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Electrochemiluminescent dinuclear Ru(II) complexes assembled with 1,1′-(1,2-ethynediyl)- or dimethlyene-bridged bis(bipyridine) ligands: Synthesis and photophysical and electrochemical properties

Minki Kim [a,1], Chang Hoon Kang [b,1], Subong Hong [a], Won-Yong Lee [b,*], Byeong Hyo Kim [a,*]

[a] Department of Chemistry, Kwangwoon University, Seoul 139-701, Republic of Korea
[b] Department of Chemistry and Center for Bioactive Molecular Hybrids, Yonsei University, Seoul 120-749, Republic of Korea

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ABSTRACT

1,2-Di(2,2′-bipyridin-5-yl)ethane (**BL1**) and 1,2-di(2,2′-bipyridin-5-yl)ethyne (**BL2**) were synthesized as new bridging ligands and coordinated to $(RuL_2(acetone)_2)(PF_6)_2$ for the preparation of various $[Ru(L)_2(BL)Ru(L)_2](PF_6)_4$-type dinuclear ruthenium complexes (where BL = **BL1**, **BL2** and L = bpy, *o*-phen, DTDP). The electrochemical redox potentials, spectroscopic properties, and relative electrochemiluminescence intensity of **BL1** and **BL2** were characterized and compared to those of well-known tris(1,10-phenanthroline)rutheniun(II) $[Ru(o\text{-phen})_3](PF_6)_2$ complex as a reference. Dinuclear Ru(II) complexes containing the conjugated bridging ligand (**BL2**) showed much more intense electrochemiluminescent responses than dinuclear Ru(II) complexes with the non-conjugated bridging ligand (**BL1**). Among the complexes with conjugated bridging ligands, $[(DTDP)_2Ru(bpy\text{-}CC\text{-}bpy)Ru(DTDP)_2](PF_6)_4$ exhibited enhanced ECL intensities as high as 3.6 times greater than that of the reference, $[Ru(o\text{-phen})_3](PF_6)_2$.

1. Introduction

Since the first report of tris(2,2′-bipyridyl)ruthenium(II) $(Ru(bpy)_3^{2+})$ as an electrochemiluminescent material [1], the electrochemiluminescence (ECL) emitted by transition metal complexes has been recognized as a powerful tool. It has been applied for the analysis of a wide range of compounds such as oxalates, alkylamines, amino acids, NADH, organic acids, and pharmaceutical compounds. This concept is also used for immunoassay and DNA probe assays by employing ECL-active species as labels on biological molecules [2].

The inherent molecular structure of central metal, ligand, and functional group attached on the ligand is the most important factor for determining ECL characteristics. In addition to using various ligands and central metals, several research groups have investigated the use of multi-metallic systems containing multiple redox centers in a molecule [3]. Further improvements can possibly be made if multi-metallic complexes can exist within a single molecular framework, even though the ECL intensity may not be proportional to the number of metals. We previously examined the application of multi-nuclear metallic complexes for improving ECL efficiency and found that some multi-nuclear metallic complexes in a single molecular framework, such as tri- to hepta-ruthenium metallodendrimers and di-ruthenium complexes, exhibited improved ECL intensities compared to simple mono-ruthenium complexes [4]. In our previous studies, we used polypyridyl ligands connected with polyamidoamine [4a], amide [4b], or ester groups [4c,d], in which spacers are bridged with extended single bonds. Most spacers that we previously used were extended with single bonds that can rotate freely, indicating that the metallic site of multi-nuclear complexes may possibly affect the ECL properties of complexes. We are interested in how ECL properties will change if the free rotation of the spacer is restricted using a proper spacer. For example, the 1,2-di(2,2′-bipyridin-5-yl)ethyne ligand will be ligated with metals in two positions opposite of the spacer without dangling around the spacer. The 1,2-di(2,2′-bipyridin-5-yl)ethyne ligand can not only fix the position of the spacer, but can also influence the degree of bipyridyl ligand conjugation. This affects the extent of metal-to-ligand charge transfer (MLCT) or localized π–π^* transition. It is of great interest to design ECL materials that are connected with 1,2-di(2,2′-bipyridin-5-yl)ethyne ligands and ligated with other proper ligands (Fig. 1). These ECL materials are expected to show improved ECL properties. Herein, we report the synthesis and physical properties of newly designed di-ruthenium complexes connected with 1,2-di(2,2′-bipyridin-5-yl)ethyne ligand. We also synthesized di-ruthenium complexes connected with 1,2-di(2,2′-bipyridin-5-yl)ethane ligand to compare physical properties. Novel dinuclear ruthenium complexes, $[Ru(L)_2(BL)Ru(L)_2](PF_6)_4$ (BL = bridging ligand, L = bpy,

* Corresponding authors. Tel.: +82 2 2123 2649 (W.-Y. Lee), tel.: +82 2 940 5247; fax: +82 2 942 4635 (B.H. Kim).
E-mail addresses: wylee@yonsei.ac.kr (W.-Y. Lee), bhkim@kw.ac.kr (B.H. Kim).
[1] These authors contributed equally to this work.

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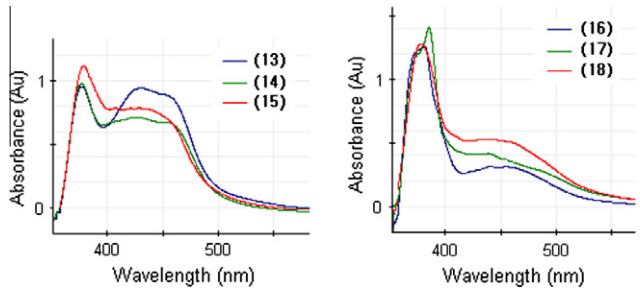


Fig. 1. UV–Vis absorption spectra of synthesized dinuclear ruthenium complexes.

o-phen, DTDP), containing new ethynyl or ethylene bridging ligands (BL) were synthesized in this study and their structures were characterized. The electrochemical redox potentials, spectroscopic properties, and relative electrochemiluminescence intensities of the complexes were also investigated in detail.

