Synthesis of Novel Electrochemiluminescent Polyamine Dendrimers Functionalized with Polypyridyl Ru(II) Complexes and Their Electrochemical Properties

Do Nam Lee, Hee Sang Park, Eun Hwa Kim, Young Moo Jun, Ja-Young Lee,[†] Won-Yong Lee,[†,*] and Byeong Hyo Kim[*]

*Department of Chemistry, Kwangwoon University, Seoul 139-701, Korea. *E-mail: bhkim@daisy.kw.ac.kr*
†Department of Chemistry and Center for Bioactive Molecular Hybrids, Yonsei University, Seoul 120-749, Korea
E-mail: wylee@yonsei.ac.kr

Polyamine dendrimers functionalized with electrochemiluminescent (ECL) polypyridyl Ru(II) complexes, dend-[CO-(CH$_2$)$_3$-mbpy·Ru(L)$_2$]$_3$(PF$_6$)$_6$ (dend: N(CH$_2$CH$_2$NH)$_3$-, L: bpy, *o*-phen, phen-Cl, DTDP), were synthesized through the complexation of dendritic polypyridyl ligands to Ru(II) complexes. Their electrochemical redox potentials, photoluminescence (PL), and relative ECL intensities were studied. The ECL emissions produced by the reaction between the electro-oxidized Ru^{3+} species of polyamine dendrimers and tripropylamine as a coreactant were measured in a static system with potential cycles between 0.8 and 1.3 V or through flow injection analysis with a potential of +1.3 V, and were compared to that of [Ru(*o*-phen)$_3$](PF$_6$)$_2$. Dend-[CO-(CH$_2$)$_3$-mbpy·Ru(bpy)$_2$]$_3$(PF$_6$)$_6$ showed an ECL intensity that was two-fold greater than that of the reference complex [Ru(*o*-phen)$_3$](PF$_6$)$_2$.

Key Words : Electrochemiluminescence, Ruthenium(II) complexes, Polyamine dendrimer

Introduction

A supramolecular system capable of performing complex functions such as the capability to absorb visible light, to produce luminescence, and to undergo reversible redox processes was initiated by Balzani's and Newkome's groups.[1-6] More recently, dendrimers that incorporate metal ions into their building blocks were studied extensively.[7-16] Metal ions can serve as branching centers, building block connectors, terminal groups, and structural auxiliaries. Transition metal complexes containing polypyridyl-type ligands exhibit attractive electrochemical and photophysical properties.[17-24] The electrochemiluminescence (ECL) phenomenon can be applied to biological technologies such as immunoassay and DNA probe assay, and it has many advantages, such as low detection limits and a wide, dynamic range over classical analysis methods. In recent years, Ru(II) complex-based ECL gained importance as a sensitive and selective detection method for the analysis of a wide range of compounds,[25-28] such as oxalate,[29] alkylamines,[30] amino acids,[31-33] NADH,[34,35] and organic acids.[36,37] In particular, the ECL observed with the tris(2,2'-bipyridyl)rutheium(II), [Ru(bpy)$_3$]$^{2+}$ system is among the most intense and best characterized.[38]

Recently, dendrimers peripherally functionalized with polypyridyl Ru(II) complex were synthesized and their photophysical and electrochemical properties were reported.[39] In addition, the ECL of a dendrimer pendant with multiple [Ru(bpy)$_3$]$^{2+}$ units shows that the intensity of this dendrimer is higher than that of monomeric units.[40,41] Therefore, dendrimers with multiple polypyridyl Ru(II) units may be used in developing new, efficient ECL materials.

The effects of ligands in a series of polypyridyl-substituted

Ru(II) complexes containing different *α*-diimine ligands on ECL intensity were studied by us and it was demonstrated that the ECL characteristics of the transition metal complexes are strongly dependent upon the local environments of metal complexes.[42-45] In a previous ECL study on PAMAM (polyamidoamine) metallodendrimers, bipyridyl (bpy) ligand was shown to be more efficient than phenanthroline (*o*-phen) ligand with regard to ECL intensity, which was not consistent with the monometallic [Ru(bpy)$_3$]$^{2+}$ or [Ru(*o*-phen)$_3$]$^{2+}$ cases.[46] In addition, the increased length of spacer of PAMAM seemed to result in an improved ECL intensity, which may have come from the sterically less-congested location of ECL-producing Ru(II) complexes. Thus, the length of spacer that connects metal complexes to dendrimers may be correlated with ECL intensity.

One of the problems with the previous PAMAM metallodendrimers was a strong background effect on ECL measurement, probably due to the inter- or intramolecular interaction of two amine groups in the core with peripheral Ru(II) complexes since the ECL emissions produced by the reaction between the electro-oxidized Ru^{3+} species of polyamine dendrimers and tripropylamine as a coreactant had been measured. The multiplicity of the inner amine functional group in metallodendrimers may be expected to affect ECL intensity.

