Dendritic Bipyridine Ligands and Their Tris(bipyridine)ruthenium(II) Chelates—Syntheses, Absorption Spectra, and Photophysical Properties

Jörg Issberner, Fritz Vögtle,* Luisa De Cola, and Vincenzo Balzani*

Abstract: Several synthetic strategies have been explored to prepare dendrimers having the $[Ru(bpy)_3]^{2+}$ complex as their core (bpy = 2,2′-bipyridine). Dendritic ligands have been synthesized by attaching branches in the 4,4′-positions of bpy. The largest dendritic bipyridine ligand contains 54 peripherical methylester units. Four Ru^{II} dendritic complexes have been prepared. Their absorption and emission spectra are very similar to those of the unsubstituted parent Ru^{II}–bipyridine complexes. The large dendritic complexes, however, exhibit a more intense emission and a longer excited-state lifetime than $[Ru(bpy)_3]^{2+}$ in aerated solutions. This is due to the shielding effect of the dendrimer branches on the Ru–bipyridine core, which limits the quenching effect of molecular oxygen. For the largest dendritic complex, which contains 54 peripherical methylester units, the excited-state lifetime in aerated acetonitrile solution is longer than 1 μs, and the rate constant for dioxygen quenching is twelve times smaller than for $[Ru(bpy)_3]^{2+}$.

Keywords
bipyridine ligands · dendrimers · dioxygen quenching · luminescence · ruthenium

Introduction

Well-defined, highly branched, and nanoscopic are the terms most often used to describe the characteristics of cascade molecules,[1] also called arborols,[2] or, more frequently, dendrimers.[3] After the first example prepared 18 years ago,[1] there has been an enormous number of publications dealing with dendrimers, particularly in the last three years.[4] Nevertheless, dendrimers continue to reveal new potential. Recently dendrimers have also become commercially available. Manufacturers of fine chemicals use the divergent synthetic approach to produce polypropyleneamine and polyamidoamine (PAMAM™) dendrimers[3] in large scale.

Owing to the high but well-defined number of functional end groups and the presence of internal cavities, dendrimers offer a wide range of unique physical and chemical properties. A particularly interesting class of dendrimers is that containing metals,[5–11] because in metal-based building blocks it is possible to incorporate specific "pieces of information" such as accessible redox potentials and low-energy excited states. Suitably designed dendrimers containing up to 22 Ru^{II} and/or Os^{II} metal complexes absorb and emit visible light, undergo a great number of redox processes, and can function as antennas for light harvesting.[5] Furthermore many dendrimers have been prepared which contain metal complexes only at their surface.[9] In contrast, only a few examples have been described of dendrimers in which the only metal center is at the core.[10] Dendrimers based on a metal porphyrin core[11] have been reported to exhibit quite interesting electrochemical[11a] and photophysical[11c] properties.

The complexes of the $[Ru(bpy)_3]^{2+}$ family (bpy = 2,2′-bipyridine) are know to show a unique combination of photophysical and redox properties.[12] Because of these porperties, they are extensively used as photocatalysts,[13] reactants in intermolecular[12] and intramolecular[14] energy- and electron-transfer processes, building blocks for the construction of supramolecular species,[15] and luminescence labels for immunoassays.[16]

In this paper we report the synthesis of bpy-based dendritic ligands and their Ru^{II} complexes. The absorption spectra and luminescence properties of the dendritic complexes and of suitable model compounds are compared and discussed. We also show that in the larger dendritic complexes (higher generations) the shielding effect of the dendrimer branches on the $[Ru(bpy)_3]^{2+}$ core strongly decreases the quenching effect of molecular oxygen.

[*] Prof. Dr. F. Vögtle, Dipl.-Chem. J. Issberner
Institut für Organische Chemie und Biochemie der Universität
Gerhard Domagk Str. 1, D-53121 Bonn (Germany)
Fax: Int. code +(228)73-5662
e-mail: voegtle@plumbum.chemie.uni-bonn.de
Prof. Dr. V. Balzani, Dr. L. De Cola
Università di Bologna, Dipartimento di Chimica "G. Ciamician"
Via Selmi 2, I-40126 Bologna (Italy)
Fax: Int. code +(51)259-456
e-mail: vbalzani@ciam.unibo.it

Results and Discussion

Synthesis: The synthesis of the new dendritic ligands was performed by a divergent strategy, using 4,4′-functionalized 2,2′-bipyridines as starting materials (Scheme 1). Following the pro-

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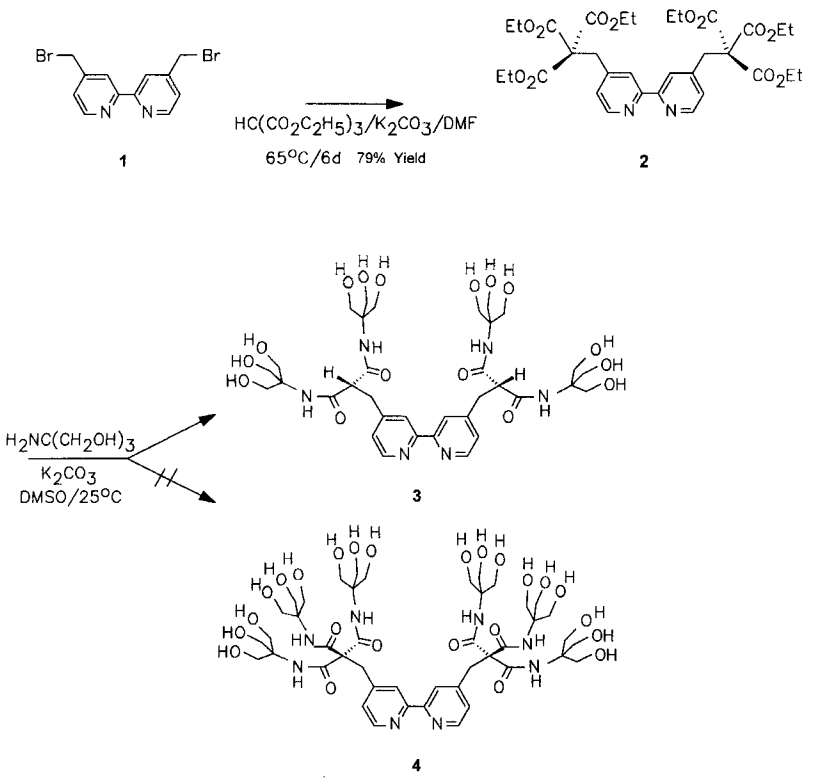
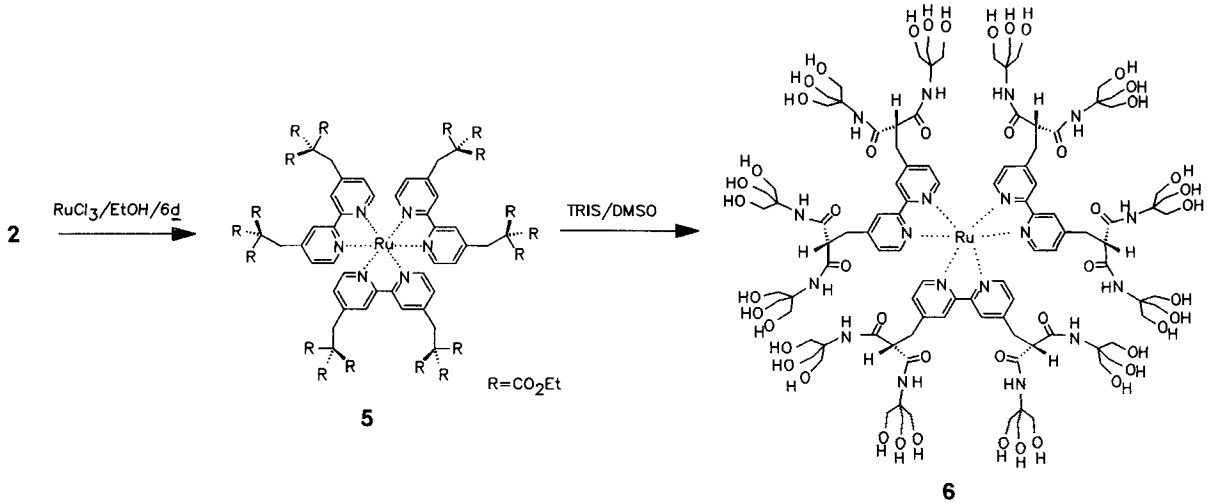


