Diastereoselective Assembly of Chiral Ru^{II}-Coordinated Depsipeptide-Dendrimers

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The synthesis, characterization and chiroptical properties of chiral dendrimers **11**–**14** formed by ruthenium coordination of2,2′-bipyridine (bpy*) ligands **4**, **7**, **8** and **10** involving two pairs of enantiomerically pure depsipeptide dendrons bound in 4,4′-position are described. In the case of the first and second generation ligands **4**, **7** and **8** the metallodendrimers **11**, **12** and **13** are formed containing a central $[Ru(bpy^*)_3]^{2+}$ core. After coordination of the third generation dendritic ligand **10** the metallodendrimer **14** with two bpy* ligands, {$[Ru(bpy^*)_2Cl_2]$ core} was isolated. The corresponding metallodendrimer **15** with three bpy* ligands was formed in traces only. Dendrimers **11**, **12** and **13** are the first chiral metallodendrimers involving an $[Ru(bpy^*)_3]^{2+}$ core. This chiral coordination motif can have either a Δ or a Λ configuration. To elucidate if there is a preference for a certain configuration ^{1}H NMR and CD spectroscopy and analytical HPLC were applied. It was found that for the first generation dendrimer **11** the corresponding diastereoisomers with Δ and Λ configuration are formed in equal amounts. On the other hand the Λ diastereoisomers of **12** and **13** are preferably formed upon coordination of the second generation dendrons **7** and **8** with all-(*R*,*R*) configuration (**8**) or mixed $(S,S)_1$-$(R,R)_2$ configuration (**7**). This demonstrates that the configuration of the outer rather than the inner layer within the depsipeptide dendrons determines which isomer is preferably formed.

Introduction

Chirality plays an important role in the interplay between structure and function of biopolymers.[1] Pivotal processes such as chiral recognition, enantioselective catalysis and clathration become feasible by correctly assembled asymmetric structures.[2] The defined globular structures of proteins and other biopolymers are encoded in the sequence of small chiral monomers (e.g., amino acids) within linear polymer chains. A distinctive folding process leads to the formation of specific three-dimensional structures. The chirality of the monomers can be amplified upon the diastereoselective formation of chiral superstructures such as α-helices.[3] In recent years much effort has been undertaken to prepare protein mimetics and to understand the amplification of chirality and chiral recognition processes.[4–6]

Chiral dendrimers are considered as model compounds for biopolymers due to their monodisperse and asymmetric globular structures.[7–11] Many of the applications envisaged for chiral dendrimers rely on the chirality of the system (e.g., biocompatibility, molecular recognition, and asymmetric catalysis). This new class of molecules also opens the possibility to study the effect of chirality in macromolecular systems. However, so far only a few examples for chiral dendrimers with indications of macromolecular asymmetry are known.[12–14] In most cases no chiral folding motifs have been detected because the structures are very flexible involving equilibria of numerous almost isoenergetical conformers.[15–29]

We have recently developed the new class of chiral depsipeptide dendrimers.[22,30] Here we found that the conformation within the dendrons is very sensitive to environmental conditions (solvent and temperature). We also obtained indications that a chiral secondary structure is stabilized in non-protic solvents such as CH_3CN. However, the nature of the corresponding preferred conformers could not be determined. A possible route to reduce conformational flexibility is the incorporation of metal-binding sites. Many examples of metallodendrimers are known.[31–35] Binding of the metal can take place in the core, in the branches, in the peripheral units or can be used for dendrimer branching itself. However, the introduction of chiral coordination motifs within metallodendrimers has received little attention. The enormous variability of the stereochemistry of metal complexes offers the possibility to study interactions within the overall structure of chiral dendrimers and is very interesting from the point of view of possible applications (enantioselective catalysis, chiral recognition). A very impressive example is the construction of conformationally rigid, topologically chiral metallodendrimers by F. M. MacDonnell et al.[36,37]

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In this work we report on the diastereoselective assembly of chiral dendritic 2,2′-bipyridine–depsipeptide ligands caused by complexation to ruthenium ions. The chiral information stored in the dendritic ligands is transferred to the octahedral metal center (Figure 1).

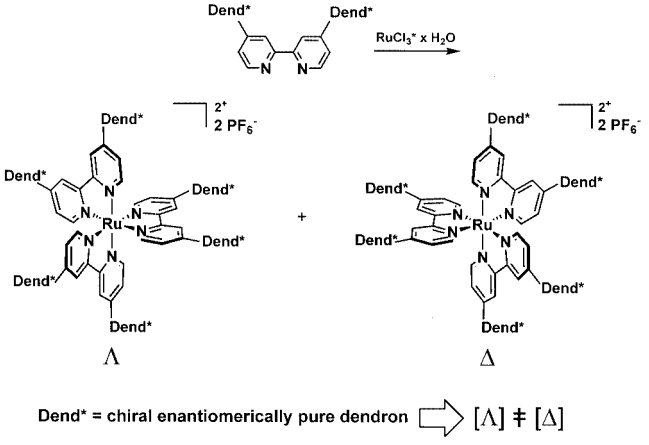


Figure 1. Diastereoselective formation of dendritic $[Ru(bpy^*)_3]^{2+}$ complexes.

The tris(2,2′-bipyridine)ruthenium(II) complexation motif was chosen as it is known to be stable both in solution and in atmospheric oxygen and that it does not racemize.[38] The configuration within the central octahedral complex is either Λ or Δ, depending on the helical arrangement (Δ: right-handed; Λ: left-handed) of the bidentate ligands.[39] Due to the chirality of enantiomerically pure 2,2′-bipyridine–depsipeptide ligands Ru complexes with Δ or Λ configuration are no longer enantiomers but represent diastereoisomers. As a consequence, the preferred formation of a specific chiral complexation motif can be expected (Figure 1). In previous work with leading contributions by Vögtle and Balzani the coordination of bipyridine (bpy) ligands to Ru was used for the assembly of dendritic architectures already.[40–46] However, up to now only achiral dendrons were assembled and the resulting dendrimers are always racemic mixtures. In the approach presented here the inherent chirality of second and third generation bpy*–depsipeptide ligands leads to diastereoselective assembly of chiral metallodendrimers.

Results and Discussion

Synthesis of the Dendritic Depsipeptide–bpy* Ligands

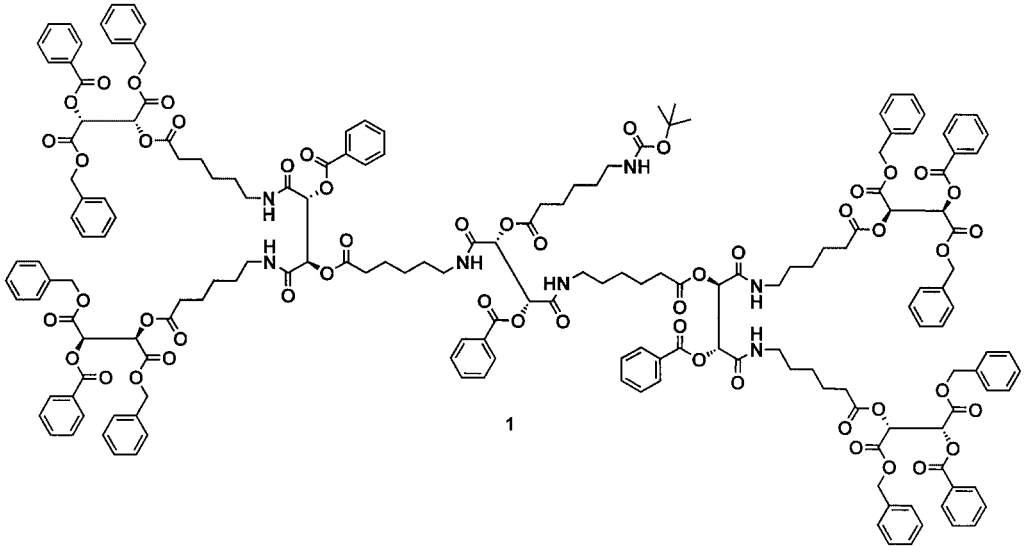
We recently reported of a new type of the chiral depsipeptide dendrons.[30] In these architectures natural and unnatural tartaric acid building blocks are connected with ω-aminocaproic acid spacers via ester and amide bonds. By the incorporation of both (*R*,*R*)- and (*S*,*S*)-tartrate building blocks in different layers of the dendrons a library of eight diastereomers and enantiomers, respectively, was prepared.

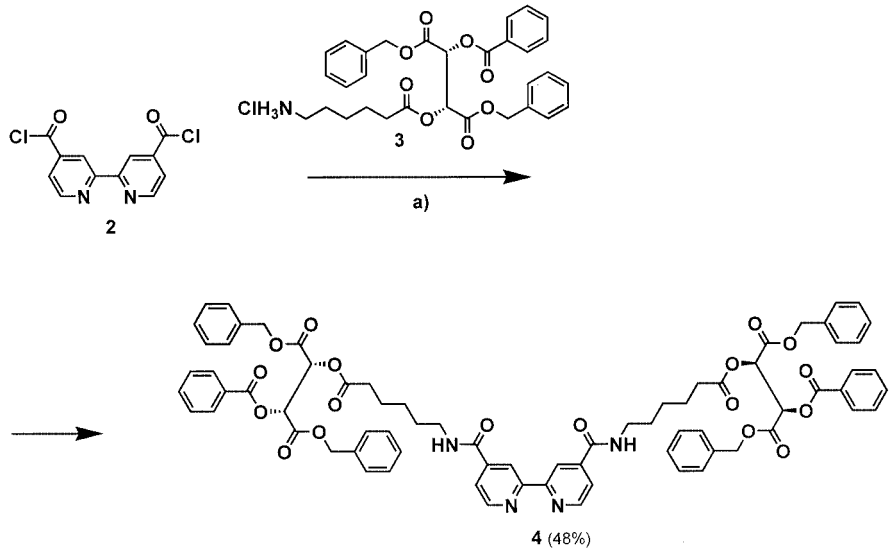
A typical representative of this family is the third generation dendron **1** with all-(*R*,*R*) configuration of the tartrate building blocks.

