Dendritic Supramolecular Assembly with Multiple Ru(II) Tris(bipyridine) Units at the Periphery: Synthesis, Spectroscopic, and Electrochemical Study

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ABSTRACT: A supramolecular assembly with eight peripheral ruthenium(II) tris(bipyridine), $[Ru(bpy)_3]^{2+}$, units covalently linked to a carbosilane dendrimer platform has been synthesized. ^{1}H NMR and MALDI-TOF mass spectrometry confirm the target structure. Spectroscopic and electrochemical studies disclose that the identical $[Ru(bpy)_3]^{2+}$ units in this system interact neither in the ground state nor in the excited state. In acetonitrile solutions of identical molar concentration of $[Ru(bpy)_3]^{2+}$ units, both the dendrimer and reference monomeric $[Ru(bpy)_2(4\text{-octoxy-}2,2'\text{-bipyridine})]^{2+}$ exhibit identical absorption and emission spectra. Cyclic voltammetry reveals that the dendrimer and monomer possess the same redox potentials of the metal-centered oxidation process $[Ru(bpy)_3]^{2+/3+}$ and the first ligand-centered reduction process $[Ru(bpy)_3]^{1+/2+}$. The abnormal redox peaks of the $[Ru(bpy)_3]^{0/1+}$ and $[Ru(bpy)_3]^{1-/0}$ transitions of the dendrimer are attributed to the accumulation of neutral dendrimer on the electrode. A preliminary study of the electrochemiluminescence (ECL) in tripropylamine−acetonitrile solution indicates that the ECL intensity of the dendrimer with eight $[Ru(bpy)_3]^{2+}$ units is 5 times higher than that of the reference monomeric species. Therefore, the molar emission, generated either by photoexcitation or by electrochemical excitation, can be amplified by incorporating multiple luminophores into a multibranch platform without significantly changing the redox and photophysical properties. The possible use of supramolecular assemblies as labels for biodiagnostics is discussed.

Introduction

Ruthenium(II) tris(bipyridine) complexes, $[Ru(bpy)_3]^{2+}$, bpy = 2,2′-bipyridine, and its other *N*,*N*-chelating analogues, e.g., those with 2,2′:6′,2″-terpyridine and 1,10-phenanthroline ligands, have been studied intensely because they are chemically very stable, and they have numerous redox states and strong photoemission under photoexcitation[1] and electrochemical excitation.[2] The photochemical, photophysical, and electrochemical aspects of these studies have been reviewed.[3] In addition to the early interest in water splitting,[4] these compounds have been exploited for artificial photosynthesis.[5] The strong specific photoluminescence and electrochemiluminescence (ECL) of $[Ru(bpy)_3]^{2+}$ compounds are increasingly used for molecular recognition[6] and for chemical analysis.[7] Ru(II) tris(bipyridine) complexes have also been used in DNA binding studies[8] and in DNA probing.[8b,9] The ECL phenomenon has been developed into a new technology in which bioconjugatable ruthenium complexes are used as the ECL labels, e.g., [4-(*N*-succimidyloxycarbonylpropyl)-4′-methyl-2,2′-bipyridine] bis(2,2′-bipyridine)ruthenium(II) dihexafluorophosphate, for immunoassays and DNA probe assays in laboratory and clinical settings.[10] Among the many advantages of this new technique over classical fluorescence or isotope labeling are the low detection limit (200 fM) and the large dynamic range (up to 6 orders). These results have been obtained after optimization of the many technical aspects of the analytical procedure.

It is thought that further improvements can be realized if labels with multiple $[Ru(bpy)_3]^{2+}$ complexes would be available. Polymers with multiple $[Ru(bpy)_3]^{2+}$ complexes attached as side groups[11] or as links in the polymer backbone[12] have been described. However, for analytical purposes it is imperative that the multiple redox groups in the label are molecularly and functionally identical. Therefore, dendrimers with multiple $[Ru(bpy)_3]^{2+}$ groups may offer the best strategy.

Lehn and Ziessel[13] have described a ligand with three bipyridine groups (L_3), and this compound was complexed with three units of $[Ru(bpy)_2]^{2+}$ to form $\{[Ru(bpy)_2]_3L_3\}^{6+}$. Its absorption in acetonitrile (λ_{max} = 446 nm with ϵ_{max} = 33 000 M^{-1} cm^{-1}) is compared with values for $[Ru(bpy)_3]^{2+}$ (λ_{max} = 452 nm with ϵ_{max} = 14 600 M^{-1} cm^{-1}).[14] This result immediately shows the importance of the proper choice of reference material. Cyclic voltammetry results also show significant deviations between the tris-Ru(II) complex and the chosen reference. Belser et al. have described another tris(bipyridine) ligand and its complexes with 1−3 $[Ru(bpy)_2]^{2+}$ moieties.[15] In each case λ_{max} = 451 nm, and values of ϵ_{max} increase as multiples of 12 400 M^{-1} cm^{-1}. The first oxidation and first reduction potentials slightly deviate from those of $[Ru(bpy)_3]^{2+}$. However, no photoluminescence intensities (λ_{max} = 640 nm against 615 nm for $[Ru(bpy)_3]^{2+}$) are available for comparison. Marvaud et al. have synthesized two hexa(bipyridine) stars (L_6) and their hexa-Ru(II) complexes. The two $\{[Ru(bpy)_2]_6L_6\}^{12+}$ compounds have λ_{max} = 456 nm with ϵ_{max} = 65 000 M^{-1} cm^{-1} and λ_{max} = 459 nm with ϵ_{max} = 68 000 M^{-1} cm^{-1}.[16] Cyclovoltammetry shows a single reversible wave for the $Ru(bpy)_3^{2+/3+}$ oxidation, indicating that the six Ru centers are equivalent and noncommunicating. Constable et al. have described a tetra(terpyridine) compound (L_4) derived from pentaerytritol.[17] The complex with four Ru centers $\{[Ru(tpy)]_4L_4\}^{8+}$ has