Scheme 1.

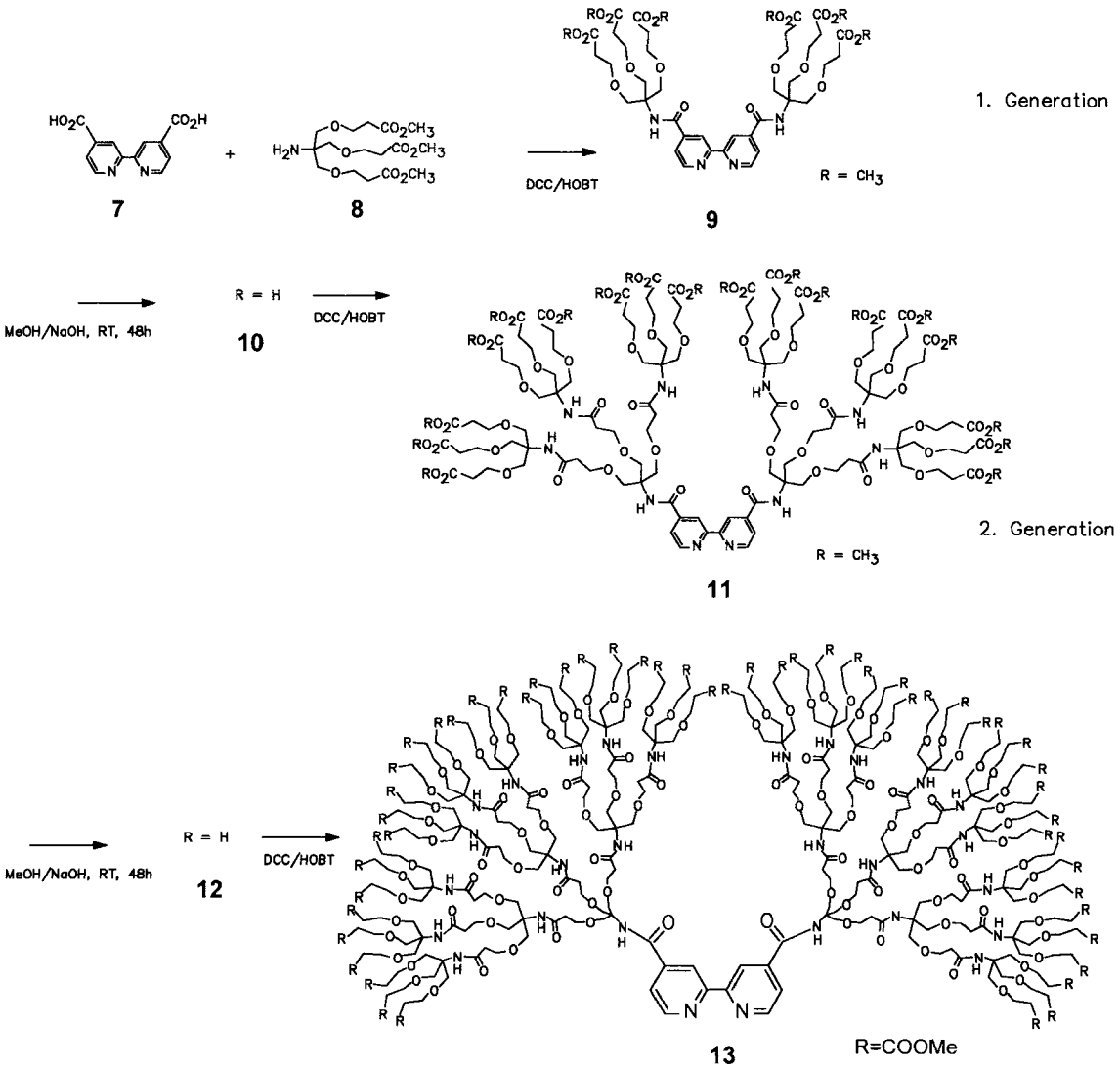
cedure reported by Newkome et al.,[17, 18] 4,4′-bis(bromomethyl)-2,2′-bipyridine[19] (**1**) was treated with triethyl methanetricarboxylate to obtain the dendritic hexaester **2** as a colorless crystalline solid. Further reaction of **2** with the monomeric branching unit tris(hydroxymethyl)aminomethane (Tris) led to formation of **3**. This dendritic bipyridine ligand bears twelve hydrophilic hydroxyl functions on its surface and is as a very hygroscopic colorless solid. The structures of **2** and **3** were readily deduced from ^{1}H and ^{13}C NMR spectra as well as from mass spectrometric analyses. The positive fast atom bombardment (FAB) mass spectrum of **3** shows the protonated molecule ion at *m/z* 801.3 and peaks at *m/z* 855.3 and 871.3 (molecular ion $+2O+Na^+$, molecular ion $+2O+K^+$). The decarboxylation reported previously[18b] was confirmed, and the desired product **4** could therefore not be obtained. Unfortunately, attempts to complex ligand **3** with Ru^{II} were unsuccessful. We assume that the dendritic surface is quite hydrophilic and that there is a strong interaction between the hydroxy functions of the dendritic ligand **3** and the Ru^{II} cation. A further possible explanation is the aggregation of the ligand, as has been shown for some related arboroles,[18] which prevents the nitrogens of the bpy ligands from coordinating the Ru^{II} ion.

