

Synthesis of Novel Ruthenium(II) Complexes Containing 2,2'-Bipyridyl and 2-(2-Pyridyl)benzimidazole Ligands and Their Electrochemiluminescent Characteristics

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The property of electrochemiluminescence (ECL) has led to a sensitive and selective detection method for the analysis of a wide range of compounds.¹ Especially, luminescent transition metal complexes have become an increasingly important class of sensor materials, because ECL, in contrast to chemiluminescence (CL), is an electron transfer reaction that results in CL emission without bond breakage or rearrangement and can be recycled. The general rule of luminescent transition metal complexes shows that the emission always arises from the lowest excited state, which is either metal-to-ligand charge transfer (MLCT) or ligand localized $\pi-\pi^*$ transition.^{2,3}

Of the numerous electrogenerated chemiluminescent materials, Ru(bpy)₃²⁺ has been the most exploited ECL compound to date.⁴ As the characteristics (emission properties, luminescent intensities, and life time) may vary depending on the local environment of the metal complexes (d-d states, spin-orbit coupling, pure $\pi-\pi^*$ phosphorescences, and emitting state energy), we are interested in developing new inorganic complexes with local environments differing from Ru(bpy)₃²⁺ or known derivatives. In the present study we report the synthesis and characterization of novel electrochemiluminescent ruthenium(II) complexes, which are expected to be potent ECL materials.

To explore new ECL compounds and to investigate the effect of ligands, a series of ruthenium(II) complexes having α -diimine ligands, such as 2,2'-bipyridyl (bpy), 2-(2-pyridyl)-benzimidazole (PBIIm-H),⁵ 2-(2-pyridyl)-*N*-methylbenzimidazole (PBIIm-Me),⁶ 4,4'-dimethyl-2,2'-bipyridyl (dmbpy) and 4-carboxymethyl-4'-methyl-2,2'-bipyridyl (mbpy-CH₂CO₂H),⁷ have been synthesized.

Various novel ruthenium complexes, [Ru(bpy)_{3-n}L_n]²⁺ (L =

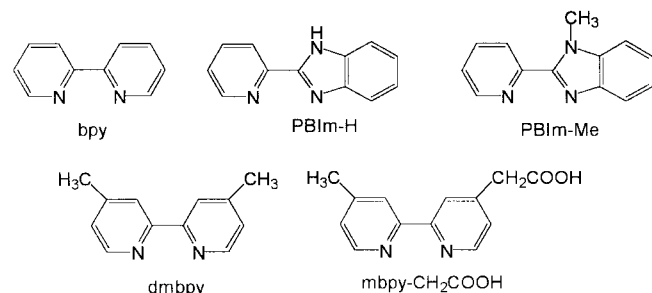
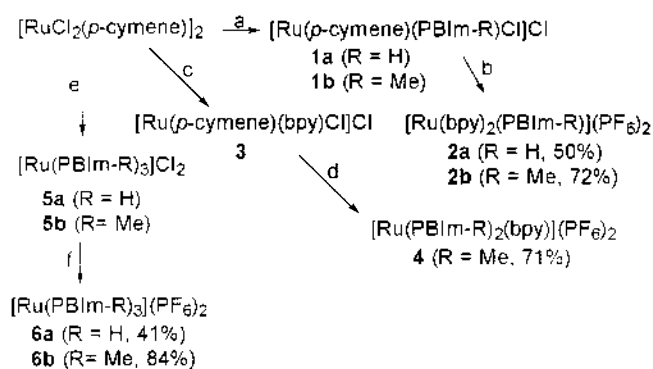


Figure 1. Chemical structures of ligands and their abbreviations.



a) PBIIm-R/EtOH, rt, 2 h. b) 2bpy/H₂O, reflux, 24 h, then NH₄PF₆. c) bpy/EtOH, rt, 2 h. d) 2PBIIm-R/H₂O, reflux, 48 h, then NH₄PF₆. e) 3PBIIm-R/EtOH, H₂O (1/2), 24 h. f) NH₄PF₆.