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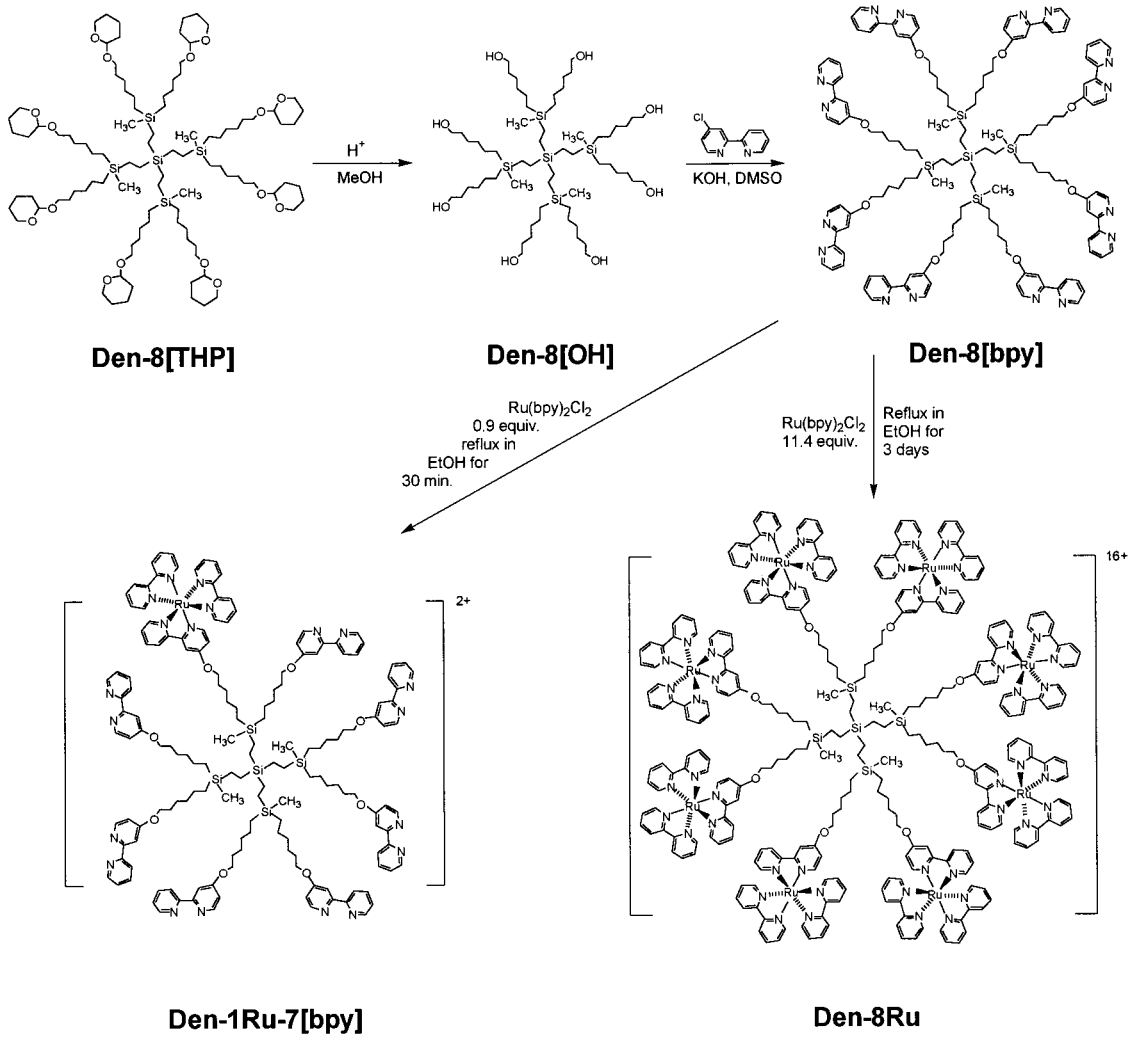
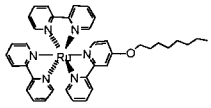
Scheme 1





Ref-Ru

λ_{max} = 482 nm with ϵ_{max} = 60 000 cm^{-1} compared to λ_{max} = 479 nm with ϵ_{max} = 15 200 cm^{-1} for the correct reference $[Ru(tpy)(4\text{-}EtOtpy)]^{2+}$. Cyclic voltammetry shows a single reversible wave for the Ru(II/III) transition that is evidence for the equivalence and independence of the four Ru(II) complexes. Most recently, Storrier et al. have described the synthesis of poly(amidoamine) PAMAM dendrimers with peripheral bipyridine groups and their Ru(II) complexes.[18] Dendrimers with nominally 4, 8 16, 32, and 64 Ru centers all have λ_{max} = 454 nm and ϵ_{max} = 44 000, 93 000, 174 000, 248 000, and 533 000 M^{-1} cm^{-1}, respectively. This result represents a significant decrease of the extinction coefficient per Ru center for the higher generation dendrimers. This may be genuine, but the presence of incomplete dendrimers and incomplete substitution reactions cannot be excluded in view of the difficulties of the synthesis and analysis of defect-free high-generation dendrimers. The electrochemical study shows a single reversible oxidation process and is taken as evidence for the simultaneous transfer of one electron from each Ru center of the dendrimer to the electrode. More complex surface phenomena associated with electroprecipitation and changes in film morphology and charge trapping are also described.

So far, from these previous studies of star-shaped and dendritic molecules with multiple peripherally placed Ru(II) bipyridine and Ru(II) terpyridine complexes, it appears that the properties associated with each Ru unit are independent of each other. This is also supported by similar redox properties of dendrimers with peripheral ferrocene groups.[19] We have prepared a supramolecular assembly with eight $[Ru(bpy)_3]^{2+}$ units (Den-8Ru in Scheme 1) based on the synthesis of carbosilane dendrimers[21] and their hydroxy derivatives[22] and studied its photophysical and electrochemical properties in comparison with those of the monomeric species $[Ru(bpy)_2(4\text{-octoxy-}2,2'\text{-bipyridine})](PF_6)_2$ (Ref-Ru). Our further interest is in the electrogenerated chemiluminescence (or electrochemiluminescence, ECL)[2,20] of dendritic systems containing multiple Ru units which, to the best of our knowledge, has not been reported. Since ECL is

the outcome of a complex chain of electrochemical reactions, follow-up chemical reactions, and photophysical processes, the comparison between monomeric and dendritic species is of great importance.

Experimental Section

Chemicals. Reagent grade solvents and reactants were used as received unless otherwise specified. *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ was prepared according to the procedure of Sullivan et al.[23]

Syntheses. Synthesis of 4-Chloro-2,2′-bipyridine. The procedure of Jones et al.[24] was followed with minor modifications. Alternatively, 2,2′-bipyridine was oxidized by the method of Wenkert and Woodward[25] and 2,2′-bipyridine *N*-oxide chlorinated according to the method of Moran.[26] 4-Chloro-2,2′-bipyridine was isolated from the 6-chloro-isomer by column chromatography (silica gel treated with 20% triethylamine in hexane, elution 20% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, 1H), 8.58 (d, 1H), 8.50 (d, 1H), 8.43 (d, 1H), 7.86 (t, 1H), 7.37 (m, 1H), 7.34 (m, 1H).

