

Copyright © 2012 American Scientific Publishers All rights reserved Printed in the United States of America

Journal of Nanoscience and Nanotechnology Vol. 12, 4317–4320, 2012

Synthesis and Properties of the Diruthenium(II) Complexes with Diimine-linked Polypyridine Bridges

Dong Hwan Kim¹, Hwa-Seon Kim¹, Woong Kyu Jo¹, Ho-Geun Ahn¹, Chee Hun Kwak², Ji-Hoon Lee³, Dong Ho Kim⁴, Ruimao Hua⁵, and Min Chul Chung^{1, *}

¹ Department of Chemistry Engineering, Sunchon National University, Sunchon, Jeonnam 540-742, Korea
 ² Department of Chemistry, Sunchon National University, Sunchon, Jeonnam, 540-742, Korea
 ³ Department of Polymer Engineering, Chungju National University, Chungju, Chungbuk 380-702, Korea
 ⁴ Jeonnam TP, Suncheon, Jeonnam, 540-856, Korea
 ⁵ Department of Chemistry, Tsinghua University, Beijing 100084, China

The diruthenium complexes, $[(bpy)_2Ru(II)-(bpy-DPDA)-Ru(II)(bpy)_2][PF_6]_4$ **3**, (bpy: 2,2'-bipyridiyl; bpy-DPDA: Bis(2,2'-dipyridylketenylidene)-*N*,*N* $-1,4-phenylenediamine}, and <math>[(bpy)_2Ru(II)-(Dbpy-DPDA)-Ru(II)(bpy)_2][PF_6]_4$ **4** {Dbpy-DPDA: Bis(2,2'-dipyridyl ketenylidene)-*N*,*N*-1,1'-(4,4'-diphenylene)diamine}, were prepared by the reaction of $(bpy)_2Ru(II)Cl_2$ with diimine-linked polypyridine bridges. These complexes were characterized by NMR, IR, UV/VIS, PL and cyclic voltammetry. In the ¹³C-NMR spectra of **3** and **4**, the carbon peaks of the Schiff Bases (>C=N-) were shifted to lower fields, and emissions were observed at 689 and 693 nm with quantum yields of 0.004 and 0.006, respectively. The electrochemistry of complexes **3** and **4** showed four-reversible waves (one oxidation wave and three reduction waves). The electrochemically measured band gaps for complexes **3** and **4** were 2.01 and 2.10 eV, respectively.

Keywords: Ruthenium, Schiff Base, Bipyridine, Pyridiyl, Cyclic Voltammogram, Emission.

1. INTRODUCTION

Recently, there have been a number of studies of binuclear compounds using π -conjugated organic materials as a bridge.^{1,2} This interest is fundamentally attributable to their potential use as materials for molecular wires, and electroluminescent materials.²⁻⁶ Welter et al. reported that the compounds of these diruthenium complexes with a semiconducting polymer used for electroluminescent devices can display two different colors (red/green), depending on the applied voltage,⁷ Diruthenium(II) complexes based on polypyridiyl ligands have attracted considerable attention due to their diverse properties. The bridging ligand, mediating the two metal centers, plays a key role in the determination of the properties of these systems. Planar polyaromatic bridging ligands have been the focus of some recent studies, due to their rigid nature.^{8,9} Although a wide variety of bridging ligands have been introduced in recent years,¹⁰ the study of dinuclear complexes, bisite bridge ligands with Schiff bases, is less common.¹¹ In this study, we explored the potential use of bi-site bridge ligands with Schiff bases in dinuclear Ru(II) complexes. We report the synthesis and characteristic electronic and photophysical properties of the new diruthenium complexes, [(bpy)₂Ru(II)-(bpy-DPDA)-Ru(II)(bpy)₂] [PF₆]₄ (**3**),{bpy: 2,2'-bipyridiyl; bpy-DPDA: Bis(2,2'-dipyridylketenylidene)-*N*,*N*-1,4-phenylenediamine}, [(bpy)₂Ru (II)-(Dbpy-DPDA)-Ru(II)(bpy)₂][PF₆]₄(**4**), {Dbpy-DPDA: Bis(2,2'-dipyridyl ketenylidene)-*N*,*N*-1,1'-(4,4'-diphenylene)diamine}, in detail.