Scheme 1

PBIIm-H, PBIIm-Me, n = 1, 2, 3), were obtained through the sequential reaction of [RuCl₂(*p*-cymene)]₂⁸ with bpy or PBIIm-R in ethanol, H₂O, or H₂O/EtOH as shown in Scheme 1. When 1 equiv of bpy or PBIIm-R was applied to [RuCl₂(*p*-cymene)]₂ in EtOH solution at room temperature, 1 or 3 was obtained quite selectively. By refluxing 1 or 3 with 2 equiv of alternative ligand in aqueous solution followed by NH₄PF₆ treatment, 2 or 4 was obtained respectively in reasonable yield. Symmetrical complexes, such as 6, were obtained by refluxing [RuCl₂(*p*-cymene)]₂ with 3 equiv of PBIIm-R (R=H, Me) in aqueous EtOH (v/v = 2 : 1) followed by NH₄PF₆ treatment.

UV-vis spectral characteristics, oxidation potential, and ECL were examined for the prepared Ru complexes. The absorption bands at 440–495 nm may be assigned to metal-to-ligand charge transfer (MLCT) transitions. Although absorption bands were appropriately matched with [Ru(bpy)₃]²⁺ (454 nm), the oxidation potentials of the imidazole ligand containing complexes were lowered substantially much more than that of [Ru(bpy)₃]²⁺ (1.14 V). Moreover, complexes containing PBIIm-H showed very low emission intensity compared with that of the [Ru(bpy)₃]²⁺, which seemed to decrease with the increasing number of benzimidazole ligands (Table 1, entries 1, 2). In the case of PBIIm-Me complexes, ECL intensity improved relative to the PBIIm-H complexes, probably because the emitting state was much further from the ground state (Table 1, entries 3–5). According to the

Table 1. Spectral data of synthesized Ru(II) complexes

Entry	Ru(II) cpd	UV-vis (nm) ^a	E _{pa} (V) ^b	ECL (%) ^c
1	[Ru(PBIm-H) ₂](PF ₆) ₂ (6a)	473	0.30	0
2	[Ru(bpy) ₂ (PBIm-H)](PF ₆) ₂ (2a)	440, 485	0.69	4
3	[Ru(PBIm-Me) ₂](PF ₆) ₂ (6b)	341, 457	0.86	0
4	[Ru(PBIm-Me) ₂ (bpy)](PF ₆) ₂ (4)	341, 456	0.98	4
5	[Ru(bpy) ₂ (PBIm-Me)](PF ₆) ₂ (2b)	341, 454	1.06	28
6	[Ru(dmbpy) ₂ (PBIm-Me)](PF ₆) ₂ (8a)	460	0.96	17
7	[Ru(dmbpy) ₂](PF ₆) ₂ (12)	456	1.02	48
8	[Ru(dmbpy) ₂ (bpy)](PF ₆) ₂ (8b)	458	1.05	60
9	[Ru(bpy) ₂ (mbpy-CH ₂ CO ₂ H)](PF ₆) ₂ (13)	341, 456	1.06	85
10	[Ru(bpy) ₂ (dmbpy)](PF ₆) ₂ (10)	452	1.06	93

^aIn ethanol or acetone. ^bMeasured in acetonitrile:H₂O at pH 7 containing 50 mM phosphate buffer as a supporting electrolyte at a glassy carbon electrode vs Ag/AgCl (3 M NaCl). ^cRelative ECL to [Ru(bpy)₃]Cl₂.

energy gap law, radiationless processes become more efficient as the emitting state approaches the ground state.^{2,3} It seems that less electron-donating ligands are desirable to increase the MLCT transition energy.

Thus, as shown in Scheme 2, 4,4'-dimethyl-2,2'-bipyridyl (dmbpy) and 4-carboxymethyl-4'-methyl-2,2'-bipyridyl (mbpy-CH₂CO₂H) were introduced to ruthenium in place of PBIm-R to observe the electronic effect of the ligands. All of the newly synthesized compounds were fully identified with ¹H NMR, IR, UV-vis and FAB mass.⁹