The BOC protecting groups of the focal amine functionalities of these dendrons can selectively be removed by treatment with HCl in ethyl acetate. The resulting dendritic ammonium chlorides were then used as coupling reagents for the attachment of the 2,2′-bipyridine ligand (Schemes 1, 2, and 3).

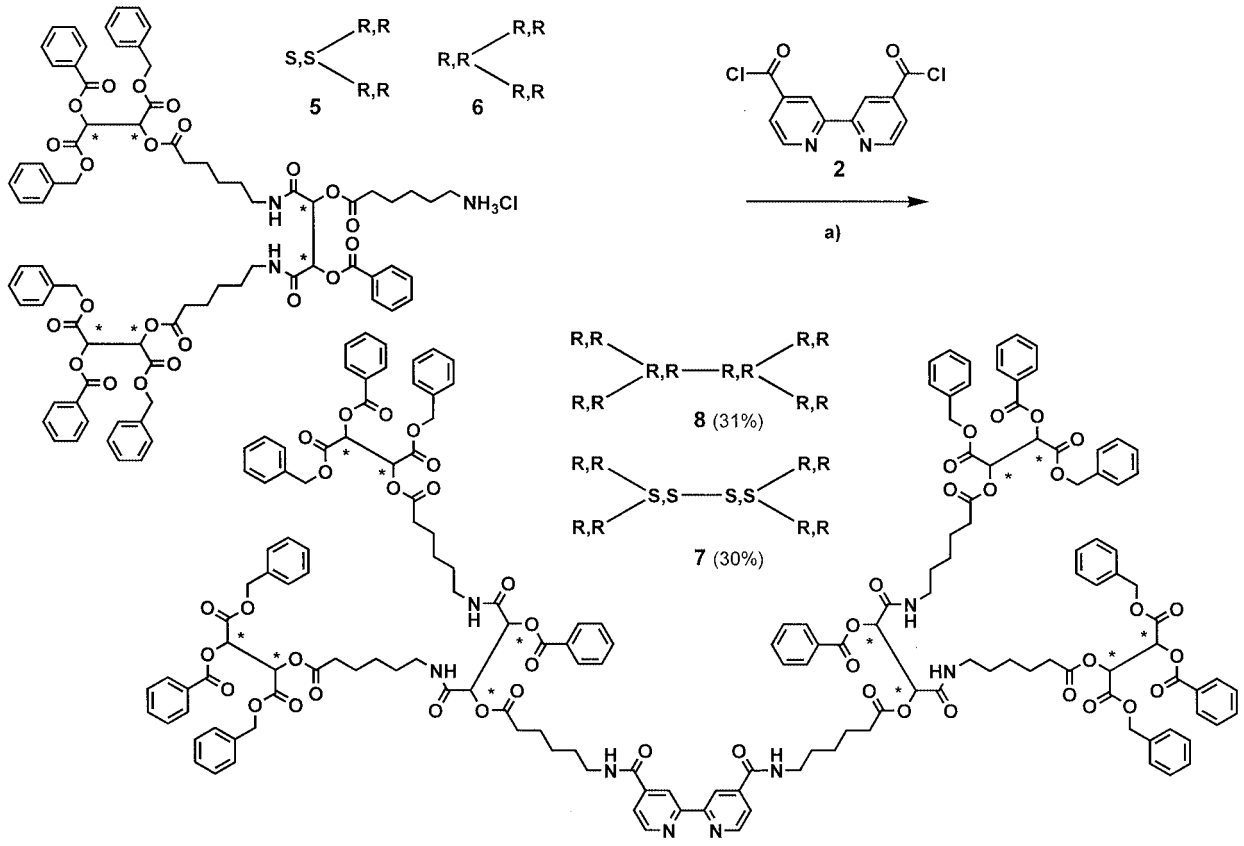
In the ligand the 4- and 4′-bpy positions were chosen as the anchor site for the dendron coupling, because in this way the attached groups point away from the metal center as far as possible. As a consequence, sufficient space for the attachment of the dendritic building blocks is provided.

The coupling was accomplished by treatment of the corresponding dendrons **3**, **5**, **6** and **9** with2,2′-bipyridine-4,4′-dicarboxylic dichloride (**2**) in dry CH_2Cl_2 at 0 °C in the presence of 2.5 equiv. of NEt_3 (Schemes 1–3). As the coupling reaction proceeded, the color of the solution turned slightly orange. Note that the chiral building blocks in the inner layer of **7** and **8** are of opposite configuration but have the same configuration (*R*,*R*) in the outer layer



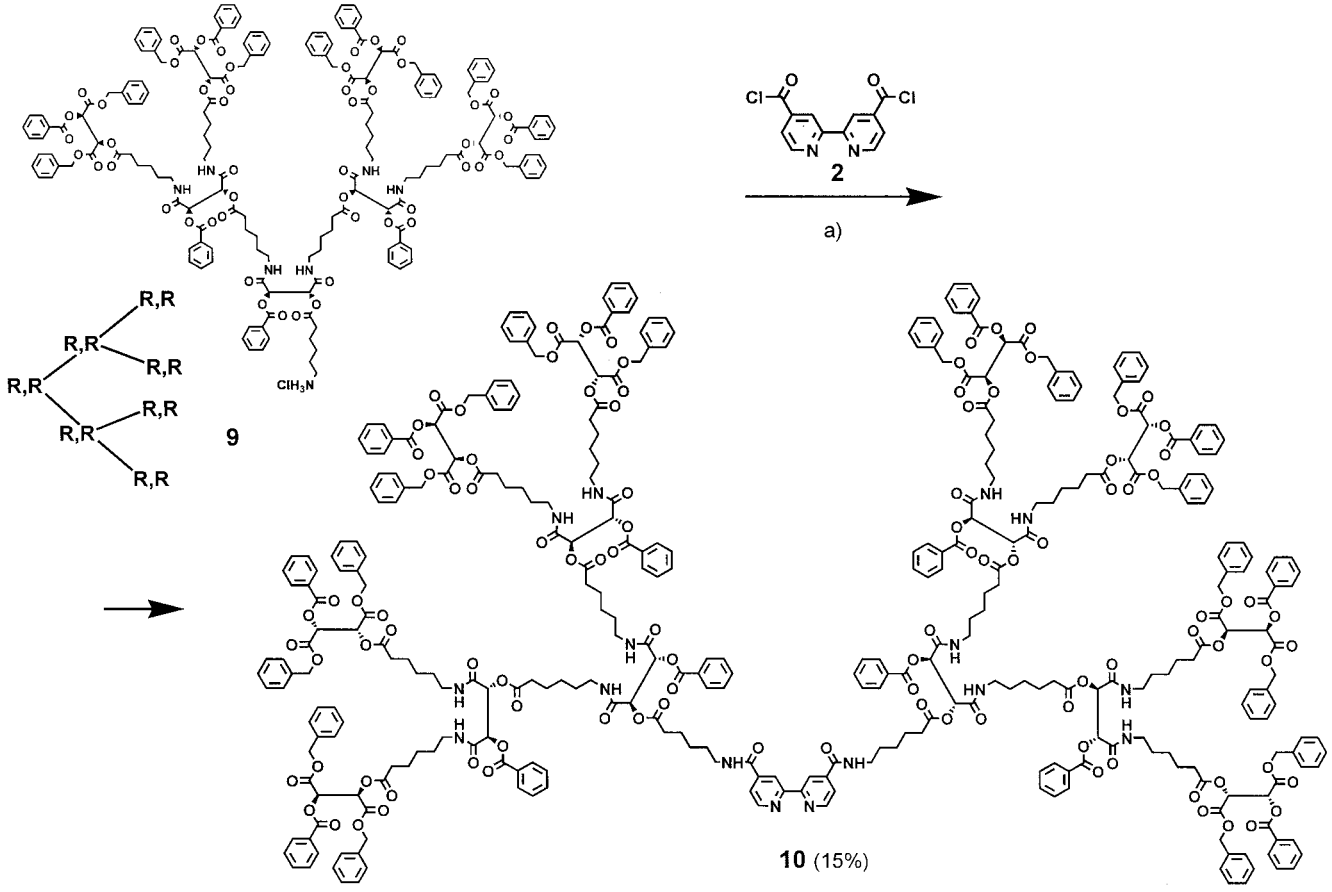


Scheme 1. Synthesis of 1st generation dendritic ligand **4**. a) NEt_3, CH_2Cl_2, 55%.



Scheme 2. Synthesis of 2nd generation dendritic ligands **7** and **8**. a) NEt_3, CH_2Cl_2, 30% (**7**), 31% (**8**).