2. EXPERIMENTAL DETAILS

2.1. General Considerations

For this experiment, THF (tetrahydrofuran), hexane, pentane, and CH_2Cl_2 were purchased from Aldrich, distilled with CaH_2 or Na/K alloy and then stored under a nitrogen atmosphere. 1,4-phenylenediamine, methanol,

J. Nanosci. Nanotechnol. 2012. Vol. 12. No. 5

^{*}Author to whom correspondence should be addressed.

¹⁵³³⁻⁴⁸⁸⁰

2,2-dipyridyl ketone, formic acid, benzidine, cis-bis(2,2'bipyridine)dichlorideruthenium(II)hydrate, ethanol, and [Cp₂Fe][PF₆] were purchased from Furuka and Aldrich and used without purification. Bis(2,2'-dipyridylketenylidene)-*N*,*N*-1,4-phenylenediamine (**Dbpy-PDA**) and Bis(2,2'-dipyridyl ketenylidene)-N,N-1,1'-(4,4'-diphylene) diamine (Dbpy-DPDA) were synthesized according to the procedures described in the literature.¹¹ All syntheses were performed using a Schlenk tube under an argon atmosphere. In addition, CD₃CN, CDCl₃ were used as the solvents for NMR, after being dried using a molecular sieve-4A and kept under an argon atmosphere. A SHI-MADZU FTIR-8700 spectrophotometer was used for the IR analysis. The ¹H-NMR and ¹³C-NMR spectra were determined by means of a Bruker AVANCE 400FT-NMR spectrometer (1 H, 400 MHz). A JASCO V-570 was used for the UV-Vis-Near-IR(NIR) analysis. The spectrofluorometer used was a JASCO FP-6500. Cyclic voltammetry (CV) was carried out in acetonitrile (0.1 M) with NBu_4PF_6 as an electrolyte using a Bioanalytical Systems Inc. E2. A Pt disk was used as the working electrode, while Pt wire and Ag/AgCl were used as the auxiliary and reference electrodes, respectively. Potentials were internally referenced to the $Cp_2Fe^{0/+}$ couple by adding Cp_2Fe at the end of the experiment.

dene)-N, N-1,4-Phenylenediamine (Dbpy-PDA), 1

¹H-NMR(CDCl₃), $\delta_{\rm H}$, 8.53 (*dq*, 4.7 Hz, 0.87 Hz, 4 H), 8.06 (dt, 8.89 Hz, 1.05 Hz, 2 H), 7.72 (td, 7.86 Hz, 1.78 Hz, 2 H), 7.46 (td, 7.73 Hz, 1.75 Hz, 2 H), $7.0 \sim 7.27$ (m, 4 H), 6.94 (dt, 79 Hz, 1.05 Hz, 72 H), 6.50 (s, 4 H); ¹³C-NMR (CDCl₃), $\delta_{\rm C}$, 166.4 (>C=N-), 156.6, 154.9, 149.2, 149.1, 146.6, 136.5, 135.7, 124.7, 124.6, 123.4, 123.0, 121.3; FT-IR (KBr, cm⁻¹), 1630, 1616, 1581,1565; Mass spectrum(m/e): 441; UV($\lambda_{abs}/nm(\varepsilon_{max}/dm^3 mol^{-1} cm^{-1})$, 244(39,349), 268(34,841), 378(10,492), E.A, Found (Cal'd), C; 76.05 (76.35), H; 4.64 (4.58), N: 19.43(19.08) for C₂₈H₂₀N₆.