2. Experimental

2.1. Materials and instrumentation

Most chemical reagents were purchased from Aldrich Chemical Co. (St. Louis, Missouri, USA) and were used as received without further purification. All the reactions were carried out under a dry nitrogen atmosphere, unless stated otherwise. Solvents were dried using the standard method. 5-Carboxylate-, 5-bromo-, and 5-methyl- substituted 2,2′-bipyridine [5], 5-(hydroxymethyl)-2,2′-bipyridine (bpy-(CH_2OH)) [6], 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one (DTDP) [4d], and *cis*-$Ru(L)_2Cl_2{\cdot}2H_2O$ [7] (L: bpy, *o*-phen, DTDP) were prepared using known literature methods.

^1H NMR spectra were recorded on a 400 MHz (Jeol, Tokyo, Japan), and chemical shifts were reported in ppm relative to the residual solvent as an internal standard. GC/MS was recorded on an HP 5973 mass spectrometer connected with HP 6890 GC (Hewlett–Packard Co., Palo Alto, California, USA) and MALDI-TOF mass spectra were recorded on a JMS-DX303 (Jeol, Tokyo, Japan). Infrared spectra (IR) were recorded on a MB104 FT-IR (ABB Bomen Inc., Zurich, Switzerland) and UV–Vis spectra were recorded on a S-3100 (Scinco, Seoul, Korea). Emission spectra were obtained with the use of a luminescence spectrometer LS 50B (excitation source at 400 nm; Perkin Elmer, Waltham, Massachusetts, USA). Flow injection analysis (FIA) was performed with the previously described ECL detection system [8].

2.2. Synthesis

2.2.1. Synthesis of 5-bromomethyl-2,2′-bipyridine (**5**) [5]

The 5-(hydroxymethyl)-2,2′-bipyridine (0.837 g, 4.5 mmol) was dissolved in a mixture of 48% HBr (1 mL) and concentrated sulfuric acid (2 mL). The resulting solution was refluxed for 6 h and then allowed to cool to room temperature, after which 10 mL of water was added. The pH was adjusted to neutral with NaOH solution and the resulting precipitate was filtered, washed with water (pH 7), and air-dried. The product was dissolved in chloroform and filtered. The solution was dried over magnesium sulfate and evaporated to dryness. Yield: 48% (536 mg), TLC (SiO_2): R_f 0.21 (20% ethyl acetate/hexane); IR (KBr, cm^{-1}) 3039 (Ar–H), 2999 (Ar–H), 2968 (C–H), 1460 (aromatic C=C), 649 (Ar–C), ^1H NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 2H, CH_2Br), 7.30–7.33 (m, 1H, Py*H*), 7.80–7.86 (m, 2H, Py*H*), 8.39–8.41 (m, 2H, Py*H*), 8.68 (m, 2H, Py*H*); MS/EI *m*/*z* 248 [M^+, 8%], 169 [M^+−Br, 100%], 141 [M^+−NCH_2-Br, 21%].

2.2.2. Synthesis of 1,2-di(2,2′-bipyridin-5-yl)ethane (**6**) [9]

5-Methyl-2,2′-bipyridine (0.600 g, 3.5 mmol) was dissolved in THF (20 mL degassed under N_2) in a 250 mL round-bottomed flask. 1.8 M LDA (4 mL, 7 mmol) was used to added dropwise using a cannula at −78 °C. After stirring at −78 °C for 2 h under N_2, 5-(bromomethyl)-2,2′-bipyridine (868 mg, 3.5 mmol) dissolved in a degassed THF solution (20 mL) was added dropwise. After warming to room temperature and stirring for 24 h, the mixture was quenched with a saturated aqueous NaCl (20 mL) solution. The organic solvent was mostly evaporated and the remaining was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporator to give a crude product. The coupling product was purified by flash column chromatography (silica gel, MeOH/CH_2Cl_2 = 1/9). Yield: 67% (792 mg), TLC (SiO_2): R_f 0.57 (10% methanol/dichloromethane); IR (KBr, cm^{-1}) 3051 (Ar–H), 3006 (Ar–H), 2916 (C–H), 2856 (C–H), 1458 (aromatic C=C), ^1H NMR (400 MHz, $CDCl_3$) δ 3.04 (d, J = 4.0 Hz, 4H, CH_2), 7.27–7.31 (m, 2H, Py*H*), 7.58–7.61 (m, 2H, Py*H*), 7.78–7.82 (m, 2H, Py*H*), 8.29–8.36 (m, 4H, Py*H*), 8.48–8.49 (m, 2H, Py*H*), 8.65–8.67 (m, 2H, Py*H*); MS/EI *m*/*z* 338 [M^+, 51%], 169 [M^+−CH_2bpy, 100%], 141 [M^+−NCH_2CH_2bpy, 20%].

