DOI: 10.1002/ejic.200900253

Long-Lived Luminescent Dendrimers with a $[Ru(dpp)_3]^{2+}$-Type Core: Synthesis and Photophysical Properties

Uwe Hahn,*[a][‡] Fritz Vögtle,*[a] Gabriele De Paoli,[b] Mara Staffilani,[b] and Luisa De Cola*[b]

Keywords: Dendrimers / Dioxygen quenching / Luminescence / N ligands / Ruthenium

Metallodendrimers built around a $[Ru(dpp)_3]^{2+}$-type core (dpp = 4,7-diphenyl-1,10-phenanthroline) were prepared containing peripheral phenyl moieties. The convergent synthesis of the ligands was accomplished by coupling dendritic branches with a focal amino function to the chelating phenanthroline precursor under the formation of sulfonamide linkages. Complexation of ruthenium ions afforded the corresponding metallodendrimers with up to 24 peripheral phenyl units in the case of the largest dendritic structure. The absorption spectra and luminescence properties of the four new dendrimers are reported. The dendritic effect is clearly visible, going from zero to second generation, as demonstrated by an elongation in the excited-state lifetime in aerated acetonitrile and improved emission quantum yields relative to the reference complex containing a $[Ru(dpp)_3]^{2+}$ core. Interestingly, the use of rigid and conjugated ruthenium-based cores results, for all dendritic structures, in luminescence lifetimes that are several microseconds long in deaerated solutions, even at room temperature.

Introduction

Dendrimers can be regarded as repeatedly oligo- or polybranched compounds with a certain degree of perfection that is related to symmetry and dispersity of the species.[1] Within their regularly branched architecture, selected chemical units can be introduced into predetermined sites, namely, in the core, the branching units or the surface.[2] Since the synthesis of the first fractal species in 1978,[3] many efforts have been devoted to the preparation of these often large and beautiful molecules. The growing interest in dendrimers over more than the last decade is based on their potential for molecular design, which offers numerous possibilities for applications in various fields such as instance medicinal chemistry[4] or photonic devices.[5]

Specifically, luminescent and redox-active dendrimers are the focus of investigations, as they might open the way towards the design and development of artificial systems. Such frameworks are capable of playing the role of light-harvesting antennae for photochemical solar-energy-conversion processes by sensory signal amplification in the presence of suitable energy or electron acceptors.[6,7] In this respect, the incorporation of photoactive metal species into a dendritic scaffold is particularly appealing, as the characteristic features of metal complexes such as electronic and optical properties can be tailored by the dendritic surrounding. This approach can lead to systems capable of performing useful and appealing new functions.[7k,8,9]

Homoleptic metallodendrimers consisting of a $[Ru(bpy)_3]^{2+}$- or $[Ru(phen)_3]^{2+}$-type core and different dendritic motifs have been intensively investigated and found to exhibit interesting luminescence and redox properties.[7h,7i,10,11] In general, there are two different developments related to metallodendritic structures: (i) the possibility to link several electro- or photoresponsive metal units within the same molecule by using, for example, polypeptide chains[12] with the use of the periphery for multiple chelation[4e,4f,13,14] or chemical recognition[15] and (ii) to prevent oxygen quenching or chemical decomposition placing the active unit in the core of the dendrimer.[7h,7i,10,11] Such strategies led to the development of, for instance, markers based on the electroluminescence of ruthenium complexes,[16] novel MRI contrast agents[4e,4f,13] and to multiarm DNA complexes for the assembly of regular DNA lattices of nanoscale dimensions.[17] Such effects can lead to the design of specific luminescent or highly stable metallocores for the control of cascade processes like energy or electron transfer and to the selective solvation of different branches with different pe-

‡ Current Address: Departamento de Química Orgánica, Universidad Autónoma de Madrid (UAM),
28049 Madrid, Spain
Fax: +34-91497-7616
E-mail: uwe.hahn@uam.es
[a] Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn,
Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany
Fax: +49-22873-5662
E-mail: voegtle@uni-bonn.de
[b] Physikalisches Institut, Westfälische Wilhelms-Universität Münster,
Mendelstrasse 7, 48149 Münster, Germany
Fax: +49-251980-2805
E-mail: decola@uni-muenster.de

ripheral groups. Finally, the dendritic effect has been clearly illustrated, as the properties of the system change and can be tuned as desired by increasing the surrounding dendritic shell.[10,11]

In particular, the shielding of the dendrons from the environment can be of great interest, for example, in biomedical applications for long-lived luminescent species that would otherwise be quenched by molecules present in solution. Also, the compartmentalisation of the metal complex could have interesting properties, as it was recently demonstrated by the use of a gadolinium core grafted onto an aspartate-based dendrimer, which gave a good relaxivity enhancement over the analogous free complex.[18] Furthermore, Gd complexes have been covalently attached to the periphery of dendritic architectures to increase the number of metal complexes and to reduce the tumbling rate as a result of the larger molecular weight.[14f]

In this paper we report the preparation of new phenanthroline-based dendritic ligands and their photoactive ruthenium(II) complexes. Hence, a series of metallodendrimers was synthesised with increasing Fréchet-type polybenzylether wedges. The photophysical properties of the complexes with dendritic shells of different size around the luminescent $[Ru(dpp)_3]^{2+}$-type core (dpp = 4,7-diphenyl-1,10-phenanthroline) and a suitable model compound are discussed. The use of such sulfonamide-linked phenanthrolines as chelating units resulted in very long-lived excited species and high emission quantum yields in aerated and deaerated solutions. The increased dendritic shell surrounding the $[Ru(dpp)_3]^{2+}$-type metal core leads to a strong influence on the quenching effect of molecular oxygen, as demonstrated by the increasing excited-state lifetimes in aerated solutions. Moreover, we observed a macroscopic dendritic pattern with seven near to equidistant shells obtained after solidification of a dendritic precursor by slow solvent evaporation.

Results and Discussion

Synthesis

The synthetic strategy for the preparation of the dendritic phenanthroline-based chelating ligands started with the preparation of the corresponding polybenzylether-type dendrons **1** and **2** with a bromide function at the focal point, which were obtained following the procedure reported by Fréchet.[19] During the preparation of the higher-generation dendrons, second generation alcohol **3** was obtained as an intermediate and disclosed interesting behaviour upon slow evaporation of the acetone solvent. A viscous oil remained on the wall of the flask, and solidification of the oily residue resulted in a fractal pattern with precise and defined shells. Figure 1 shows an image of a 100-mL flask with the macroscopic pattern and seven near-to-equidistant shells of the branched structure. To the best of our knowledge, this is the first example for a macroscopic pattern based on a nonpolymeric dendritic structure.[20] Similar fractal structures were successfully reproduced by slow evaporation of solutions of **3** in acetone and subsequent solidification.

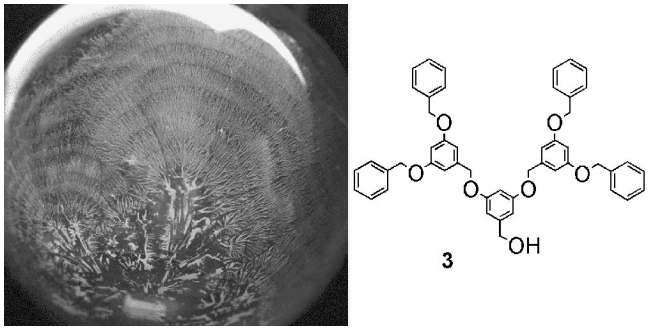
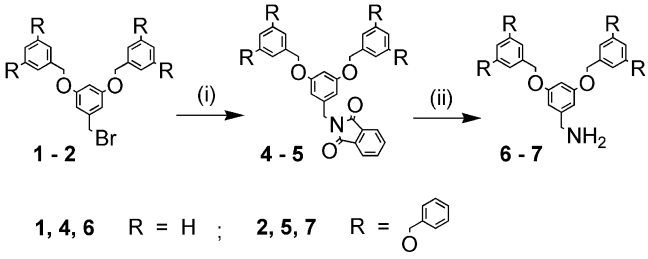


Figure 1. Fractal pattern of second generation benzyl alcohol **3** showing seven distinct equidistant shells.