(Scheme 2). The 2,2′-bipyridine derivative **2** was obtained by treatment of 2,2′-bipyridine-4,4′-dicarboxylic acid with thionyl chloride ($SOCl_2$, 24h, reflux). The diacid itself was synthesized by oxidation of the commercial available 4,4′-dimethyl-2,2′-bipyridine with $KMnO_4$ according to a procedure described by Nolte et al.[47] The yields of the coupling decreased by going from the first (**4**, 48%) to the second (**7**, 30%; **8**, 31%) and to the third (**10**, 15%) generation dendrons. However, other coupling procedures and protocols mediated by DCC (DCC, HOBt, NEt_3) or EDC (EDC, NEt_3) gave even lower yields (< 10%) or no product at all. After column chromatography (silica) the desired dendritic bipyridine ligands **4**, **7**, **8** and **10** were obtained in analytically pure form as colorless solids. They are highly soluble in apolar and polar aprotic solvents such as CH_2Cl_2, CH_3CN, EtAc and readily soluble in polar protic solvents



Scheme 3. Synthesis of 3rd generation dendritic ligand **10**. a) NEt_3, CH_2Cl_2, 15%.

such as CH_3OH, EtOH. They were completely characterized by ^1H and ^{13}C NMR and UV/Vis spectroscopy and elemental analysis. FAB mass spectrometry confirmed the expected molecular weights.

Dendritic Bipyridine Complexes

The metallodendrimers **11** (Scheme 4), **12**, **13** (Scheme 5), **14** (Scheme 6) and **15** were formed upon complexation of the dendritic ligands **4**, **7**, **8** and **10** with $RuCl_3 \cdot xH_2O$ (35–40% Ru) according to a literature procedure.[42,44]

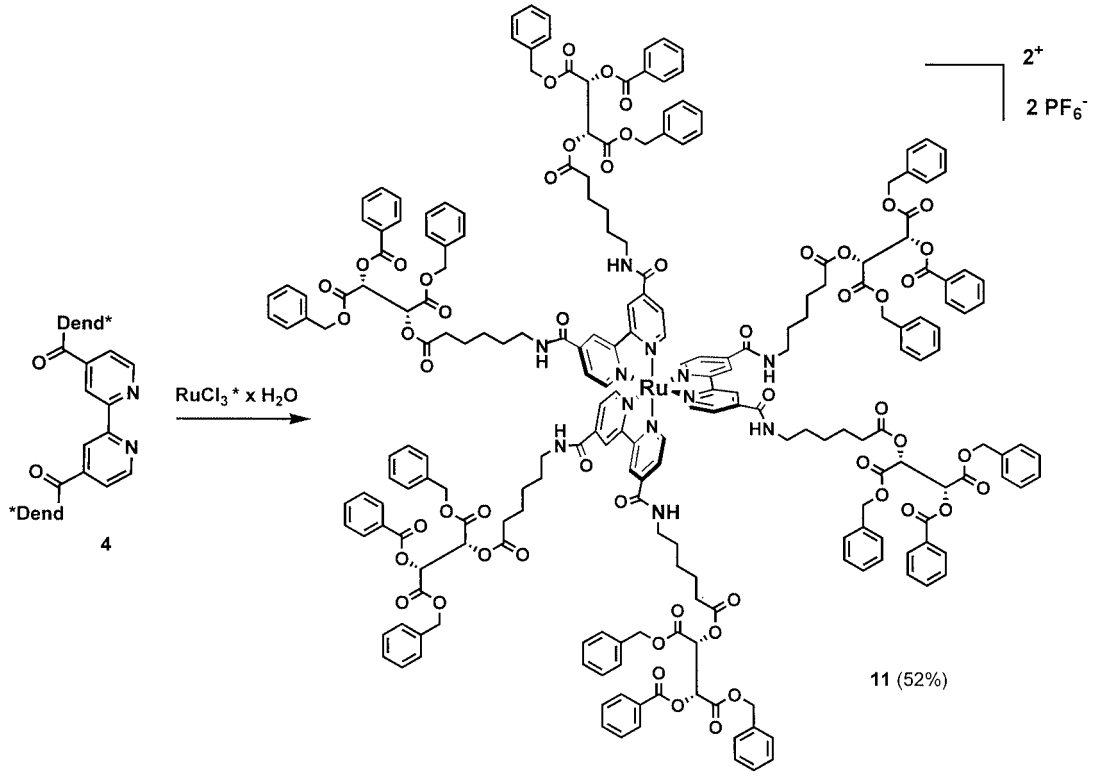
For this purpose the corresponding dendritic bpy* ligand was added to a solution of ruthenium trichloride in a mixture of chloroform/ethanol (1:1, v/v) and the resulting dark red solution was refluxed at 77 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was diluted with CH_2Cl_2 and extracted with an aqueous solution of saturated NH_4PF_6 to facilitate anion exchange. In comparison to complexes with chloride counterions, the dendrimers with hexafluorophosphate ions are easier to separate on silica gel. Purification by column chromatography afforded the dendritic tris(2,2′-bpy*)ruthenium(II) complexes **11** (52%), **12** (20%) and **13** (24%), which exhibit D_3 symmetry. In the case of the third generation ligand **10** a MALDI-TOF mass spectrum of the crude reaction mixture clearly showed the formation of the dendritic tris(2,2′-bpy*)ruthenium(II) complex **15** with a signal at m/z = 19976 corresponding to $[M - PF_6]^+$. The formation of **15** was further supported by the characteristic emission of the metal-to-ligand charge transfer (MLCT) excited states of tris(bpy)ruthenium(II) compounds upon irradiation at 366 nm. Unfortunately, all efforts to isolate **15** failed due to overlapping and smearing bands during column chromatography. Instead the C_2-symmetric bis(2,2′-bpy*)-ruthenium(II) dendrimer **14** (33% yield) was isolated as the major reaction product.

All dendrimers except **15** were characterized by ^1H and ^{13}C NMR and UV spectroscopy. FAB and/or MALDI-TOF mass spectrometry confirmed the expected molecular weights of **11**, **12**, **13** and **14**.

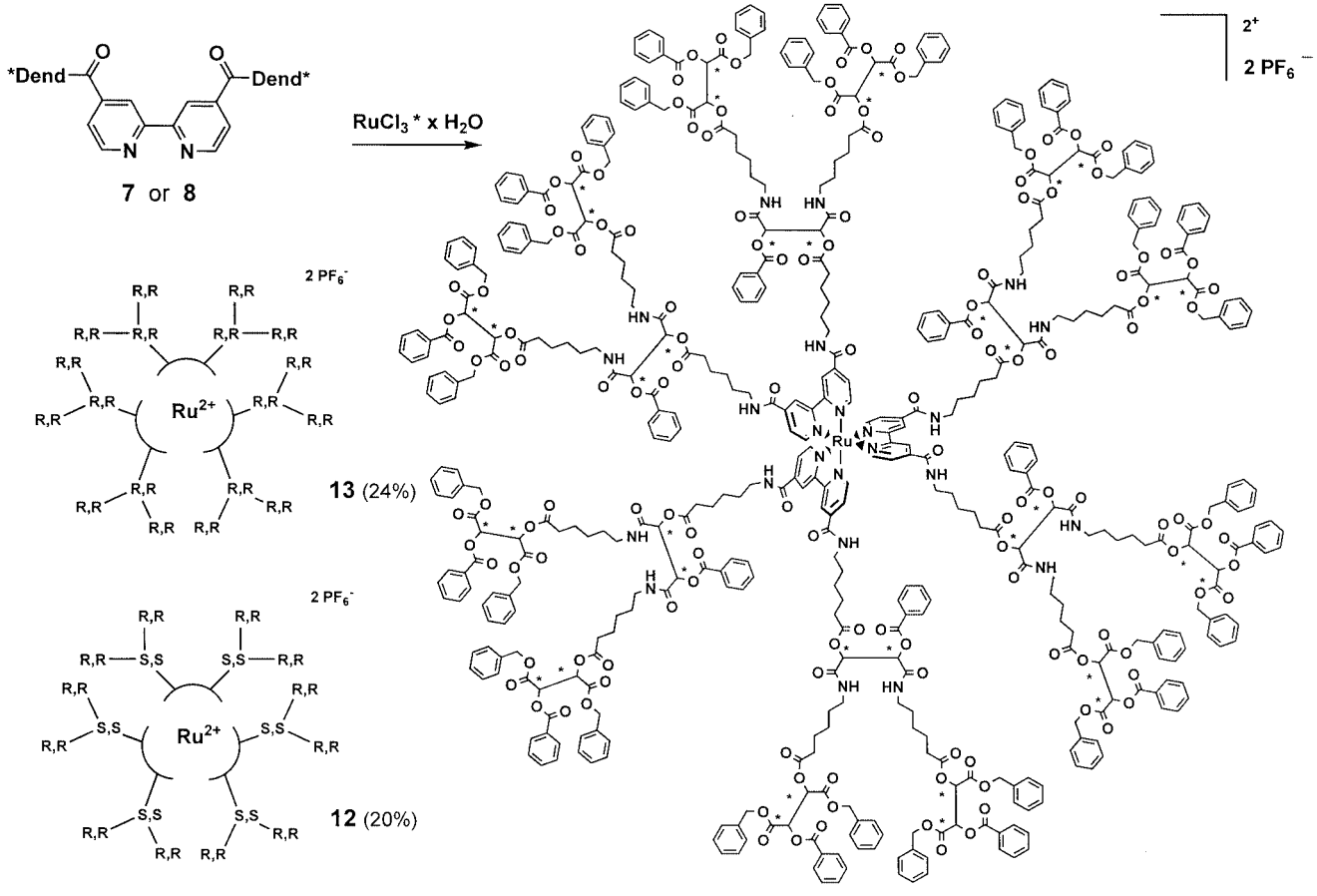
Spectroscopic and Chiroptical Properties

