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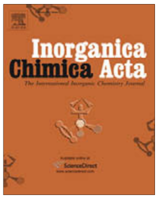

Synthesis and properties of electrochemiluminescent dinuclear Ru(II) complexes assembled with ester-bridged bis(bipyridine) ligands

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ABSTRACT

New bridging ligands, such as bpy-($COOCH_2$)-bpy (BL1), mbpy-$(CH_2)_3COOCH_2$-bpy (BL2), bpy-COO$(CH_2)_6$OOC-bpy (BL3), and bpy-$COOCH_2PhPhCH_2OOC$-bpy (BL4), have been synthesized and coordinated to $[RuL_2(acetone)_2](PF_6)_2$ for various $[Ru(L)_2(BL)Ru(L)_2](PF_6)_4$-type dinuclear ruthenium complexes (where BL = BL1, BL2, BL3, BL4, and L = bpy, *o*-phen, DTDP). Their electrochemical redox potentials, spectroscopic properties and relative electrochemiluminescence were investigated in detail. All dinuclear Ru complexes exhibit MLCT (metal-to-ligand charge transfer) absorption and luminescence bands in the visible region. ECL intensities of dinuclear ruthenium(II) complexes were affected not only by the kind of the ligand, but also by the nature of the bridging ligand. Among the synthesized dinuclear Ru complexes, $[(DTDP)_2Ru(mbpy)\text{-}(CH_2)_3COOCH_2\text{-}(bpy)Ru(DTDP)_2](PF_6)_4$ exhibited enhanced ECL intensities as high as 2.9 times greater than that of the reference, $[Ru(o\text{-}phen)_3](PF_6)_2$.

1. Introduction

Electrogenerated chemiluminescence (ECL, also known as electrochemiluminescence) has been recognized as a sensitive and selective detection tool in Life Science and Analytical Chemistry, i.e. for the analysis of a wide range of compounds such as oxalates, alkylamines, amino acids, NADH, organic acids, and pharmaceutical compounds [1]. It has also been developed into a new technology for immunoassay and DNA probe assays by employing ECL-active species as labels on biological molecules with advantages over classical fluorescence or isotope labeling [1b–e, 2]. Recently, a number of luminescent polynuclear transition-metal complexes have been synthesized, which could be applied not only to the above-mentioned fields but also to the various fields such as molecular electronics, photochemical molecular devices, and information storage [3].

After the first report in 1972, tris(2,2′-bipyridyl)ruthenium(II) ($Ru(bpy)_3{}^{2+}$) has been the most widely used and thoroughly studied ECL-active molecule because of its strong luminescence, good solubility in both aqueous and organic solutions, and capability to undergo reversible one-electron-transfer redox processes [4]. The ECL of the $Ru(bpy)_3{}^{2+}$/tripropylamine (TPA) system is one of the most efficient and most common. Its ECL mechanism is well documented and a simplified ECL reaction scheme is shown below [5]:

$$Ru(bpy)_3{}^{2+} \rightarrow Ru(bpy)_3{}^{3+} + e^- \tag{1}$$

$$Ru(bpy)_3{}^{3+} + TPA \rightarrow Ru(bpy)_3{}^{2+} + TPA^{\cdot} \tag{2a}$$

$$TPA \rightarrow TPA^{\cdot} + e^- \tag{2b}$$

$$Ru(bpy)_3{}^{3+} + TPA^{\cdot} \rightarrow [Ru(bpy)_3{}^{2+}]^* + \text{oxidized products of TPA} \tag{3}$$

$$[Ru(bpy)_3{}^{2+}]^* \rightarrow Ru(bpy)_3{}^{2+} + \text{light (610 nm)} \tag{4}$$

Generally, the emission of luminescent transition metal complexes always arises from the lowest excited state, which is either a metal-to-ligand charge transfer (MLCT) or localized π–π^* transition. The ECL characteristics of transition metal complexes strongly depend on the local environment of the complex related to the metal, ligand, and the concentration of an analyte. Thus, the nature of the central metal, ligand, functional group and network might be considered as an important factor. So, we have studied the relationship based on ECL intensity and local environment [6]. As a weak donor ligand, such as *o*-phenanthroline, raised the MLCT band energies of Ru(II) complexes, the ECL intensity of Ru(II) complexes was increased correspondingly. In addition, from the previous study on the metallodendrimers, it was observed that the ECL intensity of dendrimers with four $[Ru(bpy)_2(L')]$ units increased as the spacer length of the bridging ligand increased, provided that the other factors were fixed [7].