Synthesis of Den-8[bpy]. Tetrahydropyran functionalized carbosilane dendrimer Den-8[THP][22] (0.57 g, 0.32 mmol) and two drops of concentrated hydrochloric acid (37%) were stirred in methanol (15 mL) at room temperature for 5 days. The methanolic solution was neutralized with a small amount of ground KOH, then evaporated, and vacuum-dried to afford 0.37 g of oily Den-8[OH] (colorless but slightly cloudy due to the presence of KOH and KCl). ^{1}H NMR (400 MHz, DMSO): δ 3.34 (t, 16 H, CH_2O), 1.37 (m, 16 H), 1.25 (bs, 48 H), 0.46 (m, 16 H), 0.33 (m, 16 H), −0.11 (s, 12 H). Den-8[OH] (0.358 g, 0.32 mmol) was dissolved in 10 mL of freshly dried DMSO, and 2 g of KOH was added. The mixture was evacuated for 10 min and saturated with argon. 4-Chloro-2,2′-bipyridine (0.74 g, 3.88 mmol, 1.52 equiv per OH) was added, and the heterogeneous mixture was stirred at 40 °C for 4 days. The resulting solution was poured into 150 mL of water and neutralized with 1 N HCl. The product was extracted with CH_2Cl_2 (4 × 200 mL). After evaporation of CH_2Cl_2, the slightly pink oil was purified by chromatography (silica gel, 25% ethyl acetate in hexane first, then 5% methanol in CH_2Cl_2) to afford 0.65 g of oil (yield 87%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, 8H), 8.44 (d, 8H), 8.43 (d, 8H), 7.93 (d, 8H), 7.79 (t, 8H), 7.28 (m, 8H), 6.80 (m, 8H), 4.07 (t, 16 H, CH_2O), 1.77 (q, 16 H), 1.36 (m, 48 H), 0.51 (m, 16 H), 0.37 (m, 16 H), −0.07 (s, 12 H). MALDI-TOF *m*/*z* 2356.2 (calcd 2355.57).

Synthesis of Den-8Ru$(PF_6)_{16}$. Den-8[bpy] (0.10 g, 0.042 mmol) and 250 mg (0.48 mmol, 1.43 equiv per arm) of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ in 20 mL of ethanol were refluxed for 3 days. The unreacted $Ru(bpy)_2Cl_2$ was filtered off. The filtrate was evaporated, and the red solid was dissolved in a small amount of water and precipitated by adding a large excess of aqueous saturated NH_4PF_6. After filtration the product was redissolved in acetone and precipitated in dried ether to yield a fine red powder that was centrifuged and vacuum-dried. Yield 0.25 g (75%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.8−7.0 (184 H), 4.25 (t, 16 H, CH_2O), 1.79 (b, 16 H), 1.47 (b, 16 H), 1.37 (b, 32 H), 0.56 (b, 16 H), 0.47 (b, 16 H), −0.05 (s, 12 H). MALDI-TOF *m*/*z* 7837.42 ([Den-8Ru − PF_6]$^+$, calcd 7837.51). See results and discussion.

Synthesis of Den-1Ru-7[bpy]$(PF_6)_2$. Den-8[bpy] (0.10 g, 0.042 mmol) and 20 mg (0.038 mmol) of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ in 10 mL of ethanol were refluxed for 30 min. The solution was evaporated, and the red solid was dissolved in a small amount of water and precipitated by adding large excess of saturated NH_4PF_6−water solution. After filtration and water washing the product was vacuum-dried at 100 °C. Yield 0.109 g (94%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.8−6.8 (72 H), 4.11 (m, 16 H, CH_2O), 1.78 (q, 16 H), 1.48 (b, 16 H), 1.38 (b, 32 H), 0.57 (b, 16 H), 0.52 (b, 16 H), −0.03 (s, 12 H). MALDI-TOF *m*/*z* 2913.26 ([Den-1Ru-7[bpy] − PF_6]$^+$, calcd 2913.97), 2768.38 ([Den-1Ru-7[bpy] − $2PF_6$]$^+$, calcd 2769.01).

Synthesis of Den-8Ru$(Cl)_{16}$. The procedure for the preparation of the compound was the same as described for Den-8Ru$(PF_6)_{16}$ except for the precipitation with NH_4PF_6. The ethanol solution of the product was dropped into dried ether followed by centrifugal separation and vacuum-drying to afford 0.73 g of product (from 0.3 g of Den-8[bpy], yield 92%).^{1}H NMR (400 MHz, DMSO-d_6): δ 9.3−7.0 (184 H), 4.23 (t, 16 H, CH_2O), 1.64 (b, 16 H), 1.33 (b, 16 H), 1.23 (b, 32 H), 0.43 (b, 16 H), 0.30 (b, 16 H), −0.14 (s, 12 H).

Synthesis of 4-Octoxy-2,2′-bipyridine. 1-Octanol (0.26 g, 0.2 mmol) and 0.5 g of KOH were stirred in DMSO for 15 min, and 0.19 g (0.1 mmol) of 4-chloro-2,2′-bipyridine was added and stirred at room temperature for 2 days. The resulting mixture was poured into 25 mL of water and neutralized with 1 N HCl. The product was extracted with CH_2Cl_2 (3 × 75 mL) and dried with $MgSO_4$. After evaporation of CH_2Cl_2, the oil was purified by chromatography (silica gel treated with 20% triethylamine in hexane, elution 20% ethyl acetate in hexane) and vacuum-dried. Yield 0.233 g (82%) colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, 1H), 8.45 (d, 1H), 8.40 (d, 1H), 7.94 (d, 1H), 7.79 (t, 1H), 7.28 (m, 1H), 6.81 (m, 1H), 4.10 (t, 2H, CH_2O), 1.80 (q, 2H), 1.45 (q, 2H), 1.27 (m, 8H), 0.86 (t, 3H).

Synthesis of $Ru(bpy)_2$(4-octoxy-2,2′-bipyridine)$(PF_6)_2$ (Ref-Ru). See Scheme 1. 4-Octoxy-2,2′-bipyridine (0.150 g, 0.527 mmol) and 0.300 g (0.576 mmol) of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ in 20 mL of ethanol were refluxed for 8 h. The resulting solution was filtered to remove unreacted *cis*-$Ru(bpy)_2Cl_2$. The filtrate was evaporated and dissolved in a small amount of water and precipitated with a large excess of saturated NH_4PF_6−water solution. After filtration the product was redissolved in acetone and precipitated in dried ether to yield fine orange particles which were centrifuged and vacuum-dried. Yield 0.45 g (86.5%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.86 (d, 1H), 8.81 (m, 4H), 8.37 (d, 1H), 8.20 (m, 4H), 8.13 (d, 1H), 8.08 (d, 1H), 8.05 (m, 4H), 7.75 (d, 1H), 7.57 (m, 5H), 7.15 (m, 1H), 4.29 (t, 2H, CH_2O), 1.84 (q, 2H), 1.48 (q, 2H), 1.29 (m, 8H), 0.87 (t, 3H). MALDI-TOF *m*/*z* 844.26 ([Ref-Ru − PF_6]$^+$, calcd 843.65), 696.34 ([Ref-Ru − $2PF_6$]$^+$, calcd 698.69), 568.32 ([Ref-Ru − $2PF_6$ − $O(CH_2)_7CH_3$]$^+$, calcd 569.47).The calculated molecular weights are based on ^{102}Ru, the isotope of greatest abundance.