2.2.3. Synthesis of 5-[(trimethylsilyl)ethynyl]-2,2′-bipyridine (**7**) [10]

(Trimethylsilyl)acetylene (0.400 g, 4.07 mmol), [$PdCl_2(PPh_3)_2$] (0.123 mg, 0.18 mmol), CuI (0.052 g, 0.27 mmol), and 6 mL of triethyl amine were added in sequence to 5-bromo-2,2′-bipyridine (0.400 g, 1.71 mmol) in 30 mL of THF (degassed under N_2) in a 100 mL round-bottomed flask equipped with a septum. The solution was stirred at room temperature for 24 h. During that time, the solution turned black with the formation of an abundant precipitate of the salt. After complete consumption of the starting material (determined by TLC), the mixture was treated with activated carbon (ca. 200 mg) and filtered over Celite. The filtrate was concentrated by rotary evaporator to give a crude product, which was purified through flash silica gel column chromatography using CH_2Cl_2 as eluent. Yield: 80% (345 mg), TLC (SiO_2): R_f 0.45 (20% ethyl acetate/hexane); IR (KBr, cm^{-1}) 3049 (Ar–H), 3006 (Ar–H), 2960 (Ar-H), 2898 (C–H), 2160 (C≡C), ^1H NMR (400 MHz, $CDCl_3$) δ 7.00–7.03 (m, 1H, Py*H*), 7.50–7.59 (m, 2H, Py*H*), 8.00–8.12 (m, *2*H, Py*H*), 8.38–8.39 (m, 1H, Py*H*), 8.44–8.45 (m, 1H, Py*H*); MS/EI *m*/*z* 252 [M^+, 38%], 237 [M^+−CH_3, 100%], 221 [M^+−2(CH_3)H, 7%], 207 [M^+−3(CH_3), 5%].

2.2.4. Synthesis of 5-ethynyl-2,2′-bipyridine (**8**) [10]

5-[(Trimethylsilyl)ethynyl]-2,2′-bipyridine (0.360 g, 1.43 mmol) was dissolved in 30 mL of THF (degassed under N_2). A solution of KOH (0.320 g, 5.72 mmol) in methanol (30 mL) was then added. The reaction was stirred at room temperature for 6 h and the solvent was removed under vacuum. The residue was purified through flash silica gel column chromatography using CH_2Cl_2 as eluent. Yield: 95% (245 mg), TLC (SiO_2): R_f 0.45 (10% methanol/dichloromethane); IR (KBr, cm^{-1}) 3298 (C≡C–H), 3190 (C≡C–H), 3049 (Ar–H), 3001 (Ar–H), 2964 (Ar–H), 2933 (Ar–H), 2096 (C≡C), ^1H NMR (400 MHz, $CDCl_3$) δ 3.29 (s, 1H, C≡C*H*), 7.26–7.33 (m, 1H, Py*H*), 7.79–7.84 (m, 1H, Py*H*), 7.88–7.90 (m, 1H, Py*H*), 8.37–8.41 (m, 2H, Py*H*), 8.67–8.69 (m, 1H, Py*H*), 8.77 (m, 1H, Py*H*); MS/EI *m*/*z* 180 [M^+, 100%] 153 [M^+−NCH, 48%], 126 [M^+−2(NCH), 9%].

2.2.5. Synthesis of 1,2-di(2,2′-bipyridin-5-yl)ethyne (**9**) [10]

For the cross-coupling reaction leading to 5-ethynyl-2,2′-bipyridine (0.150 g, 0.83 mmol), the 5-bromo-2,2′-bipyridine (0.200 g, 0.83 mmol) was dissolved in benzene at 80 °C. When a clear solution was obtained, [$Pd(PPh_3)_4$] (0.092 g, 0.08 mmol) and 5 mL of triethylamine were added. After 24 h of heating at 80 °C, the solvent was removed under vacuum and the residue was purified

by flash column chromatography (silica gel, MeOH/CH_2Cl_2 = 1/9). Yield: 48% (133 mg), TLC (SiO_2): R_f 0.28 (10% methanol/dichloromethane); IR (KBr, cm^{-1}) 3053 (Ar-H), 3008 (Ar–H), 2923 (Ar–H), 2850 (Ar–H), 1456 (aromatic C=C), 798 (Ar–C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.35 (m, 2H, Py*H*), 7.82–7.86 (m, 2H, Py*H*), 7.97–8.00 (m, 2H, Py*H*), 8.43–8.46 (m, 4H, Py*H*), 8.70–8.71 (m, 2H, Py*H*), 8.85–8.86 (m, 2H, Py*H*); HRMS: *m*/*z* calc. for $C_{22}H_{14}N_4$: calc. for 336.1375, found 336.1369.

2.2.6. General procedure for syntheses of dinuclear ruthenium complexes

$AgPF_6$ (202 mg, 0.8 mmol) was added to a solution of *cis*-$Ru(L)_2Cl_2 \cdot 2H_2O$ (L = bpy, *o*-phen, DTDP, 0.4 mmol) dissolved in acetone (10 mL, degassed under N_2), and the mixture was stirred for 2 h at room temperature. After reaction completion, AgCl was removed by filtration. After acetone evaporation, the residue was dissolved in DMF (5 mL), a bridging ligand (BL = bpy-CH_2CH_2-bpy, bpy-CC-bpy, 0.1 mmol) was added to the solution, and the mixture was heated for 3 h at 90 °C. After cooling to room temperature, the residue was treated with a saturated aqueous solution of NH_4PF_6, which gave a red precipitate. The solid was filtered and recrystallized from acetone/ethyl acetate. Red crystals were obtained in 32–52% yield.

*2.2.6.1. [(bpy)$_2$Ru(bpy-CH_2CH_2-bpy)Ru(bpy)$_2$](PF$_6$)$_4$ (**13**).* Yield: 39% (68 mg), UV (acetone) λ_{max} (ε) 430 nm (21,200 $M^{-1}cm^{-1}$); PL (acetone) 581 nm, IR (KBr, cm^{-1}) 3118 (Ar–H), 3087 (Ar–H), 2923 (C–H), 1708 (C=C), 1604 (aromatic C=C), 1465 (aromatic C=C), 1446 (aromatic C=C), 840 (Ar–C), 761 (Ar–C), ^{1}H NMR (400 MHz, acetone-d_6) δ 2.63 (s, 4H, CH_2), 7.38–7.39 (m, 10H, Py*H*), 7.48 (m, 2H, Py*H*), 7.65–7.73 (m, 12H, Py*H*), 8.03–8.07 (m, 10H, Py*H*), 8.33–8.35 (m, 2H, Py*H*), 8.43–8.49 (m, 10H, Py*H*); MALDI-TOF: m/z 1601 [M^+-PF_6].