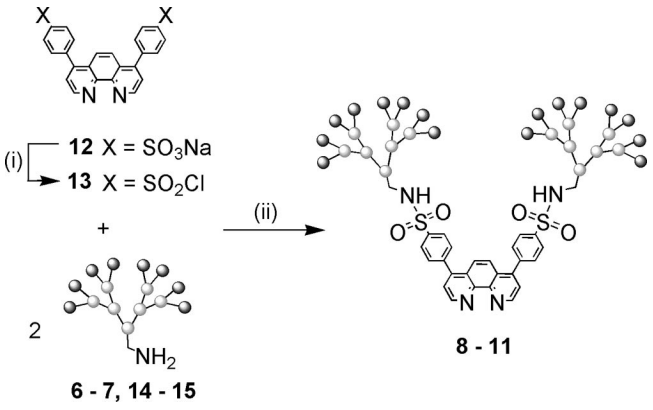
Conversion of the dendritic bromides into the corresponding amines **6** and **7** was achieved by using the classical Gabriel synthesis for primary amines.[21] Reaction with potassium phthalimide in DMF gave imides **4** and **5** in high yields, which were then subjected to hydrazinolysis.[22] Accordingly, the reaction with hydrazine hydrate in dry ethanol under reflux conditions afforded dendritic amines **6** and **7** as colourless solids in medium to high yields after purification by column chromatography (Scheme 1).



Scheme 1. Reagents and conditions: (i) Potassium phthalimide, DMF, 80 °C, 2 h; (ii) addition of N_2H_4. H_2O at 100 °C, EtOH, 100 °C, 2 h.

In contrast, as part of the convergent strategy, commercially available bathophenanthroline disulfonic acid disodium salt **12** was treated with phosphorus(V) chloride and phosphoryl chloride at 110 °C to yield sulfonyl chloride **13** as a colourless amorphous solid (Scheme 2). Conjugation of the amino-functionalised fractal species with phenanthroline derivative **13** afforded targeted dendritic ligands **10** and **11**, which are referred to as "sulfobathophenanthrolines" (SBP). The reaction was accomplished in dry chloroform in the presence of triethylamine and yielded amorphous yellowish solids after purification by column chromatography on silica gel. Similarly, two non-dendritic sulfonamide linked ligands **8** and **9** were prepared with the use of butylamine (**14**) or benzylamine (**15**), respectively (Figure 2). Ligand **8** served as a reference compound during the studies. The butyl chains impart solubility, but do not constitute a bulky group able to significantly shield the ruthenium centre, whereas benzylic derivative **9** can be regarded as the simple analogue of the series of polyben-

zylether-substituted dendrimers. The structures of all the new dpp-chelating ligands could be readily deduced by ^1H and ^{13}C NMR spectroscopy as well as by FAB mass spectrometry.



Scheme 2. Reagents and conditions: (i) PCl_5, $POCl_3$, 110 °C, 3 h (95%); (ii) Et_3N, $CHCl_3$, 1 d, room temp. (light spheres represent the ether aryl branching units, dark spheres represent phenyl end groups).

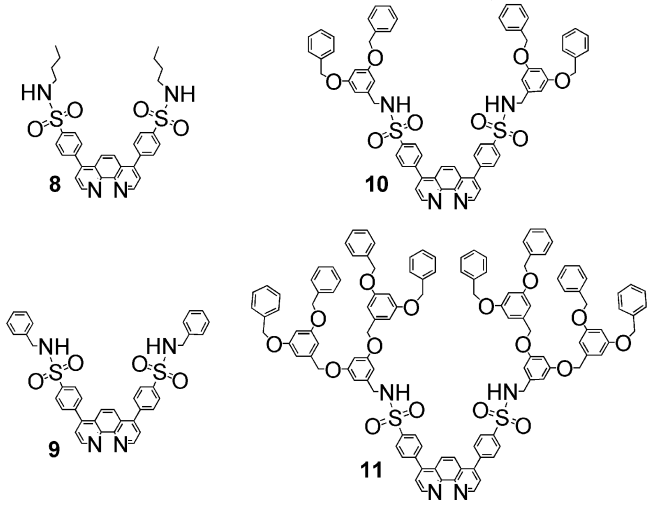


Figure 2. Sulfobathophenanthroline (SBP) ligands **8**–**11**.

The preparation of metallodendrimers RuG0 to RuG2 and RuRef (Figure 3) was performed under irradiation in a microwave oven. Hence, a solution of the corresponding SBP ligands **8**–**11** (3 equiv.) and ruthenium(III) chloride (1 equiv.) in ethylene glycol was heated for 2 min at 200 W in the presence of a few drops of water. The reaction mixture turned bright orange in colour, thus indicating the formation of the $[Ru(dpp)_3]^{2+}$-type complexes. Exchange of the counterions to hexafluorophosphate and subsequent purification by column chromatography on silica gel and gel permeation chromatography gave the desired metallodendrimers. Regardless of the dendritic generation, all ruthenium-based complexes were obtained as glassy dark orange com-

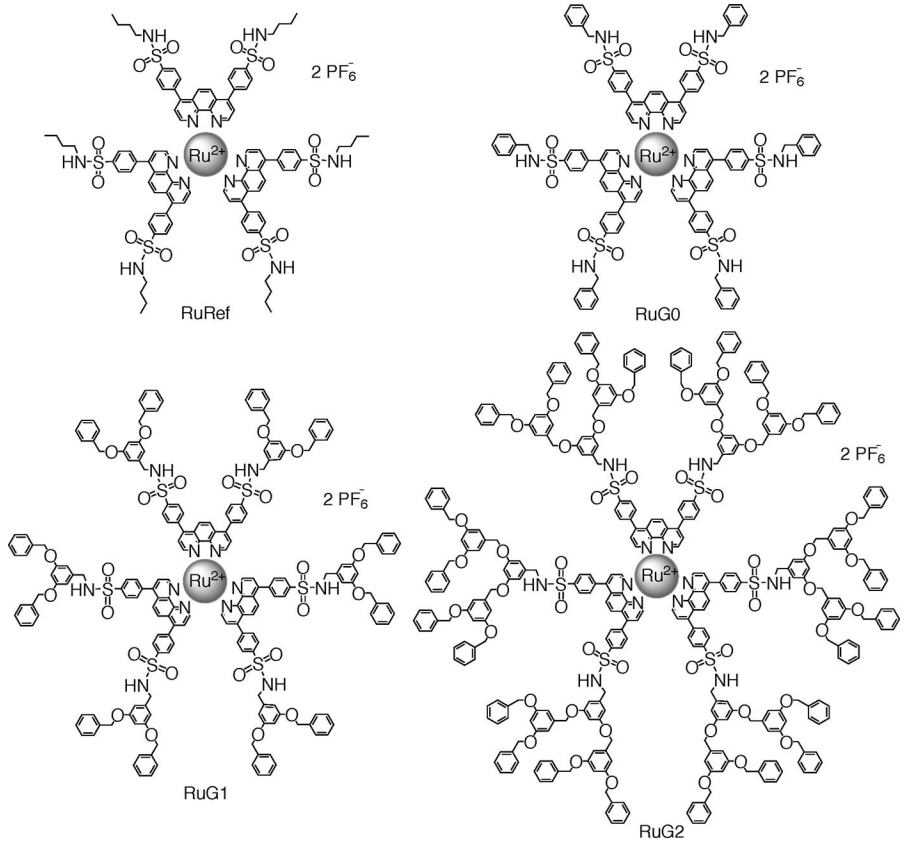


Figure 3. Dendritic metal complexes RuG0 to RuG2 with phenyl end groups and reference complex RuRef with butyl terminal groups.

pounds. The structures of all dendritic ruthenium complexes could also be readily deduced by ^1H and ^{13}C NMR spectrometry and MALDI-TOF mass spectrometry.