In this paper, the synthesis of polyamine dendrimers surrounded by three units of electrochemiluminescent polypyridyl ruthenium(II) complexes was undertaken as this might reduce the background effect on ECL intensity due to the amine of dendrimer, which was observed in the ECL measurement of PAMAM dendrimers. In addition, new ligands, such as phen-Cl and DTDP, were introduced to the peripheral Ru(II) complexes to study the effect of ligands on

ECL efficiency. Through the complexation of dendritic polypyridyl ligands with a long spacer group to ruthenium— *i.e.*, polyamine dendrimers that were surface-modified with polypyridyl ruthenium(II) complexes—dend-[CO-(CH₂)₃-mbpyRu(L)₂]₃(PF₆)₆ (L: bpy, *o*-phen, phen-Cl, DTDP) was prepared and the effect of ligands and of a dendritic network on ECL behavior was studied for the purpose of developing more sensitive ECL materials.

Experimental Section

Materials and Instrumentation. All the reactions were carried out under a dry nitrogen atmosphere, unless otherwise stated. The solvents were purchased and dried using the standard method. Most of the chemical reagents were purchased from Aldrich Chemical Co. and were used as received without further purification in most cases. 4-(3-Carboxypropyl)-4'-methyl-2,2'-bipyridine,[47] 1,3-dihydro-1, 1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one (DTDP),[48] and *cis*-Ru(L)₂Cl₂·2H₂O (L: bpy, *o*-phen, phen-Cl, DTDP)[49] were prepared using the known literature methods.

¹H NMR spectra were recorded on a 300 MHz Jeol instrument. Chemical shifts were reported in ppm relative to a residual solvent as an internal standard. GC/MS was recorded on an HP 6890 mass spectrometer and MALDI-TOF mass was recorded on a JMS-DX303 (JEOL Co.). Infrared spectra (IR) were recorded on a Nicolet 205 FT-IR and UV-vis spectra were recorded on a Shimadzu UV-240 or a Sinco S-3100. Emission spectra were obtained with the use of a Perkin Elmer luminescence spectrometer LS 50B (excitation source at 400 nm). Flow injection analysis (FIA) was performed with the use of the previously described ECL detection system.[42]

FIA Experimental Conditions. In the FIA experiments, the dual platinum electrode was polished prior to each experiment with 0.05 *μ*m alumina, sonicated, and rinsed with methanol followed by water. The flow cell was assembled and placed in the FIA system. The buffered carrier stream flow rate was 2.0 mL/min. The working electrode was held at a potential of +1.3 V (vs the Ag quasi-reference electrode). Ru(II) complex solution and tripropylamine (TPA) solutions were prepared in pH 7.0 phosphate buffer and 30 mM TBAP with acetonitrile. TPA solutions (0.3 mM) were mixed with 0.24 or 0.30 mM Ru(II) complex solutions (molar ratio; 1 : 1, 3 : 1). A mixture of Ru(II) complex and TPA was injected and passed through the cell. Blank injections were made in all studies. Blanks were prepared by mixing the given concentration of Ru(II) complex solution and the same buffer (1 : 1 v/v). Corrected ECL signals were obtained by subtracting the ECL signals for blank solutions from the observed ECL signals for TPA. For all studies, the ECL signal was calculated on the basis of the maximum peak height.

In the static mode, the working electrode was cleaned prior to each experiment by repeated potential cycling (0 ~ +1.2 V) in 0.2 mM sulfuric acid. During the course of the

ECL measurement, the potential of the working electrode was cycled from 0.5 V ~ +1.3 V with a scanning rate of 100 mV/s.

Synthesis.

Synthesis of Dendrimer Ligand: 4-(3-Carboxypropyl)-4'-methyl-2,2'-bipyridine (410 mg, 1.6 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC, 330 mg, 1.6 mmol), and 1-hydroxybenzotriazole (HOBt, 217 mg, 1.6 mmol) were dissolved in *N,N*-dimethylacetamide (DMAc) 5 mL and stirred at room temperature for 24 hrs. The precipitated *N,N'*-dicyclohexylurea (DCU) was filtered off. Tris(2-aminoethyl)amine (30 *μ*L, 0.2 mmol) dissolved in DMAc 1 mL was slowly added into filtrate and stirred. After DMAc was distilled off at low pressure, the residue was dissolved in minimum methanol. This solution was added dropwise to diethyl ether 250 mL to precipitate the solid. The solid was filtered and washed with diethyl ether. The filtrate was evaporated to remove diethyl ether and then the product was purified by basic alumina column chromatography (MeOH/CH₂Cl₂ = 2 : 98) and obtained in 53% yield.

