



## Research paper

Highly packed and stretched polyterpyridinyl Ru<sup>2+</sup> complexes and their photophysical and stability propertiesDie Liu<sup>1</sup>, Zhilong Jiang<sup>1</sup>, Meng Wang, Xiaoyu Yang, Haisheng Liu, Tun Wu, Pingshan Wang<sup>\*</sup>

Department of Organic and Polymer Chemistry, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China

## ARTICLE INFO

## Article history:

Received 4 May 2016

Received in revised form 4 June 2016

Accepted 6 June 2016

Available online 8 June 2016

## Keywords:

Polyterpyridine

Terpyridine-ruthenium complexes

Photophysical

Non-emissive

## ABSTRACT

Two unique trinuclear terpyridine-ruthenium complexes having similar components placed at different angles were successfully synthesized and fully characterized for the purpose of determining the photophysical and electronic properties. The corresponding UV–vis absorptions and similar electrochemical properties showed characteristic MLCT transitions in both complexes. However, complex C2 displayed an intense emission at 77 K, as expected, where highly packed complex C1 is almost non-emissive. This result may be due to that a distinct configuration adopted by the complex impacts ligand field strength.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, ruthenium-polypyridyl complexes have attracted considerable attention due to their photosensitive applications as a result of their unique electrochemical and photophysical properties [1–3]. Among these complexes, the robust, bis-tridentate octahedral ruthenium complexes are one of the most common and provide an ideal building block for construction of multi-nuclear complexes. For example, multinuclear Ru<sup>2+</sup> coordination systems can be adjusted by using different polyterpyridine derivatives upon complexations [3,4]. It is known that tpy-Ru<sup>2+</sup>-tpy systems show rather poor excited properties and are almost non-emissive compared with that of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> at room temperature [5]. Much work has been done to improve the luminescent properties of ruthenium-polypyridyl complexes by incorporating different substituents to the polypyridine ligand [6], or by using heterocycles or cyclometalating ligands which change the coordination sphere [7–9]. An idealized terpyridine related metallo-organic octahedral architecture should afford a longer excited-state lifetime, a more conjugated ligand with higher delocalization. Such structure can possess excellent photoelectric properties, since the higher energy of the metal-centred (<sup>3</sup>MC) states increases the energy gap between the metal-to-ligand charge transitions (<sup>3</sup>MLCT) and <sup>3</sup>MC states [8,9]. Therefore, the ligand environment is of great importance for the photophysical properties of ruthenium-polypyridyl

complexes. In this paper, two trinuclear terpyridyl-ruthenium complexes were synthesized and characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Further, their photophysical and stability properties were investigated by UV–vis spectra, Emission spectra, cyclic voltammetry (CV) and ESI-MS.

## 2. Results and discussion

Tristerpyridine Ligands L1 and L2 with similar structures and both bearing three terpyridyl units were synthesized using a Suzuki coupling with two newly designed bromo-substituted terpyridines (see ESI, Scheme S1), 6,6''-dibromoterpyridine and 5,5''-dibromoterpyridine. The structures of L1 and L2 were characterized through <sup>1</sup>H NMR (Figs. 1 and 2), <sup>13</sup>C NMR and ESI-MS (see ESI). The ruthenium complexes C1 and C2 were synthesized by reacting L1 or L2 with (2,2':6',2''-terpyridine)ruthenium trichloride (tpyRuCl<sub>3</sub>) in ethylene glycol at 395 K for 24 h (Scheme 1).

<sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>1</sup>H ROESY (see ESI), ESI-MS (Fig. 3) along with the <sup>13</sup>C NMR spectra (see ESI) were used for further characterization of C1 and C2. The <sup>1</sup>H NMR spectra for the ligands and complexes have been assigned; the shifts of <sup>1</sup>H NMR spectra are shown in Fig. 1 for C1 and Fig. 2 for C2. Compared with the ligands, the complexes show significant downfield shift in the 3',5'-tpy protons and 3,3''-tpy protons owing to the lower electron density after coordination. Both 6,6''-tpy protons show a dramatic upfield shift because of the shielding effect from the metal centers. As usual, the Ph-H in the 4'-phenyl terpyridine tends to shift downfield after coordination because of the reduced electron density [10]. To our

\* Corresponding author.

E-mail address: [chemwps@csu.edu.cn](mailto:chemwps@csu.edu.cn) (P. Wang).<sup>1</sup> These authors contributed equally to this work.

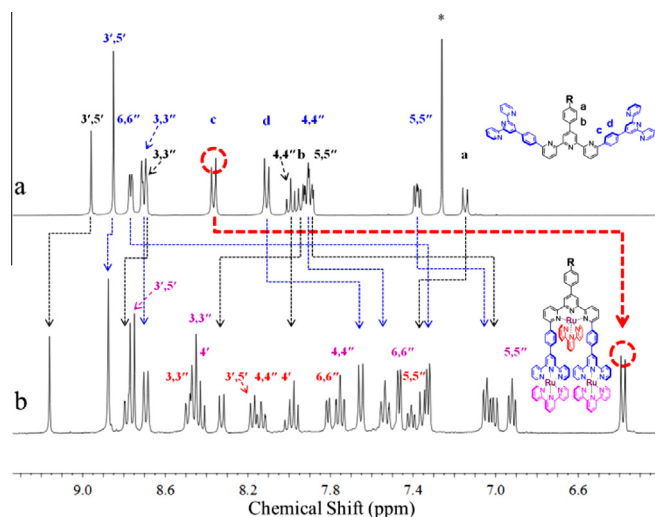


Fig. 1.  $^1\text{H}$  NMR spectra of (a) ligand **L1** in  $\text{CDCl}_3$ ; (b) complex **C1** in  $\text{CD}_3\text{CN}$ .