Characterization.^{1}H NMR spectra were obtained on a Varian Inova (400 MHz) spectrometer. Measurements of the diffusion coefficients were made with a Bruker Avance AMX-300 NMR spectrometer in acetonitrile-d_6 at 21 °C. The pulse-gradient spin-echo (PGSE) sequence of Stejskal and Tanner[27a] was used. Details of the method have been given previously.[27b] MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectra were recorded on a Perseptive Biochemistry Voyager-DE STR Maldi spectrometer operated in linear mode using dithranol as the matrix. UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Emission spectra were obtained with a Fluorolog spectrofluorometer. The relative photoluminescence intensities were obtained by comparing the integrated emission spectra of the compounds with that of $Ru(bpy)_3(PF_6)_2$. Both absorption and emission measurements were carried out in argon-saturated acetonitrile solutions at room temperature.

Cyclic voltammetry in acetonitrile was performed according to the previously described protocol 2.[28] The airtight cell, loaded with a column of basic alumina powder (Aldrich, standard grade, ~150 mesh), was vacuum-dried at 250 °C for 2.5 h. After the cell cooled to room temperature, tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Fluka, electrochemical grade) was added to the cell followed by evacuation of the cell at room temperature for 30 min. Under protection of argon, 10 mL of acetonitrile (Fisher Scientific, HPLC grade) was introduced into the cell to form a 0.1 M $TBAPF_6$ solution. The solution was dried and deaerated by multiple circulation through the alumina-filled column. The ruthenium complex was then added. All steps and measurements were conducted under argon. A Pt disk (diameter 1 mm, area 0.785 mm^2) sealed in a soft glass rod was employed as the working electrode. It was polished with diamond polishing paste (1 μm), rinsed thoroughly with acetone and acetonitrile, and dried by a warm air flow. Pt and Ag wires were used as counter and quasi-reference electrodes, respectively. Potentials versus the

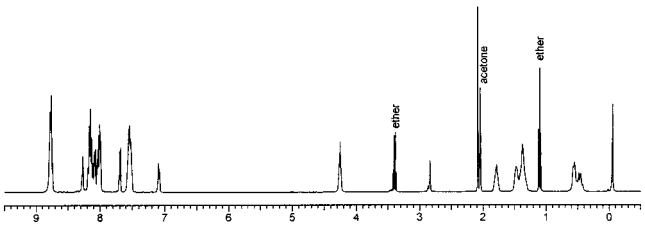


Figure 1. ^{1}H NMR spectrum of Den-8Ru$(PF_6)_{16}$ in acetone-d_6.

Ag quasi-reference electrode were then rescaled by Ag/AgCl and calibrated with the ferrocene/ferrocenium redox couple (0.35 V vs Ag/AgCl). A Solartron SI 1287 electrochemical interface was used for cyclic voltammetry. The scan rate in all experiments was 100 mV s^{-1} and the temperature was 20 °C, unless otherwise stated.

ECL measurements were carried out in the $TBAPF_6$ (0.1 M)−tripropylamine (TPA, 0.15 M)−acetonitrile system[29] at 1 mM Ru unit concentration. A pair of parallel platinum foils (6 × 24 mm) were employed as working and counter electrodes in a quartz cell. A silver wire was used as quasi-reference electrode. The outside of the working electrode faced the photocounting detector of the Fluorolog spectrometer. Before the solution was prepared, acetonitrile had been saturated with argon by Ar bubbling for 30 min. No further measures were taken during the ECL measurement in the open cell.

Results and Discussion

Synthesis and Structural Characterization. The synthesis of Den-8Ru from Den-8[THP] is shown in Scheme 1. The 2,2′-bipyridine is linked to the dendrimer via a Williamson-type reaction as used in the work of Marvaud et al.[16] As a result, our ^{1}H NMR spectra of Den-8[bpy] and Den-8Ru show the same patterns as the corresponding compounds prepared by Marvaud. In the ^{1}H NMR spectrum of Den-8Ru$(PF_6)_{16}$ (see Figure 1), the peaks in the alkyl region originate from the dendrimer core (0.56 to −0.05 ppm), and the spacers $-CH_2(CH_2)_4$-CH_2O- (4.25 to 1.37 ppm) and the integrations of individual peaks are consistent with the dendrimer structure. The assignment of peaks in the aryl region is difficult because of the existence of diastereomers[16a,30] as a result of the helical chirality of the octahedral six-coordinate Ru center. However, the total peak integration of 184 aryl protons satisfactorily matches the 124 protons in the alkyl region. It should be noted that the solvents used in the purification of Den-8Ru can hardly be removed. The presence of ether is identified in the ^{1}H NMR spectrum of Den-8Ru$(PF_6)_{16}$, whereas ether and ethanol are found in Den-8Ru$(Cl)_{16}$. If the ether drying procedure is not used, a large amount of water is found in Den-8Ru$(PF_6)_{16}$, despite high vacuum-drying at 100 °C for 1 day. Since water is a harmful impurity within the potential range of our electrochemical study, we prefer a small amount of ether. From the signal integration, the molar ratio of ether to Den-8Ru$(PF_6)_{16}$ is approximately 3:1, which accounts for 2.7 wt %.

Mass spectroscopy is now employed as a powerful tool in the structural characterization of dendrimers. Metallodendrimers containing multiple Ru centers have been characterized by MALDI-TOF, ES (electrospray), and FAB MS (fast atom bombardment mass spectrometry) techniques.[18,19a,30,31] Figure 2 shows the full range of MALDI-TOF spectra of Den-8Ru and Den-1Ru-7[bpy]. Successive loss of PF_6 moieties has been observed in many metallodendrimers containing Ru centers.[18,19a,30,31] This appears to be the only fragmentation in Den-1Ru-7[bpy]. The assigned fragmentation products with their observed and calculated masses are collected in Table 1 for the case of Den-8Ru. The first four rows are fragments formed by consecutive loss of PF_6 from the target Den-8Ru. The appearance of the large peaks ascribed to $[(\text{Den-7Ru}) - n\text{PF}_6]^+$ and $[(\text{Den-6Ru}) - n\text{PF}_6]^+$ (rows 5−9 in Table 1) raises a question with respect to the integrity of the target molecular structure. Compounds with this structural defect, i.e., the absence of one or more complete $[Ru(bpy)_3]^{2+}$ groups, may be due to incomplete Williamson reaction, i.e., in the transformation from Den-8[OH] to Den-8[bpy]. This possibility can, however, be ruled out by comparison of the ^{1}H NMR peak of the CH_2O protons of Den-8[OH] and Den-8[bpy]. The transformation of $-CH_2OH$ to $-CH_2O$-bpy causes a shift from 3.34 ppm (t, $-CH_2OH$) to 4.07 ppm (t, $-CH_2O$-bpy). See also the ^{1}H NMR peak at 4.25 in Figure 1. The ^{1}H NMR of Den-8[bpy] provides therefore definite evidence for the complete transform of $-CH_2$-OH to $-CH_2O$-bpy. Furthermore, integration of all and each aromatic ^{1}H peak from bpy and comparison with the peaks of the dendrimer core also indicate complete conversion. It must therefore be concluded that the $[(\text{Den-7Ru}) - n\text{PF}_6]^+$ and $[(\text{Den-6Ru}) - n\text{PF}_6]^+$ species are due to fragmentation during ionization of the perfect Den-8Ru. This type of fragmentation at the ether bond is also found in the MALDI-TOF spectrum of Ref-Ru (see Experimental Section and Supporting Information).