A different synthetic pathway is shown in Scheme 2. The dendritic hexaester **2** was first complexed with Ru^{II} to yield the complex **5**. Subsequent reaction with Tris in DMSO at room temperature gave the metallo-"micellanol"[20] **6**. The identity and integrity of the dendritic tris(bipyridine)ruthenium(II) complex **6** were proven by ^{1}H and ^{13}C NMR spectroscopy and by means of the high-field shift of the bipyridine protons in the 6,6′-positions. Compounds **5** and **6** show the characteristic absorption and emission spectra of Ru–bipyridine complexes (vide infra). Further growth of the dendrimer beyond generation one was not possible by this synthetic method.

An alternative iterative synthesis was then pursued to obtain dendritic bipyridine ligands of higher generation and molar mass by using 2,2′-bipyridine-4,4′-dicarboxylic acid (**7**) as starting material (Scheme 3). A similar synthetic approach was previously reported[21] for the preparation of metal porphyrins. Following standard methods, well-known in peptide chemistry, the diacid **7** was treated with the monomeric branching unit **8** to yield the hexaester **9** (Scheme 3). This hexaester was readily hydrolyzed with a NaOH solution in methanol/water to give the hygroscopic hexaacid **10**, which could again be treated with the monomeric branching unit **8**. The first-, second-, and third-generation dendrimers (**9**, **11**, and **13**, respectively) are colorless oils, which were purified by columm chromatography. The largest dendritic bipyridine **13** contains 54 peripherical methyl ester units and has a molar mass



Scheme 2. TRIS: tris(hydroxymethyl)aminomethane.



Scheme 3. DCC: dicyclohexylcarbodiimide; HOBT: 1-hydroxy-1*H*-benzotriazole hydrate.

of 10 kDa. The formation of the dendrimers was established by ^{1}H and ^{13}C NMR spectroscopy and by positive-FAB and MALDI-TOF mass spectrometry.

The tris(bipyridine)ruthenium(II) chelates **14** and **15** were synthesized from the dendritic bipyridines **9** and **11**, respectively. Under the experimental conditions used (refluxing the ligand with Ru^{III} chloride in ethanol for 14 days) complete transesterification (-OMe to -OEt) occurred in the case of the first-generation dendrimer, whereas for the second-generation dendrimer only a small amount of the transesterification product was observed. The reason for this difference in behavior is probably the fact that the second-generation dendrimer has a denser surface than the first-generation dendrimer.

Remarkably the complexation of Ru^{II} with the third-generation ligand **13** did not proceed smoothly under the same experimental conditions. The characteristic metal-to-ligand charge-transfer (MLCT) bands in the visible region of the Ru^{II}–polypyridine complexes could hardly be observed. We assume that the conversion from the transoid structure of the free ligand to the cisoid conformation needed for metal chelation is hindered by the dendritic branches. Another possible explanation is the competition of the donor centers in the dendritic part of the ligand with the bpy nitrogen atoms.

Spectroscopic and Photophysical Properties: The absorption and emission spectra of compounds **6** in water and **15** in acetonitrile solution at 298 K are displayed in Figure 1, which also shows the absorption and emission spectra of the parent $[Ru(bpy)_3]^{2+}$ complex in acetonitrile solution. Table 1 gives a summary of the spectroscopic and photophysical data for compounds **5**, **6**, **14**, and **15**, and for the parent $[Ru(bpy)_3]^{2+}$ complex.

Since the dendrimer branches do not possess chromophoric groups, the absorption spectra of the dendritic complexes show exclusively the bpy-centered bands in the UV region and the metal-to-ligand charge-transfer (MLCT) bands in the visible region, characteristic of the Ru^{II}–polypyridine complexes. In compounds **5** and **6**, where the groups directly linked to the bpy ligand are saturated hydrocarbons, the maximum of the visible band is shifted less than in the case of compounds **14** and **15**, where the substituents are amido groups. The length of the dendrimer branches does not seem to play an important role in the absorption spectra.

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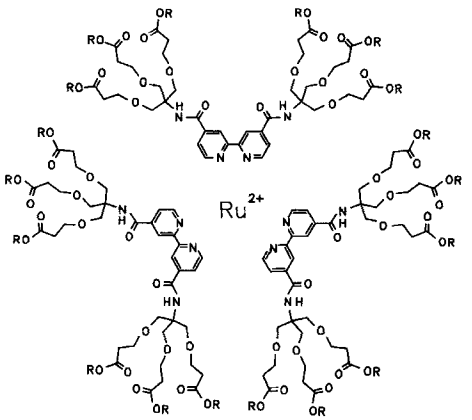
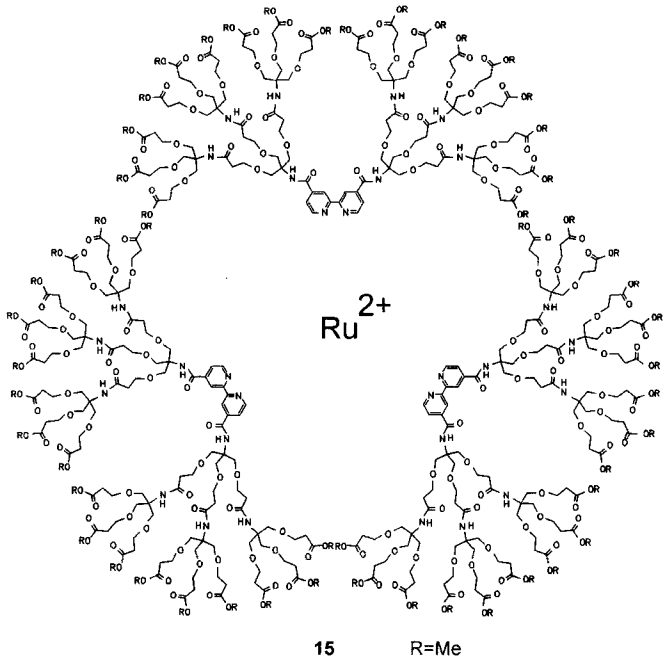


14 R=Et



15 R=Me

In Ru–polypyridine complexes emission originates from the lowest, formally spin-forbidden, ^{3}MLCT level. The wavelength of the maximum of the emission band is clearly more sensitive to the chemical nature of the group directly linked to the bpy ligand than to the length of the dendrimer branches. For compounds **5** and **6** the emission maximum at 298 K is very close to that of $[Ru(bpy)_3]^{2+}$, whereas for compounds **14** and **15** the emission maximum is red-shifted, as is the case for amido-substituted bpy complexes.[114a] The same effect can also be observed in a rigid matrix at 77 K. The emission lifetime in a rigid matrix at 77 K is very similar for all the compounds examined.