N-[2-(Bis-{4-(4'-methyl-[2,2']bipyridinyl-4-yl)-butyrylamino}-ethyl)-amino]-ethyl]-4-(4'-methyl-[2,2']bipyridinyl-4-yl)-butyramide (dend-[CO-(CH₂)₃-mbpy]₃; 1) Alumina TLC (2% MeOH/CH₂Cl₂) R_f 0.44; C₅₁H₆₀N₁₀O₃; ¹H NMR (300 MHz, CD₃OD) δ 8.43 (t, *J* = 4.5 Hz, 6H), 8.04-8.03 (d, *J* = 4.0 Hz, 6H), 7.21 (m, 6H), 3.20 (t, *J* = 6.0 Hz, 6H), 2.67 (t, *J* = 7.5 Hz, 6H), 2.56 (t, *J* = 6.0 Hz, 6H), 2.40 (s, 9H), 2.23 (t, *J* = 7.4 Hz, 6H), 1.97-1.89 (m, 6H).

General Procedure for the Syntheses of Metallodendrimers: *cis*-Ru(L)₂Cl₂·2H₂O (L = bpy, *o*-phen, phen-Cl, DTDP, 0.32 mmol each) was dissolved into the mixture of degassed methanol and a small amount of acetone. Dendritic ligand (45 mg, 0.053 mmol) dissolved in methanol was added into the above solution and was refluxed for 48 hrs. After cooling, the excess amount of aqueous NH₄PF₆ was added, and then the solvent was evaporated until a precipitate was formed. The precipitate was filtered and washed with ethanol. The product was purified by alumina column chromatography using MeOH/CH₂Cl₂(1 : 99) as eluent. Red solid was recrystallized from ethyl acetate/acetone and obtained in 31-44% yield.

Hexakis(2,2'-bipyridine){N-[2-Bis-{4-4'-methyl-[2,2']-bipyridinyl-4-yl}-butyrylamino]-ethyl}-amino]-ethyl]-4-(4'-methyl-[2,2']bipyridinyl-4-yl)butyramide]ruthenium(VI) (dend-[CO-(CH₂)₃-mbpy·Ru(bpy)₂]₃(PF₆)₆; 2) UV-vis (Acetone) λ_max (ε) 454 nm (34,412 M⁻¹cm⁻¹); IR (KBr) 3423, 3085, 2967, 1669, 1621, 1452, 840 cm⁻¹; ¹H NMR (300 MHz, Acetone-*d₆*) δ 8.66-8.53 (m, 18H), 8.02 (m, 12H), 7.89 (t, *J* = 6.0 Hz, 12H), 7.68 (d, *J* = 5.6 Hz, 6H), 7.42 (m, 12H), 7.24 (m, 6H), 3.02 (m, 6H), 2.71 (m, 12H), 2.39 (s, 9H), 2.13 (t, *J* = 4.0 Hz, 6H), 1.91 (m, 6H); MALDI-TOF MS m/z 2827.8 ((M-PF₆⁻)⁺, calc. 2827.6), 2682.7 ((M-2PF₆⁻)⁺, calc. 2682.6), 2539.7 ((M-3PF₆⁻)⁺, calc. 2537.6).

Hexakis(1,10-phenanthroline){N-[2-Bis-{4-4'-methyl-[2,2']-bipyridinyl-4-yl}-butyrylamino]-ethyl}-amino)-ethyl]-4-(4'-methyl-[2,2']bipyridinyl-4-yl)butyramide]ruthenium(VI) (dend-[CO-(CH₂)₃-mbpy·Ru(o-phen)₂]₃(PF₆)₆; 3) UV-vis (Acetone)

λ_{max} (ε) 442 nm (37,196 M^{-1}cm^{-1}); IR (KBr) 3428, 3085, 2928, 1739, 1656, 1430, 1253, 844 cm^{-1}; ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.76-8.62 (m, 18H), 8.47 (m, 6H), 8.35-8.30 (m, 12H), 8.17-8.15 (m, 6H), 7.93-7.90 (m, 6H), 7.74-7.64 (m, 12H), 7.19 (m, 6H), 3.05 (m, 6H), 2.75 (m, 12H), 2.45 (br, s, 9H), 2.09 (br, s, 6H), 2.00 (m, 6H); MALDI-TOF MS m/z 2971.6 ((M-PF$_6$)$^-$, calc. 2971.6), 2826.5 ((M-2PF$_6$)$^-$, calc. 2826.6), 2681.5 ((M-3PF$_6$)$^-$, calc. 2681.6).

