Inorganic Chemistry Communications 43 (2014) 10–14

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Preparation, photophysical, and electrochemical properties of three trinuclear Ru(II) complexes: Bridging ligands composed of 2,2′-bipyridine and 4,5-diazafluorene fragments

Feixiang Cheng [a,*], Chixian He [a], Mingli Ren [a], Lifeng Yao [a], Ning Tang [b]

[a] College of Chemistry and Chemical Engineering, Qujing Normal University, Qujing 655011, PR China
[b] College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history:
Received 10 September 2013
Accepted 19 January 2014
Available online 25 January 2014

Keywords:
Ru(II) complex
2,2′-Bipyridine
4,5-Diazafluorene
Photophysics
Electrochemistry

ABSTRACT

Three bridging ligands 5,5′-bis[(4,5-diazafluoren-9-ylimino)methyl]-2,2′-bipyridine (L^1), 5,5′-bis[2-(4,5-diazafluoren-9-ylimino)phenoxymethyl]-2,2′-bipyridine (L^2), 5,5′-bis[4-(4,5-diazafluoren-9-ylimino) phenoxymethyl]-2,2′-bipyridine (L^3), and corresponding Ru(II) complexes $[(bpy)_6Ru_3(L^{1-3})](PF_6)_6$ (bpy = 2,2′-bipyridine) have been synthesized. The three ligands have two kinds of nonequivalent chelating sites: one involving the 2,2′-bipyridine moiety, and the other involving the 4,5-diazafluorene moiety. The emission intensities of complexes $[(bpy)_6Ru_3(L^2)]^{6+}$ and $[(bpy)_6Ru_3(L^3)]^{6+}$ are almost equal to that of complex $[(bpy)_6Ru_3(L^1)]^{6+}$ in CH_3CN solution at room temperature, but weaker than that of complex $[(bpy)_6Ru_3(L^1)]^{6+}$ in EtOH–MeOH (4:1, v/v) glassy matrix at 77 K. Cyclic voltammetry and differential pulse voltammetry studies of the three complexes show one Ru(II)-centered oxidation at around 1.33 V for the $Ru^{II/III}$ couple.