Although there are plenty of factors affecting ECL intensity, the inherent molecular structure seems to be much more important

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than others. Thus, multi-nuclear metallic complexes for improving the ECL efficiency were actively studied in the recent years [8]. Therefore, it is thought that further improvements can be made if multiple Ru(II) complexes would exist within a single molecule, even though the ECL intensity may not be proportional to the number of Ru metals. It is of great interest to design ECL materials that are expected to show excellent ECL properties by the controlling MLCT energy, multiplicity of chromophore and network. Moreover, since the amine groups in metallodendrimers are likely to affect their background ECL signals, it seems to be possible that the background signal can be controlled by eliminating the amine moieties from the dendrimer network [9]. Therefore, it is expected that the introduction of new ester-bridged ligand as a new spacer to dinuclear ruthenium complex may bring on the changes in electrochemical properties and lead to better ECL efficiency.

In this study, novel dinuclear ruthenium complexes, $[Ru(L)_2(BL)Ru(L)_2](PF_6)_4$ (BL = bridging ligand, L = bpy, *o*-phen, DTDP), containing new ester bridging ligands (BL) have been synthesized and their structures were characterized. In addition, their electrochemical redox potentials, spectroscopic properties, and relative electrochemiluminescence (ECL) were investigated in detail.

2. Experimental

2.1. Materials and instrumentation

Most of the chemical reagents were purchased from Aldrich Chemical Co. and were used as received without further purification in most cases. All the reactions were carried out under a dry nitrogen atmosphere, unless otherwise stated. The solvents were dried using the standard method. 2,2′-Bipyridine-5-carboxylic acid [10], 5-(hydroxymethyl)-2,2′-bipyridine(bpy-(CH_2OH)) [11], 4′-methyl-2,2′-bipyridine-4-butanoic acid [11], 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one (DTDP) [12], and *cis*-$Ru(L)_2Cl_2 \cdot 2H_2O$ [13] (L: bpy, *o*-phen, DTDP) were prepared using the known literature methods.

^1H NMR spectra were recorded on a 400 MHz Jeol instrument, and chemical shifts were reported in ppm relative to a residual solvent as an internal standard. GC/MS spectra were recorded on an HP 5973 mass spectrometer connected with HP 6890 GC and MALDI-TOF mass spectra were recorded on a JMS-DX303 (JEOL Co.). Infrared (IR) spectra were recorded on a MB104 FT-IR (ABB Bomen Inc.), and UV–Vis spectra were recorded on 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 [6a].

2.2. 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 a 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 (Hamamatuse 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 the studies. Corrected ECL signals were obtained by subtracting the ECL signals for blank solutions from the observed ECL signals for TPA.