^1H NMR Spectroscopy

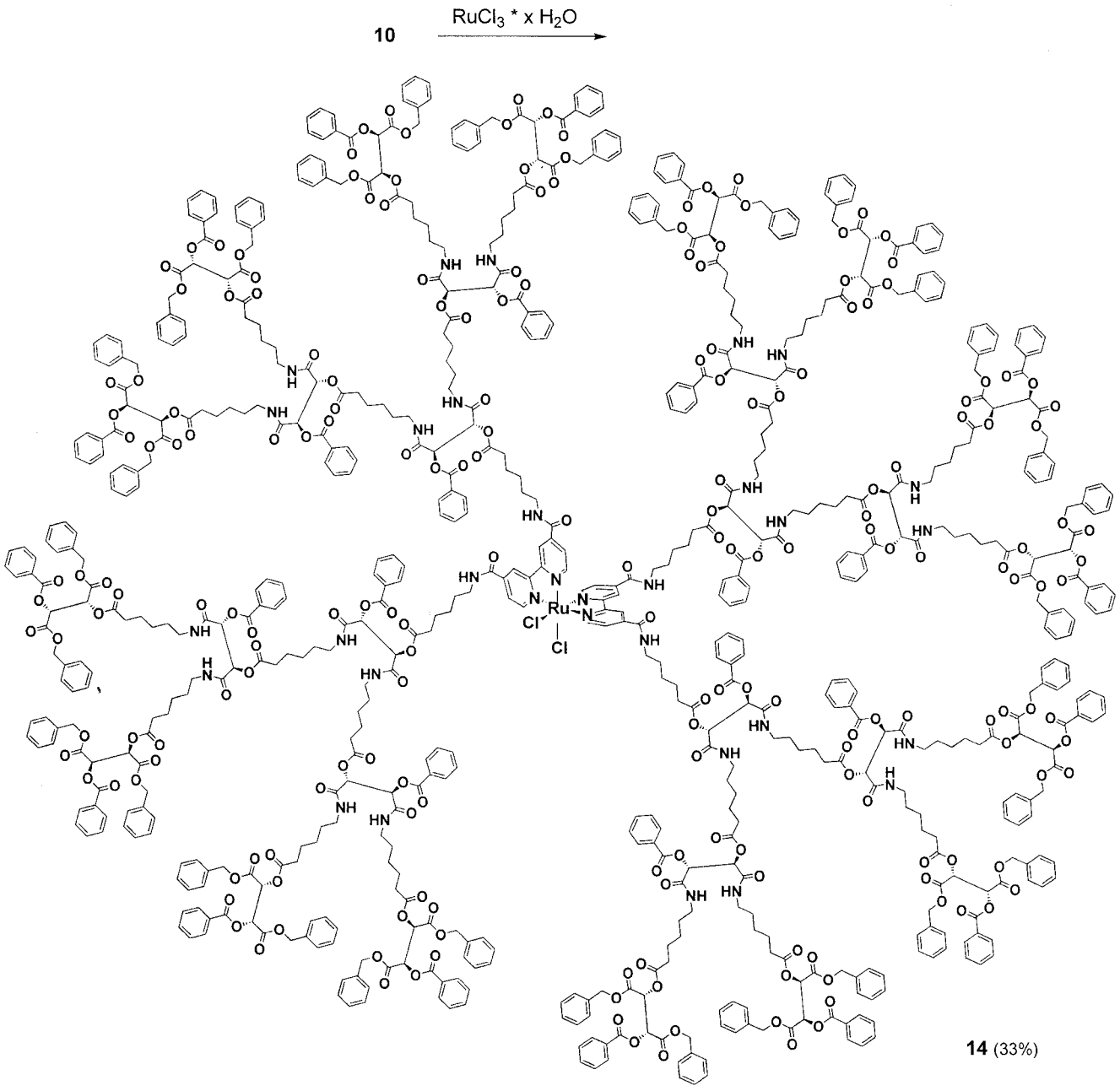
A characteristic feature of the dendritic bpy* ligands **4**, **7**, **8** and **10** is the C_2-symmetric architecture with one set of topologically different C and H atoms for both dendrons. The characteristic resonances and splitting patterns of the dendrons have already been described in a previous paper and after coupling to the bipyridine these resonances basically do not change.[30] As a representive example for all



Scheme 4. Synthesis of 1st generation metallodendrimer **11**.



Scheme 5. Synthesis of 2nd generation metallodendrimers **12** and **13**.

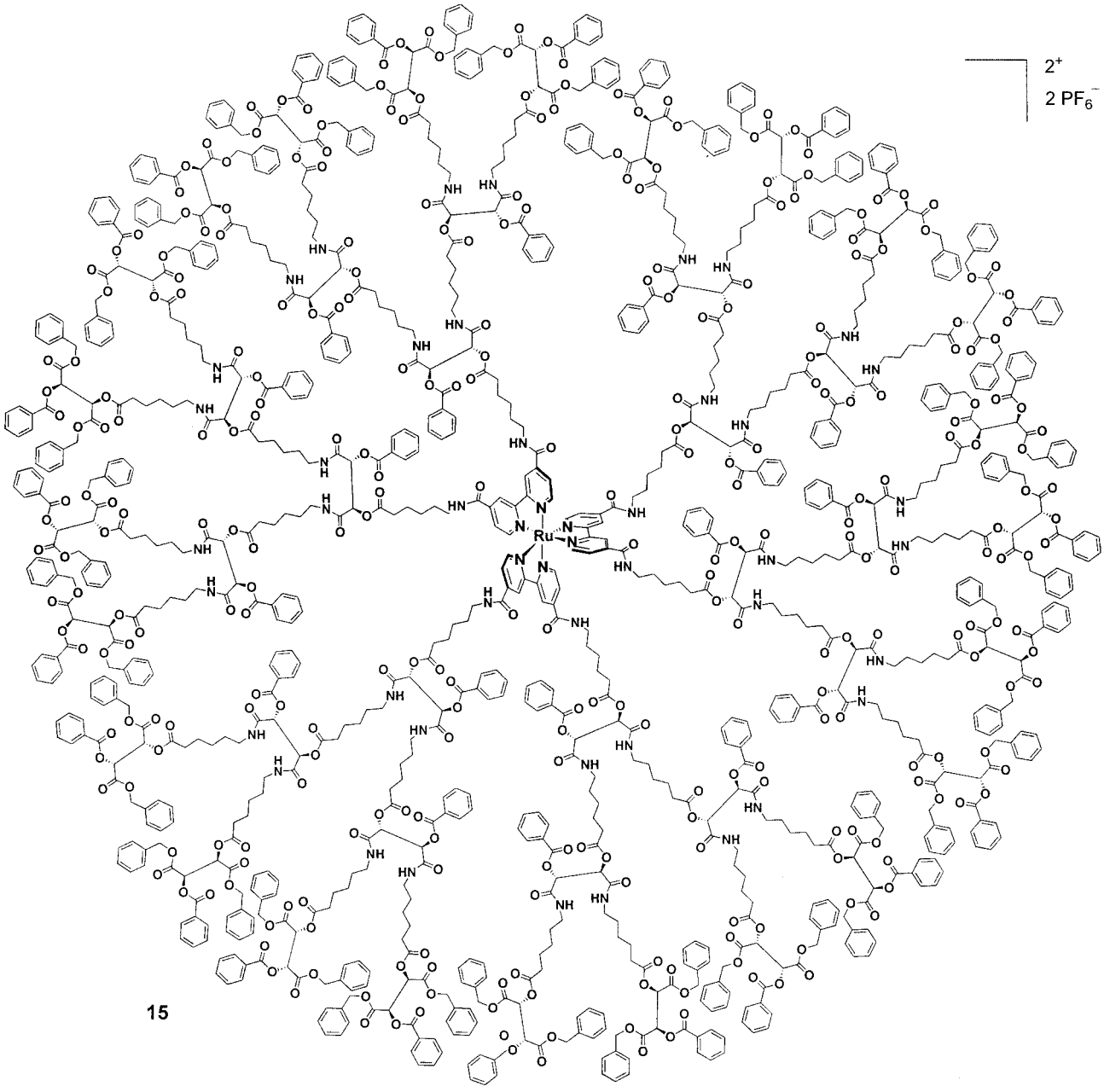


Scheme 6. Synthesis of 3rd generation bis(2,2′-bpy*)ruthenium(II) dendrimer **14**.

dendritic ligands the spectrum of first generation ligand **4** is shown in Figure 2.

The 6,6′- and 5,5′-protons of the bipyridine ring resonate as a well-resolved doublet of a doublet at δ = 7.7 ppm and as a doublet at δ = 8.7 ppm, respectively. The signal of the 3,3′-protons appears at δ = 8.6 ppm as a long-range-coupled doublet. These resonances are of value to provide evidence for a successful and complete complexation of the Ru^{2+} ions. In Figure 2 also the ^{1}H NMR spectrum of metallodendrimer **11** is shown. The signals of the 6,6′- and 5,5′-protons as well as those of the 3,3′-protons are shifted upfield. However, a proper assignment is difficult due to closely overlapping signals (Figure 2). The assignment of the signals was carried out on the basis of ^{1}H NMR spectroscopic data in the literature and two-dimensional NMR techniques.

In principle, an NMR spectrum of a mixture of the Δ and Λ forms should show two sets of signals, because they represent pairs of diastereomers. However, in the present cases the differences in the ^{1}H NMR spectra are hardly observable. In the metallodendrimer **11** the resonances of the 6,6′-protons appear as a broad doublet at δ = 7.7 ppm. The 3,3′-protons resonate as one broad signal at δ = 7.8 ppm. Overlapping signals of the aromatic protons of the dendrons prevent an exact analysis. The NMR spectra of larger dendrimers **12**, **13** and **14** are even more complex. As a



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consequence, the determination of the configuration and the Δ/Λ ratio is not possible by the analysis of the NMR spectra.