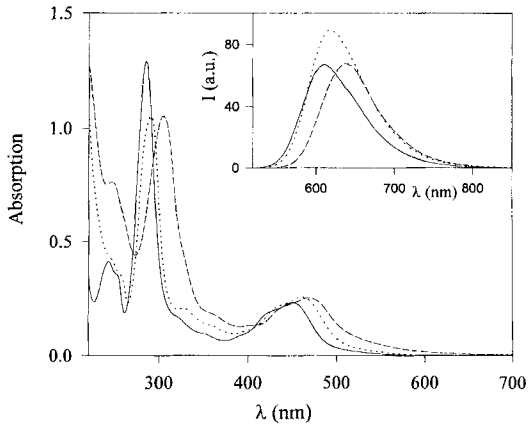


Figure 1. Absorption and emission (inset) spectra, at room temperature, of $[Ru(bpy)_3]^{2+}$ in acetonitrile solution (—), compound **6** in water (· · · · ·), and compound **15** in acetonitrile solution (– – –). The concentration is 1.6×10^{-5} M in all cases. The emission intensities are given in arbitrary units; quantum yields are given in Table 1.

The most interesting results concern the excited-state lifetime and the luminescence quantum yield in fluid solution at 298 K. In air-equilibrated solution, which is the usual condition for most applications, all the novel compounds exhibit a more intense emission and a longer excited-state lifetime than the parent $[Ru(bpy)_3]^{2+}$ complex. In the case of compound **15**, the excited-state lifetime is more than five times longer than for $[Ru(bpy)_3]^{2+}$. This is due to both the chemical nature of the group directly linked to the bpy ligand and the length of the dendrimer branches. The latter effect becomes particularly clear if we compare the data of compounds **14** and **15**, where the groups directly linked to the bpy ligands are the same. In deaerated solutions the lifetime of **15** is shorter than that of **14**, whereas in aerated solutions the situation is reversed. This indicates that the increase in length of the branches slightly decreases the intrinsic lifetime of the Ru–bpy core, but in aerated solution the excited state of the compound with longer branches **15** is less quenched by dioxygen than the excited state of the smaller compound **14**. On going from **5** to **6** the effect is even larger, but it

Table 1. Spectroscopic and photophysical data for the tris(bipyridine)ruthenium(II) complexes.

	Absorption [a]	Emission					
		298 K [a]			77 K [b]		
	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)	λ_{max}, nm	τ, μs	$\Phi \times 10^2$	λ_{max}, nm	τ, μs	k_q [c], $M^{-1}s^{-1}$
$[Ru(bpy)_3]^{2+}$	450 (13400)	611	172 [d]	1.6 [d]	582	4.8	2.5×10^9
			990 [e]	6.2 [e]			
5	459 (14100)	611	287	3.5	583	5.4	1.3×10^9
			960 [e]	10 [e]			
6 [f]	460 (15300)	618	580	3.7	– [h]	– [h]	1.3×10^9
			730 [e]	5.1 [e]			
14	465 ([g])	630	760	7.0	602	5.5	0.43×10^9
			1940 [e]	12 [e]			
15	468 ([g])	638	1010	6.2	606	5.5	0.22×10^9
			1740 [e]	13 [e]			

[a] Acetonitrile solution, unless noted otherwise. [b] Butyronitrile solution, unless noted otherwise. [c] Rate constant for quenching by dioxygen at 298 K. [d] Aerated solution. [e] Deaerated solution. [f] H_2O solution. [g] Oily compound, difficult to weigh. [h] Not measured.

should be pointed out that the latter compound was examined in a different solvent.

The quenching of the luminescent ^{3}MLCT level of Ru^{II}–polypyridine compounds by dioxygen contained in the solvent is a well-documented phenomenon.[22] Although some of the details of the quenching mechanism are still the object of controversy, energy transfer and electron transfer are both involved. The quenching rate constant k_q can be calculated from the Stern–Volmer equation[12, 23] [Eq. (1)], where τ° and τ are the

$$\tau^\circ/\tau = 1 + k_q\tau^\circ[O_2] \quad (1)$$

excited-state lifetimes in deaerated and air-equilibrated solutions, respectively, and $[O_2]$ is the concentration of dioxygen in the air-equilibrated solution (1.9×10^{-3} M in acetonitrile and 0.29×10^{-3} M in water at 298 K).[24] The k_q values obtained by Equation (1) for the various compounds are listed in the last column of Table 1. The quenching constant decreases by a factor of about 6 on going from $[Ru(bpy)_3]^{2+}$ to compound **14**, and further decreases by a factor of 2 from **14** to **15**. The less effective quenching effect of dioxygen on the luminescent ^{3}MLCT level of the Ru^{II}–bpy core in the dendrimers can be assigned to one or more of the following factors: 1) decrease in the diffusion rate constant with the increasing volume of the compound; 2) lower solubility of dioxygen in the interior of the dendrimer; 3) preferential "solvation" of the metal-complex core by the dendrimer branches, hindering suitable orbital overlap for energy or electron transfer.

Conclusions

We have explored several strategies to prepare Ru^{II} complexes of dendritic bipyridine ligands. By an iterative synthesis based on 2,2′-bipyridine-4,4′-dicarboxylic acid as starting material we succeeded in preparing bpy-based dendrimers up to the third generation. By using dendritic bpy ligands, four new Ru^{II} complexes were prepared. These complexes exhibit the expected absorption and emission properties of Ru^{II}–polypyridine compounds. However, their excited-state lifetime in air-equilibrated solutions is longer than expected. A comparative analysis of the results obtained shows that the dendrimer branches protect the Ru–bpy core from dioxygen quenching. A long lifetime of the luminescent excited state 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 timescale.[25] We plan to perform systematic investigations by using a variety of quenchers in order to elucidate the details of the protection effect caused by the dendrimer branches.