2.3. Synthesis of the Bis(2,2'-dipyridyl ketenylidene)-*N*,*N*-1,1'-(4,4'-diphenylene)Diamine (Dbpy-DPDA), 2

¹H-NMR(CDCl₃), $\delta_{\rm H}$, 8.5 (*tq*, 4.8 Hz, 0.87 Hz, 4 H), 8.13 (d, 7.9 Hz, 2 H), 7.77 (td, 7.82 Hz, 1.77 Hz, 2 H), 7.49 (td, 7.73 Hz, 1.74 Hz, 2 H), 7.11~7.29 (m, 8 H), 7.0 (dt, 7.79 Hz, 1.05 Hz, 2 H), 6.74 (dt, 8.5 Hz, 2.33 Hz, 4 H); ¹³C-NMR (CDCl₃), $\delta_{\rm C}$, 167.6 (>C=N-), 157.9, 156.2, 150.6, 150.4, 137.8, 137.4, 137.2, 128.2, 125.9, 124.9, 124.6, 122.9; FT-IR (KBr, cm⁻¹), 1614, 1586, 1510, 1463; UV(λ_{abs} /nm), 222(16,696), 270(27,703), 304(41,616), E.A, Found (Cal'd), C; 76.45(76.05), H; 4.64(4.68), N: 16.43(16.27) for C₃₄H₂₄N₆.

2.4. Synthesis of the [(bpy)₂ Ru(II)-(Dbpy-PDA)-Ru(II)(bpy)₂][PF₆]₄ Complex, 3

A solution of $(bpy)_2RuCl_2 \cdot xH_2O$ (250 mg, 0.5 mmol) and bis(2-2'-dipridiyl kentenylidene)-N,N-1,4-phenylenediamine (bpy-PDA, 105 mg, 0.238 mmol)) in 30 ml of ethanol/water (2:1) and CHCl₃ (2 ml) was heated at 80 °C for 2 hrs. The mixture was heated under argon until the complete consumption of the starting materials was observed. After the solution cooled to room temperature, a solution of ammoniumhexafluorophosphate in water was added, and upper liquid was removed. The precipitate was washed with water $(3 \times 10 \text{ ml})$, and passed short alumina using the acetonitrile. The fractions containing the pure complex were evaporated to dryness and recrystallized from acetonitrile/toluene. Complex 3 was finally obtained with 55% yield.

¹H-NMR(CD₃CN), $\delta_{\rm H}$, 8.42 (*d*, 8 Hz, 4 H), 8.34 (*d*, 8 Hz, 4 H), 8.22 (dd, 3.6 Hz, 0.7 Hz, 4 H), 8.13 (dq, 7.9 Hz, 1.0 Hz, 4 H), 8.09 (td, 8.4 Hz, 1.46 Hz, 4 H), 7.99 (td, 7.8 Hz, 1.4 Hz, 4 H), 7.93 (td, 8.05 Hz, 1.44 Hz, 4 H), 7.66 (dt, 5.77 Hz, 0.72 Hz, 4 H), 7.60 (dt, 5.6 Hz, 0.7 Hz, 4 H), 7.49~7.54 (m, 4 H), 7.26~7.31 (*m*, 8 H); ¹³C-NMR (CD₃CN), $\delta_{\rm C}$, 188.2 (>C=N-), 159.1, 158.7, 157.3, 155.0, 154.6, 153.5, 140.3, 140.0, 130.7, 129.3, 129.2; FT-IR (KBr, cm⁻¹), 1970, 1682, **2.2.** Synthesis of the Bis(2,2'-dipyridyl ketenyli-characteristic states of the Bis(2,2'-dipyridyl ketenyli-teristic states of the Bis(2,2'-dipyridyl keteny 246(35,870), 286(78,787), 428(13,596), 488(9,580).

E.A, Found (Cal'd), C; 44.30 (44.21), H; 2.64 (2.84), N: 10.43(10.62) for $C_{68}H_{52}F_{24}N_{14}P_4Ru_2$.

2.5. Synthesis of the [(bpy)₂ Ru(II)-(Dbpy-DPDA)-Ru(II)(bpy)₂][PF₆]₄ Complex, 4

Complex 2 was prepared using the same procedure as that for complex 1 except that Bis(2,2'-dipyridyl ketenylidene)-N, N-1, 1'-(4, 4'-diphylene) diamine (**bpy-DPDA**) was used instead of Bis(2,2'-dipyridyl ketenylidene)-N,N-1,4phenylenediamine (bpy-PDA). Finally, complex 4 was obtained. (yield: 62%).