Hexakis(5-chloro-1,10-phenanthroline){N-[2-Bis-{4-4'-methyl-[2,2']bipyridinyl-4-yl}-butyrylamino]-ethyl}-amino}-ethyl}-4-(4'-methyl-[2,2']bipyridinyl-4-yl)butyramide} Ruthenium(VI) (dend-[CO-(CH₂)₃-mbpy·Ru(phen-Cl)₂]₃(PF₆)₆; 4) UV-vis (Acetone) λ_{max} (ε) 441 nm (39,444 M^{-1}cm^{-1}); IR (KBr) 3428, 3080, 2928, 1661, 1621, 1422, 1253, 844 cm^{-1}; ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.82-8.50 (m, 24H), 8.30-8.22 (m, 6H), 8.01-7.91 (m, 6H), 7.75-7.68 (m, 12H), 7.18 (br s, 6H), 2.87 (m, 6H), 2.55 (br, s, 6H), 2.44 (br, s, 15H), 2.04 (br, s, 6H), 1.91 (m, 6H); MALDI-TOF MS m/z 3178.3 ((M-PF$_6$)$^+$, calc. 3177.2), 3034.8 ((M-2PF$_6$)$^+$, calc. 3032.2).

Hexakis(1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one){N-[2-Bis-{4-4'-methyl-[2,2']-bipyridinyl-4-yl}-butyrylamino]-ethyl}-amino}ethyl}-4-(4'-methyl-[2,2']bipyridinyl-4-yl)butyramide} Ruthenium(VI) (dend-[CO-(CH₂)₃-mbpy·Ru(DTDP)₂]₃(PF₆)₆; 5) UV-vis (Acetone) λ_{max} (ε) 457 nm (37,636 M^{-1}cm^{-1}); IR (KBr) 3428, 3098, 2976, 1756, 1665, 1426, 1192, 844 cm^{-1}; ^{1}H NMR (300 MHz, Acetone-d_6) δ 9.07-8.95 (m, 12H), 8.68 (m, 6H), 8.49 (m, 6H), 8.17-7.95 (m, 12H), 7.70 (m, 12H), 7.21 (m, 6H), 2.80 (m, 6H), 2.55 (br, s, 6H), 2.48-2.45 (m, 15H), 2.09 (m, 6H), 2.00 (m, 6H), 1.72-1.61 (m, 72H); MALDI-TOF MS m/z 3620.5 ((M-PF$_6$)$^-$, calc. 3621.4), 3476.8 ((M-2PF$_6$)$^+$, calc. 3476.4).

Results and Discussion

Syntheses. It was shown in the previous studies that the ECL intensities of the PAMAM dendrimers functionalized with multiple ECL Ru(II) complexes were greater than that of [Ru(bpy)₃]$^{2+}$.[46] However, the ECL measurements of these

metallodendrimers showed a strong background effect that might decrease the effectiveness of ECL due to the reaction of amine groups in the dendrimer core to the peripheral Ru(II) complexes. Thus, polyamine was chosen as a new dendritic core to reduce the effect of amine groups and to develop a new, sensitive ECL material. Polyamine dendrimer was functionalized with an electrochemiluminescent Ru(II) complex containing polypyridyl ligand through the following steps to produce multiple luminescence.