Experimental Section

Materials and Methods: Chemicals were purchased from Aldrich and used as received except for CH_2Cl_2, which was dried using molecular sieves 4 Å. 4,4′-Bis(bromomethyl)-2,2′-bipyridine (**1**), 4,4-bis(carboxylic acid)-2,2′-bipyridine[19] (**7**), and the monomeric branching unit **8** were prepared according to published literature.[21b] Thin layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (Merck 1.05554). The sheets were examined by UV light (λ = 254 nm). Column chromatography was carried out using silica gel 60 (Merck 15101). Melting points were determined on a Kofler microscope heater (Reichert, Wien) and are not corrected. Microanalyses were performed by the Microanalytical Department at the "Institut für Organische Chemie und Biochemie der Universität Bonn".[26] Low-resolution mass spectra were obtained on an A. E. I. (Manchester, UK) MS 50 operating in electron impact mode (EIMS); fast atom bombardment mass spectra (FAB-MS) were recorded on a Kratos Concept 1H spectrometer. The matrix used was *m*-nitrobenzyl alcohol. MALDI spectra were recorded on a Kratos Kompakt MALDI3, with 9-nitroanthracene, 5-chlorosalicylic acid, or 1,8-dihydroxyanthracene matrices. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 250 (250 MHz (^{1}H), 62.9 MHz (^{13}C)) or on a Bruker AM 400 (400 MHz (^{1}H), 100.6 MHz (^{13}C)) spectrometer. Absorption spectra were measured in acetonitrile solution, unless otherwise noted, at room temperature with a Perkin-Elmer Lambda 6 spectrophotometer. Corrected luminescence experiments were performed in air-equilibrated acetonitrile or water solution at room temperature and in freshly distilled butyronitrile at 77 K. Luminescence spectra were obtained with a Perkin-Elmer LS 50 spectrofluorimeter. Luminescence decay measurements were performed with an Edinburgh single photon counting machine. Analysis of the decay curves was performed by employing either purpose-written nonlinear iterative programs or commercial programs. When necessary, deaeration of the solutions was performed by repeated freeze–thaw–freeze cycles. Luminescence quantum yields were measured following the method described by Demas and Crosby[28] using $[Ru(bpy)_3]^{2+}$ as a standard ($\Phi = 2.8\times10^{-2}$ in aerated water solution).[29] Experimental errors: λ, ±2 nm; ε, ±10%; τ, ±5%; ϕ, ±20%. The nomenclature used to indicate the dendrimers is that suggested by Newkome et al.[30]

6-Cascade 2: A solution of 4,4′-bis(bromomethyl)-2,2′-bipyridine (2.00 g, 5.8 mmol) in dry toluene/DMF (40 mL, 3/2 *v*/*v*) was added to a suspension of triethylmethanetricarboxylate (6.85 g, 29.5 mmol) and potassium carbonate (4.10 g, 29.7 mmol) in dry toluene/DMF (50 mL, 3/2 *v*/*v*) at 50 °C. The reaction mixture was stirred for 4 d at 65 °C and then filtered. The solvent was removed in vacuo, and the remaining residue was dissolved in toluene (100 mL) and washed with brine, 7% NaOH, and brine. The organic layer was dried (Na_2SO_4), and the solvent was removed in vacuo to yield **2** as colorless crystals. 2.95 g (79% yield). M.p.: 114 °C (cyclohexane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.21 (t, 18H, ^3J(H,H) = 7.2 Hz; CH_3), 3.57 (s, 4H; CH_2), 4.22 (q, 12H, ^3J(H,H) = 7.2 Hz; CH_2), 7.25 (dd, 2H, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.2 Hz; arom. CH), 8.29 (d, 2H, ^4J(H,H) = 1.2 Hz; arom. CH), 8.51 (dd, 2H, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.2 Hz; arom. CH); ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 13.96 (CH_3), 38.1 (CH_2), 62.6 (H_2CO), 66.5 (CC=O), 123.4, 125.6, 145.9, 149.0, 155 (pyridine C, CH), 166.5 (C=O); MS-50 (180 °C, 70 eV, 300 mA): *m*/*z* (%): found: 644.2585 (Dev. 0.4, 66.8%), $C_{32}H_{40}N_2O_{12}$ (644.682): calcd. C 59.62, H 6.25, N 4.35; found C 59.70, H 6.32, N 4.31.

12-Cascade 3: Potassium carbonate (967 mg, 7.00 mmol) was added to a solution of the hexaester **2** (752.7 mg, 1.17 mmol) and α,α,α-tris(hydroxymethyl)methylamine (Tris) (848.6 mg, 7.00 mmol) in dry DMSO (10 mL). This reaction mixture was stirred for 12 h at room temperature, the solvent removed in vacuo, and the residue dissolved in a small quantity of DMSO/H_2O. After addition of dry acetone **3** precipitated as a hygroscopic colorless solid; 652 mg (67% yield). ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = 3.08 (s, 4H, CH_2), 3.22 (s, 6H, CH), 3.47 (d, 8H, ^2J(H,H) = 10.8 Hz; CH_2), 3.55 (d, 8H, ^2J(H,H) = 11.1 Hz; CH_2), 4.6–5.1 (brs, OH), 7.27 (d, 2H, ^3J(H,H) = 4.8 Hz; arom. CH), 7.4–7.7 (s, NH), 8.23 (s, 2H, arom. CH), 8.51 (d, 2H, ^3J(H,H) = 4.8 Hz; arom. CH); ^{13}C NMR (75.47 MHz, [D$_6$]DMSO, 25 °C): δ = 30.7 (CH_2), 59.7 (CH_2OH), 61.7 (CR_4), 63.34 (CR_4), 78.5 (CCO), 122.8, 126.0, 146.0, 148.7, 155.0 (pyridine C, CH), 170.2 (CONH); FAB$^+$-MS (m-NBA): *m*/*z*: 801.3, 833,3, 855.3, 871.3, 965.2 ([*M*+H]$^+$, [*M*+2O]$^+$[*M*+2O+Na]$^+$, [*M*+2O+K]$^+$, [*M*+2O+Cs]$^+$), $C_{34}H_{52}N_6O_{16}$ (800.82).