Photophysical Characterisation

The UV/Vis absorption spectra of investigated complexes RuRef and RuG0 to RuG2 in acetonitrile solutions are depicted in Figure 4. The spectroscopic data for all new dendritic complexes are summarised in Table 1. The UV/Vis spectra of phenyl-terminated complexes RuG0 to RuG2 are very similar to the profile obtained for reference compound RuRef. The spectra are dominated by an intense, sharp, diphenylphenanthroline intraligand (^{1}IL) transition bands located at λ_{max} = 277 nm and the typical weaker featureless d_π(Ru) → π*(phen) metal-to-ligand-charge-transfer (^{1}MLCT) bands at about λ_{max} = 450 nm. The molar extinction coefficient of the IL bands increases along the dendrimer generation, that is, from the lowest generation RuG0 to the highest generation complex RuG2. The expected enhanced absorption can be assigned to the augmented number of chromophoric 1,3-dimethyleneoxybenzene units when going from generation 0 to 2. As the luminescent $[Ru(dpp)_3]^{2+}$-type core remains the same in all complexes investigated, no spectral changes were expected in the ^{1}MLCT region. Indeed, the peripheral substitution had virtually no influence on the ^{1}MLCT bands, thus proving that the attachment of the dendritic branches does not substantially affect the electronic properties of the $[Ru(dpp)_3]^{2+}$-type core in all dendritic architectures described herein.

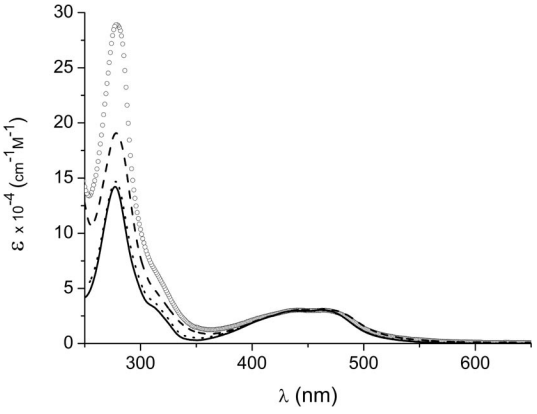


Figure 4. UV/Vis spectra of RuRef (—), RuG0 (· · ·), RuG1 (— —) and RuG2 (○○○) in acetonitrile.

The emission spectra of the series of metallodendrimers are shown in Figure 5. All four new complexes emit from the lowest ^{3}MLCT excited state, at the same wavelength as reference compound RuRef, that is, at $\lambda_{max} \approx 622$ nm, independently from the excitation wavelength (Table 1). This rather broad and structureless red-orange emission is resolved into a vibrational progression in glassy matrix at 77 K (inset in Figure 5).

A dendritic effect was observed for the emission quantum yields and excited-state lifetimes in air-equilibrated acetonitrile. As can be clearly seen in Figure 5, upon excitation

Table 1. Photophysical data.

	298 K[a]					77 K[b]	
	λ_{max}[c] (nm)	τ[d] (μs)	Φ_{em}[d]	τ[e] (μs)	Φ_{em}[e]	λ_{max}[c] (nm)	τ (μs)
RuRef	622	0.26	0.013	6.7	0.34	598	8.2
RuG0	623	0.27	0.015	6.5	0.32	597	8.3
RuG1	623	0.45	0.025	6.6	0.30	598	8.7
RuG2	621	0.73	0.031	6.6	0.29	600	9.5

[a] Acetonitrile solution. [b] Butyronitrile glass matrix. [c] Emission maxima wavelength. [d] Air-equilibrated solution. [e] Deaerated solution, $[Ru(bpy)_3]Cl_2$ in H_2O (Φ_{em} = 0.028) used as reference emitter for quantum yields calculations.

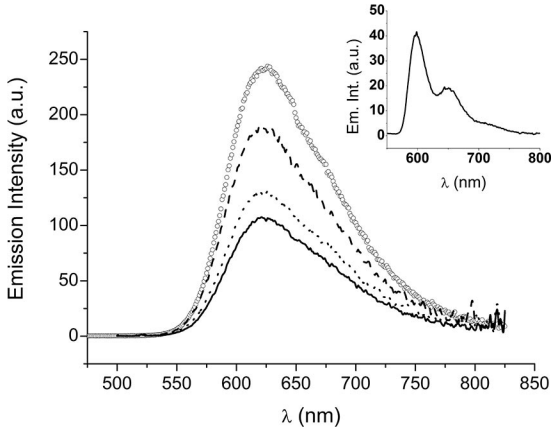


Figure 5. Emission spectra of RuRef (—), RuG0 (· · ·), RuG1 (— —) and RuG2 (○○○) in air-equilibrated acetonitrile (λ_{exc} = 450 nm). Inset: Luminescent spectrum of RuRef in a butyronitrile matrix at 77 K, λ_{exc} = 420 nm. All the other profiles – not shown – are the same.

in the isoabsorptive wavelength (420 nm), increasing generation leads to an increase in the emission intensity. The emission quantum yields double going from RuG0 to RuG2 and the same is observed for the excited-state lifetimes. For model complex RuRef, a value of 260 ns was measured, which is similar to the value obtained for RuG0 (270 ns) with peripheral benzyl moieties. Interestingly, in contrast to these values, the lifetimes increase in the series RuG0, RuG1 and RuG2, being 270, 450 and 730 ns, respectively. The improved emission properties, mirroring a dendritic effect, can be explained by the sterically more demanding substituents. Hence, incorporation of the fractal wedges at the periphery of the metallodendritic entities leads to more efficient shielding of the ruthenium core by dioxygen and/or solvent interactions. The less effective dioxygen quenching of the ^{3}MLCT excited state of the ruthenium core upon increasing the dendrimer generation may depend on different factors such as a decrease in the diffusion rate constant of the metal complex, which thereby lowers the probability of encountering a molecule of oxygen and a lower solubility of the dioxygen within the dendrimer framework.