*2.2.6.2. [(o-phen)$_2$Ru(bpy-CH_2CH_2-bpy)Ru(o-phen)$_2$](PF$_6$)$_4$ (**14**).* Yield: 32% (59 mg), UV (acetone) λ_{max} (ε) 428 nm (25,400 M^{-1} cm^{-1}); PL (acetone) 629 nm, IR (KBr, cm^{-1}) 3085 (Ar–H), 2923 (Ar–H), 1703 (C=C), 1469 (aromatic C=C), 1429 (aromatic C=C), 838 (Ar–C), 721 (Ar–C), ^{1}H NMR (400 MHz, acetone-d_6) δ 2.54 (s, 2H, CH_2), 7.38–7.42 (m, 1H, Py*H*), 7.68–7.77 (m, 3H, Py*H*), 7.81–7.82 (m, 1H, Py*H*), 7.88–7.99 (m, 3H, Py*H*), 8.13–8.20 (m, 3H, Py*H*), 8.34–8.49 (m, 6H, Py*H*), 8.63–8.65 (m, 1H, Py*H*), 8.70–8.75 (m, 3H, Py*H*), 8.80–8.85 (m, 2H, Py*H*); MALDI-TOF: *m*/*z* 1697 [M^+-PF_6-3H].

*2.2.6.3. [(DTDP)$_2$Ru(bpy-CH_2CH_2-bpy)Ru(DTDP)$_2$](PF$_6$)$_4$ (**15**).* Yield: 52% (119 mg), UV (acetone) λ_{max} (ε) 426 nm (22,000 M^{-1} cm^{-1}); PL (acetone) 587 nm, IR (KBr, cm^{-1}) 3110 (Ar–H), 2974 (Ar–H), 2935 (Ar–H), 2873 (C–H), 1749 (C=C), 1708 (C=O), 1602 (aromatic C=C), 1467 (aromatic C=C), 842 (Ar-C), 727 (Ar-C), ^{1}H NMR (400 MHz, acetone-d_6) δ 1.62–1.77 (m, 48H, CH_3), 2.79 (s, 4H, CH_2), 7.37–7.40 (m, 2H, Py*H*), 7.73–7.85 (m, 9H, Py*H*), 7.92–8.01 (m, 5H, Py*H*), 8.11–8.25 (m, 6H, Py*H*), 8.40–8.48 (m, 4H, Py*H*), 8.66–8.68 (m, 2H, Py*H*), 8.75–8.77 (m, 2H, Py*H*), 8.97–9.02 (m, 4H, Py*H*), 9.10–9.13 (m, 4H, Py*H*); MALDI-TOF: m/z 2137 [M^+-PF_6].

*2.2.6.4. [(bpy)$_2$Ru(bpy-CC-bpy)Ru(bpy)$_2$](PF$_6$)$_4$ (**16**).* Yield: 47% (82 mg), UV (acetone) λ_{max} (ε) 441 nm (24,800 M^{-1} cm^{-1}); PL (acetone) 579 nm, IR (KBr, cm^{-1}) 3120 (Ar–H), 3083 (Ar–H), 2962 (Ar–H), 2925 (Ar–H), 2867 (Ar–H), 1992 (C≡C), 1604 (aromatic C=C), 1465 (aromatic C=C), 838 (Ar–C), ^{1}H NMR (400 MHz, acetone-d_6) δ 7.53–7.62 (m, 5H, Py*H*), 7.97–8.06 (m, 5H, Py*H*), 8.12–8.30 (m, 7H, Py*H*), 8.77–8.82 (m, 6H, Py*H*); MALDI-TOF: *m*/*z* 1597 [M^+-PF_6].

*2.2.6.5. [(o-phen)$_2$Ru(bpy-CC-bpy)Ru(o-phen)$_2$](PF$_6$)$_4$ (**17**).* Yield: 41% (75 mg), UV (acetone) λ_{max} (ε) 438 nm (24,200 M^{-1} cm^{-1}); PL (acetone) 627 nm, IR (KBr, cm^{-1}) 3085 (Ar–H), 2925 (Ar–H), 2850 (Ar–H), 2225 (C≡C), 1699 (aromatic C=C), 1465 (aromatic C=C), 840 (Ar–C), ^{1}H NMR (400 MHz, acetone-d_6) δ 7.44–7.47 (m, 1H, Py*H*), 7.70–7.74 (m, 2H, Py*H*), 7.93–7.99 (m, 2H, Py*H*), 8.01–8.03 (m, 1H, Py*H*), 8.14–8.18 (m, 3H, Py*H*), 8.20–8.24 (m, 2H, Py*H*), 8.36–8.42 (m, 4H, Py*H*), 8.50–8.51 (m, 1H, Py*H*), 8.65–8.66 (m, 1H, Py*H*), 8.72–8.74 (m, 2H, Py*H*), 8.82–8.86 (m, 4H, Py*H*); MALDI-TOF: *m*/*z* 1718 [M^+-PF_6+Na+3H].