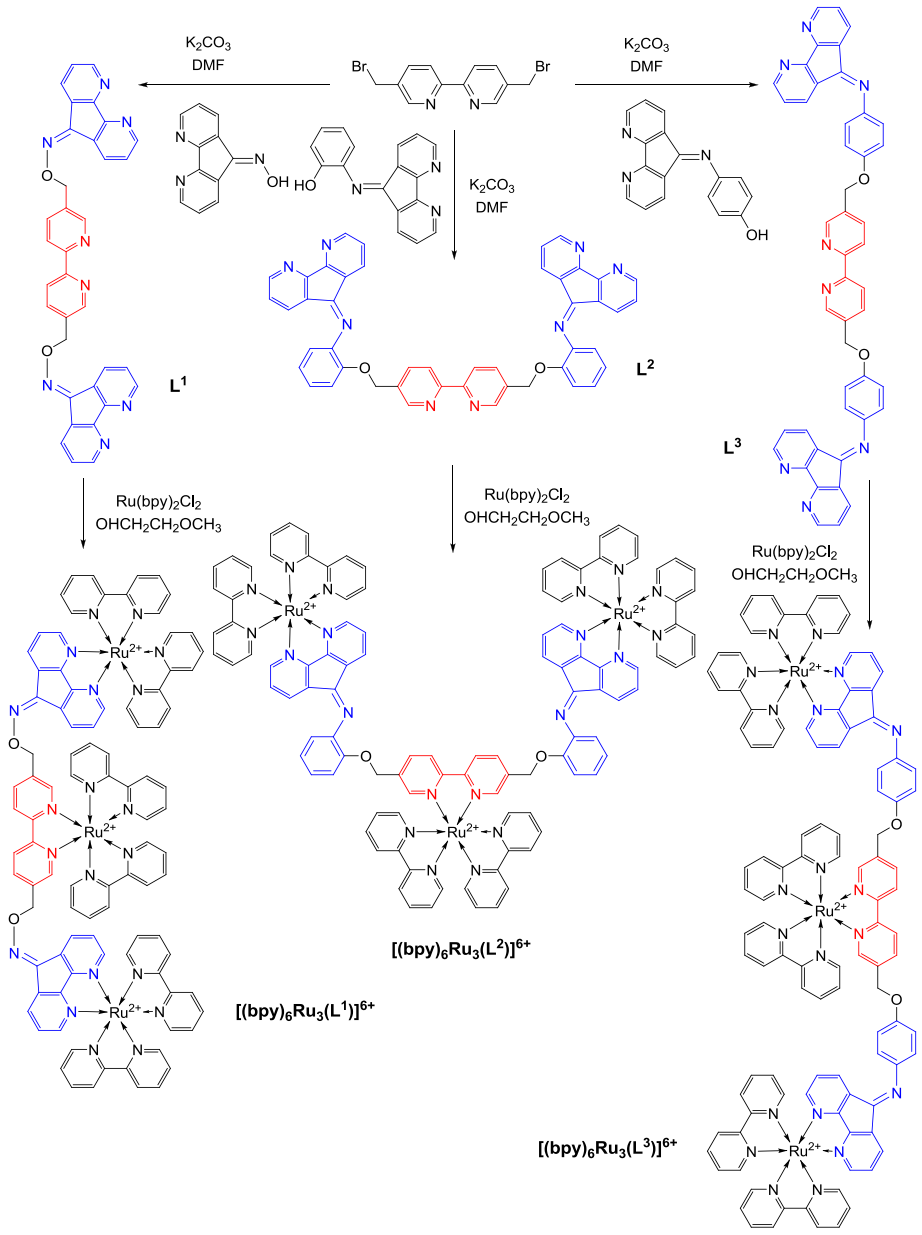
Ru(II) polypyridine complex is considered as a building block for designing photomolecular devices because of a unique combination of its suitable photophysical and electrochemical properties [1,2]. The efficiency of photoactive processes in polynuclear complexes is strongly regulated by the size, shape, and electronic nature of the bridging ligands [3,4]. Therefore, the choice of suitable bridging ligands is crucial to obtain polynuclear complexes capable of showing luminescence, of exhibiting interesting electrochemical properties, and of giving rise to photoactive processes. A wide range of bridging ligands containing 2,2′-bipyridine or 1,10-phenanthroline (phen) as chelating units have been prepared in recent years. However, the vast majority of such studies have focused on systems containing symmetric bridging ligands. The study of polynuclear Ru(II) complexes, bridged with ligands containing two kinds of nonequivalent coordinating sites, has attracted less attention [5–7]. 4,5-Diazafluoren-9-one (dafone) is structurally similar to bpy and phen. However, dafone has a different electronic property from that of bpy and phen; as a consequence, Ru(II) complexes containing 4,5-diazafluorene group have different photophysical and electrochemical properties from the $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ based complexes [8,9]. Toward the aim of synthesizing new polynuclear Ru(II) complexes with interesting photophysical and electrochemical properties, herein, we describe the synthesis and characterization of three bridging ligands incorporating two kinds of nonequivalent chelating sites: one involving the 2,2′-bipyridine moiety, and the other involving the 4,5-diazafluorene moiety. The absorption and emission spectra, and electrochemical properties of the three complexes are also presented and discussed.

An outline of the synthesis of the three ligands and their Ru(II) complexes is presented in Scheme 1. Ligands L^1, L^2 and L^3 were synthesized in moderate yields by the reaction of 5,5′-bis(bromomethyl)-2,2′-bipyridine [10] with 4,5-diazafluoren-9-oxime, 9-(2-hydroxy) phenylimino-4,5-diazafluorene, and 9-(4-hydroxy)phenylimino-4,5-diazafluorene [11,12], respectively, in DMF solution under nitrogen atmosphere [13]. The three Ru(II) complexes were prepared by refluxing $Ru(bpy)_2Cl_2 \cdot 2H_2O$ [14] and ligands in 2-methoxyethanol solution for 12 h under nitrogen atmosphere, and isolated as their PF_6^- salts [15]. These compounds were characterized by ^1H NMR, ESI-MS, IR, and elemental analysis.