Furthermore, the dendritic branches are rather rigid, as is the core, resulting in a reduction in the radiationless deactivation that derives from vibronic coupling and molecular motions. This effect is very evident in the deaerated excited-

state lifetimes with values of several microseconds (see Table 1), which are strongly elongated in comparison to the usual values observed for most of the polypyridine systems. Such behaviour is similar to that reported for the diphenyl phenanthroline complexes[23] and is attributed to the rigidity and extended delocalisation of the charge on the coplanar phenyl substituents. Moreover, it is interesting to notice that the dendritic branches are linked to the central core by sulfonyl amide functional groups. Hence, such functionalities confer a slight electron-withdrawing character to the coordinated ligands, which results in an extended charge delocalisation upon light excitation. Such rigidity and electronic effects are evident from the redshifted emission maxima relative to the unsubstituted phenanthroline compounds described in the literature[24] and by the very long excited-state lifetimes observed also at low temperature. The excited-state lifetimes at 77 K in a butyronitrile matrix also show a size dependent behaviour, as there is a constant increase going from RuG0 to RuG2 (see Table 1). To the best of our knowledge, few examples of metal complexes have shown a clear dependence on the generation of the dendrimers in relation to the photophysical properties even in rigid matrices.[25]

Also, the ruthenium core, as a result of the rigidity and cage-type[26] arrangement of the coordinated ligands, is almost insensitive to the deactivation to the energetically accessible metal-centred ^{3}MC states. In fact, the MLCT state can be associated with an activated surface crossing to an upper lying ^{3}MC excited state, which can then undergo fast deactivation to the ground state and/or ligand dissociation. For the corresponding tris(phenanthroline) ruthenium complex the variation in the excited-state lifetime, going from room temperature in deaerated solution to 77 K in a rigid matrix, is at least a factor of eight.[27] In our case, the change in lifetimes upon gelation of the solvent is very small (from 6.6 to about 8.5 μs), indicating that the radiative and nonradiative processes are very similar at any temperature. Therefore, we conclude that even if the ^{3}MC state as expected is populated, it is then depopulated back to the emitting ^{3}MLCT without undergoing severe radiationless deactivation. A similar behaviour was observed for cage-type complexes[26] in which, besides no large change in excited-state lifetimes with changing temperature, no photoisomerisation and a high photostability were demonstrated.

Conclusions

Four new metal complexes constructed around a $[Ru(dpp)_3]^{2+}$-type core comprising either butyl chains in the case of the reference compound or dendritic polybenzylether substituents of varying size were prepared. The highest generation complex contains 24 terminal phenyl groups. Investigation of the photophysical properties of the four metallodendrimers revealed that the presence of the dendritic substituents, at the chelating ligands of the ruthenium ion, has no significant influence on the energy of the excited states of the luminescent metal core. However, dendritic effects are observed for the excited-state lifetimes and emission quantum yields. Furthermore, the lack of a large variation between room and low temperature lifetimes point to a kinetic stabilisation of the dendritic structure and reduction of radiationless processes. This could be of great interest for diagnostic applications, in which long excited-state lifetime and improved emission properties are required.

Experimental Section

General: All reagents were used as purchased from commercial sources without further purification. Compounds **1** and **2** were prepared according to previously described procedures in the literature.[19] Solvents were dried by using standard techniques prior to use. All reactions were performed in standard glassware under an inert argon atmosphere. Reactions were monitored by thin-layer chromatography by using TLC plates precoated with silica gel 60 F_{254} (Merck). Column chromatography was carried out on Merck silica gel 60, 40–63 μm (230–400 mesh). Gel permeation chromatography was performed by using a Biorad, Biobeads SX-1 instrument. ^{1}H and ^{13}C NMR spectra were recorded by using Bruker (Avance 300 and AM 400 MHz) instruments; the solvent signal was used for internal calibration. Mass spectra were recorded with a MS-50 from A.E.I., Manchester, GB (EI), a Concept 1H from Kratos Analytical Ltd., Manchester, GB (FAB) and a MALDI-TOF Spec-E from Micromass, GB (MALDI). Microwave-supported complexations were performed in a Discover S-Class device from CEM Corp. Matthews, NC, United States. UV/Vis spectra were recorded with a Hewlett Packard 8453 diode-array spectrophotometer. Emission and excitation spectra were recorded with a Spex 1681 spectrophotometer. All the emission spectra were corrected for the photomultiplier response. Time-resolved emission studies were performed at single wavelength by using a continuously tuneable (400–700 nm) Coherent Infinity XPO laser as excitation source. The emission light was collected in an Oriel monochromator, detected by a P28 PMT (Hamamatsu), and recorded with a Tektronix TDS3052 (500 MHz) oscilloscope. A photodiode was used as external trigger source. Luminescence quantum yields were measured in optically dilute ($A<0.15$) solutions by using $[Ru(bpy)_3]Cl_2$ in H_2O ($\Phi_{em} = 0.028$)[28] as reference emitter. Estimated experimental errors in the reported data are as follows: absorption and emission maxima ±2 nm, emission lifetimes 8%, emission quantum yields ±20%. Where required, deaerated solutions were prepared by a freeze–pump–thaw technique on a vacuum line.

General Procedure for the Preparation of the Dendritic Phthalimides: A solution of the appropriate dendritic bromides **1** or **2** (1.0 mmol) and potassium phthalimide (1.3 mmol) in DMF (15 mL) was heated at 80 °C for 2 h. The solution was cooled to room temperature and aqueous NaOH (2 N, 200 mL) was added. The aqueous phase was extracted several times with CH_2Cl_2, the collected organic phase was dried with $MgSO_4$, the solvent was evaporated and the crude product was purified by column chromatography.

Compound 4: Bromide **1** (2.50 g, 6.52 mmol) and potassium phthalimide (1.57 g, 8.48 mmol) in dry DMF (90 mL). Column chromatography (SiO_2, CH_2Cl_2) yielded **4** as a colourless solid (2.90 g, 99%). M.p. 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.77 (s, 3 H, NCH_2), 5.04 (s, 4 H, OCH_2), 6.51 (t, J = 2 Hz, 1 H, H_{ar}), 6.70 (t, J = 2 Hz, 2 H, H_{ar}), 7.33–7.44 (m, 20 H, H_{ar}), 7.72 (dd, J = 6, 3 Hz, 2 H, H_{ar}), 7.85 (dd, J = 6, 3 Hz, 2 H, H_{ar}) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 41.7, 70.1, 101.5, 107.7, 123.8, 128.0, 128.4, 128.9, 132.4, 134.7, 137.0, 138.7, 160.1, 168.0 ppm. MS (70 eV, EI): *m*/*z* (%) = 449 (12), 91 (100).

Compound 5: Bromide **2** (1.50 g, 1.86 mmol) and potassium phthalimide (0.44 g, 2.39 mmol) in dry DMF (30 mL). Column chromatography (SiO_2; CH_2Cl_2/cyclohexane, 5:1) yielded **5** as a colourless oil (1.60 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.77 (s, 2 H, NCH_2), 4.93 (s, 4 H, OCH_2), 5.04 (s, 8 H, OCH_2), 6.51 (t, *J* = 2 Hz, 1 H, H_{ar}), 6.54 (t, *J* = 2 Hz, 2 H, H_{ar}), 6.69 (d, *J* = 2 Hz, 6 H, H_{ar}), 7.25–7.44 (m, 20 H, H_{ar}), 7.70 (dd, *J* = 6, 3 Hz, 2 H, H_{ar}), 7.83 (dd, *J* = 6, 3 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.8, 70.3, 70.4, 101.7, 102.0, 107.9, 123.7, 127.5, 128.3, 128.9, 132.4, 134.2, 139.0, 139.4, 160.1, 160.5, 168.2 ppm. MS (MALDI-TOF, matrix DHB): *m*/*z* = 896 $[M + H]^+$.

General Procedure for the Preparation of the Dendritic Amines: A suspension of the appropriate dendritic phthalimide **4** or **5** (1.0 mmol) in dry ethanol was heated at 100 °C until the solid was dissolved. Concentrated hydrazine hydrate was then added, and the solution was heated at 100 °C for 2 h. The reaction mixture was cooled to room temperature and ethyl ether (50 mL) and aqueous KOH (50 mL, 20%) were added. The organic phase was separated, the aqueous phase was extracted several times with ethyl ether, and the collected organic phase was washed twice with water and dried with $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography.