*2.2.6.6. [(DTDP)$_2$Ru(bpy-CC-bpy)Ru(DTDP)$_2$](PF$_6$)$_4$ (**18**).* Yield: 44% (100 mg), UV (acetone) λ_{max} (ε) 436 nm (26,200 M^{-1} cm^{-1}); PL (acetone) 590 nm, IR (KBr, cm^{-1}) 3110 (Ar–H), 2974 (Ar–H), 2935 (Ar–H), 2873 (Ar–H), 1967 (C≡C), 1602 (aromatic C=C), 1467 (aromatic C=C), 840 (Ar–C), ^{1}H NMR (400 MHz, acetonitrile-d_3) δ 1.61–1.73 (m, 48H, CH_3), 7.29–7.32 (m, 2H, Py*H*), 7.53–7.62 (m, 6H, Py*H*), 7.71–7.81 (m, 10H, Py*H*), 7.94–7.96 (m, 2H, Py*H*), 8.03–8.10 (m, 4H, Py*H*), 8.20–8.21 (m, 2H, Py*H*), 8.48–8.52 (m, 4H, Py*H*), 8.74–8.77 (m, 4H, Py*H*), 8.84–8.88 (m, 4H, Py*H*); MALDI-TOF: *m*/*z* 2137 [M^+-PF_6+4H].

2.3. Electrochemical and ECL measurements

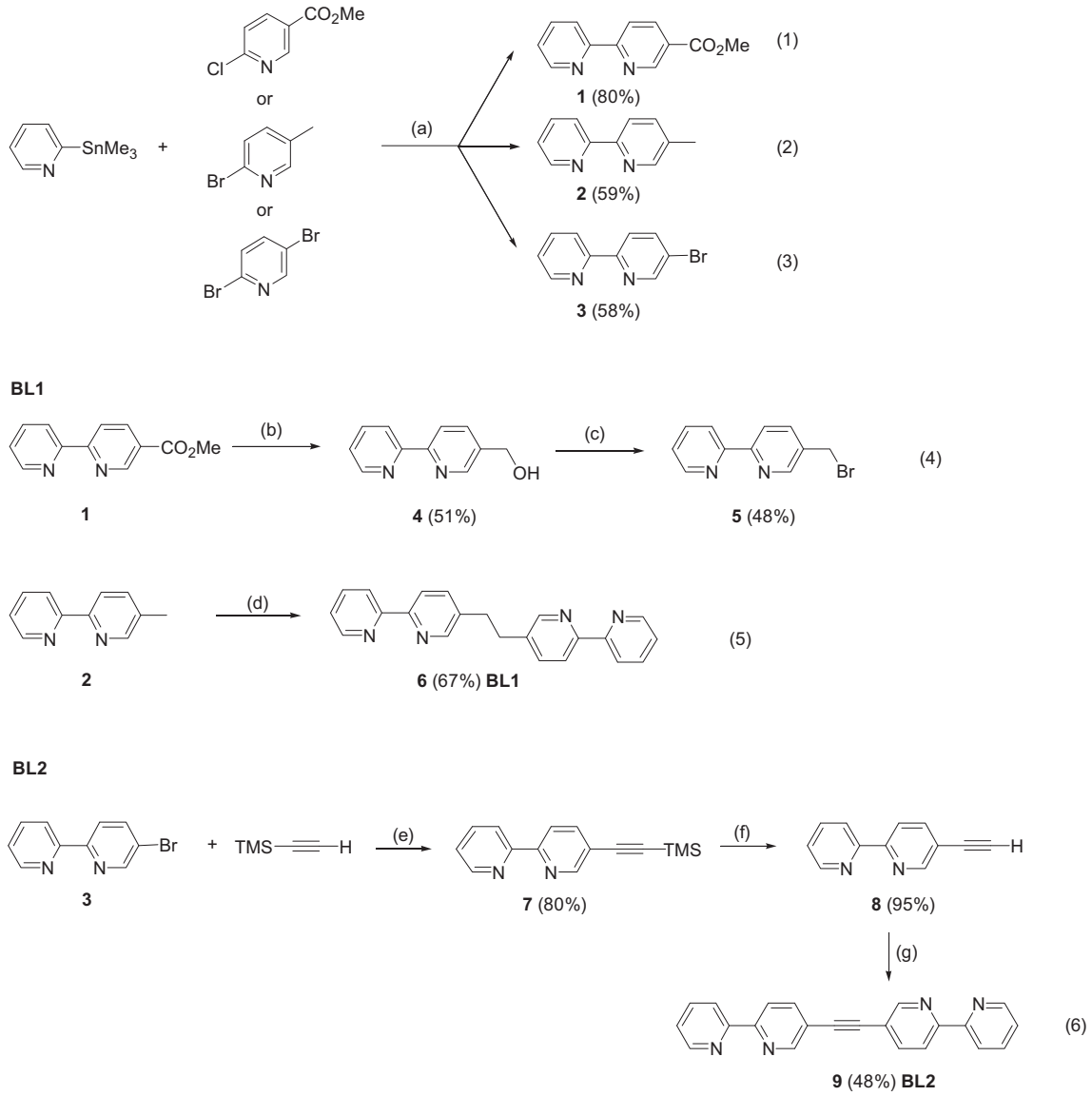
Cyclic voltammetric experiments were performed with an EG & G 273A potentiostat (Oak Ridge, TN, USA). A conventional three-electrode system was employed with a platinum wire as counter electrode, glassy carbon (0.07 cm^2) electrode as a working electrode, and an Ag/AgCl (3 M NaCl) reference electrode. The photon counting system used was a Hamamatsu Photonics HC 135-02 photon counting module (Hamamatsu city, Japan) in conjunction with a computer for recording the output. The electrochemical cell was also used in the ECL experiments. The ECL cell was placed directly in front of the photomultiplier tube (PMT) window. Prior to the electrochemical and ECL experiments, the working electrode was polished with 0.05 μm alumina, sonicated, and rinsed with methanol followed by water. Ru(II) complex solution and tripropylamine (TPA) solutions were prepared in the same 50 mM pH 7.0 phosphate buffer containing acetonitrile (v/v, 80%). TPA solutions (1 mM) were mixed with 0.5 mM synthesized Ru(II) complex solutions (1:1 v/v) and also blank solutions were prepared by mixing the given concentration of Ru(II) complex solution and the same buffer (1:1 v/v) without TPA. During the course of the ECL measurement, the potential of the working electrode was cycled from 0.7 V to +1.4 V with a scanning rate of 100 mV/s. ECL measurements were also performed for blank solutions in all studies. Corrected ECL signals were obtained by subtracting the ECL signals for blank solutions from the observed ECL signals for TPA.