The UV–vis absorption spectra of the three complexes have been studied in CH_3CN solution, at a working concentration of 5×10^{-6} mol/L. The energy maxima and absorption coefficients are summarized in Table 1, and the spectra are shown in Fig. 1. Assignments of the absorption bands of the complexes have been made on the basis of the well-documented optical transitions of analogous Ru(II) polypyridyl complexes [16–19]. The absorption spectra of the complexes exhibit three well-resolved bands. Those at ca. 287 and 240 nm can be assigned to intraligand $\pi \rightarrow \pi^*$ transitions centered on the 2,2′-bipyridine. The lowest energy band at around 445 nm is attributed to MLCT, $d\pi \rightarrow \pi^*$ transition, which consists of overlapping $d\pi(Ru) \rightarrow \pi^*(bpy)$ and $d\pi(Ru) \rightarrow \pi^*(L)$ components. The three bridging ligands contain two kinds of chelating units with different accepting properties (2,2′-bipyridine and

* Corresponding author at: Qujing Normal University, Sanjiang Road, Qilin District, Qujing, Yunnan, PR China.

1387-7003/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2014.01.013



Scheme 1. Synthesis of ligands L^{1-3} and Ru(II) complexes $[(bpy)_6Ru_3(L^{1-3})](PF_6)_6$.

Table 1
UV–vis absorption and emission data for the three Ru(II) complexes.

Complex	Absorption	Emission [a]	
	λ_{max}, nm ($10^4\varepsilon$, M^{-1} cm^{-1})	λ_{max}, nm, Φ (298 K)	λ_{max}, nm, Φ (77 K)
$[(bpy)_6Ru_3(L^1)](PF_6)_6$	444 (3.69) 287 (20.08) 244 (7.52)	643 (0.016)	649 (0.326)
$[(bpy)_6Ru_3(L^2)](PF_6)_6$	447 (4.12) 287 (18.76) 237 (10.67)	627 (0.018)	641 (0.164)
$[(bpy)_6Ru_3(L^3)](PF_6)_6$	447 (3.89) 287 (19.73) 241 (9.27)	627 (0.017)	641 (0.161)

[a] The emission quantum yields are calculated relative to $Ru(bpy)_3^{2+}$ ($\Phi_{std} = 0.062$) in deoxygenated CH_3CN solution at 298 K or relative to $Ru(bpy)_3^{2+}$ ($\Phi_{std} = 0.376$) in EtOH–MeOH (4:1, v/v) glassy matrix at 77 K; the uncertainty in quantum yields is 15%.

4,5-diazafluorene), which results in the appearance of a non-symmetrical MLCT band. The MLCT absorption maxima of complexes $[(bpy)_6Ru_3(L^2)]^{6+}$ and $[(bpy)_6Ru_3(L^3)]^{6+}$ are red-shifted by about 3 nm compared with that of complex $[(bpy)_6Ru_3(L^1)]^{6+}$ due to the extension of the corresponding π framework of ligands L^2 and L^3.

The emission band maxima and emission quantum yields of the three Ru(II) complexes are summarized in Table 1. Upon excitation into the MLCT band, the three complexes show almost equal emission intensities in CH_3CN solution at room temperature (Fig. 2). The emission properties of Ru(II) polypyridyl complexes generally follow the energy gap law [20,21]. The ^{3}MLCT state is reasonably long-lived and is thought to be deactivated by three processes: radiative decay k_r, radiationless decay k_{nr}, and thermal population of a higher lying excited state, $k_o\exp(-\Delta E/RT)$. For the last process, the thermally accessible excited state has been designated as a ligand field excited state, and the energy of the ligand field state should