Supramolecular dendrimers with a $[Ru(bpy)_3]^{2+}$ core and naphthyl peripheral units

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We report the synthesis and the photophysical properties of first and second generation dendrimers built around a $[Ru(bpy)_3]^{2+}$ core (bpy = 2,2′-bipyridine) and bearing 12 and 24 naphthyl units, respectively, in the periphery. The metallodendrimers were obtained by complexation of ruthenium trichloride with bipyridine ligands carrying dendritic wedges in the 4,4′-positions. Since the chromophoric groups present in the dendritic complexes are separated by aliphatic connections, interchromophoric interactions are weak and the absorption spectra of the metallodendrimers are essentially equal to the summation of the spectra of the chromophoric groups which are present in their structures. The 'free' wedges show an intense emission band in the region of the naphthyl-type units. Such a band, however, is almost completely absent in the emission spectra of the metallodendrimers, which exhibit the visible emission band characteristic of their $[Ru(bpy)_3]^{2+}$-type unit, regardless of the excitation wavelength. These results show that a very efficient energy-transfer process takes place from the potentially fluorescent excited states of the aromatic units of the wedges to the metal-based dendritic core (antenna effect). We have also found that the dendrimer branches protect the Ru–bpy based core from dioxygen quenching.

Introduction

Dendrimers are a new class of well defined macromolecules exhibiting a tree-like structure,[1] first derived by the 'cascade molecule' approach.[2] Dendrimer chemistry was initially developed in the field of organic chemistry. More recently, a number of dendrimers based on metal complexes have been synthesized.[3–9] Metal complexes are characterized by a precise molecular geometry related to the characteristic coordination number of the metal ion and can exhibit valuable properties such as absorption of visible light, luminescence, and reduction and oxidation levels at accessible potentials. By using metal complexes it is therefore possible to incorporate in the dendritic structure specific 'pieces of information' that, when placed in suitable sites of the array, can be used to perform valuable functions.[3] From a structural viewpoint, most of the metal-containing dendrimers can be classified according to four categories:[3e] (i) dendrimers built around a metal complex as a core; (ii) dendrimers containing metal complexes as peripheral units; (iii) dendrimers containing metal complexes in the branches; (iv) dendrimers based on metals as branching centers. Continuing our collaboration in the field of photoactive dendrimers,[10] we report here the synthesis and the photophysical properties of first and second generation dendrimers built around a $[Ru(bpy)_3]^{2+}$ core (bpy = 2,2′-bipyridine) and bearing 12 and 24 naphthyl units, respectively, in the periphery. One reason of interest in these compounds is due to the fact that both the $[Ru(bpy)_3]^{2+}$ core[11] and the peripheral naphthyl units[12] are luminescent species, with well defined energy levels. It seems reasonable to expect that UV excitation of the peripheral naphthyl units can be followed by energy transfer to the $[Ru(bpy)_3]^{2+}$ core, thereby causing sensitized emission of visible light. Energy transfer in dendrimers is an important topic related to a variety of applications, including the construction of antenna supramolecular systems capable of harvesting sunlight.[13–15] Another interesting aspect of the investigated compounds is whether the organic branches of the dendrimer protect the luminescent core from oxygen quenching.[10a]

Results and discussion

Synthesis

Dendritic benzylic bromides of the first and second generation with naphthalenyl units at the periphery (Fig. 1) were prepared following the general procedure developed by Hawker and Fréchet.[16] According to such a convergent approach, the synthesis of the dendritic wedges starts from the units that will ultimately be found at the periphery. In the first step, the reaction of 3,5-dihydroxybenzylalcohol **1** with two equivalents of 2-bromomethylnaphthalene **2** yields the first generation benzylic alcohol **3**. The reaction was carried out in boiling acetone in the presence of potassium carbonate and a catalytic amount of 18-crown-6. After purification, the benzylic alcohol **3** was obtained as a colorless solid. The conversion of **3** to the first generation benzylic bromide **4**, obtained as a colourless solid compound, was achieved with PBr_3[17] in dry toluene or benzene at 0 °C. Reaction of the first generation benzylic bromide with **1** under the same conditions described above (boiling acetone, K_2CO_3, 18-crown-6, 48 h) gave the second-generation alcohol **5**, which was treated again with PBr_3 to give the corresponding second generation benzylic bromide **6** (Fig. 1).

The synthesis of the new dendritic ligands (Fig. 2) was performed using 4,4′-dimethyl-2,2′-bipyridine as the starting