3. Results and discussion

3.1. Synthesis

To examine the influence of the bridging ligands on ECL properties, new dinuclear ruthenium complexes that are covalently connected with 1,1′-(1,2-ethynediyl)- or dimethylene-bridged bis(bipyridine) ligands were designed and synthesized. While a dimethylene-bridged spacer is more freely rotated between the bipyridine ligands, 1,2-ethynediyl-bridged spacers can restrict the free rotation of the spacer and extend the degree of bipyridyl ligand conjugation in the spacer. ECL properties may be affected accordingly.

Multi-step synthesis of these two bridging ligands was carried out as outlined in Scheme 1. The first bridging ligand, dimethylene-bridged bis(bipyridine) ligand **6**, was synthesized using modified literature methods. This ligand's spacer has a flexible geometry because of the compound's dimethylene unit. First,



Scheme 1. Synthesis of bridging ligands, **BL1** and **BL2**. (a) $(PPh_3)_2PdCl_2$, *m*-Xylene, reflux, 10 h; (b) $NaBH_4$, EtOH, reflux, 4 h; (c) 48% HBr, H_2SO_4, rt, 6 h; (d) 1) 1.8 M LDA, THF, −78 °C, 2 h, 2) **5**, THF, −78 °C → rt, 24 h; (e) $(PPh_3)_2PdCl_2$, CuI, Et_3N, THF, rt, 24 h; (f) KOH, MeOH, THF, rt, 7 h; (g) **3**, $Pd(PPh_3)_4$, Et_3N, benzene, reflux, 24 h.

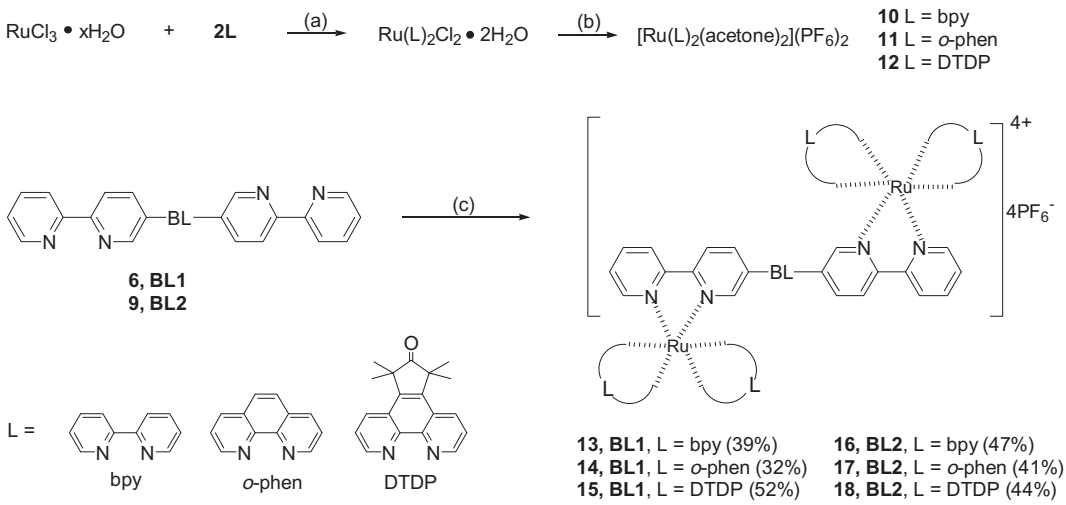
5-bromomethyl-2,2′-bipyridine (**5**) was prepared from 2,2′-bipyridine-5-carboxylate (**1**) (Eq. 4, Scheme 1). 2,2′-Bipyridine-5-carboxylate (**1**) was reacted with $NaBH_4$/EtOH to obtain precursor 5-(hydroxymethyl)-2,2′-bipyridine (**4**). Then, **4** was transformed into **5** by treatment with 48% HBr and H_2SO_4 at room temperature. Lithiated 5-methyl-2,2′-bipyridine (**2**) was added to the THF solution of **5** at −78 °C. The temperature was then raised to room temperature and the solution was stirred for 24 h. As a result, bridging ligand (**BL1**), 1,2-di(2,2′-bipyridin-5-yl)ethane (**6**) was obtained in reasonable yield (Eq. 5, Scheme 1).

A three step process was performed to synthesize the second bridging ligand (**BL2**), 1,2-di(2,2′-bipyridin-5-yl)ethyne (**9**), which has geometry fixed with a triple bond. At room temperature, **3** was coupled with (trimethylsilyl)acetylene in the presence of $PdCl_2(PPh_3)_2$, CuI, and diisopropylamine in THF to produce 5-[(trimethylsilyl)ethynyl]-2,2′-bipyridine (**7**) in 80% yield. 1,2-Di(2,2′-bipyridin-5-yl)ethyne (**9**) was obtained by desilylation of **7**–**8** using KOH and MeOH in THF. This was followed by a coupling reaction with **3** in the presence of $Pd(PPh_3)_4$ and diisopropylamine in benzene at reflux (Eq. 6, Scheme 2).