UV/Vis Spectroscopy

Figure 3 shows the UV/Vis spectra of the ligands **4** and **7** and the corresponding dendrimers **11** and **12** in acetonitrile. The spectra of **7** and **8** (not shown)and **12** and **13** (not shown) are almost identical because the different configurations of the chiral building blocks have no influence on the UV/Vis-spectroscopic behavior. The $[Ru(bpy^*)_3]^{2+}$ core leads to ligand-centered (LC) bands at 305 nm and to characteristic metal-to-ligand charge transfer (MLCT) bands at 455 nm for **11** and **12**. Clearly separated from the absorptions of the core are the π-π* transitions of the dendritic benzene chromophores at 237 nm. One can clearly see, that the size of the dendrons (generation number) does not substantially influence the electronic transitions in the $[Ru(bpy^*)_3]^{2+}$ core.

However, the molar absorptivity (ε) of the dendron-based benzene chromophores is roughly proportional to their number. The UV/Vis spectrum of a metallodendrimer can therefore be regarded as the superposition of the spectra of three pairs of depsipeptide dendrons and one $[Ru(bpy^*)_3]^{2+}$ core. In the spectrum of the bis(bpy*) complex **14** the characteristic absorptions of the $[Ru(bpy^*)_3]^{2+}$ core are replaced with a band at 305 nm in the UV region and two broad bands at 405 and 590 nm in the visible region for the $[Ru(bpy^*)_2Cl_2]^{2+}$ core (Figure 4).

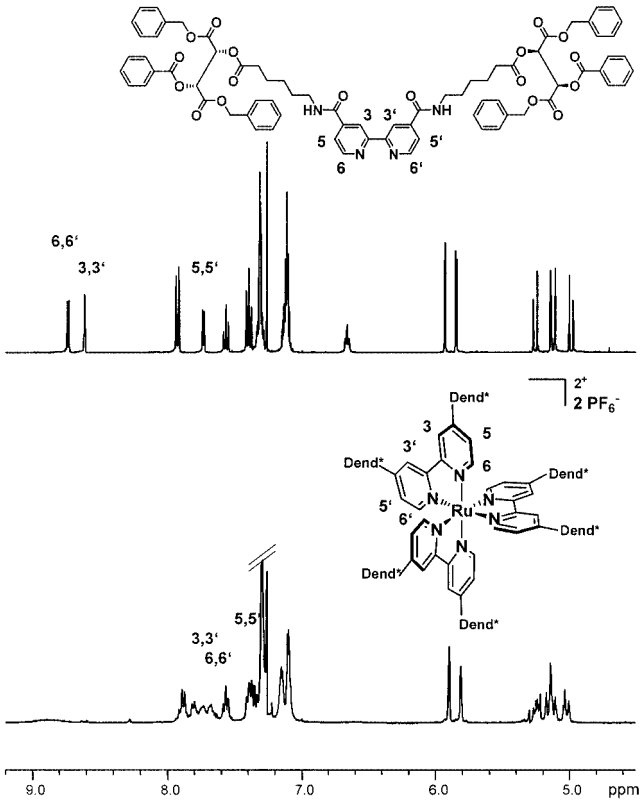

Figure 2. ^1H NMR spectra (δ = 9.2–4.6 ppm region) of dendritic ligand **4** and its ruthenium(II) complex **11** in $CDCl_3$.

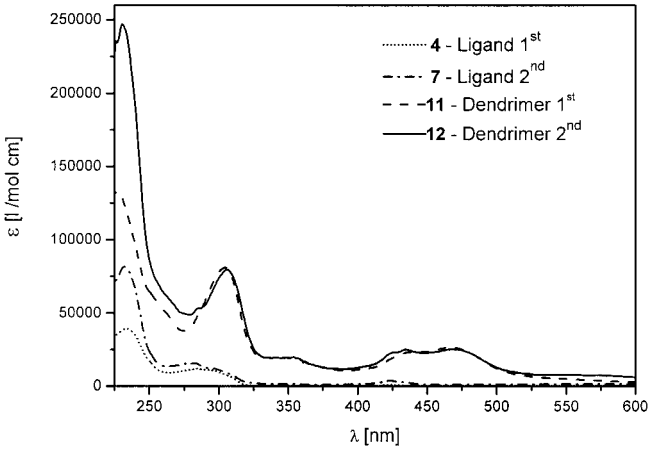

Figure 3. Electronic absorption spectra of **4**, **7**, **11** and **12** in CH_3CN.

Again, the UV spectrum represents the superposition of the spectra of two third generation ligands **10** and one $[Ru(bpy^*)_2Cl_2]^{2+}$ core. The coordination geometry of bis(2,2′-bipyridine)ruthenium(II) complexes such as **14** can be *cis* or *trans*, depending on the equatorial or axial position of the two monodentate chlorine ligands. The *cis* form, however, is known to have only two visible absorptions at around 590 and 430 nm, compared with three for the *trans* form.[48] Our data are therefore consistent with the C_2-symmetric *cis* isomer.

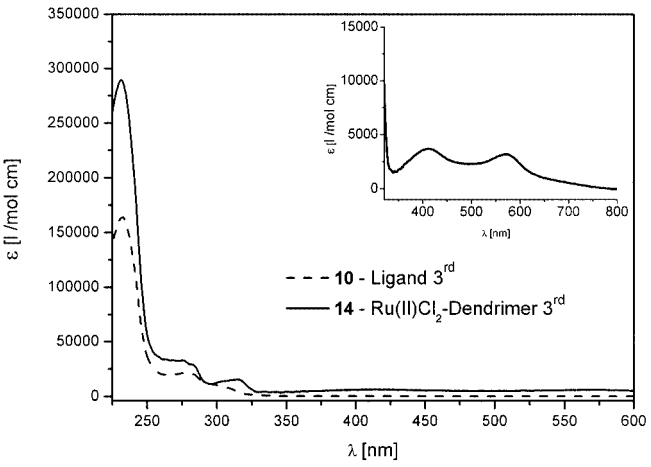

Figure 4. Electronic absorption spectra of **10** and **14** in CH_3CN. The inset shows the electronic absorption spectrum of **14** in the region between 350 and 800 nm on a larger scale.

Circular Dichroism Spectra

The clearly separated absorptions in the UV/Vis region of the complexes **11**, **12**, **13** and **14** are ideally suited to probe the chiral environment around the metal center by means of CD spectroscopy. The dendritic shell should not have any significant influence on the CD and UV/Vis spectroscopic properties of the $[Ru(bpy^*)_3]^{2+}$ cores. A variety of CD spectra of non-dendritic complexes with $[Ru(bpy)_3]^{2+}$ cores in the Λ or Δ configuration have been reported.[49–51] Characteristic are two overlapping LC bands at 290 and 310 nm, as well as a broad MLCT band (spanning ca. 200 nm) with a midpoint at 450 nm. The absolute configuration around the metal center can be assigned by comparison with spectra from complexes with known absolute configuration from the sign of the Cotton effects of the LC bands. Complexes with a large positive/negative LC band with maxima at 305 and 285 nm, arising from exciton coupling of the long-axis-polarized transitions of the three bipyridine ligands, involve a Λ configuration.[51,52] The absolute values and positions of the bands vary significantly with the electron-donating or -withdrawing ability of the ligands. These results enabled us to determine whether the complexation of the dendritic bpy* ligands **4**, **7**, **8** and **10** with ruthenium is diastereoselective and to determine the absolute configuration of the preferably formed diastereoisomer. Figure 5 shows the CD spectra of the metallodendrimers **11** and **12** as well as those of the corresponding ligands **4** and **7**. In the spectrum of the first generation dendrimer **11** two weak bands centered at 305 and 455 nm can be observed. However, the typical sequence of bands with positive and negative signs for complexes containing $[Ru(bpy)_3]^{2+}$ cores is missing and the magnitude of the Cotton effects is very small. Therefore, it can be concluded that if at all only a very weak diastereoselectivity is associated with the formation of **11**.

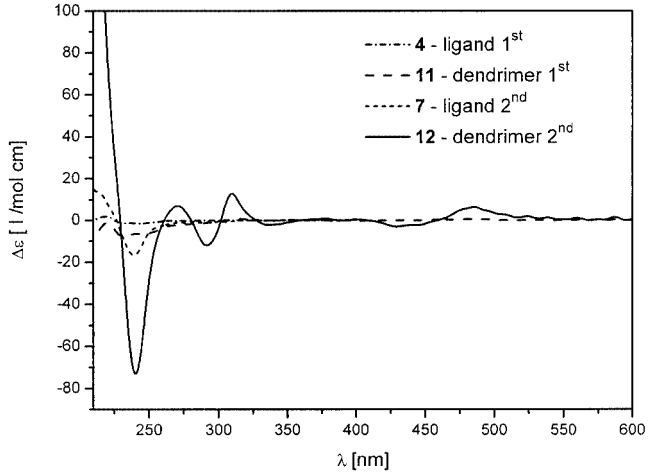

Figure 5. CD spectra of **4**, **7**, **11** and **12** in CH_3CN.

In contrast to these findings is the spectrum of the second generation dendrimer **12**. The bands at 305 and 290 nm with consecutive positive and negative values and the broad MLCT band at 455 nm are characteristic for a $[Ru(bpy)_3]^{2+}$ core in the Λ configuration. However, the magnitude of the diastereomeric excess is difficult to predict from the CD spectrum, as it is known that the intensities and the shape of the bands are very ligand-sensitive.[52] Suitable enantiopure model compounds for our system are not available in the literature. The reported data of chiral complexes with a $[Ru(bpy)_3]^{2+}$ core cover a broad range for the intensity of the ligand-centered band, ranging from $\Delta\varepsilon$ = 90 to 300, depending strongly on the system.[49–51] The actual intensity on the corresponding band in **12** is $\Delta\varepsilon$ = 20.