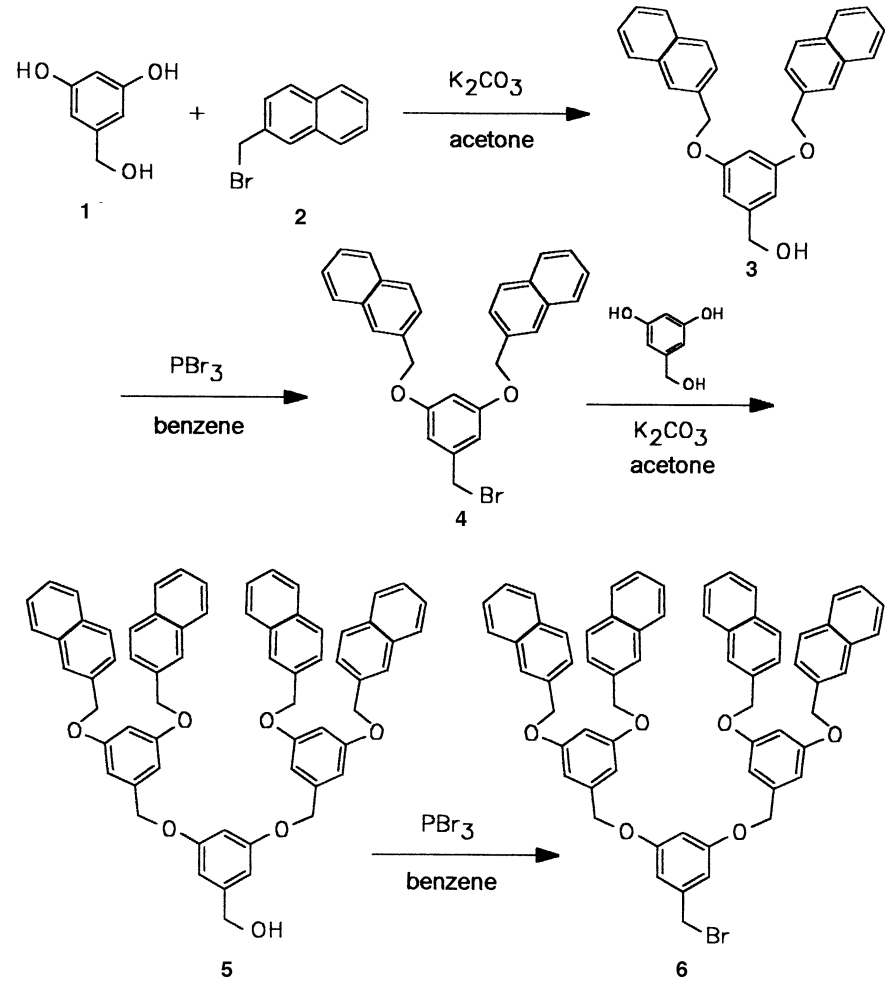


Fig. 1 Synthesis of the dendritic wedges with naphthyl units at periphery.

material. Treatment of 4,4′-dimethyl-2,2′-bipyridine with an excess of LDA in dry THF at −10 °C afforded the orange dilithio compound **7**.[18] After 45 min this species was quenched by addition of a dendritic benzylic bromide which leads to the symmetric 4,4′-disubstituted dendritic bipyridine-ligands **8** and **9** of the first and the second generation, respectively. Column chromatography on silica-gel gave the desired products in *ca.* 60% yield. The structures of the new ligands were

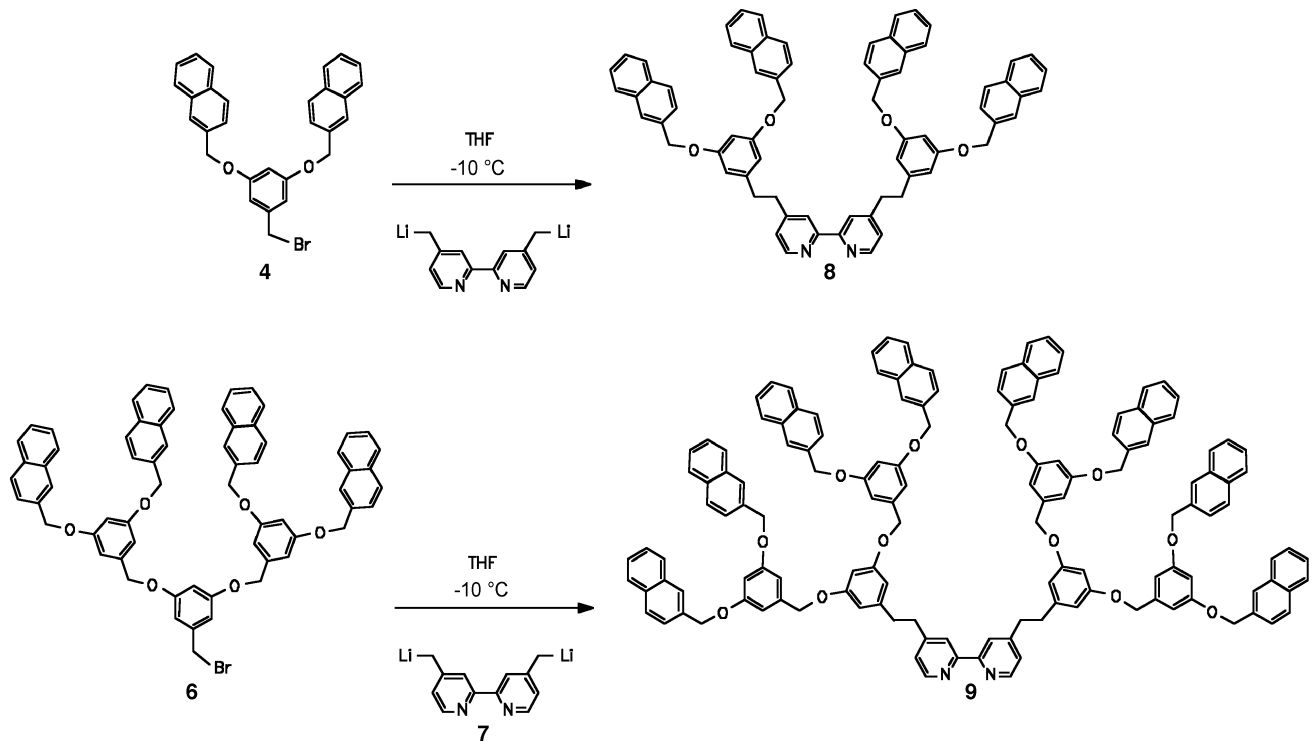
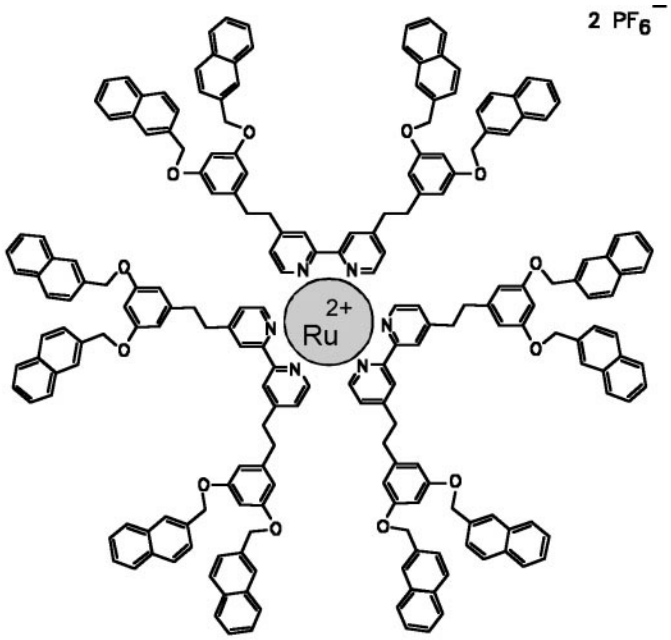