For the coordination reactions of bridging ligands to the Ru metal shown in Scheme 2, dinuclear ruthenium complexes $[Ru(L)_2(BL)Ru(L)_2](PF_6)_4$ (L = bpy, *o*-phen, DTDP) **13**–**18** were obtained in reasonably good yields. This was done by the complexation of bridging ligands **6** and **9** to $[cis\text{-}Ru(L)_2(acetone)_2]^{2+}$(L = bpy, *o*-phen, DTDP), **10**–**12** in DMF at 90 °C. The final products, **13**–**18**, were fully characterized with ^1H NMR, IR, UV–Vis, and MALDI-TOF mass spectra.

3.2. Absorption and emission spectra of dinulear Ru(II) complexes

Absorption and photoluminescence emission spectral data of the newly synthesized dinuclear Ru(II) complexes, **13**–**18**, were obtained at the concentration of 0.5×10^{-4} M in acetone. Metal-to-ligand charge transfer (MLCT) transitions were observed between 426 and 441 nm depending upon the bridging ligand and the terminal ligand in monomeric Ru(II) complexes (Fig. 1). The maximum absorption wavelengths of dinuclear Ru(II) complexes containing conjugated 1,2-di(2,2′-bipyridin-5-yl)ethyne bridging ligand (**BL2**) (**16**, **17**, and **18**) were red shifted about 10 nm



Scheme 2. Synthesis of various bridged dinuclear ruthenium complexes. (a) DMF, reflux, 10 h; (b) $AgPF_6$, acetone, rt, 2 h; (c) 1) **10**, **11**, or **12**, DMF, 90 °C, 3 h; 2) aq. NH_4PF_6.

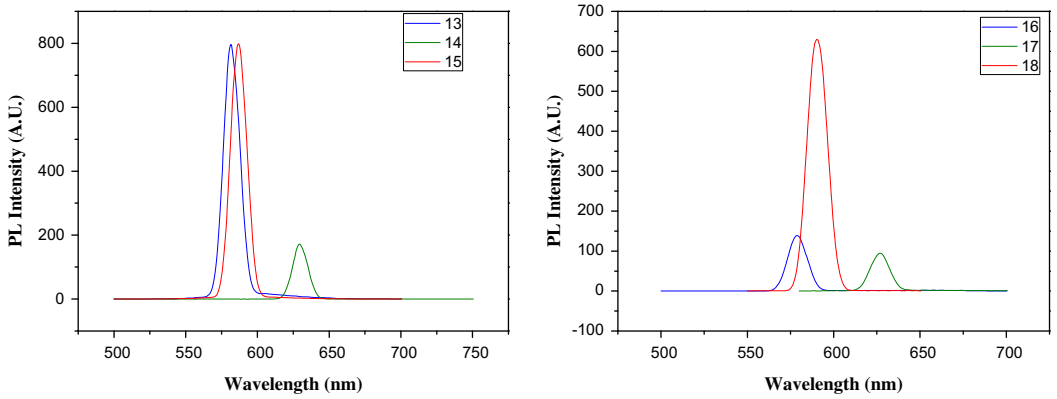


Fig. 2. PL data of synthesized dinuclear ruthenium complexes.

compared to those of dinuclear Ru(II) complexes with non-conjugated dimethlyene-bridged bis(bipyridine) bridging ligand (**BL1**) (**13**, **14**, and **15**). These results indicate that the degree of bridging ligand conjugation affects the extent of MLCT or localized π–π^* transition. The maximum absorption wavelengths of dinuclear Ru(II) complexes with the same bridging ligand seems to be affected mainly by the nature of the terminal ligands in monomeric Ru(II) complexes. Thus, their absorption bands are slightly different within a 5 nm range.

However, the maximum PL wavelengths of **BL2** bridged dinuclear Ru(II) complexes containing a DTDP terminal ligand are slightly red-shifted compared to the **BL1** bridged dinuclear Ru(II) complexes. Other **BL2** bridged dinuclear Ru(II) complexes containing bpy and *o*-phen are slightly blue-shifted compared to the **BL1** bridged dinuclear Ru(II) complexes (Fig. 2).

3.3. Electrochemical and ECL characteristics

Cyclic voltammograms of dinuclear Ru(II) complexes, **13**–**18**, were obtained at the concentration of 0.5 mM prepared in a mixture solution (1:1, v/v) of 50 mM phosphate buffer (pH 7) and acetonitrile. All the dinuclear Ru(II) complexes showed quasi-reversible one-electron processes for Ru(II)/Ru(III) oxidation–reduction with half-wave potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$) within 1.13 – 1.31 V versus Ag/AgCl (3 M NaCl), as summarized in Table 1. Peak separation, ΔE_p, between the anodic and cathodic peaks was in the range of 60–100 mV. The ratios of anodic to cathodic currents, I_{pa}/I_{pc}, were close to 1.0, confirming the quasi-reversible redox behavior of newly synthesized dinuclear Ru(II) complexes. In addition, all the dinuclear Ru(II) complexes showed single quasi-reversible waves. This result indicates that the Ru(II) centers in dinuclear Ru(II) complexes are electrochemically equivalent.

Although all the dinuclear Ru(II) complexes exhibited similar electrochemical properties, as shown in the CV data in Table 1, the half-wave potentials were slightly different depending on the bridging ligand and the ligand in each monomeric Ru(II) complex. For dinuclear Ru(II) complexes containing *o*-phen and DTDP ligands in a monomeric Ru(II) complex, the **BL2** bridging ligand caused the oxidation potential of dinuclear Ru(II) complexes to shift cathodically compared to those obtained with a **BL1** bridging ligand. This result indicates that the **BL2** bridging ligand with a triple bond increases the electron density of the resulting Ru(II) complex relative to that of a Ru(II) complex containing the **BL1** bridging ligand with a single bond. The donor abilities of dinuclear Ru(II) complexes with a **BL2** bridging ligand are stronger than those of Ru(II) complexes with a **BL1** bridging ligand, leading to a cathodic potential shift.

