed. In general, the values of the quenching constants decrease with increasing number and size of the dendritic branches. For MV²⁺ the quenching constant is more than 1 order of magnitude smaller than that of the “naked” [Ru(bpy)₃]²⁺ complex. The results show that several, sometimes contrasting, factors intervene in determining the actual value of the quenching rate constant.

Experimental Section

Materials, Methods, and Measurements. Chemicals were purchased from Aldrich and Fluka and used as received. 4,4'-Dimethyl-2,2'-bipyridine, the monomeric branching units **6**, **7**, and **8**, and 1-bromo-3-(4'-*tert*-butylphenoxy)propane (**12**) were prepared according to published literature.¹³ Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F254 (Merck 1.05554). The sheets were examined by UV light (λ = 254 nm). Column chromatography was carried out with silica gel 60 (Merck 15101). Melting points were determined on a Kofler microscope heater (Reichert, Vienna) and are not corrected. Mass spectra were obtained on an A.E.I. (Manchester, UK) MS 50 operating in electron impact mode (EIMS). MALDI spectra were recorded on a TofSpec E (Micromass, Manchester, UK). The ¹H and ¹³C NMR spectra were recorded on a Bruker AM 250 (250 MHz (¹H), 62.9 MHz (¹³C)) or on a Bruker AM 400 (400 MHz (¹H), 100.6 MHz (¹³C)). A description of the equipment and procedures employed for the absorption, luminescence, and electrochemical experiments can be found in ref 33 and in the Supporting Information.

X-ray Structural Analysis of 4,4'-Bis[[3',5''-bis[3''',5'''-bis(benzyloxy)]benzyloxy]phenylethyl]-2,2'-bipyridine (2). Crystal data: C₁₁₀H₉₆N₂O₁₂, *M* = 1637.89 g mol^{−1}, colorless crystal of 0.20 × 0.10 × 0.08 mm, triclinic, space group *P* $\bar{1}$ (No. 2), *a* = 10.096(1) Å, *b* = 11.270(1) Å, *c* = 20.127(1) Å, α = 81.47(1)°, β = 75.94(1)°, γ = 73.40(1)°, *V* = 2121.2(3) Å³, *Z* = 1, *d*_{calc} = 1.282 Mg m^{−3}, μ(Mo Kα)

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= 0.083 mm⁻¹, $F(000) = 866$; Nonius Kappa CCD diffractometer; θ range for data collection, 1.89–28.20°; index ranges, $-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$; temperature, 123(2) K; wavelength, 0.71073 Å (Mo K α); monochromator, graphite; reflections collected, 12136, independent reflections, 6836 ($R_{\text{int}} = 0.061$); refinement method, full-matrix least squares on F^2 ; data/restraints/parameters = 6828/0/560; goodness-of-fit on F^2 , 0.763; final R indices [$I > 2\sigma(I)$], $R1 = 0.039$, $wR2 = 0.071$; R indices (all data), $R1 = 0.113$, $wR2 = 0.081$; largest difference peak and hole, 0.147 and $-0.179 \text{ e}\text{\AA}^{-3}$. The structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 114186).

Acknowledgment. This work was supported in Germany by Volkswagen Stiftung and in Italy by MURST (Supramo-

lecular Devices Project), University of Bologna (Funds for Selected Research Topics), and EU (TMR grant FMRX-CT96-0031). G. C. Azzellini wishes to thank Fapesp (Fundação de Amparo à Pesquisa do Estado de São Paulo—Brazil) for financial support.

Supporting Information Available: Synthetic procedures, characterization, equipments and methods for absorption, luminescence and electrochemical experiments, and X-ray crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA990430T