Interesting to note are the dendron-based bands at 240 and 220 nm. In comparison with the free dendritic ligand **7** the intensity of the band at 240 nm increases five- to sixfold. An even much more pronounced increase is observed for the band at 220 nm. We assume that these dramatic effects are due to the formation of chiral superstructures within the dendritic branches caused by the helical arrangement of the dendrons around the $[Ru(bpy^*)_3]^{2+}$ core.

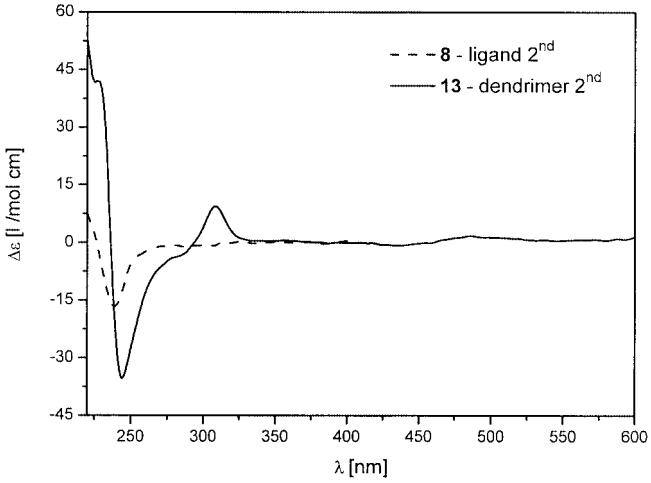

Figure 6. CD spectra of **8** and **13** in CH_3CN.

In comparison with **7** the configuration of the inner tartrate building block within the ligand **8** unit is (*R*,*R*) instead of (*S*,*S*). The CD spectrum of the related dendrimer **13** is shown in Figure 6.

Here, also the Λ configuration of the $[Ru(bpy^*)_3]^{2+}$ core is favored. However, the diastereoselectivity of the formation of Λ-**13** is lower than that of Λ-**13**. Obviously, the preference of the Λ form is mainly caused by the configuration of the outer rather than the inner layer of tartrate building blocks. In the case of the complex **14** no preference was found for a certain configuration (Figure 7).

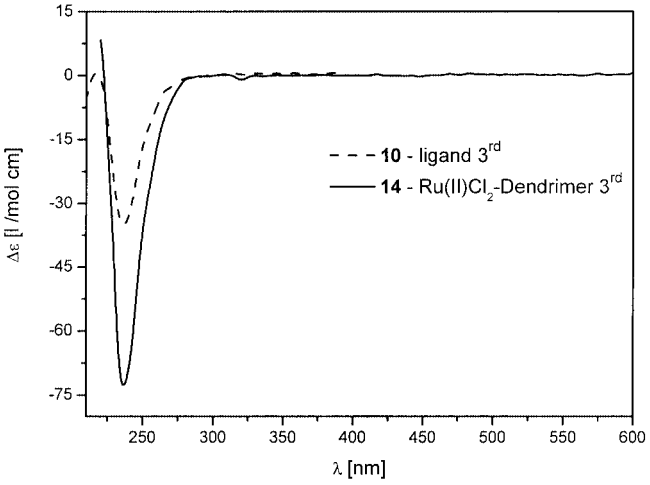

Figure 7. CD spectra of **10** and **14** in CH_3CN.

The CD spectrum can be seen as the superposition of two spectra of ligand **10**. It seems that at least two dendritic ligands are necessary to create a fit-misfit situation for complexation of the last dendritic ligand.

Analytical HPLC

The Λ/Δ ratio of the diastereoisomeric mixtures of **11** and **12** was investigated by analytical HPLC. The retention times were determined using a Nucleosil column ($CHCl_3$/MeOH, 91:9) with a flow rate of 0.8 mL/min at room temperature. For the first generation metallodendrimer **11** two peaks were found at 5.71 and 5.92 min with a relative ratio of 50:50. This is in agreement with the CD spectra and shows that with the relatively small first generation dendron **4** no diastereoselectivity is associated with the coordination to ruthenium.

For the second generation metallodendrimer **12** two peaks at 2.77 and 3.06 min (Nucleosil column, 1 mL/min, $CHCl_3$/MeOH, 95:5) in a 64:36 ratio were observed. This corresponds to a diastereomeric excess of 28% in favor of the Λ over the Δ isomer. Attempts to separate the mixtures by preparative HPLC proved unsuccessful, mainly due to the poor peak separation of the diastereoisomers.

Conclusions

In this work we describe the synthesis and characterization of the first examples of chiral dendrimers involving the

coordination of bpy* ligands to an Ru^{II} core. Each bpy* ligand contains two pairs of enantiomerically pure depsipeptide dendrons **4**, **7**, **8** and **10** of generation one to three. Threefold coordination of such dendritic bpy* ligands to the Ru^{II} center leads to octahedral coordination motifs with either Λ or Δ configuration. As a consequence, in each case diastereoisomers are formed. Upon coordination of the bpy* ligand **4** involving first generation dendrons with (*R*,*R*) configuration of the tartrate units the Δ and Λ isomers are formed in equal amounts. However, coordination of both the corresponding second generation ligands with all-(*R*,*R*) configuration **8** or mixed (*R*,*R*)-(*S*,*S*) configuration **7** leads to a diastereoselective preference of the Λ configuration. Obviously, the configuration of the outer rather than the inner tartrate layer determines which isomer is preferably formed. This in turn indicates that the geometry of the whole ligand rather than the local structure of the inner tartrate building blocks determines the stereoselectivity of the coordination process. As a consequence, the conformational freedom of the second generation dendrons **7** and **8** seems to be restricted at least when coordinated within the chiral dendrimers **12** and **13.** In the case of the third generation ligand **10** only the twofold coordinated complex **14** could be isolated.

Experimental Section

General Remarks: All starting materials were purchased from commercial sources or prepared using known literature procedures. 4,4′-Dimethyl-2,2′-bipyridine was oxidized with $KMnO_4$ following a procedure by Nolte et al.[47] The preparation of **3**, **5** and **7** has been described in our previous publication.[30] The solvents were dried using standard techniques. Reactions were monitored by thin layer chromatography using DC silica gel $60F_{254}$ (Merck) aluminium plates. ^1H and ^{13}C NMR spectra were recorded with JEOL GX 400, JEOL EX 400, and JEOL A 500. The chemical shifts are given in ppm relative to $SiMe_4$ or the solvent peak as standard reference. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quadruplet) and m (multiplet). Broad resonances are described as broad (b). An asterisk indicates the central tartrate protons. Mass spectra were measured with Micromas Zab Spec (FAB) on a Finnigan MAT 900 with 3-nitrobenzyl alcohol as the matrix. IR spectra were recorded with Bruker FT-IR IFS 88. Circular dichroism (CD) measurements were carried out with a Jasco J 710 using optical grade solvents and quartz glass cuvettes with a 10-mm path length. Optical rotations were performed with a Schmidt&Haensch Polatronic E Digitalpolarimeter. UV spectroscopy was performed using a UV-3102 by Shimadzu. Products were isolated by flash column chromatography (FC) (silica gel 60, particle size 0.04–0.063 nm, Merck).

General Procedure for the Preparation of the Dendritic Bipyridine Ligands: 2,2′-Bipyridine-4,4′-dicarboxylic acid was dissolved in $SOCl_2$ and refluxed for 24 h. After removal of the excess of $SOCl_2$ in vacuo, the resulting dicarboxylic dichloride was dissolved in dry CH_2Cl_2 under nitrogen. The dendritic hydrochloride and NEt_3 were added at 0 °C and the solution was stirred for 24 h. During the reaction, the color of the solution turned to pink. After the reaction was complete, the solution was diluted with CH_2Cl_2 and extracted three times with an aqueous solution of saturated $NaHCO_3$ and one time with an aqueous solution of saturated NaCl. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to yield a crude product, which was purified by column chromatography.

Compound 4, Dendritic $(R,R)_1$ Ligand First Generation: Compound **4** was synthesized according to the general procedure with compound **3** (1.53 g, 2.62 mmol), NEt_3 (570 μL, 4.1 mmol) and with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (204 mg, 0.73 mmol) in dry CH_2Cl_2 (20 mL). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 20:1; R_f = 0.25). Yield 450 mg (48%) white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 4 H, CH_2), 1.63 (m, 8 H, CH_2), 2.22 (m, 4 H, CH_2COO), 3.48 (m, 4 H, CH_2N), 4.98 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.10 (m, 4 H, CH_2-Bn), 5.22 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.81 (d, ^3J = 3 Hz, 2 H, *CH), 5.91 (d, ^3J = 3 Hz, 2 H, *CH), 6.65 (br., 2 H, CONH), 7.09 (m, 10 H, Bn), 7.29 (m, 10 H, Bn), 7.37 (m, 4 H, Bz), 7.54 (m, 2 H, Bz), 7.71 (dd, ^3J = 5, ^4J = 1.5 Hz, 2 H, Pyr-CH), 7.91 (m, 4 H, Bz), 8.59 (d, ^4J = 1.5 Hz, 2 H, Pyr-CH), 8.71 (d, ^3J = 5 Hz, 2 H, Pyr-CH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.8, 25.9, 28.6 (CH_2), 33.1 (CH_2COO), 39.7 (CH_2N), 67.8, 67.9 (CH_2-Bn), 70.7, 71.2 (*CH), 117.7, 122.3 (Pyr-C, CH), 128.3, 128.4, 128.5, 128.6, 129.9, 130.1, 133.9, 134.5, 134.9 (Ph), 143.2, 150.3, 156.2 (Pyr-C, CH), 165.2, 165.7, 165.9, 166.1, 172.2(C=O) ppm. MS (FAB): *m*/*z* (%) = 1303 (100) $[M + H]^+$, 1213 (20) $[M - Bn]^+$, 744 (40), 590 (20). UV/Vis (CH_3CN): λ_{max} (ε) = 285 (12000), 234 (39000) nm. $C_{74}H_{70}O_{18}N_4 \cdot H_2O$ (1321.4): calcd. C 67.26, H 5.49, N 4.24; found C 67.42, H 5.52, N 3.98.