Dendritic polypyridyl ligand was synthesized by a modified procedure of the known literature method.[39] As shown in Scheme 1, dend-[CO-(CH₂)₃-mbpy] (1) was obtained in 53% yield from the reaction of 4-(3-carboxypropyl)-4'-methyl-2,2'-bipyridine, N,N'-dicyclohexylcarbodiimide (DCC), and 1-hydroxybenzotriazole (HOBt), followed by the addition of polyamine dendrimer.
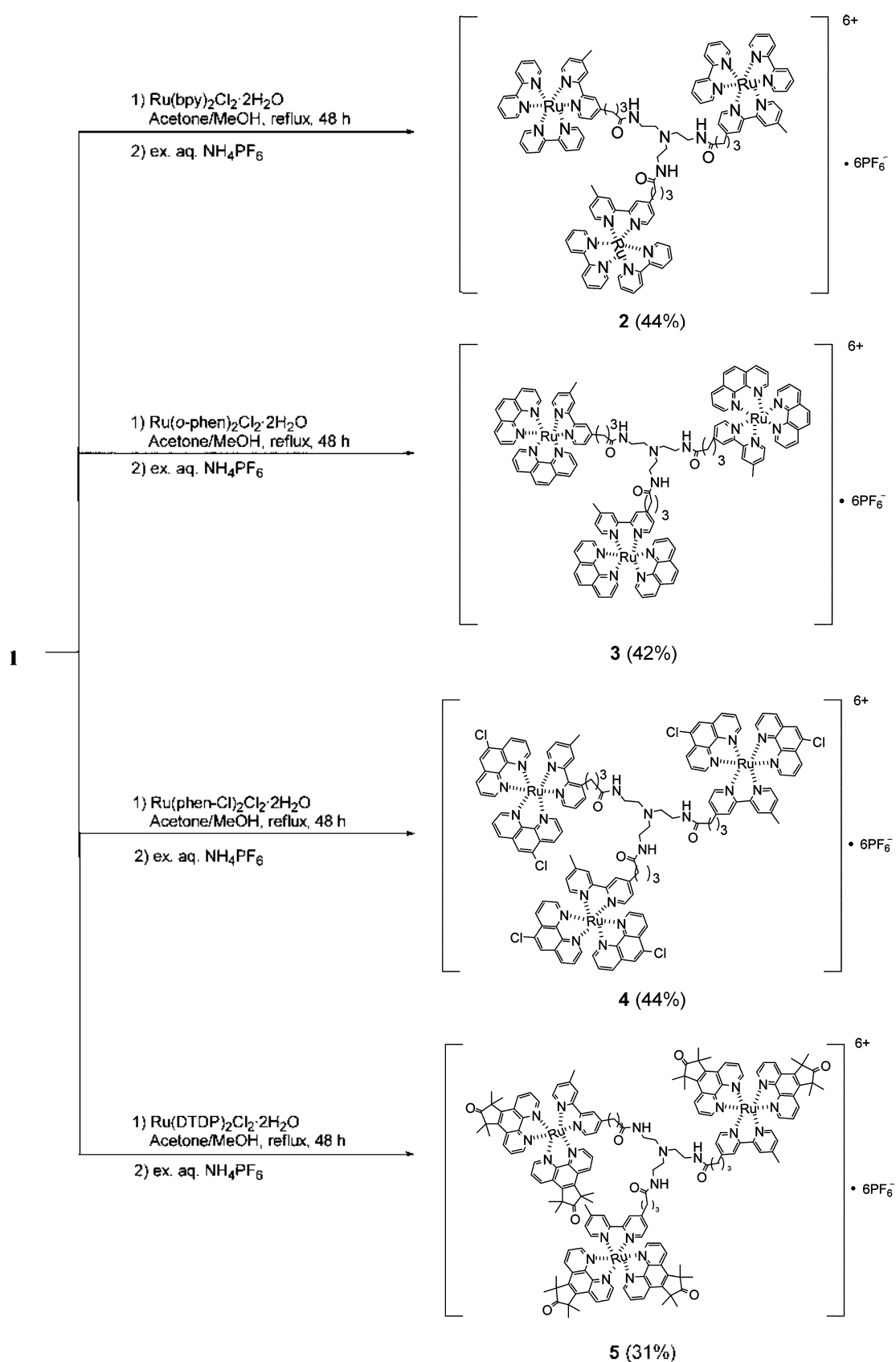
The coordination of dendrimer ligands to the Ru metal is shown in Scheme 2. Dend-[CO-(CH₂)₃-mbpy·Ru(L)₂]₃Cl₆ (L: bpy, o-phen, phen-Cl, DTDP) was formed from the reaction of cis-Ru(L)₂Cl₂·2H₂O and dend-[CO-(CH₂)₃-mbpy]₃ (1) in acetone/methanol at reflux. It was treated with NH₄PF₆ to obtain the complexes as hexafluorophosphate salts.

^{1}H NMR spectroscopy and Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry were used for the characterization of the metallodendrimer structures. The ^{1}H NMR of metallodendrimers provides an evidence of the coordination of dendrimer ligand on the Ru(II) complex from the ^{1}H peak of polypyridyl ligand compared with the peaks of the dendrimer core. In the MALDI-TOF MS, peaks, which were attributed to the successive loss of a PF₆ ion, were observed for all dendritic complexes, as shown in Table 1.

Absorption and Emission Spectra of Metallodendrimers. Absorption and emisssion spectra of metallodendrimers **2-5** for the photophysical properties were obtained in acetone (Table 2). All metallodendrimers functionalized with polypyridyl ruthenium(II) complexes exhibited an intense absorption of around 450 nm, which was ascribed to the metal-to-ligand charge transfer (MLCT) transition (Fig. 1). The absorption wavelength of metallodendrimers **3** and **4**
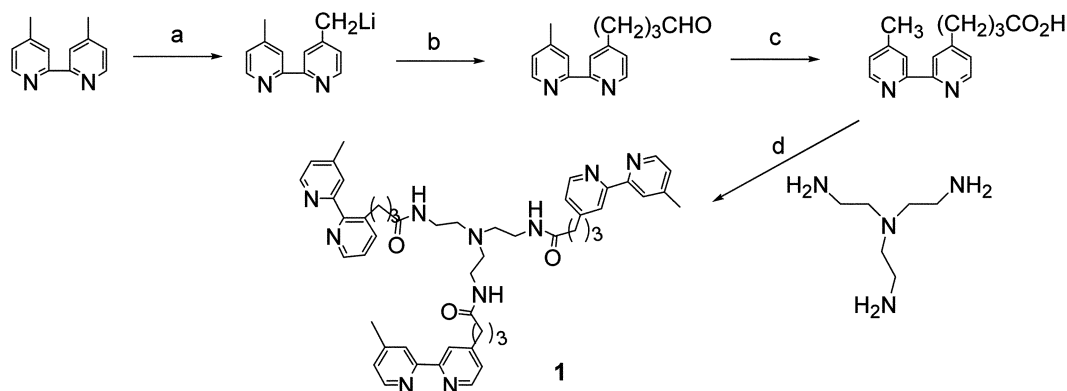
Scheme 1. a) LDA, THF, −78 °C, 2 hrs; b) 2-(2-bromoethyl)-1,3-dioxolane, r.t., overnight, then 1.0 M HCl, 60 °C, 3 hrs (39% for two steps); c) KMnO₄, acetone, r.t., overnight (76%); d) DCC, HOBt, DMAc, r.t., 24 hrs (53%).