Besides these series of peaks, there are small peaks in the MALDI-TOF spectrum of Den-8Ru that can be assigned to the absence of one or more $Ru(bpy)_2$ groups, i.e., to structures of the general formula $[(\text{Den-}m\text{Ru}-(8 - m)\text{bpy}) - n\text{PF}_6]^+$ as given in rows 10 and 11 of Table 1. The fragments in rows 12 and 13 originate from [Den-7Ru-bpy], which suffers further loss of one or two $[Ru(bpy)_3]^{2+}$ moieties. The loss of multiple PF_6 moieties was not observed in these cases. These mass peaks may arise from fragmentation but can also be due to an incomplete complexation step from Den-8[bpy] to Den-8Ru. An estimation based on the peak heights suggests that complexation is at least 96% complete. As already shown from the NMR result and as will be shown later when discussing the absorption and emission spectra of Den-8Ru and Ref-Ru, this estimate must be considered to be a lower limit.

Absorption and Emission. Figure 3 shows the absorption and emission spectra of 40 μM (based on Ru units) Den-8Ru and Ref-Ru in argon saturated acetonitrile at 293 K. The absorption and emission spectra are completely overlaid, with a metal-to-ligand charge transfer (MLCT) absorption maximum at 455 nm and an emission maximum at 618 nm. The detailed data are listed in Table 2. As shown in Table 2, neither $Ru(bpy)_3(PF_6)_2$ nor Den-1Ru-7[bpy] is good reference materials for Den-8Ru. The relative emission intensity of Den-8Ru given in Table 2 is on the basis of the Ru unit concentration. Therefore, the molar emission intensity of Den-8Ru is 8 times larger than for Ref-Ru, and the photoluminescence efficiencies of Den-8Ru and Ref-Ru are identical and about 75% of the efficiency of $Ru(bpy)_3(PF_6)_2$. As mentioned in the Introduction, literature data for dendritic systems with Ru centers exclusively on the periphery are rather incomplete. The two supramolecular assemblies with six Ru centers described by Marvaud et al. chemically resemble best Den-8Ru because their Ru centers are also linked to the central core via 4-alkoxy[bpy] links.[16] See Scheme 1. However, the authors reported a low $\epsilon_{456} \approx 1.1 \times 10^4$ M^{-1} cm^{-1} per

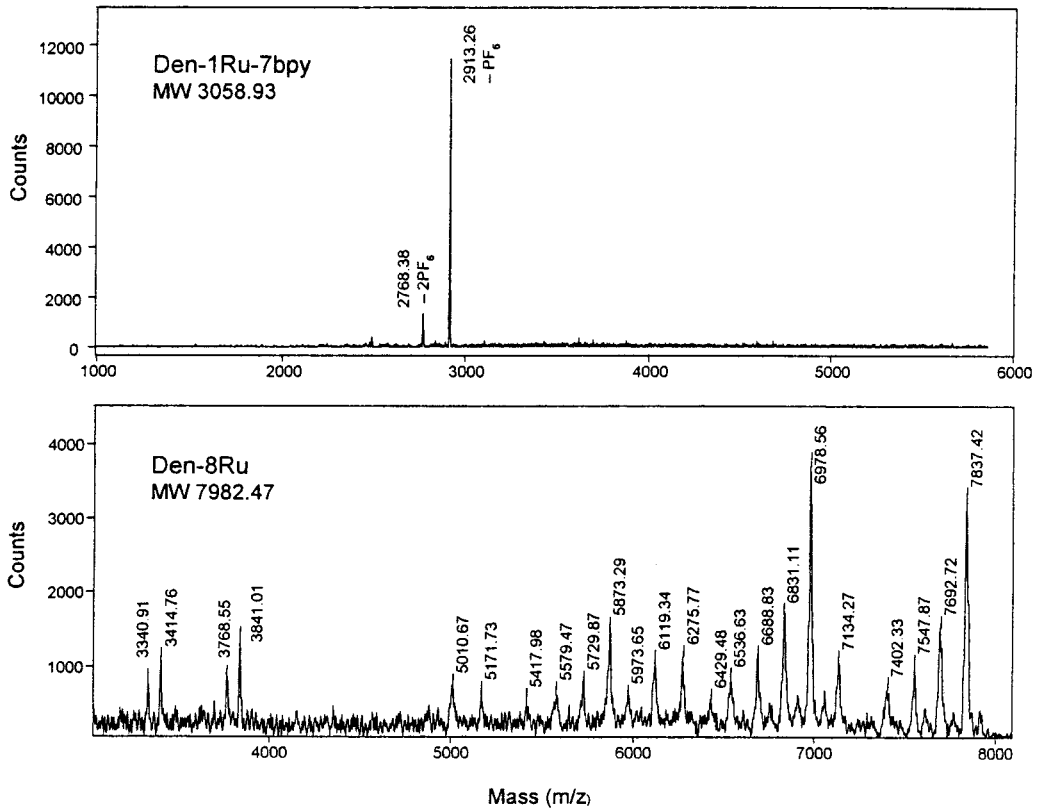


Figure 2. MALDI-TOF mass spectra of Den-1Ru-7[bpy] and Den-8Ru$(PF_6)_{16}$.