The ECL characteristics of newly synthesized dinuclear Ru(II) complexes were studied in the presence of tripropylamine as a co-reactant for the Ru(II) ECL oxidation–reduction system. Tripropylamine was used in this study because it is the best characterized among a variety of coreactants [2]. ECL emissions were

Table 1
UV, PL, CV and ECL data of synthesized dinuclear ruthenium complexes.

Entry	Ru(II) cpd	BL^n	UV (nm)[a]	PL (nm)[a]	E_{pa} (V)[b]	E_{pc} (V)[b]	ECL[c]
1	$[(bpy)_2Ru(BL^1)Ru(bpy)_2](PF_6)_4$**(13)**	**BL1**:bpy-(CH_2CH_2)-bpy	430	581	1.16	1.09	0.2
2	$[(o\text{-phen})_2Ru(BL^1)Ru(o\text{-phen})_2](PF_6)_4$**(14)**		428	629	1.36	1.26	0.1
3	$[(DTDP)_2Ru(BL^1)Ru(DTDP)_2](PF_6)_4$**(15)**		426	587	1.36	1.26	0.1
4	$[(bpy)_2Ru(BL^2)Ru(bpy)_2](PF_6)_4$**(16)**	**BL2**:bpy-(C≡C)-bpy	441	579	1.22	1.16	1.2
5	$[(o\text{-phen})_2Ru(BL^2)Ru(o\text{-phen})_2](PF_6)_4$**(17)**		438	627	1.20	1.14	1.2
6	$[(DTDP)_2Ru(BL^2)Ru(DTDP)_2](PF_6)_4$**(18)**		436	590	1.20	1.14	3.6

[a] In acetone (0.5×10^{-4} M).
[b] Measured in acetonitrile/50 mM phosphate buffer (pH 7.0) at a glassy carbon electrode vs Ag/AgCl (3 M NaCl).
[c] ECL relative to $[Ru(o\text{-phen})_3](PF_6)_2$.

obtained for each dinuclear Ru(II) complex upon sufficiently sweeping the positive potential to simultaneously oxidize the complex and tripropylamine in static solution systems. The dinuclear Ru(II) complexes containing the conjugated bridging ligand (**BL2**) showed a much more intense electrochemiluminescent response than the dinuclear Ru(II) complexes with the non-conjugated bridging ligand (**BL1**). In addition, the ECL intensities of dinuclear Ru(II) complexes with the conjugated bridging ligand (**BL2**) were stronger than those of the reference $[Ru(o\text{-phen})_3](PF_6)_2$ complex. As summarized in Table 1, the ECL intensities of the dinuclear ruthenium(II) complexes, **16** and **17**, were around 20% higher than that of the complex. Among the newly synthesized complexes, **18** shows the strongest electrochemiluminescent intensity. Its ECL intensity was 3.6 times higher than that of the reference complex. However, the ECL intensities of dinuclear Ru(II) complexes with the non-conjugated ligand (**BL1**) were much weaker than that of the reference complex. The ECL intensity of dinuclear ruthenium(II) complex **13** was 20% that of the reference complex. Also, ECL intensity for the dinuclear ruthenium(II) complexes **14** and **15** was only 10% that of the reference complex. These results indicate that the nature of the bridging ligand in dinuclear Ru(II) complexes strongly affects the ECL response of resulting dinuclear Ru(II) complexes. The conjugated bridging ligand used in the present study can hinder free rotation of the metallic sites of the dinuclear complexes and increase the degree of conjugation of the bipyridyl ligand. This affects the extent of metal-to-ligand charge transfer (MLCT) or localized π–π^* transition. Therefore, the conjugated bridging ligand in dinuclear Ru(II) complexes might be more effective at producing strong ECL responses than the non-conjugated bridging ligand. In dinuclear Ru(II) complexes with a **BL2** bridging ligand, the ECL intensities are also dependent upon the nature of the ligand. Ru(II) complexes with a DTDP ligand exhibited higher ECL intensities than those with bpy and *o*-phen ligands. The ECL behavior among different ligands within the monomeric Ru(II) complex is identical to our previous works with dinuclear Ru(II) complexes containing ester-bidged bis(bipyridine) ligands [4d].

4. Conclusion

New dinuclear ruthenium(II) complexes with the non-conjugated bridging ligand, **13**–**15**, and with the conjugated bridging ligand, **16**–**18**, were synthesized in reasonably good yields from reactions of $[Ru(L)_2(acetone)_2]^{2+}$ and the corresponding bridging ligand. The absorption spectra of dinuclear ruthenium(II) complexes exhibited an intense band at around 430–440 nm, which was assigned to MLCT. The emissions of dinuclear ruthenium(II) complexes were observed at around 579–629 nm depending on the nature of the bridging ligand. Three dinuclear ruthenium(II) complexes with the conjugated **BL2** bridging ligand (**16**, **17**, **18**) showed greater ECL intensities than others with the non-conjugated **BL1** bridging ligand (**13**, **14**, **15**). The ECL intensities of the dinuclear Ru(II) complexes were affected not only by the kind of ligand with in monomeric Ru(II) complexes, but also by the nature of the bridging ligand. Due to their very strong ECL intensity, newly prepared dinuclear ruthenium(II) complexes (**18**) could be utilized as sensitive ECL materials for the biochemical analysis of a variety of bioactive amine compounds and substrates that can produce NADH in dehydrogenase enzyme reactions.

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