1) Ru(bpy)$_2$Cl$_2$·2H$_2$O
Acetone/MeOH, reflux, 48 h

2) ex. aq. NH$_4$PF$_6$

2 (44%)

1) Ru(*o*-phen)$_2$Cl$_2$·2H$_2$O
Acetone/MeOH, reflux, 48 h

2) ex. aq. NH$_4$PF$_6$

3 (42%)

1) Ru(phen-Cl)$_2$Cl$_2$·2H$_2$O
Acetone/MeOH, reflux, 48 h

2) ex. aq. NH$_4$PF$_6$

4 (44%)

1) Ru(DTDP)$_2$Cl$_2$·2H$_2$O
Acetone/MeOH, reflux, 48 h

2) ex. aq. NH$_4$PF$_6$


5 (31%)

1

Scheme 2

was blue-shifted from 448 nm of [Ru(*o*-phen)$_3$](PF$_6$)$_2$, while the absorption wavelength of metallodendrimers **2** and **5** was

red-shifted.
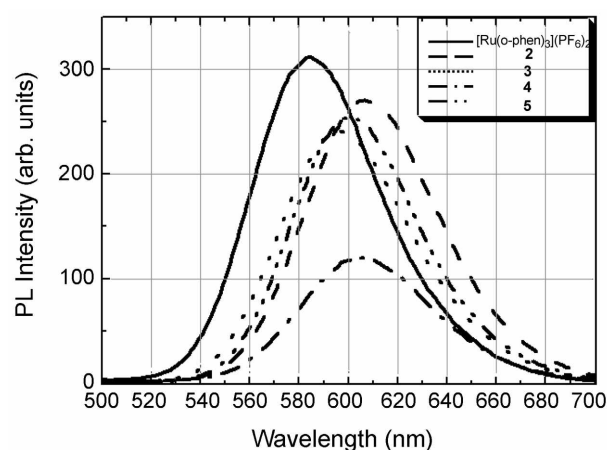
Ru(II) dendrimers **2-5** are all luminescent in acetone

Table 1. Assignment of MALDI-TOF fragments from dend-[CO-(CH$_2$)$_3$-mbpy-Ru(L)$_3$]$_3$(PF$_6$)$_6$

Entry	Ru(II) cpd	[M-PF$_6$]$^+$ (m/z)	[M-2PF$_6$]$^+$ (m/z)	[M-3PF$_6$]$^+$ (m/z)
1	2	2827.8	2682.7	2539.7
2	3	2971.6	2826.5	2681.5
3	4	3178.3	3034.8	–
4	5	3620.5	3476.8	–
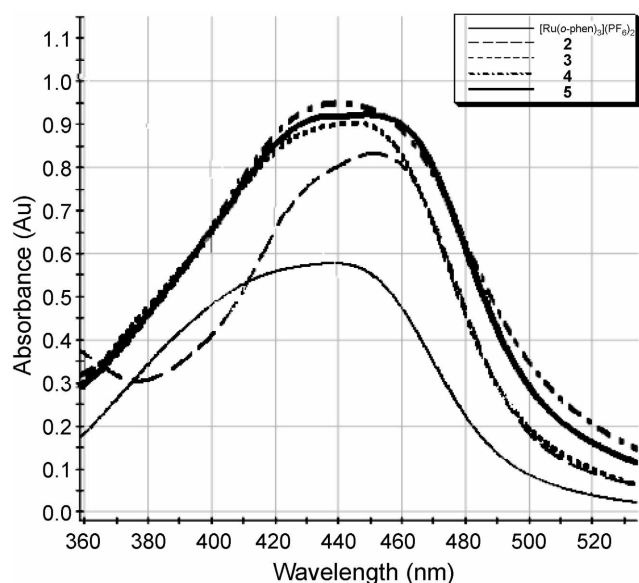
Figure 1. UV-vis absorption spectra of synthesized metallodendrimers.