Table 1. Assignment of MALDI-TOF Fragments from Den-8Ru

fragment	observed *m/z*	calculated *m/z*
$[Den\text{-}8Ru - PF_6]^+$	7837.42	7837.51
$[Den\text{-}8Ru - 2PF_6]^+$	7692.72	7692.55
$[Den\text{-}8Ru - 3PF_6]^+$	7547.87	7547.59
$[Den\text{-}8Ru - 4PF_6]^+$	7402.33	7402.63
$[Den\text{-}7Ru - PF_6]^+$	6978.50	6978.97
$[Den\text{-}7Ru - 2PF_6]^+$	6831.11	6834.01
$[Den\text{-}7Ru - 3PF_6]^+$	6688.83	6689.05
$[Den\text{-}6Ru - PF_6]^+$	6119.34	6120.43
$[Den\text{-}6Ru - 2PF_6]^+$	5973.65	5975.47
$[Den\text{-}7Ru\text{-}1[bpy] - PF_6]^+$	7134.27	7134.15
$[Den\text{-}6Ru\text{-}2[bpy] - PF_6]^+$	6429.48	6430.78
$[Den\text{-}6Ru\text{-}1[bpy] - PF_6]^+$	6275.77	6275.60
$[Den\text{-}5Ru\text{-}1[bpy] - PF_6]^+$	5417.98	5417.06

Ru unit and do not provide emission data for their compounds.

Our results demonstrate that multiple identical $[Ru(bpy)_3]^{2+}$ units peripherally built onto a dendrimer system retain the ground-state and excited-state photophysical properties of Ref-Ru. When compared with $Ru(bpy)_3(PF_6)_2$, the absorption and emission energy are different, and the emission efficiency is lower due to a substitution effect rather than an assembly effect.

Voltammetric Studies. The cyclic voltammograms of Ref-Ru, Den-8Ru, and Den-1Ru-7[bpy] are displayed in Figure 4. The numerical results of the voltammetric study are listed in Table 3. For Ref-Ru, a single monoelectronic oxidation process (metal-centered) and three successive monoelectronic reduction processes (ligand-centered) display very good reversibility. In addition to the four reversible waves, an irreversible peak is found at −2.5 V (see dotted curve). All these features are very similar to those of $Ru(bpy)_3(PF_6)$.[2] As a general reference, the electrochemical data of $Ru(bpy)_3(PF_6)_2$ measured under the same experimental conditions are also given in Table 3. As expected, Den-8Ru also exhibits a single metal-centered oxidation process with half-wave potential of 1.17 V identical to that of Ref-Ru. However, unlike the Ref-Ru, the ligand-centered reduction of Den-8Ru shows an interesting phenomenon. The first reduction occurs at −1.39 V and shows the characteristics of a reversible one-electron transfer. The peak current is at the same level as that of the oxidation process at 1.17 V. However, after the compound undergoes the second reduction and becomes neutral, we find, on switching back, a very sharp anodic peak associated with the $[Ru(bpy)_3]^{0/1+}$ transition. Similarly, on further negative going we find a cathodic peak at −1.95 V (see dotted curve) associated with the $[Ru(bpy)_3]^{1-/0}$ process. It has the same sharpness as the anodic half-wave of the $[Ru(bpy)_3]^{0/1+}$ transition. This

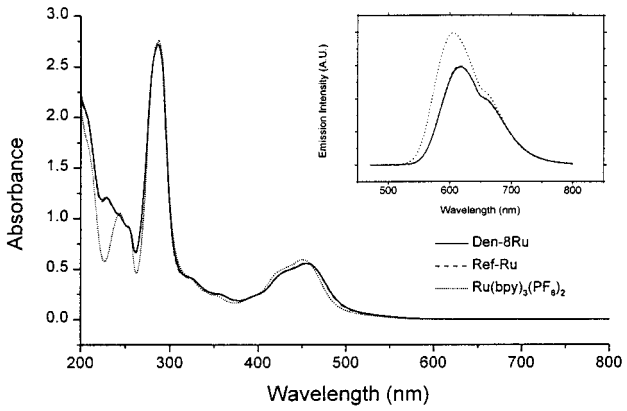


Figure 3. UV−vis absorption and emission spectra (inset) of Den-8Ru$(PF_6)_{16}$, Ref-Ru$(PF_6)_2$, and Ru$(bpy)_3(PF_6)_2$ in acetonitrile at 293 K. The Ru unit concentration is 40 μM in each case.

Table 2. Photophysical Data in Acetonitrile at 293 K

	absorption			emission[c]		
compound	λ_{max} (nm)	$\epsilon \times 10^{-4}$ (M^{-1} cm^{-1})	$\epsilon \times 10^{-4}$ (M^{-1} cm^{-1})/Ru[a]	λ_{max} (nm)	I_{rel}[d]	τ (ns)
Ref-Ru	229	3.01				
	286	6.82				
	455	1.40		618	0.75	905[e]
Den-1Ru-7[bpy]	455[b]	1.68				
Den-8Ru	229	24.24	3.03			
	286	544.8	6.81			
	455	11.12	1.39	618	0.75[a]	935[e]
$Ru(bpy)_3(PF)_6$	244	2.64				
	287	6.91				
	451	1.48		610	1.00	850−1100[f]

[a] Values of the extinction coefficient per Ru center. [b] In addition to the MLCT absorption at 455 nm, there are stronger absorptions due to bpy in the UV range. [c] Den-8Ru and Ref-Ru were excited at 455 nm, and decay measurements were directed to the emission maximum. $Ru(bpy)_3(PF_6)_2$ was excited at 451 nm. [d] I_{rel} is the emission intensity relative to $Ru(bpy)_3(PF_6)_2$ obtained by comparing the integrated spectra with that of $Ru(bpy)_3(PF_6)_2$. [e] The emission decays were found to be best fit by double-exponential functions for both Ref-Ru and Den-8Ru. For Ref-Ru, the best fit is $A_1 = 0.954$, $\tau_1 = 905$ ns, $A_2 = 0.046$, $\tau_2 = 13\,920$ ns. For Den-8Ru, the best fit is $A_1 = 0.692$, $\tau_1 = 746.5$ ns, $A_2 = 0.308$, $\tau_2 = 1284$ ns, but acceptable monoexponential fitting with $\tau = 935$ ns was applied to the decay. [f] The reported lifetime for $Ru(bpy)_3(PF_6)_2$ varies. See refs 14 and 32.

type of wave shape has been reported early in poly(vinylferrocene)/THF and poly(vinylferrocene)/CH_2Cl_2 systems and is associated with electroprecipitation of the redox product.[33,34] Recently, in studying ferrocenyl-functionalized dendrimer, Cuadrado et al. found the same behavior.[35] The cyclic voltammograms obtained in our systems are more interesting because the electroprecipitation of the neutral species is reflected in the further reduction process as well as in the immediate reoxidation process upon scan reversal. It is interesting to note that, instead of the stepwise process, the $[Ru(bpy)_3]^{1-}$ species in Den-8Ru is reoxidized in a one-step, three-electron process to $[Ru(bpy)_3]^{2+}$ units showing a wave with a peak potential that slightly varies, with the switching potential, between −1.31 and −1.38 V. An earlier study on Ru(1,10-phenanthroline)$_3(ClO_4)_2$ has shown a similar behavior, i.e., after two stepwise reductions, the reversal potential scan leads to a combined anodic peak.[36]

We expected Den-1Ru-7[bpy] to be a preferred reference for Den-8Ru in terms of its chemistry and size. However, although Den-1Ru-7[bpy] has a similar metal-centered reversible redox process at 1.165 V, it does not exhibit three distinct ligand-centered reduction peaks. The reduction peak at −2.341 V (see dotted curve) seems to be due to the reduction of the seven bipyridine groups. The extinction coefficient of Den-1Ru-7[bpy] listed in Table 2 is also very different from those of Den-8Ru and Ref-Ru. The microevironment created by the seven bipyridine groups seems to have a significant influence on the properties of Den-1Ru-7[bpy].