Fig. 2 Synthesis of the dendritic bipyridine ligands.

readily confirmed by ^{1}H and ^{13}C NMR spectra, and MALDI-TOF mass spectrometric analysis.

The complexation of the dendritic ligands with ruthenium trichloride gave the metallodendrimers **10** and **11** (Fig. 3). The dendritic bipyridine-ligands and ruthenium trichloride (3 : 1 stoichiometric ratio) were dissolved in a mixture of chloroform and ethanol (2 : 1 v/v) and gently heated under reflux for five days. The reaction mixture turned from dark violet to bright orange, which indicates the formation of the tris-bipyridine ruthenium complex. In this reaction, Ru(III) is reduced to Ru(II) by ethanol. The reaction products were purified by column or plate chromatography and were obtained as orange, highly viscous, oily compounds. Further purification was obtained by exchanging the chloride counter ions with hexafluorophosphate ions.

Because of their highly branched, organic dendritic wedges, the ruthenium complexes **10** and **11** hardly show any salt-like character. They are insoluble in water, but soluble in a wide



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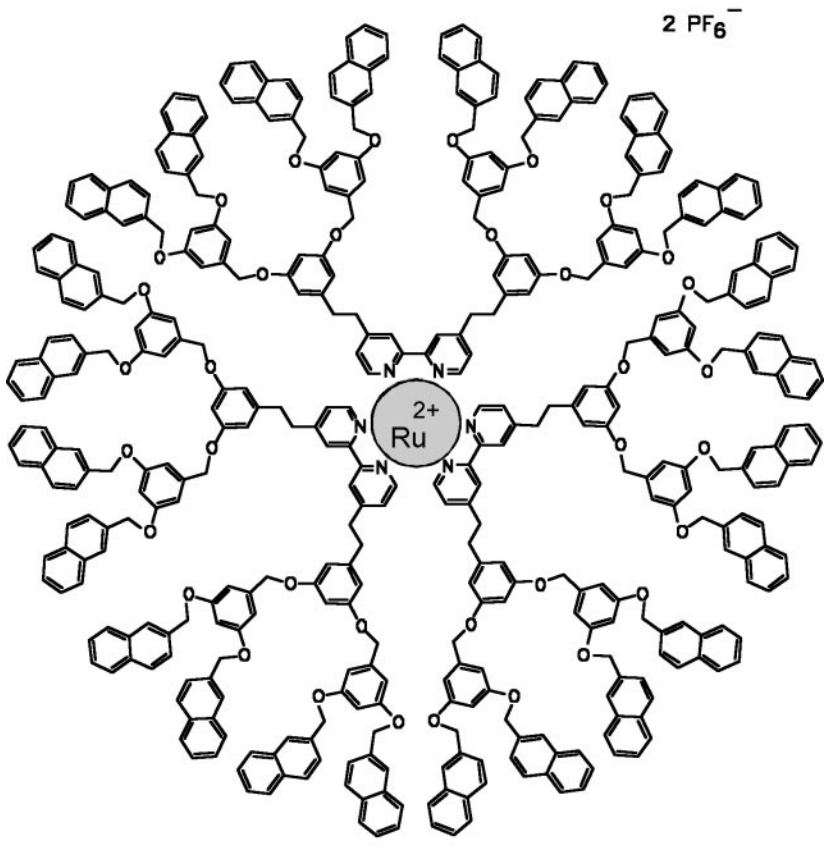

11

Fig. 3 Dendrimers with a $[Ru(bpy)_3]^{2+}$ core and naphthyl peripheral units.