Figure 2. Photoluminescence spectra of synthesized metallodendrimers (excitation at 400 nm).

solution at room temperature. However, the luminescence of all metallodendrimers was observed at above 600 nm, which was relatively red-shifted compared to the luminescence of [Ru(*o*-phen)$_3$](PF$_6$)$_2$, which was emitted at 584 nm (Fig. 2).

Electrochemical and ECL Characteristics. Cyclic voltammograms of the metallodendrimers were obtained in phosphate buffer at pH 7.0 with acetonitrile (less than 60% (v/v)). They showed a quasi-reversible one-electron process for Ru(II)/Ru(III) oxidation-reduction, with half-wave potentials within the range of 0.92 < E$_{1/2}$ < 0.97 V vs. Ag/AgCl (3 M NaCl) (E$_{1/2}$ = (E$_{pa}$ + E$_{pc}$)/2) (Table 2). This behavior was confirmed by the fact that the separation of the anodic and cathodic peak potentials, ΔE$_p$, and the ratios of

anodic to cathodic currents, I$_{pa}$/I$_{pc}$ were close to 80 mV and 1.0, respectively (Table 2). All metallodendrimers showed similar electrochemical properties. However, the oxidation potentials of metallodendrimers were shifted near 0.1 V cathodically compared to that of [Ru(*o*-phen)$_3$](PF$_6$)$_2$.

ECL measurement experiments were carried out in Ru(II) complex solutions containing tripropylamine as a coreactant in the FIA or static systems. ECL emissions were obtained for each of the complexes upon sweeping the potential sufficiently positive to oxidize both the complex and tripropylamine. The ECL intensities of Ru(II) dendrimers containing phen-Cl ligand (**4**) were relatively small (Table 2, entry 4; 75%) compared to that of the [Ru(*o*-phen)$_3$](PF$_6$)$_2$ complex. The ECL intensities of the other three Ru(II) dendrimers (Table 2: entries 2, 3, and 5) were greater than that of the [Ru(*o*-phen)$_3$](PF$_6$)$_2$ complex. The ECL intensities of Ru(II) dendrimers containing bpy ligand or DTDP ligand were two-fold greater than that of [Ru(*o*-phen)$_3$]-(PF$_6$)$_2$, which is known to have an ECL intensity around two-fold greater than that of [Ru(bpy)$_3$](PF$_6$)$_2$.[42]

In addition, the ECL intensity per Ru(II) unit of the polyamine dendrimer surrounded by 3 units of electrochemiluminescent polypyridyl ruthenium(II) complexes containing bpy ligand was greater than that of the previous PAMAM dendrimers surrounded by 4 units of electrochemiluminescent polypyridyl ruthenium(II) complexes. This result is possibly due to the decreased background effect of amine group in the core and the less sterically crowded

Table 2. Spectral data of synthesized metallodendrimers

Entry	Ru(II) cpd	UV (nm)^a	PL (nm)	E$_{pa}$ (V)^b	E$_{pc}$ (V)^b	ΔE$_p$ (mV)	ECL (%)^c
1	[Ru(*o*-phen)$_3$]$^{2+}$	448	584	1.16	1.09	70	100
2	2	454	606	0.96	0.88	80	223
3	3	442	596	0.96	0.89	70	130
4	4	441	608	1.01	0.92	90	75
5	5	457	600	0.97	0.89	80	201

^{a}In acetone. ^{b}Measured in acetonitrile/H$_2$O at pH 7 containing phosphate buffer and 30 mM TBAP at a glassy carbon electrode vs Ag/AgCl (3 M NaCl). ^{c}ECL relative to [Ru(*o*-phen)$_3$](PF$_6$)$_2$ (100%)
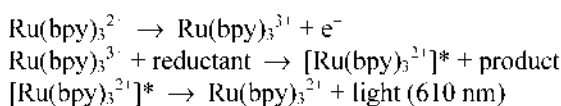
Table 3. TPA molar ratio effect on ECL intensity

Entry	Ru(II) cpd	ECL ^{a} (%)	ECL ^{b} (%)
1	**2**	210	223
2	**3**	126	130
3	**4**	25	75
4	**5**	159	201

^{a}Molar ratio TPA to Metallodendrimer (1 : 1). ^{b}Molar ratio TPA to Metallodendrimer (3 : 1)

structure of the present polyamine dendrimer compared to the previous PAMAM dendrimers.