Compound 6: Phthalimide **4** (2.90 g, 6.45 mmol) and hydrazine hydrate (4.38 mL) in dry ethanol (200 mL). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 10:1) gave **6** as a colourless solid (1.62 g, 78%). M.p. 170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 2 H, NH_2), 3.71 (s, 2 H, NCH_2), 4.95 (s, 4 H, OCH_2), 6.41 (t, *J* = 2 Hz, 1 H, H_{ar}), 6.51 (d, *J* = 2 Hz, 2 H, H_{ar}), 7.22–7.36 (m, 20 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.5, 70.1, 100.5, 106.2, 127.6, 128.0, 128.6, 136.9, 145.3, 160.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 319.1 (42), 91.0 (100).

Compound 7: Phthalimide **5** (1.60 g, 1.83 mmol) and hydrazine hydrate (1.23 mL) in dry ethanol (55 mL). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 100:1 to 20:1) gave **7** as a colourless viscous oil (1.00 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 2 H, NH_2), 3.80 (s, 2 H, NCH_2), 4.95 (s, 4 H, OCH_2), 5.02 (s, 8 H, OCH_2), 6.50 (d, *J* = 2 Hz, 1 H, H_{ar}), 6.56 (t, *J* = 2 Hz, 2 H, H_{ar}), 6.69 (d, *J* = 2 Hz, 6 H, H_{ar}), 7.30–7.48 (m, 20 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.6, 69.9, 70.1, 100.4, 101.5, 106.1, 106.4, 127.6, 128.1, 128.6, 136.7, 139.4, 145.9, 145.3, 160.1, 160.2 ppm. MS (MALDI-TOF, matrix DHB): *m*/*z* = 766.38 $[M + Na]^+$, 744.40 $[M + H]^+$.

Compound 13: A mixture of 4,7-diphenyl-1,10-phenanthroline disulfonic acid disodium salt hydrate (**12**; 2.10 g, 3.9 mmol), PCl_5 (3.30 g, 15.9 mmol) and $POCl_3$ (3 drops) was heated at 110 °C for 3 h under dry conditions. Volatile phosphorus products condensed on the cold zones of the glass flask were removed at 110 °C under reduced pressure over 7 h. Benzene (150 mL) was added to the crude product, the mixture was stirred for 10 min and the solution was decanted from the solid residue. This procedure was repeated three times with $CHCl_3$ (100 mL). The residue was then dried in vacuo to yield **13** as a colourless amorphous solid (1.47 g, 95%), which was used as obtained.

General Procedure for the Preparation of the SBP Ligands: A solution of the appropriate amine **6**, **7**, **14** or **15** (2.2 mmol) and triethylamine (2.2 mmol) in dry $CHCl_3$ (20 mL) was stirred at room temperature for 15 min. Sulfonyl chloride **13** (1.0 mmol) was then added, and the suspension was stirred for 1 d at room temperature. The solid was filtered off, the solvent was evaporated and the crude product was purified by column chromatography.

Compound 8: Butylamine (**14**; 128 mg, 1.75 mmol), triethylamine (177 mg, 1.75 mmol) and sulfonyl chloride **13** (370.0 mg, 0.70 mmol) in dry $CHCl_3$ (15 mL). Gradient column chromatography (SiO_2; CH_2Cl_2/MeOH, 20:1 to 8:1) gave **8** as a yellowish amorphous solid (240 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7 Hz, 6 H, CH_3), 1.28 (sextet, *J* = 7 Hz, 4 H, CH_3CH_2), 1.48 (p, *J* = 7 Hz, 4 H, $CH_3CH_2CH_2$), 3.04 (q, *J* = 7 Hz, 4 H, $NHCH_2$), 5.48 (t, *J* = 7 Hz, 2 H, NH), 7.48 (d, *J* = 5 Hz, 2 H, H_{ar}), 7.68 (m, 6 H, H_{ar}), 8.05 (m, 4 H, H_{ar}), 9.15 (d, *J* = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ = 13.7, 19.8, 19.8, 43.3, 123.9, 124.1, 126.2, 127.3, 128.1, 129.7, 133.7, 141.4, 146.8, 150.2 ppm. MS (FAB): *m*/*z* (%) = 603.1 (100).

Compound 9: Benzylamine (**15**; 0.13 mL, 1.19 mmol), triethylamine (0.17 mL, 1.19 mmol) and sulfonyl chloride **13** (244.0 mg, 0.46 mmol) in dry $CHCl_3$ (15 mL). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 20:1) gave **15** as a yellowish amorphous solid (102.1 g, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.26 (s, 4 H, $NHCH_2$), 5.55 (br. s, 2 H, NH), 7.16–7.28 (m, 10 H, H_{ar}), 7.48 (d, *J* = 5 Hz, 2 H, H_{ar}), 7.67 (m, 6 H, H_{ar}), 8.00 (m, 4 H, H_{ar}), 9.21 (d, *J* = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.3, 123.7, 123.9, 126.0, 127.2, 127.8, 128.0, 129.0, 133.6, 136.2, 138.8, 141.3, 146.5, 146.7, 150.0 ppm. MS (MALDI-TOF): *m*/*z* (%) = 671.3 (26), 244.1 (100).

Compound 10: Dendritic amine **6** (240.0 mg, 0.75 mmol), triethylamine (0.11 mL, 0.75 mmol) and sulfonyl chloride **13** (180.4 mg, 0.34 mmol) in dry $CHCl_3$ (10 mL). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 20:1) gave **10** a yellowish amorphous solid (107.2 g, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.08 (d, *J* = 6 Hz, 4 H, $NHCH_2$), 4.73 (s, 8 H, OCH_2), 5.68 (t, *J* = 6 Hz, 2 H, NH), 6.20–6.40 (m, 6 H, H_{ar}), 7.14–7.28 (m, 20 H, H_{ar}), 7.40 (d, *J* = 5 Hz, 2 H, H_{ar}), 7.58 (m, 6 H, H_{ar}), 7.98 (m, 4 H, H_{ar}), 9.12 (d, *J* = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.4, 70.0, 101.3, 106.9, 123.7, 123.9, 125.9, 126.9, 127.4, 128.1, 128.6, 129.4, 133.5, 136.5, 138.8, 141.5, 146.4, 146.6, 149.9, 160.1 ppm. MS (FAB): *m*/*z* (%) = 1095.3 (70), 456.1 (100).

Compound 11: Dendritic amine **7** (300.0 mg, 0.40 mmol), triethylamine (0.06 mL, 0.40 mmol) and sulfonyl chloride **13** (97.0 mg, 0.18 mmol) in dry $CHCl_3$ (15 mL). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 20:1) gave **10** a yellowish amorphous solid (89.2 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (d, *J* = 6 Hz, 4 H, $NHCH_2$), 4.78 (s, 16 H, OCH_2), 4.86 (s, 8 H, OCH_2), 5.06 (t, *J* = 6 Hz, 2 H, NH), 6.37–6.43 (m, 16 H, H_{ar}), 6.53 (m, 2 H, H_{ar}), 7.20–7.41 (m, 42 H, H_{ar}), 7.52 (m, 6 H, H_{ar}), 7.95 (m, 4 H, H_{ar}), 9.03 (m, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.3, 69.8, 70.2, 101.4, 106.2, 106.9, 123.7, 123.9, 125.9, 127.1, 127.4, 127.5, 128.0, 128.6, 129.4, 133.5, 136.6, 136.9, 138.6, 138.9, 141.6, 146.4, 150.0, 160.1, 160.2 ppm. MS (FAB): *m*/*z* (%) = 1944.7 (3), 303.1 (100).