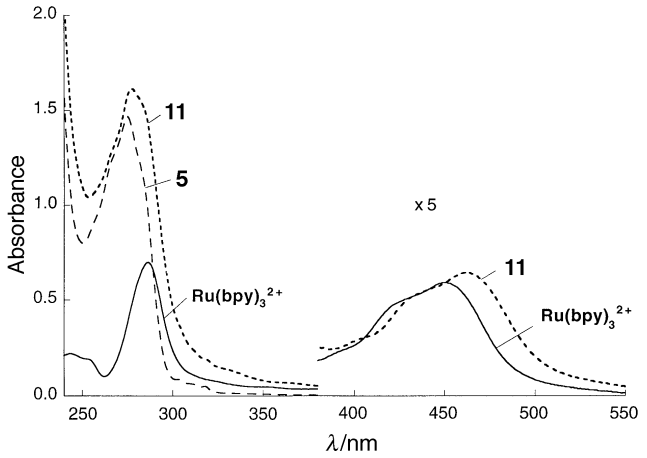

Fig. 4 Absorption spectra at 298 K in acetonitrile solution of dendrimer **11** (8.0×10^{-6} M), wedge **5** (4.8×10^{-4} M) and $[Ru(bpy)_3]^{2+}$ (8×10^{-6} M).

spectrum of organic solvents. The structures of the dendritic ruthenium complexes were readily deduced from ^1H and ^{13}C NMR spectra, and from MALDI-TOF mass spectrometry.

Spectroscopic and photophysical properties

The dendritic complexes **10** and **11** are multicomponent (supramolecular) species.[19] From a spectroscopic and photophysical viewpoint, they can be considered as comprising a $[Ru(bpy)_3]^{2+}$-type chromophoric unit bearing branches of type **3** and **6**, respectively, appended at the 4,4′-positions of the 2,2′-bipyridine ligands. Such branches are multicomponent species in their own right since they contain 1,3-dimethoxybenzene- and 2-naphthyl-type chromophoric units.

The chromophoric groups present in the dendritic complexes **10** and **11** are separated by aliphatic connections. Therefore interchromophoric interactions are expected to be weak and the absorption spectra of **10** and **11** should substantially be equal to the summation of the spectra of the chromophoric groups which are present in their structures. Fig. 4, in which the absorption spectra of dendrimer **11**, wedge **5** and $[Ru(bpy)_3]^{2+}$ (taken as a model compound for the dendritic core) are displayed, shows that the above expectation is substantially fulfilled.

The three types of chromophoric groups contained in the dendritic complexes **10** and **11**, namely, the $[Ru(bpy)_3]^{2+}$-, dimethoxybenzene-, and naphthyl-type units, are potentially luminescent species. The luminescent properties exhibited by the two dendrimers and by model compounds of their component units are presented in Table 1. The luminescence spectrum of the wedge **5** [Fig. 5(a)] shows an intense emission

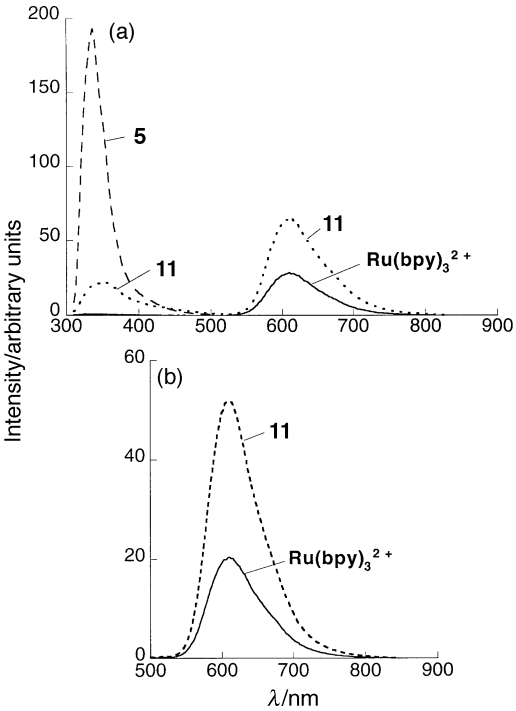

Fig. 5 (a) Luminescence spectra of dendrimer **11**, wedge **5** and $[Ru(bpy)_3]^{2+}$ on excitation at 270 nm. The absorption of the solution was 0.160 in all cases. (b) Luminescence spectra of dendrimer **11** and $[Ru(bpy)_3]^{2+}$ on excitation at 450 nm. The absorbance of the solution was 0.120 in both cases.

band in the region of the dimethoxybenzene- and naphthyl-type units. Such a band, however, is almost completely absent in the emission spectra of dendrimers **10** and **11**, which exhibit the visible emission band characteristic of the $[Ru(bpy)_3]^{2+}$-type chromophoric group, regardless of the excitation wavelength (Table 1, Fig. 5). A quantitative comparison of the emission intensity in the UV region of wedge **5** and dendrimer **11** upon excitation at 270 nm, which is mainly absorbed by the dimethoxybenzene- and naphthyl-type units in the dendrimer, shows that at least 90% of the emission of the chromophoric groups of the wedges is quenched in the dendrimer [Fig. 5(a)]. Comparison of the emission intensity at 610 nm of $[Ru(bpy)_3]^{2+}$ and dendrimer **11** upon excitation (i) with 450 nm light, which in **11** is absorbed only by the $[Ru(bpy)_3]^{2+}$-type core and (ii) with 270 nm light, which in **11** is mainly absorbed by the wedges, shows that the light absorbed by the dimethoxybenzene- and naphthyl-type units of the wedges is almost as efficient as the light absorbed by the core as far as the intensity of the 610 nm band is concerned (Table 1, Fig. 5). These results show that a very efficient energy-transfer process

Table 1 Luminescence data[a]