¹H-NMR(CD₃CN), $\delta_{\rm H}$, 8.49 (*d*, 8.1 Hz, 4 H), 8.41 (d, 8.1 Hz, 4 H), 8.29 (d5, 5.6 Hz, 0.61 Hz, 4 H), 8.20 (ddd, 7.94 Hz, 1.65 Hz, 0.58 Hz, 4 H), 8.16 (td, 8.05 Hz, 1.23 Hz, 4 H), 8.06 (td, 7.8 Hz, 1.4 Hz, 4 H), 8.0 (td, 8.05 Hz, 1.44 Hz, 4 H), 7.7 (dt, 5.73 Hz, 0.7 Hz, 4 H), 7.67 (dt, 5.6 Hz, 0.7 Hz, 4 H), 7.56~7.60 (m, 4 H), 7.33~7.60 (m, 8 H), 7.26 (d, 8.8 Hz, 2 H), 6.65 (d, 8.7 Hz, 2 H), ¹³C-NMR (CD₃CN), $\delta_{\rm C}$, 186.3 (>C=N-), 157.1, 156.7, 155.4, 153.0, 152.7, 151.6, 138.5, 138.2, 138.1, 128.8, 127.4, 127.2, 124.6, 124.2; FT-IR (KBr, cm^{-1}), 1973, 1669, 1659, 1604, 840; UV(λ_{abs} /nm), 246(33,537), 288(79,207), 428(11,989), 496 (9,190); E.A, Found (Cal'd), C; 44.45(44.21), H; 2.74(2.93), N: 10.53 (10.20) for C₇₄H₅₆F₂₄N₁₄P₄Ru₂.

J. Nanosci. Nanotechnol. 12, 4317-4320, 2012

Synthesis and Properties of the Diruthenium(II) Complexes with Diimine-linked Polypyridine Bridges



Scheme 1. Preparation of diruthenium complexes.

3. RESULTS AND DISCUSSION

Bis(2,2'-dipyridyl ketenylidene) diamine compounds (1,2) were prepared by gently melting 2 eq. of the diamines (1:1,4-phenylene diamine, 2: 1,1'-(4,4'-diphenylene)diamine) and 1 eq. of the ketene for 30 min (Scheme 1). In the NMR spectrum, the carbon peaks of the Schiff Bases (>C=N-) were observed at 166.4~167.6 ppm, which is typical for Schiff Bases. The chemical shifts of the Schiff Bases were in the range of 188.2~186.3 ppm for complexes 3 and 4, due to the ruthenium bond to the dipyridylketenylidene bridge ligand. In general, compounds 3 and 4 are dark-red in color in dilute solution. The absorption spectra of 3 and 4 in acetonitrile are shown in Figure 1. Table I lists the absorption maxima values and extinction coefficients of these complexes and a reference complex $(Ru(bpy)_3^{+2})$. The electronic absorption spectra of complexes 3 and 4 in acetonitrile at room temperature are shown in Figure 1. The three peaks at 246, 428 and 488 nm for complex 3 were assigned as the $\operatorname{Ru}(d\pi) \to \operatorname{bpy}(\pi^*)$ transitions. For complexes 3 and 4, the intense peaks at 286 and 288 nm, respectively, were assigned as the ligand centered (LC) bpy $\pi \to \pi^*$ transitions, and the intense peaks at 340 nm was attributed to metal centered (MC)Ru $d \rightarrow d$ transitions such as the characteristic transition for



Fig. 1. UV/Vis absorption and emission spectra ($\lambda_{\text{excitation}}$: 428 nm) of complex 3, and 4 in MeCN at 298 K.

J. Nanosci. Nanotechnol. 12, 4317-4320, 2012

Complexes	UV/Vis (λ_{max}/nm)	PL (nm)	φ	E_g (eV)	$ au$ (μ s)	k_r (s ⁻¹)	${\Sigma k_{ m nr} \over ({ m s}^{-1})}$	
3	220,246 286, 340 428, 488	689	0.004	2.01	8.6	465	1.15× 10 ⁵	
4	246,288 340, 428 496	693	0.006	2.10	10.2	882	9× 10 ⁵	
Ru (bpy) ^{+2,9}	451,344 322,287	605	0.062	2.60	0.89	6.9×10^{5}	10×10^5	

 Table I.
 Photophysical data for complexes in CH₂CN solution at 295 K.

octahedral d^6 metal complexes.²⁰ Both of the new complexes are luminescent in degassed solution, displaying a single, broad emission band. The luminescences of complexes **3** and **4** ($\lambda_{max} = 689$ and 693 nm, respectively) are substantially red-shifted with respect to that of the reference complex (Ru(bpy)₃⁺², $\lambda_{max} = 622$ nm). As an absorption, this is attributed to the lowering of the bridge (N^N) π^* orbital energy due to its increased conjugated as compared to bpy. The relatively long luminescence life time, τ , of the complexes, which is in the range of 8.6~10.2 μ s in degassed solution at room temperature (Table I), is also suggestive of their having a significantly ligand-centered character in the excited state.