General Procedure for the Preparation of the Metallodendrimers: A solution of the corresponding SBP ligands **8**–**11** (3 equiv.) and ruthenium(III) chloride dihydrate (1 equiv.) in ethylene glycol and a few drops of water was heated for 2 min at 200 W in the microwave. The solvent was removed under reduced pressure, the counterions were changed to hexafluorophosphate and the crude product was purified by column chromatography and gel permeation chromatography.

Compound RuRef: SBP ligand **8** (60.0 mg, 0.100 mmol), ruthenium(III) chloride dihydrate (8.1 mg, 0.039 mmol) in ethylene glycol (3 mL) and water (4 drops). Column chromatography (SiO_2;

CH_2Cl_2/MeOH, 30:1 to 15:1) and gel permeation chromatography (CH_2Cl_2) gave RuRef as a dark orange glassy product (23.8 mg, 67%). ^1H NMR (400 MHz, [D$_6$]acetone): δ = 0.80 (t, J = 7 Hz, 18 H, CH_3), 1.29 (sextet, J = 7 Hz, 12 H, CH_3CH_2), 1.44 (p, J = 7 Hz, 12 H, $CH_3CH_2CH_2$), 2.96 (q, J = 6 Hz, 12 H, $NHCH_2$), 6.52 (t, J = 6 Hz, 6 H, NH), 7.83–7.94 (m, 18 H, H_{ar}), 8.02–8.09 (m, 12 H, H_{ar}), 8.29 (s, 6 H, H_{ar}), 8.72 (d, J = 5 Hz, 6 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 13.9, 20.3, 32.4, 43.7, 127.7, 128.9, 129.8, 131.1, 134.3, 137.5, 143.1, 148.5, 149.7, 154.0 ppm. MS (MALDI-TOF): m/z (%) = 2053.436 (100) $[M - PF_6]^+$, 1908.473 (100) $[M - 2PF_6]^+$.

Compound RuG0: SBP ligand **9** (47.2 mg, 0.070 mmol), ruthenium(III) chloride dihydrate (4.87 mg, 0.023 mmol) in ethylene glycol (3 mL) and water (4 drops). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 50:1 to 10:1) and gel permeation chromatography (CH_2Cl_2) gave RuG0 as a dark orange glassy product (15.2 mg, 27%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.20 (br. s, 12 H, $NHCH_2$), 7.05–7.30 (br. m, 30 H, H_{ar}), 7.82–7.92 (br. m, 18 H, H_{ar}), 7.97–8.11 (m, 12 H, H_{ar}), 8.19 (s, 6 H, H_{ar}), 8.73 (d, J = 5 Hz, 6 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.7, 127.1, 127.7, 128.2, 128.7, 129.1, 129.8, 131.1, 134.3, 137.4, 138.2, 143.3, 148.5, 149.6, 153.9 ppm. MS (MALDI-TOF): m/z (%) = 2258.0 (21) $[M - PF_6]^+$, 2114.1 (38) $[M - 2PF_6]^+$, 671.2 (100) [Ligand].

Compound RuG1: SBP ligand **10** (76.7 mg, 0.070 mmol), ruthenium(III) chloride dihydrate (4.84 mg, 0.023 mmol) in ethylene glycol (3 mL) and water (4 drops). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 50:1 to 10:1) and gel permeation chromatography (CH_2Cl_2) gave RuG1 as a dark orange glassy product (18.5 mg, 22%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.11 (br. s, 12 H, $NHCH_2$), 4.86 (s, 24 H, OCH_2), 6.35 (s, 6 H, H_{ar}), 6.45 (s, 12 H, H_{ar}), 7.14–7.31 (br. m, 60 H, H_{ar}), 7.70–7.79 (m, 18 H, H_{ar}), 7.96–8.04 (m, 18 H, H_{ar}), 8.60 (m, 6 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.7, 70.4, 101.7, 107.7, 127.1, 127.8, 128.4, 128.6, 129.2, 129.7, 131.0, 134.3, 137.2, 138.0, 140.6, 143.5, 148.4, 149.5, 153.8, 160.8 ppm. MS (MALDI-TOF): m/z (%) = 3533.6 (100) $[M - PF_6]^+$.

Compound RuG2: SBP ligand **11** (51.6 mg, 0.027 mmol), ruthenium(III) chloride dihydrate (1.84 mg, 0.009 mmol) in ethylene glycol (3 mL) and water (4 drops). Column chromatography (SiO_2; CH_2Cl_2/MeOH, 50:1 to 10:1) and gel permeation chromatography (CH_2Cl_2) gave RuG2 as a dark orange glassy product (16.3 mg, 29%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.00 (br. s, 12 H, $NHCH_2$), 4.83 (s, 48 H, OCH_2), 4.88 (s, 24 H, OCH_2), 6.24–6.42 (m, 18 H, H_{ar}), 6.56 (m, 36 H, H_{ar}), 7.00–7.24 (m, 120 H, H_{ar}), 7.50 (m, 18 H, H_{ar}), 7.73–7.91 (m, 18 H, H_{ar}), 8.33 (m, 6 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.3, 69.8, 70.2, 101.9, 102.1, 106.9, 107.3, 127.1, 128.4, 128.6, 128.8, 129.1, 129.8, 131.1, 134.3, 137.4, 138.2, 140.0, 143.3, 144.2, 148.5, 149.6, 153.9, 160.7, 160.8 ppm. MS (MALDI-TOF): m/z (%) = 6075.8 (17) $[M - PF_6]^+$, 1943.2 (100) [Ligand].

Acknowledgments

Financial assistance by the Bundesministerium für Bildung und Forschung (BMBF) and Roche Diagnostics, Penzberg (Dr. H.-P. Josel, Dr. R. Herrmann) is gratefully acknowledged. M. S. wishes to thank the Universiteit von Amsterdam. We would like to thank Prof. Dr. C. A. Schalley and Dr. R. M. Williams for valuable discussions. The International Research Training Group (IRTG 1444) is also acknowledged for financial support.

[1] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons*, VCH, Weinheim, **2001**; b) J. M. J. Fréchet, D. A. Tomalia, *Dendrimers and Other Dendritic Polymers*, Wiley, Chichester, **2001**; c) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules*, VCH, Weinheim, **1996**; d) F. Vögtle, G. Richardt, N. Werner, *Dendritische Moleküle*,Vieweg+Teubner, Wiesbaden, **2007**; e) F. Vögtle, G. Richardt, N. Werner, *Dendrimer Chemistry*, Wiley-VCH, Weinheim, **2009**.

[2] a) C. A. Schalley, F. Vögtle (Eds.), *Topics in Current Chemistry Vol. 228: Dendrimers V*, Springer, Heidelberg, **2003**, and previous volumes I–IV; b) S. Hecht, J. M. J. Fréchet, *Angew. Chem.* **2001**, *113*, 76–94; *Angew. Chem. Int. Ed.* **2001**, *40*, 74–91; c) F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, B. Windisch, *Prog. Polym. Sci.* **2000**, *25*, 987–1041; d) M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 934–955; *Angew. Chem. Int. Ed.* **1999**, *38*, 884–905.

[3] E. Buhleier, W. Wehner, F. Vögtle, *Synthesis* **1978**, *2*, 155–158.