		298 K[b]			77 K[c]	
		λ_{max}/nm	τ/ns	Φ	λ_{max}/nm	τ/μs
$Ru(bpy)_3^{2+}$ [d]	(λ^{exc} = 450 nm)	611	172 990[e]	0.016	582	4.8
2-Methylnaphthalene[e,f]	(λ^{exc} = 265 nm)	336	59	0.32		
1,4-Dimethoxybenzene[e,g]	(λ^{exc} = 303 nm)	321	2.9	0.21		
Dendrimer **10**	(λ^{exc} = 450 nm)	613	240 1100[e]	0.030	585	5.0
	(λ^{exc} = 270 nm)	613		0.027		
Dendrimer **11**	(λ^{exc} = 450 nm)	610	412 915[e]	0.046	582	5.7
	(λ^{exc} = 270 nm)	611		0.038		

[a] Aerated solution, except otherwise noted. [b] Acetonitrile solution. [c] Butyronitrile solution. [d] From ref. 10*a*. [e] Deaerated solution. [f] Non-polar solvent, structured band, from ref. 12*a*. [g] Non-polar solvent, broad band, from ref. 12*a*; a closer model compound would be 1,2-dimethoxybenzene, data of which are not available.

takes place from the potentially fluorescent excited states of the aromatic units of the wedges to the metal-based dendritic core (antenna effect[13–15]).

As one can see from the data collected in Table 1, in deaerated solution the luminescence lifetime of the $[Ru(bpy)_3]^{2+}$-type core of dendrimers **10** and **11** is very close to that of the $[Ru(bpy)_3]^{2+}$ model compound. In aerated solution, however, the luminescence lifetime of **10** is about 40% longer than that of the $[Ru(bpy)_3]^{2+}$ model compound, and that of **11** more than twice as long. These data show that the dendrimer branches protect the Ru–bpy based core from dioxygen quenching, as it has been previously observed for other similar dendrimers.[10a] 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.[20] It is also interesting to note that, owing to the very high absorbance by the naphthyl groups in the near UV spectral region (Fig. 4) and the high energy transfer efficiency from the naphthyl units to the $[Ru(bpy)_3]^{2+}$ core, even extremely diluted solutions (10^{-7} M) of dendrimer **11** exhibit strong visible emission upon UV excitation.

Conclusions

First and second generation dendrimers built around a $[Ru(bpy)_3]^{2+}$ core and bearing 12 and 24 naphthyl units, respectively, in the periphery have been synthesized. The fluorescence of the aromatic wedges is almost completely quenched in the dendrimers as a consequence of a very efficient energy-transfer process to the metal-based dendritic core (antenna effect). The dendrimer wedges protect the $[Ru(bpy)_3]^{2+}$ core from dioxygen quenching, so that in aerated solutions the quantum yield of the Ru-based phosphorescence of the second generation dendrimer is about three times that of $[Ru(bpy)_3]^{2+}$.

Experimental

Materials and methods

Chemicals were purchased from Aldrich and Fluka and used as received. 4,4′-Dimethyl-2,2′-bipyridine, was prepared according to published literature methods.[21] Thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel 60 F254 (Merck 1.05554). The sheets were examined by UV light ($\lambda = 254$ nm). Column chromatography was carried out using silica gel 60 (Merck 15101). Plate chromatography was carried out using alox 60 plates (Merck 1.05788.0001). Melting points (uncorrected) were determined on a Kofler microscope heater (Reichert, Vienna). Mass spectra were obtained on an A.E.I. (Manchester, UK) MS 50 operating in the electron impact mode (EIMS). MALDI spectra were recorded on a TofSpec E (Micromass, Manchester, UK). The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 [250 MHz (^1H), 62.9 MHz (^{13}C)], or on a Bruker AM 400 [400 MHz (^1H), 100.6 MHz (^{13}C)].

Absorption spectra were measured in acetonitrile solution at 298 K with a Perkin–Elmer Lambda 6 spectrophotometer. Luminescence spectra were obtained with a Perkin–Elmer LS 50 spectrofluorimeter in air-equilibrated acetonitrile at room temperature and in freshly distilled butyronitrile at 77 K. Luminescence decay measurements were performed with an Edinburgh single-photon counting instrument. When necessary, deaeration of the solution was performed by repeated freeze–thaw–freeze cycles. Luminescence quantum yields were measured following the method indicated by Demas and Crosby[22] using $Ru(bpy)_3^{2+}$ as a standard ($\Phi = 2.8 \times 10^{-2}$ in aerated water solution).[23] Experimental errors: λ, ± 2 nm; ε, $\pm 10\%$; τ, $\pm 5\%$; Φ, $\pm 20\%$.

General procedure for the preparation of the dendritic benzyl alcohols

A mixture of the corresponding benzyl bromide, 3,5-dihydroxybenzyl alcohol **1**, potassium carbonate and 18-crown-6 in dry acetone was heated at reflux for 48 h under argon. After cooling the mixture was evaporated to dryness under reduced pressure. The residue was dissolved in 200 ml dichloromethane and washed with water twice. The combined water layers were extracted with dichloromethane three times. Finally the combined organic layers were dried with Na_2SO_4 and evaporated to dryness. The crude products were purified by recristalisation or column chromatography.