The emission quantum yields, Φ_R , were measured at 20 °C according to the following equation (for the buffer solutions, no refractive index correction was made).¹²

$$\Phi_R = \Phi_{\rm ref} (I_s A_{\rm ref} / I_{\rm ref} A_s) \tag{1}$$

where *I* is the emission intensity calculated from the area under the emission spectrum from 500 to 800 nm, *A* is the absorbance, and the subscripts *s* and ref stand for the samples and reference, respectively, An acetonitrile solution of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ was used as a standard with $\Phi_{\text{ref}} = 0.062^{.9,13}$ The luminescence quantum yields (Φ_R) of **3** and **4** were 0.004 and 0.006, respectively. Assuming that the formation of the emissive state occurs with unity efficiency, one may obtain an estimate of the unimolecular

 Table II.
 Electrochemical properties for complexes in Acetonitrile at 298 K.

	Oxida	tion (V)	$\frac{\text{Reduction (V)}}{E_{1/2}, (\Delta_{a,p}, \text{mV})}$		
	$E_{1/2}, (2$	$\Delta_{a,p}, mV$			
$\frac{[(bpy)_2Ru(bpy-DPDA]}{Ru(bpy)_2]^{4+}, 3}$	1.26(82)	-0.75(74)	-1.29(78)	-1.39(82)	
$ \begin{array}{c} [(bpy)_2 Ru(Dbpy-DPDA] \\ Ru(bpy)_2]^{4+} \end{array} $	1.40(82)	-0.70(75)	-1.30(75)	-1.50(80)	
$\frac{[(bpy)_2Ru(bpy-Et-bpy]}{Ru(bpy)_2]^{4+,15}}$	1.38(90)	-0.92(1e)	-1.16(1e)	-1.35(2e)	
$\frac{[(bpy)_2Ru(bpy-Bu-bpy]}{Ru(bpy)_2]^{4+,15}}$	1.35(90)	090(1e)	-1.12(1e)	-1.33(2e)	
[Ru(bpy) ₃] ^{2+, 9}	1.27(65)	-1.35(1e)	-/154(1e)	-1.79(e)	

RESEARCH ARTICLE



Fig. 2. Cyclic Voltammogram of complex 4 at 298 K (0.1 M MeCN solution of $(Bu_4N)(PF_6)$, scan rate: 100 mV/s, Reference Fe/Fe⁺: 0.43 V).

radiative (k_r) and nonradiative (Σk_{nr}) decay rate constants by the application of Eqs. (2) and (3).

$$\tau = 1/(k_r + \Sigma k_{\rm nr}) \tag{2}$$

$$\Phi_R = k_r / (k_r + \Sigma k_{\rm nr}) = k_r \cdot \tau \tag{3}$$

The inspection of the parameters so obtained (Table I) confirms that the lower emission quantum yield of the complexes compared to that of the reference complexes $(\text{Ru}(\text{bpy})_3^{+2}, k_r = 6.9 \times 10^5, k_{nr} = 1.05 \times 10^6)$ is due to the reduced radiative rate constant and the higher nonradiative decay.

The oxidation and reduction potentials for all of the complexes were determined by cyclic voltammetry. The redox potentials for compounds **3** and **4** are listed in Table II. The observed couples are all 'reverse,' where the term reversibility used here implies that the separation between the anodic and cathodic peak potentials was less than 100 mV for a one-electron process and no degradation products were observed on the following scan. The $E_{1/2}$ values of ΔE were calculated by subtraction of the cathodic potentials from the anodic potentials for a specific redox couple (Fig. 2).