18-Cascade 5: $RuCl_3\cdot3H_2O$ (65 mg, 0.25 mmol) was added to a solution of **2** (488 mg, 0.76 mmol) in ethanol (40 mL). The reaction mixture was refluxed for 6 d. The solvent was removed in vacuo, and the residue dissolved in hot water. After addition of NH_4PF_6 an orange solid precipitated. The solid was filtered and washed several times with brine and dried in vacuo to give **5**. Yield (54%), M.p. 63–65 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.20 (t, 54H, ^3J(H,H) = 7.1 Hz; CH_3), 3.64 (s, 12H, CH_2), 4.24 (q, 36H, ^3J(H,H) = 7.1 Hz; CH_2), 7.36 (dd, 6H, ^3J(H,H) = 4.4 Hz, ^4J(H,H) = 1.51 Hz; arom. CH), 7.49 (d, 6H, ^3J(H,H) = 5.8 Hz; arom. CH), 8.25 (d, 6H, ^4J(H,H) = 1.5 Hz; arom. CH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C):

0947-6539/97/0305-0710 $ 17.50+.50/0 Chem. Eur. J. 1997, 3, No. 5

δ = 13.8 (CH_3), 37.4 (CH_2), 62.9 (H_2CO), 66.1 (CCO), 125.9, 130.3, 147.8, 150.7, 155.9 (pyridine C, CH), 166.0 (C=O); FAB$^+$-MS (m-NBA): *m/z*: 2179.7, 2107.6 ($M^+ = [C_{96}H_{120}N_6O_{36}RuPF_6]^+$, $M^+ - C_3H_5O_2$), 2034.7, 1961.6 ($M^+ = [C_{96}H_{120}N_6O_{36}Ru]^+$, $M^+ - C_3H_5O_2$) 1017.4 (M^{2+}); $[C_{96}H_{120}N_6O_{36}Ru](PF_6)_2$ (2325.04).

36-Cascade 6: Potassium carbonate (321 mg, 2.3 mmol) was added to a solution of the ruthenium(II) complex **5** (300 mg, 0.13 mmol) and "Tris" (Tris(hydroxymethyl)aminomethane) (281 mg, 2.3 mmol) in dry DMSO (5 mL). The reaction mixture was stirred for 15 h at room temperature, and filtered. The solvent was removed in vacuo, and the residue dissolved in a small quantity of DMSO/H_2O. After addition of dry acetone an orange-red solid precipitated (304 mg, 83%). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 3.44 (s, 12H), 3.55–3.71 (m, 72H, CH_2OH), 7.27 (m, 6H, pyridyl H), 7.6 (m, 6H, arom. H), 8.38 (mbr, 6H, arom. H); ^{13}C NMR (100.6 MHz, D_2O, 25 °C): δ = 35.4 ($ArCH_2$), 61.4 (CH_2OH), 63.2, 62.34 (CR_4), 63.26 (CH_2OH), 63.75 (CH_2), 122.8, 123.0, 126.0, 126.2, 155.0 (pyridine-C,CH), 171.4 (CONH); $C_{102}H_{156}N_{18}O_{48}RuP_2F_{12}$ (2793.45).

6-Cascade 9: 4,4′-Bis(carboxy)-2,2′-bipyridine (**7**) (0.98 g, 4 mmol) and 1-hydroxy-1*H*-benzotriazole hydrate (HOBT) (1.10 g, 8 mmol) were dissolved in dry THF (60 mL). This solution was cooled to −5 °C, and 1,1,1-tris(carboxyethoxymethyl)aminomethane trimethyl ester (**8**) (3.03 g, 8 mmol) was added. A solution of dicyclohexylcarbodiimide (DCC) (1.75 g, 8.5 mmol) in dry THF (15 mL) was added at −5 °C by means of a syringe. This reaction mixture was stirred for 2 h at −5 °C and warmed to room temperature overnight. The precipitate was filtered off, and the solvent removed in vacuo. The residue was dissolved in AcOEt and washed twice with sat. $NaHCO_3$ solution, citric acid solution (2N), and brine. The organic layer was dried (Na_2SO_4) and the solvent removed in vacuo to yield **9** as a colorless oil. 2.4 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.50 (t, 12H, ^3J(H,H) = 6.2 Hz, CH_2), 3.53 (s, 18H, CH_3), 3.66 (t, 12H, ^3J(H,H) = 6.2 Hz, CH_2), 3.76 (s, 12H, CH_2), 6.74 (s, 2H, NH), 7.65 (dd, 2H, ^3J(H,H) = 5.0 Hz, ^4J(H,H) = 1.6 Hz; arom. CH), 8.64 (d, 2H, ^4J(H,H) = 1.6 Hz, arom. CH), 8.74 (d, 2H, ^3J(H,H) = 5.0 Hz; arom. CH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 34.6 (CH_2), 51.5 (CH_3), 60.3 (Cq), 66.7 (CH_2), 68.9 (CH_2), 118.4, 121.5, 143.5, 149.8, 156.2 (pyridine-C, CH), 165.5 (CONH), 172.0 (CO_2Me); EI: *m/z* : 935 ($[M - CH_3O]^+$, 100); $C_{44}H_{62}N_4O_{20}$ (967.99).

6-Cascade 10: A solution of the dendritic hexaester **9** (1.00 g, 1.03 mmol) in methanol (75 mL) and NaOH (25 mL, 10% in water) was stirred at room temperature 48 h. The pH of the solution was adjusted to 5, and the solvent was removed in vacuo. The residue was dissolved in THF and filtered. After removal of the solvent in vacuo compound **10** was obtained as a colorless very hygroscopic solid (0.87 g, 95%). ^{1}H NMR (250 MHz, [D$_8$]THF, 25 °C): δ = 2.46 (t, 12H, ^3J(H,H) = 6.3 Hz, CH_2), 3.60 (t, 12H, ^3J(H,H) = 6.2 Hz, CH_2), 3.73 (s, 12H, CH_2), 7.74 (dd, 2H, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.6 Hz; arom. H), 7.8 (s, 2H; NH), 8.66 (d, 2H, ^4J(H,H) = 1.6 Hz; arom. CH), 8.46 (d, 2H, ^3J(H,H) = 5.15 Hz; arom. CH), ^{13}C NMR (62.7 MHz, [D$_8$]THF, 25 °C): δ = 35.0, 61.1, 67.1, 68.2, 120.8, 128.6, 136.6, 149.3, 157.5 (pyridine-C, CH), 165.7 (CONH), 172.9 (CO_2H); FAB$^+$-MS (m-NBA): *m/z* (%): 883.2 ($[M+H]^+$, 100); 905.2 ($[M+Na]^+$, 10), 838.2 ($[M - COOH]^+$, 10); $C_{38}H_{50}N_4O_{20}$ (882.3).