3,5-Bis(2′-naphthalenylmethyloxy)benzyl alcohol 3

13 g (0.058 mol) 2-bromomethylnaphthalene **2**, 3.74 g (0.0267 mol) 3,5-dihydroxybenzyl alcohol **1**, 9.21 g (0.0667 mol) dry potassium carbonate, and 1.5 g (5.7 mmol) 18-crown-6 were dissolved in 500 ml dry acetone. The crude product was recrystallised from toluene–*n*-hexane (v/v 3 : 1). Colorless solid 13 g (46% yield). Mp 86 °C. HRMS-EI (70 eV): *m/z* (%) 420.1 (M^+ 4.2), 280.1 (3.9), 141.1 (100), 115.1 (10.3). Found 420.1727, calc. $C_{29}H_{24}O_3$: 420.1729. ^1H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 1H, OH), 4.62 (s, 2H, CH_2OH), 5.19 (s, 4H, CH_2O), 6.63 (t, $^4J_{HH} = 2.2$ Hz, 1H, phenyl-H), 6.67 (d, $^4J_{HH} = 2.3$ Hz, 2H, phenyl-H), 7.46–7.52 (m, 6H, naphthalene-H), 7.81–7.86 (m, 8H, naphthalene-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.58 (CH_2OH), 70.51 (OCH_2), 101.74, 106.14, 125.62, 126.42, 126.58, 126.68, 128.07, 128.3, 128.73, 133.39, 133.6, 134.62, 143.87, 160.5.

3,5-Bis[3′,5′-bis(2″-naphthalenylmethyloxy)benzyloxy]benzyl alcohol 5

5.5 g (11.4 mmol) 3,5-bis(2′-naphthalenylmethyloxy)benzyl bromide **4**, 0.7 g (4.96 mmol) 3,5-dihydroxybenzyl alcohol **1**, 1.7 g (12.3 mmol) dry potassium carbonate and 260 mg 18-crown-6 were dissolved in 200 ml dry acetone. The crude product was purified by column chromatography: SiO_2, dichloromethane, $R_f = 0.45$. Colorless solid, 2.5 g (53.3% yield). Mp 117 °C. MALDI-TOF-MS (matrix: 2,4-dihydroxybenzoic acid (DHB)); *m/z* 967.027 $[M + Na]^+$, 983.016 $[M + K]^+$. $C_{65}H_{52}O_7$ (945.12). ^1H NMR (400 MHz, $CDCl_3$): δ 4.56 (s, 2H, CH_2OH), 4.96 (s, 4H, CH_2O), 5.16 (s, 8H, CH_2O), 6.56 (t, $^4J_{HH} = 2.2$ Hz, 1H, phenyl-H), 6.59 (d, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 6.68 (t, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 6.72 (d, $^4J_{HH} = 2.2$ Hz, 4H, phenyl-H), 7.45–7.53 (m, 12H, naphthalene-H), 7.8–7.84 (m, 16H, naphthalene-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.4 (CH_2OH), 70.14, 70.45 (CH_2O), 101.52, 101.94, 105.92, 106.7, 125.63, 126.38, 126.52, 126.7, 128.02, 128.27, 128.67, 133.33, 133.54, 134.51, 139.672, 143.81, 160.26, 160.45.

General procedure for the preparation of the dendritic benzyl bromides

To an ice cooled mixture of the corresponding benzyl alcohol dissolved in dry toluene or dry benzene was added PBr_3 dropwise under argon. The reaction mixture was stirred for 3 h at room temperature and then poured into water and extracted with dichloromethane five times. In order to improve the separation of the organic and the water layer, some ethanol was added to the dichloromethane. Finally the combined organic layers were dried with Na_2SO_4 and evaporated to dryness. The crude products were purified by column chromatography.

3,5-Bis(2′-naphthalenylmethyloxy)benzyl bromide 4

8.78 g (0.021 mol) 3,5-bis(2′-naphthalenylmethyloxy)benzyl alcohol **3**, 0.72 ml (7.7 mmol) PBr_3 and 50 ml benzene. Column chromatography: SiO_2, dichloromethane–

cyclohexane (1 : 1 v/v), $R_f = 0.23$. Colorless solid; 7.7 g (77% yield). Mp 114 °C. HRMS-EI (70 eV): *m/z* (%) 484.1, 482.1 (M^+ 2.5, 2.49), 403.2 (2.5), 342.0 (1), 280.1 (5), 263.1 (2.1), 220.0 (1.5), 141.1 (100), 115.1 (1.8). Found 482.0882. Calc. $C_{29}H_{23}O_2Br$: 482.0883. ^1H NMR (250 MHz, $CDCl_3$): δ 4.43 (s, 2H, CH_2Br), 5.19 (s, 4H, CH_2O), 6.65 (t, $^4J_{HH} = 2.2$ Hz, 1H, phenyl-H), 6.71 (d, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 7.48–7.54 (m, 6H, naphthalene-H), 7.84–7.88 (m, 8H, naphthalene-H). ^{13}C NMR (62.86 MHz, $CDCl_3$): δ 33.78 (CH_2Br), 70.44 (OCH_2), 102.45, 108.42, 125.23, 125.45, 126.29, 126.43, 126.6, 126.74, 126.92, 127.74, 127.9, 128.13, 128.36, 128.59, 133.25, 133.44, 134.22, 139.99, 160.25.