The general behavior of the complexes was very similar to that of analogous diruthenium complexes.^{13, 14}

4. CONCLUSION

The reaction of 2 eq. of the diamine with the kentene gave the bis(2,2'-dipyridyl ketenylidene) diamine compounds (1 and 2). In the NMR spectrum, the carbon peaks of the Schiff Bases (>C=N-) were observed at 166.4~167.6 ppm, which is typical for Schiff bases. The chemical shifts of the Schiff Bases were in the range of 188.2~186.3 ppm for complexes 3 and 4. The absorption spectra of 3 and 4 in acetonitrile are shown in Figure 1.

The Ru($d\pi$) \rightarrow bpy(π^*) transitions are observed at 246, 428 and 488 nm. The ligand centered (LC) bpy $\pi \to \pi^*$ transitions (of complexes 3 and 4) are observed at 286 and 288 nm, respectively. The luminescences of complexes **3** and **4** ($\lambda_{\text{max}} = 689$, 693, respectively) are substantially red-shifted with respect to that of the reference complex (Ru(bpy)₃⁺², $\lambda_{max} = 622$). The luminescence quantum yields (Φ_R) of **3** and **4** are 0.004 and 0.006, respectively. From the radiative (k_r) and nonradiative (Σk_{nr}) , it can be inferred that the lower emission quantum yield of the complexes compared to that of the reference complexes $(\text{Ru}(\text{bpy})_3^{+2}, k_r = 6.9 \times 10^5, k_{\text{nr}} = 1.05 \times 10^6)$ is due to the reduced radiative rate constant and higher nonradiative decay. The oxidation and reduction potentials for all of the complexes were determined by cyclic voltammetry. Oxidations of the ruthenium center were observed in the region between +1.20 and 1.40 V for complexes 3 and 4, whereas the reduction of the two coordinated ligands and one bridge were observed in the negative potential region. The oxidation peak was not split for the binuclear complexes, indicating that the metal centers are not in strong electronic communication with each other. The electrochemically measured band gaps were 2.01 and 2.10 eV for complexes 3 and 4, respectively.

Acknowledgments: This work was supported by GT-FAM of the Sunchon National University through the Regional Innovation Center Program (RIC). Professor Hua was supported by the Brain Pool Program of the Korea Research Fund (061S-4-3-0027).

References and Notes

- 1. R. M. Metzger, Chem. Rev. 103, 3803 (2003).
- 2. N. Robertson and C. A. McGowan, Chem. Soc. Rev. 32, 96 (2003).
- M. Akita, Y. Tanaka, C. Naitoh, T. Ozawa, N. Hayashi, M. Takeshita, A. Inagaki, and M.-C. Chung, *Organometallics* 25, 5261 (2006).
- M. C. Chung, X. Gu, B. A. Etzenhouser, A. M. Spuches, P. T. Rye, S. K. Seetharaman, D. J. Rose, J. Zubieta, and M. B. Sponsler, *Organometallics* 22, 3485 (2003).
- T. Nagamura, Novel Materials and Device for Molecular Electronics and Photonics, CMC (2003), p. 287.
- J. M. Marshall and D. Dimova-Malinovska, Photovoltaic and Photoactive Materials-Properties, Technology and Application, Kulwer Academic Pub., Norwell (2002), p. 97.
- S. Welter, K. Brunner, J. W. Hofstraat, and L. De Cola, *Nature* 42, 52 (2003).
- 8. J. Bolger, A. Gourdon, E. Show, and J.-P. Launay, *Inorg. Chem.* 35, 2937 (1996).
- 9. D. Gut, I. Goldberg, and M. Koi, Inorg. Chem. 42, 3483 (2003).
- Balzani, A. Juris, M. Venturi, S. Campagna, and S. Serroni, <u>*Chem.*</u> *Rev.* 96, 759 (1996).
- A. A. H. Saeed and A. Y. Khedar, *Canadian J. Appl. Spect.* 39, 173 (1994).
- 12. G. F. Strouse, J. R. Schoonover, R. Duesing, S. Boyde, W. E. Jones, and T. J. Meyer, *Inorg. Chem.* 34, 473 (1995).

Received: 7 May 2010. Accepted: 2 June 2011.

J. Nanosci. Nanotechnol. 12, 4317-4320, 2012