Compound 7, Dendritic $(S,S)_1$-$(R,R)_2$ Ligand Second Generation: Compound **7** was synthesized according to the general procedure with compound **5** (529 mg, 0.363 mmol), NEt_3 (125 μL, 0.9 mmol) and with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (50 mg, 0.18 mmol) in dry CH_2Cl_2 (15 mL). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 20:1; R_f = 0.13). Yield 165 mg (30%) white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (m, 36 H, CH_2), 2.15 (m, 8 H, CH_2COO), 2.40 (t, ^3J = 7 Hz, 4 H, CH_2COO), 3.10 (m, 8 H, CH_2N), 3.41 (t, ^3J = 7 Hz, 4 H, CH_2N), 5.01 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.06 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.09 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.12 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.16 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.18 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.21 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.25 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.74 (d, ^3J = 3 Hz, 2 H, *CH), 5.77 (d, ^3J = 3 Hz, 2 H, *CH), 5.80 (d, ^3J = 3 Hz, 2 H, *CH), 5.87 (d, ^3J = 3 Hz, 2 H, *CH), 5.88 (d, ^3J = 3 Hz, 2 H, *CH), 5.91 (d, ^3J = 3 Hz, 2 H, *CH), 6.38 (br., 4 H, CONH), 7.10 (m, 20 H, Bn), 7.29 (m, 20 H, Bn), 7.40 (m, 12 H, Bz), 7.55 (m, 6 H, Bz), 7.67 (dd, ^3J = 5, ^4J = 1.5 Hz, 2 H, Pyr-CH), 7.89 (m, 8 H, Bz), 7.91 (m, 4 H, Bz), 8.61 (d, ^4J = 1.5 Hz, 2 H, Pyr-CH), 8.72 (d, ^3J = 5 Hz, 2 H, Pyr-CH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.9, 24.0, 24.2, 25.9, 28.7, 28.9 (CH_2), 33.1, 33.2, 33.7 (CH_2COO), 39.3, 39.4, 39.8 (CH_2N), 67.7, 67.9 (CH_2-Bn), 70.7, 71.2, 72.4, 72.8 (*CH), 118.1, 121.9 (Pyr-C, CH), 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 129.9, 130.0, 133.7, 134.0, 134.5, 134.8 (Ph), 142.9, 150.1, 156.1 (Pyr-C, CH), 164.9, 165.0, 165.5, 165.6, 165.7, 165.8, 166.1, 166.2, 171.9, 172.2 (C=O) ppm. MS (FAB): *m*/*z* (%) = 3062 (100) $[M + H]^+$, 2972 (15) $[M - Bn]^+$, 1623 (10), 1469 (10), 1427 (10), 1313 (20). UV/Vis (CH_3CN): λ_{max} (ε) = 285 (15000), 232 (81000) nm. $C_{170}H_{170}O_{46}N_8$ (3061.2): calcd. C 66.70, H 5.60, N 3.66; found C 66.52, H 5.58, N 3.37.

Compound 8, Dendritic $(R,R)_1$-$(R,R)_2$ Ligand Second Generation: Compound **8** was synthesized according to the general procedure with compound **6** (486 mg, 0.333 mmol), NEt_3 (116 μL, 0.835 mmol) and with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (45 mg, 0.16 mmol) in dry CH_2Cl_2 (15 mL). The crude product was

purified by column chromatography (silica, CH_2Cl_2/MeOH, 20:1; R_f = 0.13). Yield 152 mg (31%) white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (m, 36 H, CH_2), 2.15 (m, 8 H, CH_2COO), 2.40 (m, 4 H, CH_2COO), 3.10 (m, 8 H, CH_2N), 3.41 (m, 4 H, CH_2N), 5.03 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.07 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.09 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.11 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.16 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.18 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.20 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.21 (d, ^2J = 12 Hz, 2 H, CH_2-Bn), 5.71 (d, ^3J = 3 Hz, 2 H, *CH), 5.74 (d, ^3J = 3 Hz, 2 H, *CH), 5.76 (d, ^3J = 3 Hz, 2 H, *CH), 5.78 (d, ^3J = 3 Hz, 2 H, *CH), 5.87 (d, ^3J = 3 Hz, 2 H, *CH), 5.91 (d, ^3J = 3 Hz, 2 H, *CH), 6.35 (br., 4 H, CONH), 7.09 (m, 20 H, Bn), 7.27 (m, 20 H, Bn), 7.39 (m, 12 H, Bz), 7.53 (m, 6 H, Bz), 7.67 (d, ^3J = 5 Hz, 2 H, Pyr-CH), 7.90 (m, 8 H, Bz), 8.00 (m, 4 H, Bz), 8.62 (s, 2 H, Pyr-CH), 8.74 (d, 2 H, ^3J = 5 Hz, Pyr-CH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.9, 24.0, 25.9, 28.7, 28.9 (CH_2), 33.1, 33.2, 33.7 (CH_2COO), 39.3, 39.4, (CH_2N), 67.7, 67.9 (CH_2-Bn), 70.7, 71.2 (*CH), 118.1, 123.3 (Pyr-C, CH), 128.3, 128.3, 128.5, 128.6, 129.9, 130.0, 130.7, 133.7, 134.5, 134.8 (Ph), 142.9, 150.2, 158.1 (Pyr-C, CH), 164.9, 165.5, 165.6, 165.7, 166.1, 166.2, 172.2 (C=O) ppm. MS (FAB): *m/z* (%) = 3062 (100) $[M + H]^+$, 2972 (5) $[M - Bn]^+$, 1781 (12), 1623 (30), 1469 (70), 1427 (10), 1313 (10). UV/Vis (CH_3CN): λ_{max} (ε) = 285 (15000), 234 (80000) nm. $C_{170}H_{170}O_{46}N_8$ (3061.2): calcd. C 66.70, H 5.60, N 3.66; found C 66.69, H 5.77, N 3.63.

Compound 10, Dendritic (*R*,*R*)$_1$-(*R*,*R*)$_2$-(*R*,*R*)$_3$ Ligand Third Generation: Compound **10** was synthesized according to the general procedure with compound **9** (233 mg, 0.035 mmol), NEt_3 (25 µL, 0.180 mmol) and with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (9.8 mg, 0.072 mmol) in dry CH_2Cl_2 (10 mL). The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 15:1; R_f = 0.14). Yield 70 mg (15%) white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (m, 72 H, CH_2), 2.20 (m, 28 H, CH_2COO), 3.10 (m, 24 H, CH_2N), 3.40 8 m, 4 H, CH_2N), 4.05 (br., 2 H, CONH), 5.15 (m, 32 H, CH_2-Bn), 5.85 (m, 28 H, *CH), 6.70 (br., 12 H, CONH), 7.08 (m, 40 H, Bn), 7.26 (m, 40 H, Bn), 7.38 (m, 28 H, Bz), 7.53 (m, 14 H, Bz), 7.68 (d, ^3J = 5 Hz, 2 H, Pyr-CH), 7.91 (m, 14 H, Bz), 8.00 (m, 14 H, Bz), 8.59 (s, 2 H, Pyr-CH), 8.71 (d, 2 H, ^3J = 5 Hz, Pyr-CH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.0, 24.3, 24.4, 25.9, 28.8, 28.9 29.2 (CH_2), 33.1, 33.6, 34.1 (CH_2COO), 39.3 (CH_2N), 67.7, 67.9 (CH_2-Bn), 70.7, 71.2, 72.9 (*CH), 119.4 (Pyr-C, CH), 128.3, 128.5, 128.6, 130.0, 133.7, 133.9, 134.0, 134.5, 134.8 (Ph), 165.0, 165.6, 165.7, 166.2, 172.0 (C=O) ppm. MS (FAB): *m/z* (%) = 6578 (10) $[M + H]^+$, 5309 (3), 5280 (3), 3184 (40), 3071 (45), 2654 (25), 1790 (10), 1313 (100). UV/Vis (CH_3CN): λ_{max} (ε) = 278 (21000), 233 (163000) nm. $C_{362}H_{370}O_{102}N_{16}$ (6576.8): calcd. C 66.11, H 5.67, N 3.41; found C 65.66, H 5.90, N 3.47.

General Procedure for the Preparation of the Dendritic Ruthenium Complexes: The dendritic bipyridine was added to a solution of ruthenium trichloride ($RuCl_3 \cdot xH_2O$; 35–40% Ru) in a mixture of chloroform/ethanol (1:1, v/v) and the resulting dark red solution was refluxed at 77 °C for 7 d. The reaction was monitored by TLC. After the reaction was complete, the mixture was diluted with CH_2Cl_2 and extracted three times with an aqueous solution of saturated NH_4PF_6 to ensure anion exchange. The combined organic layers were concentrated to dryness without further drying.