18-Cascade 11: The dendritic hexaacid **10** (0.98 g, 4 mmol) and HOBT (0.8 g, 5.2 mmol) were dissolved in dry THF (40 mL). This solution was cooled to −5 °C, and **8** (2.00 g, 5.3 mmol) was added. A solution of DCC (1.2 g, 5.8 mmol) in dry THF (15 mL) was added at −5 °C by means of a syringe. The reaction mixture was stirred for 2 h at −5 °C and warmed to room temperature overnight. After the mixture had been stirred for 3 d at room temperature, the precipitate was filtered off and the solvent removed in vacuo. The residue was dissolved in AcOEt and washed twice with sat. $NaHCO_3$ solution, citric acid solution (2N), and brine. The organic layer was dried (Na_2SO_4) and the solvent was removed in vacuo to yield **11** as a colorless oil. 1.73g (76%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.41–2.57 (t, 48H, ^3J(H,H) = 6.3 Hz, CH_2), 3.51–3.70 (m, 150H, OCH_2CH_2, CH_2O, OCH_3), 6.1–6.2 (brs, 8H, NH), 7.7 (brs,. 2H, arom. CH), 8.6–8.8 (m, 4H, arom. CH), ^{13}C NMR (62.7 MHz, $CDCl_3$, 25 °C): δ = 34.9, 35.0, 37.6, 51.8, 60.1, 61.0, 67.0, 67.9, 69.5, 69.9, 118.9, 121.6, 143.6, 149.8, 156.2 (pyridine C, CH), 165.5 (CONH), 170.9 (CONH), 172.2 (CO_2Me); FAB$^+$-MS (m-NBA): *m/z* (%): 3051.7 ($[M+H]^+$, 100); 2965.9 (70); $C_{134}H_{212}N_{10}O_{11}$ (3051.18) calcd. C 52.0, H 7.00, N 4.59; found C 52.43, H 7.11, N 4.65.

18-Cascade 12: A solution of **11** (1.00 g, 1.03 mmol) in methanol (75 mL) and NaOH (25 mL, 10% in water) was stirred at room temperature 48 h. The pH of the solution was adjusted to 5, and the solvent was removed in vacuo. The residue was dissolved in THF and filtered. After removal of the solvent in vacuo compound **12** was obtained as a colorless very hygroscopic solid (0.87g, 95%), which was used for further reaction without purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.35–2.6 (t, 48H, ^3J(H,H) = 6.3 Hz, OCH_2CH_2), 3.55–3.75 (m, 75H, OCH_2CH_2, CH_2O, OCH_3), 6.1 (s, 8H, NH), 8.2 (brd, 2H), 8.5 (d, 2H, J(H,H) = 8.3 Hz), 9.1 (brs, 2H); $C_{116}H_{180}N_{10}O_{11}$ (2802. S).

54-Cascade 13: The dendritic acid **12** (1.42 g, 0.5 mmol) and HOBT (1.4 g, 9.1 mmol) were dissolved in dry THF (40 mL). The solution was cooled to 0 °C and **8** (3.60 g, 9.5 mmol) was added. A solution of *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide metho-*p*-toluenesulfonate (4 g, 9.4 mmol) in dry THF (15 mL) was added at 0 °C by means of a syringe. This reaction mixture was stirred for 2 h at 0 °C and warmed to room temperature overnight. After the mixture had been stirred for 1 week at room temperature, the precipitate was filtered off and the solvent removed in vacuo. The residue was dissolved in AcOEt and washed twice with sat. $NaHCO_3$ solution, citric acid solution (2N), and brine. The organic layer was dried (Na_2SO_4) and the solvent was removed in vacuo to yield **13** (2.13 g, 45%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.35–2.6 (m, 156H, OCH_2CH_2), 3.45–3.80 (m, 474H, OCH_2CH_2, CH_2O, OCH_3), 6.1 (brs, 26H, NH), 7.3–7.8 (m, 6H, pyridine CH); ^{13}C NMR (62.7 MHz, $CDCl_3$, 25 °C): δ = 22.1, 24.9, 25.6, 27.8, 33.8, 34.5, 34.6, 37.1, 37.2, 51.6, 53.4, 59.7, 66.7, 66.8, 67.5, 67.9, 68.5, 69.0, (pyridine C, CH not observed), 170.8, 171.0, 172.1 (CONH, CO_2Me); $C_{404}H_{662}N_{28}O_{212}$ (9303. V) calcd. C 52.16, H 7.17, N 4.22; found C 51.96, H 7.14, N 4.28.

Ruthenium(II) complex with 9 (14): $RuCl_3 \cdot 3H_2O$ (41 mg, 0.15 mmol) was added to a solution of **9** (457 mg, 0.47 mmol) in ethanol (25 mL). The reaction mixture was refluxed for 14 d. The solvent was removed in vacuo and the residue dissolved in hot water. After addition of NH_4PF_6 an orange oil was formed. The solution was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and the solvent removed in vacuo to yield **14** as an orange-red oil (450 mg, 76%). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1,20 (t, 54H, ^3J(H,H) = 7.2 Hz), 2.54 (t, 36H, ^3J(H,H) = 6.1 Hz), 3.71 (t, 12H, ^3J(H,H) = 6.1 Hz), 3.79 (s, 36H), 4.05 (q, 36H, ^3J(H,H) = 7.2 Hz), 7.01 (s, 6H, CONH), 7.77–7.85 (m, 12H), 8.97(s, 6H); ^{13}C NMR (62.7 MHz, $CDCl_3$, 25 °C): δ = 14.1, 34.8, 60.4, 61.0, 66.8, 68.7, 122.6, 125.9, 144.5, 152.1, 156.6 (pyridine-C, CH), 163.2 (CONH), 171.7 (CO_2Et). MALDI-TOF-MS (9-nitroanthracene): *m/z* (%): 3393.6 ($[M - PF_6]^+$, 100) calcd.: 3398.3; $C_{150}H_{222}N_{12}O_{60}RuP_2F_{12}$ (3544.46).

Ruthenium(II) complex with 11 (15): $RuCl_3 \cdot 3H_2O$ (41 mg, 0.15 mmol) was added to a solution of **11** (457 mg, 0.47 mmol) in ethanol (25 mL). The reaction mixture was refluxed for 14 d. The solvent was removed in vacuo and the residue dissolved in hot water. After adition of NH_4PF_6 an orange oil was formed. The solution was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and the solvent was removed in vacuo to yield **15** as an orange-red oil. (450 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.27–2.62 (m, 144H; CH_2), 3.53–3.77 (m, 450H; CH_2), 6.14–6.34 (s, 24H, CONH), 7.71–7.78 (brs, 6H, arom. CH), 8.73–8.8 (m, 12H; arom. CH); ^{13}C NMR (62.7 MHz, $CDCl_3$, 25 °C): δ = 14.2, 34.6 (2×), 34.9, 37.1 (2×), 51.6, 59.7, 66.6, 69.0, (pyridine C, CH not observed), 165.5 (CONH), 170.9, 172.0 (CONH), 172.1 (CO_2Me); MALDI-TOF-MS (ClSs): *m/z* (%): 9559.3 ($[M+CH_2]^+$, 100); $C_{402}H_{636}N_{30}O_{204}RuP_2F_{12}$ (9544.55).