3,5-Bis[3′,5′-bis(2′′-naphthalenylmethyloxy)benzyloxy]benzyl bromide 6

2.5 g (2.64 mmol) 3,5-bis[3′,5′-bis(2-naphthalenylmethyloxy)-benzyloxy]benzyl alcohol **5**, 0.095 ml (0.88 mmol) PBr_3, 50 ml benzene. Column chromatography: SiO_2, dichloromethane–cyclohexane (5.5 : 4.5 v/v), $R_f = 0.23$. Colourless solid 1.46 g (55% yield). Mp 108 °C. MALDI-TOF-MS (matrix: DHB); *m/z* 1030.617 $[M + Na]^+$, 1046.617 $[M + K]^+$. $C_{65}H_{51}O_6Br$ (1008.02). ^1H NMR (400 MHz, $CDCl_3$): δ 4.35 (s, 2H, CH_2Br), 4.95 (s, 4H, CH_2O), 5.19 (s, 8H, CH_2O), 6.5 (t, $^4J_{HH} = 2.2$ Hz, 1H, phenyl-H), 6.59 (d, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 6.66 (t, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 6.72 (d, $^4J_{HH} = 2.2$ Hz, 4H, phenyl-H), 7.45–7.52 (m, 12H, naphthyl-H), 7.8–7.84 (m, 16H, naphthyl-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.97 (CH_2Br), 70.33, 70.58 (CH_2O), 102.11, 102.47, 106.79, 108.54, 125.64, 126.43, 126.58, 126.74, 128.08, 128.31, 128.76, 133.4, 133.61, 134.56, 139.46, 143.09, 160.25, 160.53.

General procedure for the preparation of the dendritic bipyridine ligands

To an anhydrous solution of diisopropylamine in THF at −10 °C under argon was added 1.6 M *n*-butyllithium in hexane. After 20 min stirring, a solution of 4,4′-dimethyl-2,2′-bipyridine in THF was added. The reaction mixture turned orange. After 45 min a solution of the dendritic benzyl bromide was added. In 5 h at room temperature the reaction mixture turned pale yellow indicating the end of the reaction. Finally the solution was poured on ice and the resulting water layer was extracted five times with dichloromethane. The combined organic layers were dried with Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography.

4,4′-Bis[3′′,5′′-bis(2′′′-naphthalenylmethyloxy)phenylethyl]-2,2′-bipyridine 8

0.57 ml (4.03 mmol) diisopropylamine, 2.39 ml (3.8 mmol) *n*-buthyllithium, 281 mg (1.53 mmol) 4,4′-dimethyl-2,2′-bipyridine, 2 g (4.3 mmol) 3,5-bis(2′-naphthalenylmethyloxy)benzyl bromide **4** in 30 ml THF. Column chromatography: SiO_2, dichloromethane–methanol (1000 : 12 v/v). Colorless solid 290 mg (68% yield). Mp 79 °C. R_f (SiO_2, dichloromethane–methanol 100:5 v/v) 0.32. MALDI-TOF-MS (matrix: DHB); *m/z* 990.0 $[M + H]^+$, 1011.9 $[M + Na]^+$, 1027.9 $[M + K]^+$. $C_{70}H_{56}O_4N_2$ (989.22). ^1H NMR (400 MHz, $CDCl_3$): δ 2.94–3.06 (m, 8H, CH_2CH_2), 5.18 (s, 8H, CH_2O), 6.54 (d, $^4J_{HH} = 2.2$ Hz, 4H, phenyl-H), 6.62 (t, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 7.1 (dd, $^3J_{HH} = 5$ Hz, $^4J_{HH} = 1.7$ Hz, 2H, pyridine-H), 7.45–7.6 (m, 12H, naphthalene-H), 7.8–7.95 (m, 16H, naphthalene-H), 8.39 (s, 2H, pyridine-H), 8.58 (d, $^3J_{HH} = 5$ Hz, 2H, pyridine-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.93, 37.15 (CH_2CH_2), 70.26, (CH_2O), 100.22, 107.93, 121.64, 124.34, 125.44, 126.17, 126.33, 126.47, 127.85, 128.07, 128.49, 133.15, 133.39, 134.48, 143.39, 148.92, 152.15, 155.65, 160.15.

4,4′-Bis[[3′′,5′′-bis[3′′′,5′′-bis(2′′′′-naphthalenylmethyloxy)]-benzyloxy]phenylethyl]2,2′-bipyridine 9

0.233 ml (1.65 mmol) diisopropylamine, 0.98 ml (1.6 mmol) *n*-buthyllithium, 121 mg (0.66 mmol) 4,4′-dimethyl-2,2′-bipyridine, 1.46 g (1.46 mmol) 3,5-bis[3′,5′-bis(2′′-naphthalenylmethyloxy)benzyloxy]benzyl bromide **6** in 30 ml THF. Column chromatography: SiO_2, dichloromethane–methanol (100 : 1 v/v). Colorless solid 806 mg (60% yield). Mp 186 °C. R_f (SiO_2, dichloromethane–methanol 100 : 1 v/v) 0.16. MALDI-TOF-MS (matrix: DHB); *m/z* 2038.789 $[M + H]^+$, 2060.75 $[M + Na]^+$, 2077.783 $[M + K]^+$. $C_{142}H_{112}O_{12}N_2$ (2038.46). ^1H NMR (400 MHz, $CDCl_3$): δ 2.85–2.98 (m, 8H, CH_2CH_2), 4.93 (s, 8H, CH_2O), 5.17 (s, 16H, CH_2O), 6.44 (d, $^4J_{HH} = 2.2$ Hz, 4H, phenyl-H), 6.48 (t, $^4J_{HH} = 2.2$ Hz, 2H, phenyl-H), 6.66 (t, $^4J_{HH} = 2.2$ Hz, 4H, phenyl-H), 6.73 (d, $^4J_{HH} = 2.2$ Hz, 8H, phenyl-H), 7.05 (dd, $^3J_{HH} = 5$ Hz, $^4J_{HH} = 1.33$ Hz, 2H, pyridine-H), 7.4–7.55 (m, 24H, naphthalene-H), 7.75–7.87 (m, 32H, naphthalene-H), 8.3 (s, 2H, pyridine-H), 8.55 (d, $^3J_{HH} = 5$ Hz, 2H, pyridine-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.21, 37.39 (CH_2CH_2), 70.23, 70.54, (CH_2O), 100.21, 101.98, 106.72, 106.78, 108.03, 121.58, 124.38, 125.65, 126.4, 126.55, 126.73, 128.06, 128.29, 128.72, 133.38, 133.59, 134.56, 139.75, 143.69, 149.45, 151.91, 156.47, 160.22, 160.51.