2.3. Synthesis

2.3.1. Synthesis of 5-hydroxymethyl-2,2′-bipyridine

An excess amount of sodium borohydride (757 mg, 20 mmol) was added in one portion to the 2,2′-bipyridine-5-carboxylate (428 mg, 2 mmol) in 50 mL of absolute ethanol. The mixture was refluxed for 4 h and cooled to room temperature, and then 50 mL of the saturated ammonium chloride aqueous solution was added to decompose the excess sodium borohydride. The ethanol was removed under vacuum, and the resulting residue was extracted with ethyl acetate (5 × 30 mL) and dried over magnesium sulfate, and the solvent was removed under vacuum. The product was purified by silica gel column chromatography ($MeOH–CH_2Cl_2$ 5:95) and was obtained as an oil. Yield: 60% (224 mg). TLC (SiO_2): R_f 0.51 (20% methanol–dichloromethane, 1 drop of ammonia water); IR (CH_2Cl_2, cm^{-1}) 3322 (O–H), 3006 (Ar-H), 2930 (C–H), 1596 (aromatic C=C), 1460 (aromatic C=C), ^1H NMR (400 MHz, acetone-d_6) δ 4.48 (s, 1H, OH), 4.75 (s, 2H, CH_2), 7.39 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H, Py*H*5′), 7.87–7.92 (m, 2H, Py*H*), 8.43–8.48 (m, 2H, Py*H*), 8.65–8.67 (m, 2H, Py*H*); MS/EI *m/z* 186 [M^+, 100%], 169 [M^+–OH, 20%], 157 [M^+–CHO, 93%].

2.3.2. General procedure for synthesis of bridging ligands with monoester link

DCC (206 mg, 1 mmol) was added to a stirred solution of 2,2′-bipyridine-5-carboxylic acid (or 4′-methyl-2,2′-bipyridine-4-butanoic acid, 1 mmol), 5-hydroxymethyl-2,2′-bipyridine (170 mg, 0.92 mmol), and DMAP (30 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature overnight. The precipitated DCU was filtered off, and the filtrate was evaporated to remove the solvent. The product was purified by silica gel column chromatography ($MeOH–CH_2Cl_2$ = 5:95) and was obtained in 84% and 61% yield, respectively.

*2.3.2.1. 2,2′-Bipyridinyl-5-methyl-2,2′-bipyridinyl-5-carboxylate; bpy-$COOCH_2$-bpy (**1**).* Yield: 84% (284 mg), TLC (SiO_2): R_f 0.42 (10% methanol–dichloromethane, 1 drop of ammonia water); IR (CH_2Cl_2, cm^{-1}) 3053 (Ar-H), 2928 (C–H), 2853 (CH_2), 1717 (C=O), 1591 (aromatic C=C), 1460 (aromatic C=C), 1269 (C–O), ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 2H, $COOCH_2$), 7.29–7.35 (m, 2H, Py*H*), 7.79–7.84 (m, 2H, Py*H*), 7.93 (dd, *J* = 8.1, 2.2 Hz, 1H, CH_2-Py*H*4), 8.40–8.52 (m, 5H, Py*H*), 8.67–8.70 (m, 2H, Py*H*), 8.79 (d, *J* = 2.2 Hz, 1H, CH_2-Py*H*6), 9.30 (m, 1H, Py*H*); HRMS: *m/z* calc. for $C_{22}H_{16}N_4O_2$: calc. for 368.1273, found 368.1260.

*2.3.2.2. 2,2′-Bipyridinyl-5-methyl-4-(4′-methyl-2,2′-bipyridinyl)butanoate; mbpy-$(CH_2)_3COOCH_2$-bpy (**2**).* Yield: 61% (258 mg), TLC (SiO_2): R_f 0.34 (5% methanol–dichloromethane, 1 drop of ammonia water); IR (CH_2Cl_2, cm^{-1}) 3050 (Ar-H), 2945 (C–H), 1746 (C=O), 1601 (aromatic C=C), 1463 (aromatic C=C), 823 (Ar-H), ^1H NMR (400 MHz, $CDCl_3$) *δ 2.02–2.10* (m, 2H, CH_2), 2.41–2.44 (m, 5H, CH_3 and CH_2COO), 2.74 (t, *J* = 7.7 Hz, 2H, Py4CH_2), 5.18 (s, 2H, Py5CH_2), 7.10–7.11 (m, 2H, Py*H*), 7.28–7.30 (m, 1H, Py*H*), 7.77–7.81 (m, 2H, Py*H*), 8.22–8.23 (m, 2H, Py*H*), 8.38–8.41 (m, 2H, Py*H*), 8.51–8.56