[4] a) U. Boas, P. M. H. Heegaard, *Chem. Soc. Rev.* **2004**, *33*, 43–63; b) S. Svenson, D. A. Tomalia in *Nanoparticles for Pharmaceutical Applications* (Ed.: A. J. Domb), American Scientific Publishers, Stevenson Ranch, CA, **2007**, pp. 233–255; c) J. Dennig, *Top. Curr. Chem.* **2003**, *228*, 227–236; d) H. Yamaguchi, A. Harada, *Top. Curr. Chem.* **2003**, *228*, 237–258; e) H. Kobayashi, M. W. Brechbiel, *Adv. Drug Deliv. Rev.* **2005**, *57*, 2271–2286; f) W. Krause, N. Hackmann-Schlichter, F. K. Maier, R. Müller, *Top. Curr. Chem.* **2000**, *210*, 261–308; g) M. W. Grinstaff, *Chem. Eur. J.* **2002**, *8*, 2839–2846; h) Y. Kim, S. C. Zimmerman, *Curr. Opin. Chem. Biol.* **1998**, *2*, 733–742; i) R. K. Tekade, P. V. Kumar, N. K. Jain, *Chem. Rev.* **2009**, *109*, 49–87; j) M. S. Muthu, S. Singh, *Nanomedicine* **2009**, *4*, 105–118.

[5] a) S.-C. Lo, P. L. Burn, *Chem. Rev.* **2007**, *107*, 1097–1116; b) P. L. Burn, S.-C. Lo, *Adv. Mater.* **2007**, *19*, 1675–1688; c) G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689–1746; d) S. Yokoyama, A. Otomo, T. Nakahama, Y. Okuno, S. Mashiko, *Top. Curr. Chem.* **2003**, *228*, 197–220; e) R. M. Crooks, B. I. Lemon III, L. Sun, L. K. Yeung, M. Zhao, *Top. Curr. Chem.* **2001**, *212*, 81–135; f) G. D. D'Ambruoso, D. V. McGrath in *Energy Harvesting Materials* (Ed.: D. L. Andrews), World Scientific Publishing, Singapore, **2005**, pp. 281–334; g) R. E. Bauer, A. C. Grimsdale, K. Müllen, *Top. Curr. Chem.* **2005**, *245*, 253–286.

[6] a) A. Juris in *Electron Transfer in Chemistry* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**, vol. 3, pp. 655–716; b) S. Campagna, S. Serroni, F. Puntoriero, C. Di Pietro, V. Ricevuto in *Electron Transfer in Chemistry* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**, vol. 5, pp. 186–214; c) W.-S. Li, W.-D. Jong, T. Aida in *Macromolecular Engineering* (Eds.: K. Matyjaszewski, Y. Gnanou, L. Leibler), Wiley-VCH, Weinheim, **2007**, vol. 2, pp. 1057–1102; d) D.-L. Jiang, T. Aida, *Prog. Polym. Sci.* **2005**, *30*, 403–422; e) M. Kawa, *Top. Curr. Chem.* **2003**, *228*, 193–204; f) V. Balzani, P. Ceroni, M. Maestri, V. Vicinelli, *Curr. Opin. Chem. Biol.* **2003**, *7*, 657–665; g) S. Campagna, C. Di Pietro, F. Loiseau, B. Maubert, N. McClenaghan, R. Passalacqua, F. Puntoriero, V. Ricevuto, S. Serroni, *Coord. Chem. Rev.* **2002**, *229*, 67–74; h) A. Adronov, J. M. J. Fréchet, *Chem. Commun.* **2000**, *18*, 1701–1710; i) T. Pullerits, V. Sundström, *Acc. Chem. Res.* **1996**, *29*, 381–389.

[7] For recent examples, see: a) H. Imahori, *J. Phys. Chem. B* **2004**, *108*, 6130–6143; b) T. H. Ghaddar, J. F. Wishard, D. W. Thompson, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2002**, *124*, 8285–8289; c) D. L. Andrews, S. Li, J. Rodriguez, J. Slota, *J. Chem. Phys.* **2007**, *127*, 134902/1–134902/7; d) T. S. Ahn, A. L. Thompson, P. Bharathi, A. Müller, C. J. Bardeen, *J. Phys. Chem. B* **2006**, *110*, 19810–19819; e) L. F. Lee, A. Adronov, R. D. Schaller, J. M. J. Fréchet, R. J. Saykally, *J. Am. Chem. Soc.* **2003**, *125*, 536–540; f) U. Hahn, M. Gorka, F. Vögtle, V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, *Angew. Chem.* **2002**, *114*, 3747–3750; *Angew. Chem. Int. Ed.* **2002**, *41*,

3595–3598; g) G. S. He, T.-C. Lin, Y. Cui, P. N. Prasad, D. W. Brousmiche, J. M. Serin, J. M. J. Fréchet, *Opt. Lett.* **2003**, *28*, 768–770; h) X. Zhou, D. S. Tyson, F. N. Castellano, *Angew. Chem.* **2000**, *112*, 4471–4475; *Angew. Chem. Int. Ed.* **2000**, *39*, 4301–4305; i) D. S. Tyson, C. R. Luman, F. N. Castellano, *Inorg. Chem.* **2002**, *41*, 3578–3586; j) J.-L. Wang, J. Yan, Z.-M. Tang, Q. Xiao, Y. Ma, J. Pei, *J. Am. Chem. Soc.* **2008**, *130*, 9952–9962; k) C. Giansante, P. Ceroni, V. Balzani, F. Vögtle, *Angew. Chem.* **2008**, *120*, 5502–5505; *Angew. Chem. Int. Ed.* **2008**, *47*, 5422–5425; l) T. Qin, G. Zhou, H. Schreiber, R. E. Bauer, M. Baumgarten, C. E. Anson, E. J. W. List, K. Müllen, *Angew. Chem.* **2008**, *120*, 8416–8420; *Angew. Chem. Int. Ed.* **2008**, *47*, 8292–8296; m) T. M. Figueira-Duarte, S. C. Simon, M. Wagner, S. I. Druzhinin, K. A. Zachariasse, K. Müllen, *Angew. Chem.* **2008**, *120*, 10329–10332; *Angew. Chem. Int. Ed.* **2008**, *47*, 10175–10178; n) M. Gingras, V. Placide, J.-M. Raimundo, G. Bergamini, P. Ceroni, V. Balzani, *Chem. Eur. J.* **2008**, *14*, 10357–10363.

[8] a) P. Ceroni, G. Bergamini, F. Marchioni, V. Balzani, *Prog. Polym. Sci.* **2005**, *30*, 453–473; b) V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, *Top. Curr. Chem.* **2003**, *228*, 159–191; c) V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero, S. Serroni, *Coord. Chem. Rev.* **2001**, *219–221*, 545–572; d) J.-F. Nierengarten, *Top. Curr. Chem.* **2003**, *228*, 87–110.

[9] For some recent examples, see: a) C. Saudan, V. Balzani, M. Gorka, S.-K. Lee, J. van Heyst, M. Maestri, P. Ceroni, V. Vicinelli, F. Vögtle, *Chem. Eur. J.* **2004**, *10*, 899–905; b) V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka, F. Vögtle, *Chem. Commun.* **2000**, *10*, 853–854; c) T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, J. R. Lawrence, I. D. W. Samuel, S.-C. Lo, P. L. Burn, *Org. Electronics* **2003**, *4*, 71–76; d) T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, I. D. W. Samuel, S.-C. Lo, P. L. Burn, *Appl. Phys. Lett.* **2003**, *82*, 4824–4826; e) J. B. Oh, M. K. Nah, Y. H. Kim, M. S. Kang, J. W. Ka, H. K. Kim, *Adv. Funct. Mater.* **2007**, *17*, 413–424; f) L. Shen, M. Shi, F. Y. Li, D. Zhang, X. Li, E. Shi, T. Yi, Y. Du, C. Huang, *Inorg. Chem.* **2006**, *45*, 6188–6197; g) J. P. Cross, M. Lauz, P. D. Badger, S. Petoud, *J. Am. Chem. Soc.* **2004**, *126*, 16278–16279; h) V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, F. Vögtle, *J. Am. Chem. Soc.* **2002**, *124*, 6461–6468; i) M. Tominaga, J. Hosogi, K. Konishi, T. Aida, *Chem. Commun.* **2000**, 719–720; j) C. Saudan, V. Balzani, P. Ceroni, M. Gorka, M. Maestri, V. Vicinelli, *Tetrahedron* **2003**, *59*, 3845–3852; k) C. Saudan, P. Ceroni, V. Vicinelli, M. Maestri, V. Balzani, M. Gorka, S.-K. Lee, J. van Heyst, F. Vögtle, *Dalton Trans.* **2004**, 1597–1600; l) B. Buschhaus, A. Hirsch, *Eur. J. Org. Chem.* **2005**, 1148–1160; m) F. E. Appoh, H.-B. Kraatz, *J. Appl. Polym. Sci.* **2009**, *111*, 709–723.