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[1] E. Buhleier, W. Wehner, F. Vögtle, *Synthesis* **1978**, 155.
[2] G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.* **1985**, *50*, 2003.
[3] D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polymer J.* **1985**, *17*, 117.

[4] For recent reviews, see: a) D. A. Tomalia, H. D. Durst, *Topics Curr. Chem.* **1993**, *165*, 193; b) J. M. Fréchet, *Science* **1994**, *263*, 1710; c) J. Issberner, R. Moors, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413; d) N. Ardoin, D. Astruc, *Bull. Soc. Chem. Fr.* **1995**, *132*, 875; e) J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, *266*, 1266; f) G. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules*, VCH, Weinheim, **1996**.

[5] a) S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Balzani, *Chem. Eur. J.* **1995**, *1*, 211; b) S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano, V. Balzani, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1493; c) S. Campagna, G. Denti, S. Serroni, M. Ciano, A. Juris, V. Balzani, *Inorg. Chem.* **1992**, *31*, 2982; d) G. Denti, S. Campagna, S. Serroni, M. Ciano, V. Balzani, *J. Am. Chem. Soc.* **1992**, *114*, 2944; e) G. Denti, S. Campagna, V. Balzani in *Mesomolecules: from Molecules to Materials* (Eds.: D. Mendenhall, A. Greensberg, J. Liebman), Chapman and Hall, New York, **1995**, p. 69.

[6] S. Achar, J. J. Vittal, R. J. Puddephatt, *Organometallics* **1996**, *15*, 43.

[7] W. T. S. Huck, F. C. J. M. van Veggel, D. N. Reinhoudt, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1213.

[8] E. C. Constable, P. Harverson, *J. Chem. Soc. Chem. Commun.* **1996**, 33.

[9] a) G. R. Newkome, C. N. Moorefield, *Macromol. Symp.* **1994**, *77*, 63; b) E. Cloutet, J.-L. Fillaut, Y. Gnanou, D. Astruc, *J. Chem. Soc. Chem. Commun.* **1994**, 2433; c) M. F. Ottaviani, S. Bossmann, N. J. Turro, D. A. Tomalia, *J. Am. Chem. Soc.* **1994**, *116*, 661; d) Y.-H. Liao, J. R. Moss, *Organometallics* **1995**, *14*, 2130.

[10] a) G. R. Newkome, R. Güther, C. N. Moorefield, F. Cardullo, L. Echegoyen, E. Pérez-Cordero, H. Luftmann, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2023; b) S. Serroni, S. Campagna, A. Juris, M. Venturi, V. Balzani, G. Denti, *Gazz. Chim. Ital.* **1994**, *124*, 423.

[11] a) P. J. Dandliker, F. Diederich, J.-P. Gisselbrecht, A. Louati, M. Gross, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2725; b) J P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati, E. M. Sanford, *ibid.* **1994**, *33*, 1739; c) R. Sadamoto, N. Tomioka, T. Aida, *J. Am. Chem. Soc.* **1996**, *118*, 3978; d) P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *ibid.* **1996**, *118*, 5708.

[12] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85.

[13] a) V. Balzani, F. Barigelletti, L. De Cola, *Top. Curr. Chem.* **1990**, *158*, 31; b) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.

[14] For some recent examples from our laboratories, see: a) P. Belser, A. von Zelewsky, M. Frank, C. Seel, F. Vögtle, L. De Cola, F. Barigelletti, V. Balzani, *J. Am. Chem. Soc.* **1993**, *115*, 4076; b) L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank, F. Vögtle, *Inorg. Chem.* **1993**, *32*, 5228; c) F. Vögtle, M. Frank, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1643; d) M. Frank, M. Nieger, F. Vögtle, P. Belser, A. von Zelewsky, L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, *Inorg. Chim. Acta*, **1996**, *242*, 281.

[15] a) V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, UK, **1991**; b) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759; c) J. L. Attwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle Eds., *Comprehensive Supramolecular Chemistry*, Elsevier, Oxford, UK, **1996**.

[16] R. Herrmann, F. Vögtle, H.-P. Josel, B. Frommberger, G. Pappert, J. Issberner "Hydrophile Metallkomplexe", Patent: DE 4439346Al, 1994 (Boehringer Mannheim).

[17] Dendritic ligands based on 5,5′ substitution of 2,2′-bipyridine have also been synthesized. Their metal complexes are in preparation in our laboratories.

[18] a) G. R. Newkome, A. Nayak, R. K. Behara, C. N. Moorefield, G. R. Baker, *J. Org. Chem.* **1992**, *57*, 358; b) G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera, G. H. Escamalia, M. J. Saunders, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 917.

[19] a) F. Köchendorfer, Dissertation, Universität Bonn, 1989; b) S. Gould, G. F. Strouse, T. J. Meyer, B. P. Sullivan, *Inorg. Chem.* **1991**, *30*, 2942.

[20] G. R. Newkome, F. Cardullo, E. C. Constable, C. N. Moorefield, A. M. W. Cargill Thomson, *J. Chem. Soc. Chem. Commun.* **1993**, 925.

[21] a) S. Mattai, P. Seiler, F. Diederich, V. Gramlich, *Helv. Chim. Acta* **1995**, *78*, 1904; b) G. R. Newkome, X. Lin, J. K. Young, *Synlett* **1992**, 53.

[22] X. Zang, M. A. J. Rodgers, *J. Phys. Chem.* **1995**, *99*, 12797. F. Wilkinson, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1993**, *22*, 113. C. Tanielian, C. Wolff, M. Esch, *J. Phys. Chem.* **1996**, *100*, 6555.

[23] M. Z. Hoffman, F. Bolletta, L. Moggi, G. Hug, *J. Phys. Chem. Ref. Data* **1989**, *18*, 219.

[24] S. L. Murov, I. Carmichael, G. L. Hug, *Handbook of Photochemistry*, Dekker, New York, **1993**.

[25] J.-C. G. Bünzli; in *Lanthanides Probes in Life, Chemical and Earth Sciences, Theory and Practice* (Eds.: J.-C. G. Bünzli, G. R. Choppin), Elsevier, New York, **1989**, p. 219.

[26] Many dendrimers show discrepancies between calculated and found elemental analysis data due to traces of impurities and inclusion of solvents as previously reported [27].

[27] P. Lange, A. Schier, H. Schmidbaur, *Inorg. Chem.* **1996**, *35*, 637-642.

[28] J. M. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.

[29] K. Nakamura, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

[30] G. R. Newkome, G. R. Baker, J. K. Young, J. G. Traynham, *J. Polym. Sci. A: Polym. Chem.* **1993**, *31*, 641.

 0947-6539/97/0305-0712 $ 17.50+.50/0