It is interesting to note that the peak currents of Den-8Ru and Ref-Ru in solutions of equimolar Ru unit are very similar in the oxidation and in the first reduction processes. According to the Randles-Sevcik equation, the peak current is given by[37]

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} c v^{1/2}$$

where n is the number of electrons simultaneously transferred in the redox process, A is the electrode area (cm^2), c is the bulk concentration of the electroactive groups (mol cm^{-3}), D is the diffusion coefficient (cm^2 s^{-1}), and v is the potential sweep rate (V s^{-1}). From the Randles−Sevcik equation, $D = 8.6 \times 10^{-6}$ cm^2 s^{-1} is obtained for Den-8Ru and Ref-Ru. Under our experimental conditions, the ratio of the peak current of Den-8Ru and Ref-Ru is given by[33,38]

$$i_{p,Den}/i_{p,Ref} = (D_{Den}/D_{Ref})^{1/2}$$

On the other hand, the diffusion coefficients of Den-8Ru and Ref-Ru, measured by PGSE NMR in acetonitrile-d_6 at 21 °C, are 6.9×10^{-6} and 10.5×10^{-6} cm^2 s^{-1}, respectively. This leads to a theoretical ratio of the peak currents equal to 0.81. Within experimental error the peak current of the first reduction process is in agreement, but the peak current of the oxidation of Den-8Ru is somewhat too high. We cannot exclude the possibility that the diffusion coefficient of Den-8Ru polyelectrolyte is slightly increased relative to that of Ref-Ru in the presence of 0.1 M electrolyte with a common anion.

ECL Observation. So far, the spectroscopic and electrochemical investigations have demonstrated that, first, the spectral characteristics and lifetime of the MLCT excited state of Den-8Ru and Ref-Ru are identical and, second, the rates of electrochemical generation of $[Ru(bpy)_3]^{3+}$ from Den-8Ru and Ref-Ru are to within 80% identical. The question is then raised whether Den-8Ru and Ref-Ru will generate the same luminescence intensity upon electrochemical excitation.

The electrochemical generation of the MLCT excited state, $[Ru(bpy)_3]^{2+*}$, can be realized by one of three reaction mechanisms, i.e., annihilation,[2,36] oxidative reduction,[29,39a,b] and reductive oxidation.[39c] Since electroprecipitation has been observed on reduction of Den-8Ru, our preliminary comparative ECL study has been carried out by the oxidative-reduction process in acetonitrile solution with tripropylamine as coreactant.[29] The ECL spectra are identical to the photoluminescence spectra for all compounds studied. We have reproducibly measured the emission under various experimental conditions. Figure 5 shows the typical ECL intensities as a function of time, when the potentials are stepped from 0 to 1.8−2.4 V vs Ag wire.[40] As a common reference, the ECL of $Ru(bpy)_3(PF_6)_2$ is also displayed in Figure 5. The relative intensity of Ref-Ru and Ru(bpy)$_3(PF_6)_2$ is similar to that of their photoluminescence, whereas Ref-Ru exhibits an integrated emission intensity that is about 1.6 times as strong as that of Den-8Ru at the same concentration of Ru units. In other words, the molar ECL emission intensity of Den-8Ru is 5 times larger than that of Ref-Ru instead of a factor 8 as observed in photoluminescence.

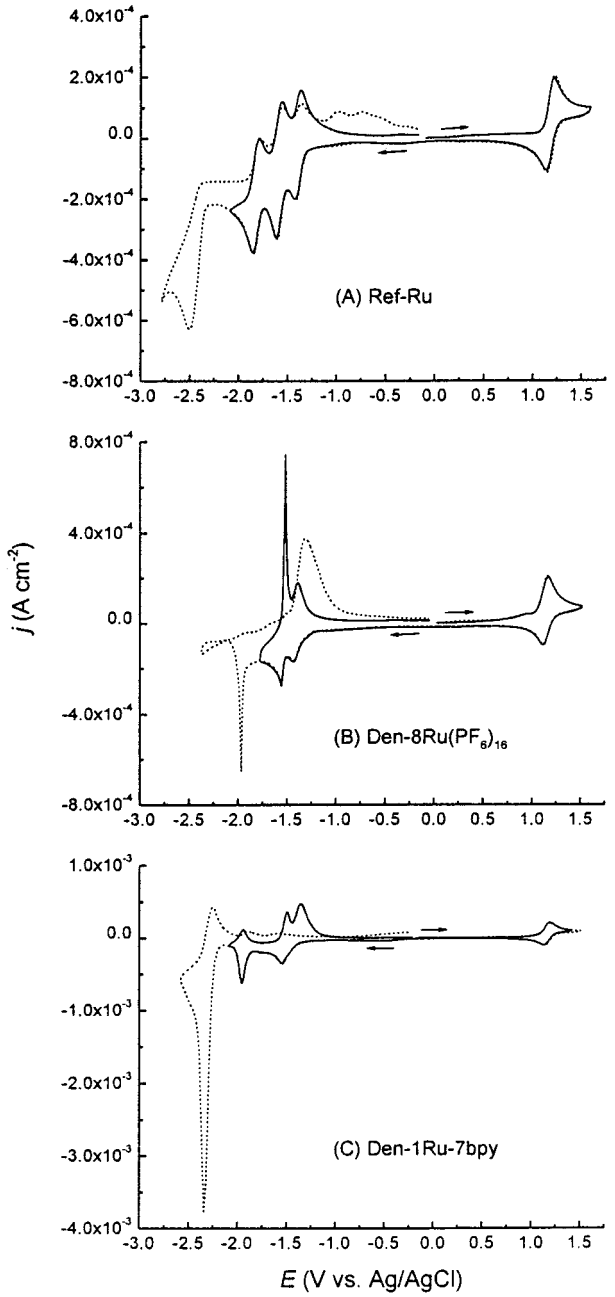


Figure 4. Cyclic voltammograms in acetonitrile at 293 K. The dotted curves show the voltammograms in extended ranges. Concentration of Ru units: 0.8 mM. Supporting electrolyte: 0.1 M $TBAPF_6$. Scan rate: 100 mV s^{-1}.