[10] a) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani, *Top. Curr. Chem.* **2007**, *280*, 117–214; b) F. Vögtle, M. Plevoets, M. Nieger, G. C. Azzellini, A. Credi, L. De Cola, V. De Marchis, M. Venturi, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 6290–6298; c) M. Plevoets, F. Vögtle, L. De Cola, V. Balzani, *New J. Chem.* **1999**, *23*, 63–69; d) G. M. Stewart, M. A. Fox, *J. Am. Chem. Soc.* **1996**, *118*, 4354–4360; e) J. Issberner, F. Vögtle, L. De Cola, V. Balzani, *Chem. Eur. J.* **1997**, *3*, 706–712; f) Y.-R. Hong, C. B. Gorman, *J. Org. Chem.* **2003**, *68*, 9019–9025; g) T. H. Ghaddar, J. F. Wishart, J. P. Kirby, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2001**, *123*, 12832–12836; h) R. Kikkeri, I. Garcia-Rubio, P. H. Seeberger, *Chem. Commun.* **2009**, 235–237.

[11] a) H. Stephan, G. Geipel, G. Bernhard, U. Hahn, F. Vögtle, *Eur. J. Inorg. Chem.* **2005**, 4501–4508; b) H. Stephan, S. Juran, K. Born, P. Comba, G. Geipel, U. Hahn, F. Vögtle, *New J. Chem.* **2008**, *32*, 2016–2022; c) N. D. McClenaghan, R. Passalacqua, F. Loiseau, S. Campagna, B. Verheyde, A. Hameurlaine, W. Dehaen, *J. Am. Chem. Soc.* **2003**, *125*, 5356–5365.

[12] a) P. D. Marcato, N. Durán, *J. Nanosci. Nanotechnol.* **2008**, *5*, 2216–2229; b) M. Montalti, L. Prodi, N. Zaccheroni in *Handbook of Photochemistry and Photobiology* (Ed.: H. S. Nalwa), American Scientific Publishers, Valencia, CA, **2003**, vol. 3, pp. 271–317; c) B. P. Gilmartin, R. L. McLaughlin, M. E. Williams, *Chem. Mater.* **2005**, *17*, 5446–5454.

[13] See, for example: a) H. Kobayashi, N. Sato, A. Hiraga, T. Saga, Y. Nakamoto, H. Ueda, J. Konishi, K. Togashi, M. W. Brechbiel, *Magn. Reson. Med.* **2001**, *45*, 454–460; b) E. C. Wiener, M. W. Brechbiel, H. Brothers, R. L. Magin, O. A. Gansow, D. A. Tomalia, P. C. Lauterbur, *Magn. Reson. Med.* **1994**, *31*, 1–8; c) E. C. Wiener, F. P. Auteri, J. W. Chen, M. W. Brechbiel, O. A. Gansow, D. S. Schneider, R. L. Belford, R. B. Clarkson, P. C. Lauterbur, *J. Am. Chem. Soc.* **1996**, *118*, 7774–7782; d) A. T. Yordanov, A. L. Lodder, E. K. Woller, M. J. Cloninger, N. Patronas, D. Milenic, M. W. Brechbiel, *Nano Lett.* **2002**, *2*, 595–599; e) A. T. Yordanov, K.-I. Yamada, M. C. Krishna, J. B. Mitchell, E. Woller, M. Cloninger, M. W. Brechbiel, *Angew. Chem.* **2001**, *113*, 2762–2764; *Angew. Chem. Int. Ed.* **2001**, *40*, 2690–2692; f) G. M. Nicolle, É. Tóth, H. Schmitt-Willich, B. Radüchel, A. E. Merbach, *Chem. Eur. J.* **2002**, *8*, 1040–1048.

[14] a) K. Takada, G. D. Storrier, J. I. Goldsmith, H. D. Abruña, *J. Phys. Chem. B* **2001**, *105*, 2404–2411; b) S. Glazier, J. A. Barron, N. Morales, A. M. Ruschak, P. L. Houston, H. D. Abruña, *Macromolecules* **2003**, *36*, 1272–1278; c) H. J. Murfee, T. P. S. Thoms, J. Greaves, B. Hong, *Inorg. Chem.* **2000**, *39*, 5209–5217; d) M. Zhou, J. Roovers, *Macromolecules* **2001**, *34*, 244–252; e) G. D. Storrier, K. Takada, H. D. Abruña, *Langmuir* **1999**, *15*, 872–884.

[15] a) A. Dirksen, U. Hahn, F. Schwanke, J. N. H. Reek, R. M. Williams, F. Vögtle, L. De Cola, *Chem. Eur. J.* **2004**, *10*, 2036–2047; b) K. Hager, A. Franz, A. Hirsch, *Chem. Eur. J.* **2006**, *12*, 2663–2679.

[16] M. Staffilani, E. Höss, U. Giesen, E. Schneider, F. Hartl, H.-P. Josel, L. De Cola, *Inorg. Chem.* **2003**, *42*, 7789–7798.

[17] a) K. M. Stewart, J. Rojo, L. X. McLaughlin, *Angew. Chem.* **2004**, *116*, 5932–5935; *Angew. Chem. Int. Ed.* **2004**, *43*, 5808–5811; b) L. A. Basile, J. K. Barton, *J. Am. Chem. Soc.* **1987**, *109*, 7548–7550; c) L. A. Basile, A. L. Raphael, J. K. Barton, *J. Am. Chem. Soc.* **1987**, *109*, 7550–7551.

[18] V. C. Pierre, M. Botta, K. N. Raymond, *J. Am. Chem. Soc.* **2005**, *127*, 504–505.

[19] a) C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647; b) C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.* **1990**, 1010–1013.

[20] The origin for this macroscopic dendritic pattern has not been further investigated.

[21] M. S. Gabon, R. W. Bradshaw, *Angew. Chem.* **1968**, *80*, 986–997; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 919–930.

[22] M. Miyaz Khan, *J. Org. Chem.* **1996**, *61*, 8063–8068.

[23] P. C. Alford, M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, D. J. Robbins, *J. Chem. Soc. Perkin Trans. 2* **1985**, 705–709.

[24] Y. Kawanishi, N. Kitamura, Y. Kim, S. Tazuke, *Riken Q.* **1984**, *78*, 212–219.

[25] V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero, S. Serroni, *Coord. Chem. Rev.* **2001**, *219*, 545–572.

[26] F. Barigelletti, L. De Cola, V. Balzani, P. Belser, A. von Zelewsky, F. Vögtle, F. Ebmeyer, S. Grammenudi, *J. Am. Chem. Soc.* **1989**, *111*, 4662–4668.

[27] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277.

[28] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697–2705.

Received: March 17, 2009
Published Online: May 11, 2009