General procedure for the preparation of the dendritic ruthenium complexes

Ruthenium trichloride (37.5% ruthenium) was added to a solution of the dendritic bipyridine ligand in a mixture of chloroform–ethanol (2 : 1 v/v). The reaction mixture was refluxed for five days. The solvent was removed and the residue was dissolved in dichloromethane and washed with water several times. The organic layer was separated and the solvent was removed. The residue was then suspended in a hot mixture of acetone and water (3 : 1 v/v). After addition of NH_4PF_6 a highly viscous oil separated from the solution. The oil was dissolved in dichloromethane and washed with water several times. The organic layer was separated. The organic layer was not dried with an inorganic salt such as Na_2SO_4 to avoid the occurrence of partial anion exchange. The solvent was removed *in vacuo* and the residue was purified by column chromatography.

Tris-[4,4′-bis[3′′,5′′-bis(2′′′-naphthalenylmethyloxy)phenylethyl]2,2′-bipyridine]ruthenium(II) dihexafluorophosphate 10

126 mg (0.131 mmol) 4,4′-bis[3′′,5′′-bis(2′′′-naphthalenylmethyloxy)phenylethyl]-2,2′-bipyridine **8**, 8.8 mg (0.033 mmol) ruthenium trichloride hydrate (37.5%). Column chromatography: Al_2O_3, chloroform, $R_f = 0.5$. Orange, high-viscous oil 69.8 mg (63% yield). MALDI-TOF-MS (matrix: DHB); *m/z* 3214.321 $[M - PF_6]^+$, 3068.427 $[M - 2PF_6]^+$. $C_{210}H_{168}O_{12}N_6RuP_2F_{12}$ (3358.68). ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ 2.7–3 (m, 24 CH_2CH_2), 5.11 (s, 24 CH_2O), 6.45 (s, 12H, phenyl-H), 6.61 (s, 6H, phenyl-H), 7.17 (s, 6H, pyridine-H), 7.37–7.48 (m, 36H, naphthalene-H), 7.65 (s, 6H, pyridine-H), 7.7–7.85 (m, 48H, naphthalene-H), 8.33 (s, 6H, pyridine-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.22, 37.49 (CH_2CH_2), 71.3, (CH_2O), 101.38, 109.53, 126.0, 127.01, 127.63, 127.8, 127.81, 129.19, 129.3, 129.57, 129.66, 134.56, 134.77, 136.3, 144.28, 154.68, 158.1, 161.63.

Tris-[4,4′-bis[[3′′,5′′-bis[3′′′,5′′′-bis(2′′′′-naphthalenylmethyloxy)]benzyloxy]phenylethyl]2,2′-bipyridine]ruthenium(II) dihexafluorophosphate 11

197 mg (0.0966 mmol) 4,4′-bis[[3′′,5′′-bis[3′′′,5′′′-bis(2′′′′-naphthalenylmethyloxy)]benzyloxy]phenylethyl]-2,2′-bipyridine **9**, 6.5 mg (0.023 mmol) ruthenium trichloride

hydrate (37.5%), Column chromatography: first: SiO_2, dichloromethane–methanol (100 : 1 v/v), $R_f = 0.3$; second: SiO_2, dichloromethane–ethyl acetate (10 : 1 v/v, $R_f = 0.8$). Orange highly viscous oil 120 mg (63% yield). MALDI-TOF-MS (matrix: DHB); m/z 6365.2 $[M - PF_6]^+$, 6225.6 $[M - 2PF_6]^+$. $C_{426}H_{336}O_{36}N_6RuP_2F_{12}$ (6506.37). ^1H NMR (400 MHz, CD_3CN–$CDCl_3$): δ 2.55–2.8 (m, 24 CH_2CH_2), 4.69 (s, 24 CH_2O), 4.86 (s, 48 CH_2O), 6.28 (s, 12H, phenyl-H), 6.34 (s, 6H, phenyl-H), 6.46 (s, 36H, phenyl-H), 6.75 (s, 6H, pyridine-H), 7.15–7.35 (m, 72H, naphthalene-H), 7.5–7.7 (m, 102H (96H naphthalene-H, 6H pyridine-H), 7.85 (s, 6H, pyridine-H). ^{13}C NMR (100 MHz, CD_3CN–$CDCl_3$): δ 35.22, 37.45 (CH_2CH_2), 68.99, 69.27(CH_2O), 99.23, 100.59, 105.97, 105.96, 107.31, 123.58, 124.86, 125.57, 125.72, 127.07, 127.22, 127.59, 132.29, 132.48, 133.76, 133.87, 138.85, 142.04, 149.52, 152.42, 155.59, 159.3, 159.45.

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