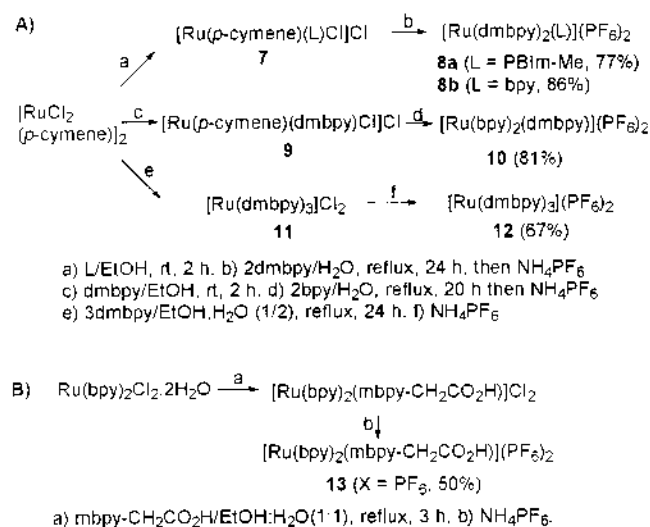
Benzimidazole (basic pK_a = 5.4-5.69)^{10a} has been shown to be more basic than pyridine (pK_a = 5.2).^{10b} and PBIm-H is a stronger donor than bpy, accordingly.¹¹ As shown in Table 1, in the case of [Ru(bpy)₂L](PF₆)₂, ECL was improved as the less electron donating ligands were introduced, *i.e.* **2a** < **2b** < **13** < **10**. The ECL tendency of **2a** to be less than **2b** is presumably interpreted as a hydrogen bonding effect of N-H in **2a** with aqueous solvent that results in the more electron donating nature of **2a** compared with **2b**. The

slightly more electron donating character of **13** compared with **10** might be due to carboxylate ion contribution in aqueous solution. Conceivably, a stronger donor ligand results in the decrease of MLCT band energies of [Ru(bpy)₂L](PF₆)₂. Moreover, a better ECL was observed if more of the less electron donating ligands was introduced in the Ru complex (for example: **6b** < **4** < **8a** < **2b** or **12** < **8b** < **10**). These results show that the trend in ECL is consistent with the donor ability of α -diimine ligands and the number of substitutions to the complex. The general tendency of the ECL vs ligand in Ru complexes could be concluded as follows: PBIm-H < PBIm-Me < mbpy-CH₂CO₂H < dmbpy < bpy. However, we estimated that the ECL of [Ru(bpy)₂L]²⁺ (L' = dmbpy or mbpy-CH₂CO₂H) is nearly equal to that of [Ru(bpy)₃]²⁺ as the hyperconjugation effect is relatively small. Further detailed study on the synthesis and characterization for novel ECL Ru complexes is in progress and will be reported in due course.

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- Spectral data of new compounds: **4**: IR (KBr): 3075, 2962, 1604, 1525, 1486, 848 cm^{-1} . UV-vis: λ_{max} = 341, 456 nm. ¹H NMR (acetone-*d*₆): δ 4.50-4.58 (m, 6H), 5.90-6.00 (m, 2H), 7.06-7.09 (m, 1H), 7.37-7.61 (m, 6H), 7.81-8.30 (m, 11H), 8.66-8.90 (m, 4H). FAB MS: m/z = 821 ([M-PF₆]⁺), 676 ([M-2PF₆]⁺), 466 ([Ru(PBIm-Me)(bpy)]⁺), 310 ([Ru(PBIm-Me)]⁺). **6b**: IR (KBr): 3050, 1600, 1510, 1480, 1440, 1420, 1400, 1335, 840 cm^{-1} . UV-vis: λ_{max} = 341, 457 nm. ¹H NMR (acetone-*d*₆): δ 4.47-4.63 (m, 9H), 5.95-6.08 (m, 3H), 6.87-6.94 (m, 1H), 7.06-7.12 (m, 2H), 7.42-7.58 (m, 6H), 7.85-7.94 (m, 3H), 8.06-8.39 (m, 6H), 8.81-8.93 (m, 3H). FAB MS: m/z = 874 ([M-PF₆]⁺), 519 ([Ru(PBIm-Me)₂]⁺). **13**: IR (KBr): 3400, 3050, 1710, 1620, 1600, 1480, 1460, 1440, 1420, 1240, 840 cm^{-1} . UV-vis: λ_{max} = 463 nm. ¹H NMR (DMSO-*d*₆): δ 2.50 (s, 5H), 7.34 (d, 2H, J = 6.0 Hz), 7.51 (m, 6H), 7.71 (m, 4H), 8.14 (t, 4H, J = 7.7 Hz), 8.70 (s, 2H), 8.81 (d, 4H, J = 7.7 Hz). FAB MS: m/z = 787 ([M-PF₆-H]⁺), 743 ([M-PF₆-CO₂-H]⁺), 413 ([Ru(bpy)₂]⁺).
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**Scheme 2**