The ECL emission of the polypyridyl ruthenium(II) complexes/amine system arises from the energetic electron transfer between the electrogenerated RuL_3^{3+} and a strong reducing intermediate (reductant) formed by the oxidation of amine-containing compounds as shown below.[25,38]

$$Ru(bpy)_3^{2} \rightarrow Ru(bpy)_3^{3+} + e^-$$
$$Ru(bpy)_3^{3+} + reductant \rightarrow [Ru(bpy)_3^{2+}]^* + product$$
$$[Ru(bpy)_3^{2+}]^* \rightarrow Ru(bpy)_3^{2+} + light (610 nm)$$

Since the present polyamine dendrimers contains four amine groups, the RuL_3 units in the dendrimers can react with amine groups in the dendrimer itself, which leads to the strong ECL background emission in the absence of conventional TPA coreactant. Thus, the present four-amine group containing dendrimers seemed to exhibit much smaller background emission than that of ten-amine group containing PAMAM dendrimers.

To examine the effect of the concentration of the coreactant, tripropylamine on ECL intensity, molar ratio variation experiments were conducted. Although the molar ratio of tripropylamine to metallodendrimer was increased from 1 : 1 to 1 : 3, very little differences in ECL intensity was observed in most cases (Table 3). However, in the case of **4**, which exhibited a relatively poor ECL intensity, the increment of tripropylamine boosted ECL intensity.

Overall, the electrochemical and ECL properties of metallodendrimers containing DTDP ligands were quite similar to those of metallodendrimers containing bpy ligands.

Relationship between the Observed ECL Intensities and the Local Environments of Metallodendrimers. The ECL intensity of [Ru(o-phen)$_3$](PF$_6$)$_2$ is known to be two-fold greater than that of [Ru(bpy)$_3$](PF$_6$)$_2$.[42] In the case of polyamine metallodendrimers, the metallodendrimer ligated with bpy showed greater ECL intensity compared to the metallodendrimer ligated with o-phen or phen-Cl. The metallodendrimer containing a DTDP ligand also showed favorably intensive ECL efficiency. The cyclic voltammetry of the metallodendrimers shows a single reversible wave (Fig. 3). This indicates that the redox potentials of the oxidation and reduction processes of metallodendrimers are similar to those of the monomer Ru(II) complex. This in turn indicates that the three Ru(II) centers are equivalent to one another and react independently. Thus, the ECL intensities of metallodendrimers can be amplified by the multiple peripheral ECL Ru(II) unit. The present ECL studies on
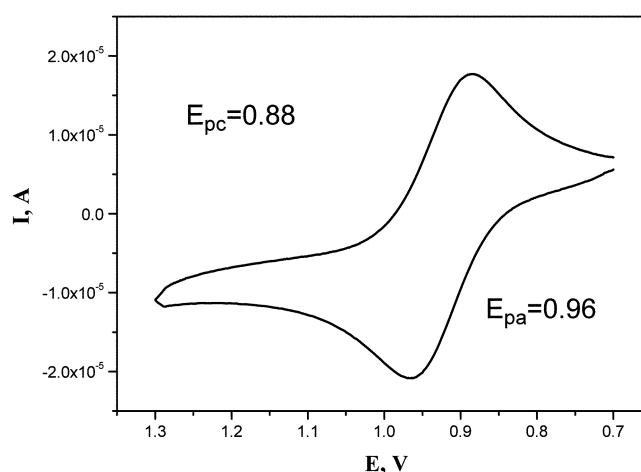
Figure 3. Cyclic voltammograms of dend-[CO-(CH$_2$)$_3$-mbpy-Ru(bpy)$_2$]$_3$(PF$_6$)$_6$ (**2**) at pH 7.0; scan rate, 100 mV/s.

metallodendrimers show that the ECL intensities of metallodendrimers (**2, 3, 5**) were improved by the three peripheral Ru(II) units that reacted independently of one another and that were affected by the nature of the ligand.

Conclusion

Metallodendrimers were synthesized in reasonable yields from the reactions of [Ru(L)$_2$(acetone)$_2$]$^{2+}$ and dendritic polypyridyl ligands that were prepared from the amide coupling reaction of polyamine with bipyridyl ligands. The relationships between the ECL intensities and the local environments of the metallodendrimers were studied. The metallodendrimers containing bpy or DTDP ligands showed greater ECL intensities than those of the metallodendrimers containing o-phen ligand. In addition, the multiplicity of the peripheral Ru(II) complex and dendritic structure improved ECL intensity. These results show a tendency similar to that shown in the previous study on the ECL of PAMAM dendrimers functionalized with ECL Ru(II) complexes. Moreover, the ECL intensities per polypyridyl Ru(II) complex unit in polyamine metallodendrimers were improved, which did not happen in polyamidoamine (PAMAM) metallodendrimers. Thus, polyamine dendrimer may be more efficient than PAMAM dendrimer for ECL due to its different core structure. Finally, dend-[CO-(CH$_2$)$_3$-mbpy-Ru(bpy)$_2$]$_3$(PF$_6$)$_6$ and dend-[CO-(CH$_2$)$_3$-mbpy-Ru(DTDP)$_2$]$_3$-(PF$_6$)$_6$ are good candidates for highly efficient ECL and light-emitting materials.

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