Compound 11, Ru^{II} Dendrimer with 4: Compound **11** was synthesized according to the general procedure with compound **4** (136 mg, 0.105 mmol) and $RuCl_3 \cdot xH_2O$ (35–40% Ru) (6.6 mg, 0.0261 mmol) in $CHCl_3$/EtOH (1:1, 10 mL) under reflux for 7 d. The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 15:1; R_f = 0.42). Yield 58 mg (52%) orange-red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (m, 36 H, CH_2), 2.20 (m, 12 H, CH_2COO), 3.37 (m, 12 H, CH_2N), 4.08 (br., 4 H, CONH), 4.99 (d, ^2J = 12 Hz, 6 H, CH_2-Bn), 5.10 (d, ^2J = 12 Hz, 6 H, CH_2-Bn), 5.16 (d, ^2J = 12 Hz, 6 H, CH_2-Bn), 5.23 (d, ^2J = 12 Hz, 6 H, CH_2-Bn), 5.78 (d, ^3J = 3 Hz, 2 H, *CH), 5.88 (d, ^3J = 3 Hz, 2 H, *CH), 7.09 (m, 30 H, Bn), 7.27 (m, 30 H, Bn), 7.36 (m, 18 H, Bz, Pyr-CH), 7.54 (m, 6 H, Bz), 7.61 (m, 6 H, Pyr-CH), 7.71 (m, 6 H, Pyr-CH), 7.85 (m, 12 H, Bz), 8.90 (br., 6 H, CONH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.1, 26.2, 28.7 (CH_2), 33.2 (CH_2COO), 40.4 (CH_2N), 67.8, 67.9 (CH_2-Bn), 70.8, 71.3 (*CH), 122.3, 123.0 (Pyr-C, CH), 126.6, 128.3, 128.4, 128.5, 128.6, 128.9, 129.2, 129.9, 130.0, 130.3, 133.7, 134.4, 134.5, 134.7 (Ph), 144.1, 151.2, 157.0 (Pyr-C, CH), 162.5, 164.9, 165.1, 165.6, 165.7, 165.8, 165.9, 172.1, 172.2, 173.8 (C=O) ppm. MS (FAB): *m/z* (%) = 4155 (30) $[M - PF_6]^+$, 3766 (20), 2219 (10), 2005 (20), 1811 (25), 1303 (20), 915 (100). IR: $\tilde{\nu}$ = 3272, 3067, 2942, 1732, 1649, 1547, 1454, 1194, 1094, 960, 837 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 470 (26000), 433 (25000), 305 (80000), 230 (129000) nm. $C_{222}H_{210}O_{54}N_{12}P_2F_{12}Ru \cdot CH_2Cl_2$ (4383.3): calcd. C 61.07, H 4.87, N 3.83; found C 60.87, H 4.90, N 4.03.

Compound 12, Ru^{II} Dendrimer with 7: Compound **12** was synthesized according to the general procedure with compound **4** (94 mg, 0.0307 mmol) and $RuCl_3 \cdot xH_2O$ (35–40% Ru) (2.2 mg, 8.78 µmol) in $CHCl_3$/EtOH (1:1, 10 mL) under reflux for 10 d. The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 15:1; R_f = 0.15). Yield 19 mg (20%) orange-red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 72 H, CH_2), 1.65 (m, 36 H, CH_2), 2.10 (m, 24 H, CH_2COO), 2.40 (m, 12 H, CH_2COO), 3.30 (m, 36 H, CH_2N), 4.10 (br., 6 H, CONH), 5.10 (m, 48 H, CH_2-Bn), 5.80 (m, 36 H, *CH), 6.80 (br., 12 H, CONH), 7.10 (m, 60 H, Bn), 7.27 (m, 60 H, Bn), 7.36 (m, 42 H, Bz, Pyr-CH), 7.53 (m, 18 H, Bz), 7.89 (br., 12 H, Pyr-CH), 7.91 (m, 36 H, Bz, Pyr-CH), 9.41 (br., 6 H, CONH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.3, 24.0, 26.1, 28.7 (CH_2), 33.1, 34.1 (CH_2COO), 39.5 (CH_2N), 67.8, 67.9 (CH_2-Bn), 70.8, 71.2 (*CH), 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 130.0, 133.7, 134.5, 134.8 (Ph), 153.0, 158.0 (Pyr-C, CH), 165.0, 165.6, 165.7, 172.0 (C=O) ppm. IR: $\tilde{\nu}$ = 3235, 2934, 1952, 1844, 1728, 1539, 1452, 1250, 1092, 1068, 839 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 470 (25000), 434 (25000), 305 (80000), 231 (247000) nm. MALDI-TOF-MS (matrix: dithranol): *m/z* = 9429 $[M - PF_6]^+$, 9288 $[M - 2\ PF_6]^+$, 9196 $[M - 2\ PF_6 - Bn]^+$.

Compound 13, Ru^{II} Dendrimer with 8: Compound **13** was synthesized according to the general procedure with compound **8** (130 mg, 0.0425 mmol) and $RuCl_3 \cdot xH_2O$ (35–40% Ru) (3.07 mg, 12.1 µmol) in $CHCl_3$/EtOH (1:1, 10 mL) under reflux for 10 d. The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 15:1; R_f = 0.15). Yield 33 mg (24%) orange-red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 72 H, CH_2), 1.65 (m, 36 H, CH_2), 2.10 (m, 24 H, CH_2COO), 2.40 (m, 12 H, CH_2COO), 3.25 (m, 36 H, CH_2N), 4.05 (br., 6 H, CONH), 5.10 (m, 48 H, CH_2-Bn), 5.80 (m, 36 H, *CH), 6.70 (br., 12 H, CONH), 7.10 (m, 60 H, Bn), 7.27 (m, 60 H, Bn), 7.35 (m, 42 H, Bz, Pyr-CH), 7.54 (m, 18 H, Bz), 7.85 (br., 12 H, Pyr-CH), 7.90 (m, 36 H, Bz, Pyr-CH), 9.00 (br., 6 H, CONH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.7, 23.0, 24.1, 26.1, 28.8 (CH_2), 33.1, 34.0 (CH_2COO), 39.0 (CH_2N), 67.8, 67.9 (CH_2-Bn), 70.8, 71.2 (*CH), 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 130.0, 131.2, 132.1, 133.7, 134.5, 134.8 (Ph), 153.0, 158.0 (Pyr-C, CH), 165.0, 165.7, 172.0 (C=O) ppm. IR: $\tilde{\nu}$ = 3232, 2933, 1952, 1844, 1728, 1539, 1452, 1249, 1092, 1068, 839 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 473 (26000), 435 (25000), 305 (85000), 230 (245000) nm. MALDI-TOF-MS (matrix: dithranol): *m/z* = 9429 $[M - PF_6]^+$, 9286 $[M - 2\ PF_6]^+$,

9196 [M – 2 PF_6 – Bn]$^+$. $C_{510}H_{510}O_{138}N_{24}F_{12}P_2Ru{\cdot}3CDCl_3$ (9935): calcd. C 62.01, H 5.23, N 3.38; found C 61.91, H 5.58, N 3.31.

Compound 14, $Ru^{II}Cl_2$ Dendrimer with 10: Compound **14** was synthesized according to the general procedure with compound **10** (58 mg, 8.82 μmol) and $RuCl_3{\cdot}xH_2O$ (35–40% Ru) (0.64 mg, 2.52 μmol) in $CHCl_3$/EtOH (1:1, 10 mL) under reflux for 14 d. The crude product was purified by column chromatography (silica, CH_2Cl_2/MeOH, 15:1; R_f = 0.13). Yield 20 mg (33%) dark-violet solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 168 H, CH_2), 2.20 (m, 56 H, CH_2COO), 3.15 (m, 56 H, CH_2N), 4.10 (br., 4 H, CONH), 5.10 (m, 64 H, CH_2-Bn), 5.80 (m, 56 H, *CH), 6.50 (br., 24 H, CONH), 7.10 (m, 80 H, Bn), 7.27 (m, 80 H, Bn), 7.40 (m, 56 H, Bz), 7.53 (m, 28 H, Bz), 7.70 (m, 2 H, Pyr-CH), 7.91 (m, 28 H, Bz), 8.05 (m, 32 H, Bz, Pyr-CH), 8.80 (m, 4 H, Pyr-CH), 10.35 (br., 2 H, Pyr-CH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.0, 24.9, 25.9, 28.7, 29.6 (CH_2), 33.0, 33.1, 33.6, 33.9 (CH_2COO), 39.3 (CH_2N), 67.7, 67.9 (CH_2-Bn), 70.1, 70.7, 71.2, 71.3, 72.3, 72.8 (*CH), 106.3, 127.5, 127.9, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 130.0, 133.6, 133.9, 134.5, 134.8, 136.7 (Ph), 160.1, 165.0, 165.3, 165.6, 165.7, 166.1, 168.3, 172.0 (C=O) ppm. IR: $\tilde{\nu}$ = 3272, 2915, 2849, 1732, 1655, 1603, 1541, 1464, 1375, 1215, 1092, 1020, 847 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 570 (5000), 411 (5000), 310 (15000), 273 (32000), 231 (290000) nm. MALDI-TOF-MS (matrix: dithranol): *m/z* = 13290 [M – Cl]$^+$, 12023, 6575 [bpy*]$^+$. $C_{724}H_{740}O_{204}N_{32}Cl_2Ru$ (13325): calcd. C 65.26, H 5.60, N 3.36; found C 65.27, H 5.97, N 3.08.

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