The electrochemiluminescence process starts with the electrochemical formation of $[Ru(bpy)_3]^{3+}$ and the simultaneous formation of $(C_3H_7)_3N^{\bullet+}$ radical cation at the electrode.[41] The radical cation is immediately deprotonated. The neutral radical $(C_3H_7)_2NC^{\bullet}HCH_2CH_3$ has a strong reducing ability and reduces $[Ru(bpy)_3]^{3+}$ to an excited state $[Ru(bpy)_3]^{2+}*$ according to

$$[Ru(bpy)_3]^{3+} + (C_3H_7)_2NC^{\bullet}HCH_2CH_3 \rightarrow [Ru(bpy)_3]^{2+}* + \text{oxidized products}$$

The excited $[Ru(bpy)_3]^{2+}*$ decays, producing luminescence. The slightly lower overall yield of electrochemiluminescence from Den-8Ru (about $^5/_8$) may be due to the possible slower diffusion of Den-8Ru to the electrode and the possible retarded reaction of the bulky oxidized Den-8Ru with the tripropylamine radical. The mechanism of oxidation of TPA and the subsequent reactions are not well understood. However, the product analysis of electrochemical dealkylation of TPA suggests the formation of the deprotonated radical as an intermediate.[42] Its strong reducing ability has been substantiated by the measurement of the redox potential of similar α-aminoalkyl radicals.[43] Whatever the exact reductant of $[Ru(bpy)_3]^{3+}$ is, it seems to be less efficient with the dendritic than the monomeric compound. Furthermore, we have to admit that the electrochemical oxidation step, although nearly identical for the two compounds in acetonitrile $TBAPF_6$, may be slightly different in the presence of TPA.

Table 3. Electrochemical Data in Acetonitrile at 293 K

compound	$E_{1/2,ox}$[a]	$\Delta E_{p,ox}$[b]	$j_{p,ox}$[c]	$E_{1/2,red}$[a]	$\Delta E_{p,red}$[b]	$j_{p,red}$[c]
Ref-Ru	1.175	0.081	1.98	−1.404	0.056	2.02
				−1.596	0.057	
				−1.831	0.061	
				−2.500[d]		
Den-1Ru-7[bpy]	1.165	0.057	2.15	−1.546[e]		
				−1.957[d]		
				−2.341[d]		
Den-8Ru$(PF_6)_{16}$	1.168	0.042	2.07	−1.390	0.045	1.72
				−1.509	0.045	
				−1.950[e]		
Den-8Ru$(Cl)_{16}$	1.175	0.036		−1.377	0.036	1.59
				−1.499	0.040	
				−1.937[e]		
Ru$(bpy)_3(PF_6)_2$	1.25	0.082	1.93	−1.380	0.058	2.00
				−1.572	0.058	
				−1.814	0.066	

[a] V vs Ag/AgCl. [b] Separation of the peak potentials (V). [c] Current intensity (10^{-4} A cm^2). [d] Reduction peak potential, irreversible. [e] Reduction peak potential, quasi-reversible.

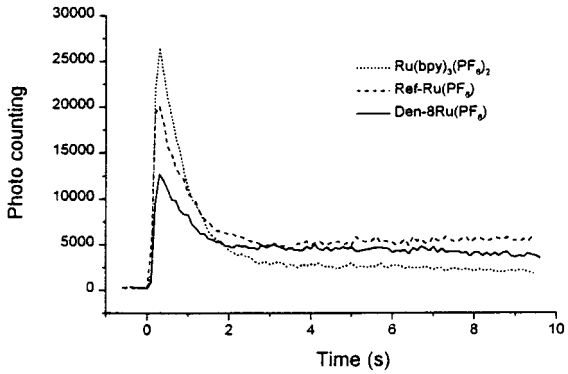


Figure 5. Electrochemiluminescence intensities as a function of time for $Ru(bpy)_3(PF_6)_2$, Ref-Ru, and Den-8Ru$(PF_6)_{16}$ in acetonitrile in the presence of 0.1 M $TBAPF_6$ and 0.15 M tripropylamine. Potential: between 1.8 and 2.4 V vs Ag wire.

Although the ECL generated from our dendritic assembly with eight Ru(II) bipyridine units is not exactly equal to the emission of the Ref-Ru complex under the same conditions, the 5-fold increase of mole-based ECL still provides a promising strategy for amplifying the luminescence signal in ECL-related analysis. As an example, a dendrimer with one bioconjugatable arm can be constructed and used as a label for ECL immunoassay and DNA probing. The solubility of these compounds in aqueous media can be improved by changing the counterion from PF_6^- to Cl^-. As a matter of fact, our Den-8Ru$(Cl)_{16}$ is sufficiently soluble in aqueous solution. The synthesis and investigation of novel bioconjugatable ruthenium complexes based on this idea are under way in our laboratory. Furthermore,

this methodology could provide a general approach to enhancing the signal intensity in analytical techniques in which signaling groups, such as radioactive isotopes, luminophores, and redox centers, etc., are linked to the analytes via a dendritic construct.

Conclusions

A supramolecular assembly with eight $[Ru(bpy)_3]^{2+}$ units at the periphery of a carbosilane dendrimer has been synthesized successfully and characterized by ^1H NMR spectroscopy and MALDI-TOF mass spectroscopy. Photophysical and electrochemical studies confirm that the identical $[Ru(bpy)_3]^{2+}$ units are noninteracting and that the dendrimer containing $[Ru(bpy)_3]^{2+}$ units behaves very much like the properly selected monomeric reference material in terms of absorption, emission, and some redox properties. The molar extinction coefficient, the luminescence intensity, and even the peak current of the redox waves of our system are simply those of the monomeric reference multiplied by the number of $[Ru(bpy)_3]^{2+}$ units. The oxidative-reduction ECL has a 5-fold enhancement over the monomeric reference compound. Since derivatives of $[Ru(bpy)_3]^{2+}$ are important labels in the ECL-based immunoassay and DNA probing, the results reported here present a strategy for the development of more efficient ECL labels that allow multiple labeling, e.g., at a single $-NH_2$ site and thus largely enhance the signal level.

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Supporting Information Available: ^1H NMR spectra of Den-8[bpy], Den-1Ru-7[bpy], Den-8Ru, and Ref-Ru, the MALDI-TOF spectrum of Ref-Ru, and the cyclic voltammogram of Den-$8Ru(Cl)_{16}$ in acetonitrile (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Due to the presence of a large amount of TPA in the solutions, the calibration of the potential with ferrocene is difficult. Therefore, we have measured the ECL for each solution at several potentials ranging from 1.8 to 2.4 V vs Ag wire. The data shown in Figure 5 are the highest emissions obtained for each individual solution.

(41) The possible chemical oxidation of TPA by $[Ru(bpy)_3]^{3+}$ can be neglected because of the low $[Ru(bpy)_3]^{2+}$ concentration.

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