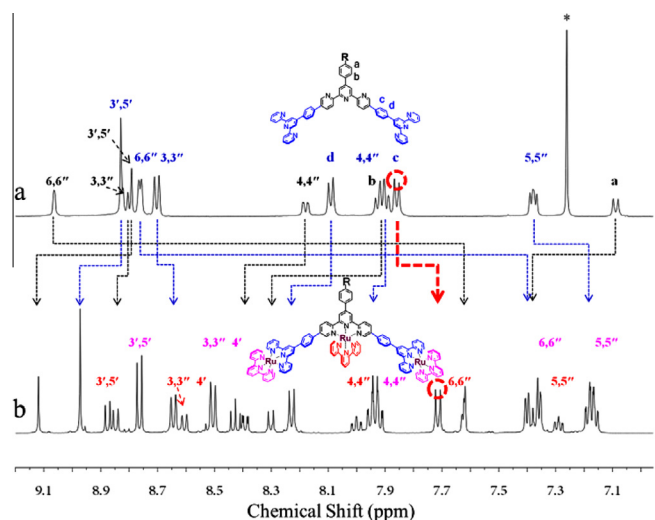


Fig. 2.  $^1\text{H}$  NMR spectra of (a) ligand **L2** in  $\text{CDCl}_3$ ; (b) complex **C2** in  $\text{CD}_3\text{CN}$ .

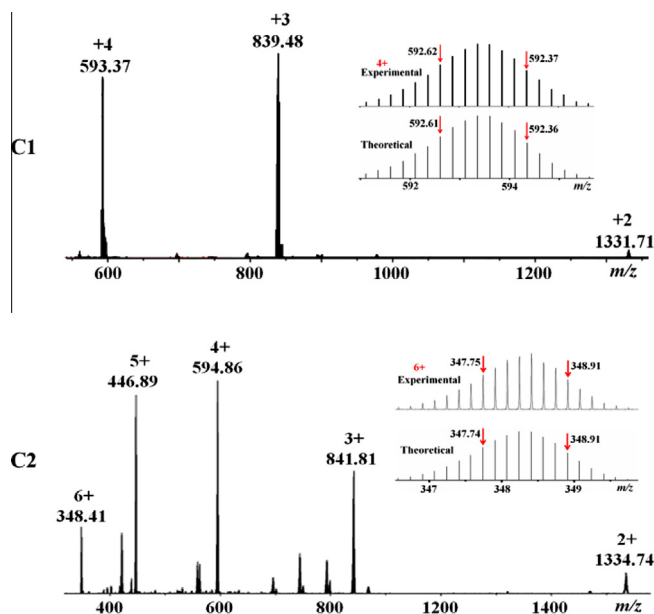
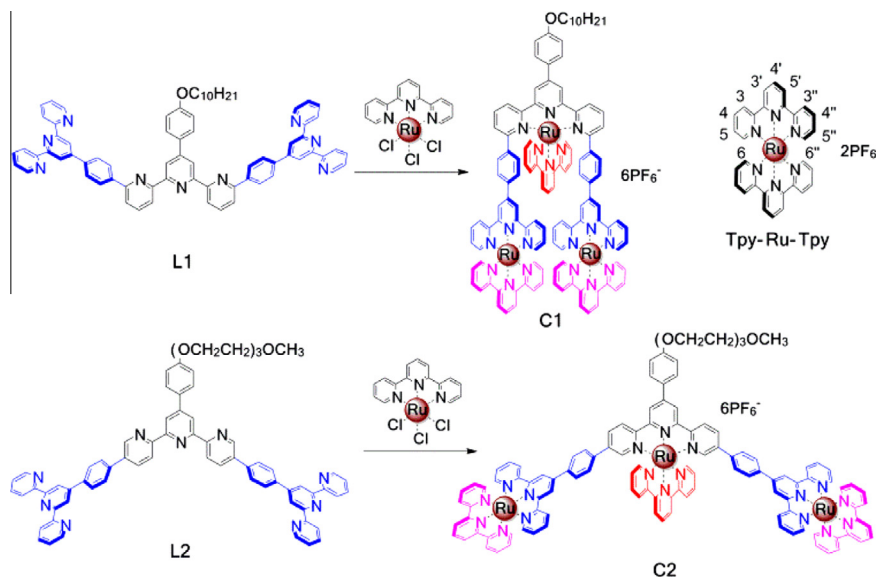


Fig. 3. ESI-MS spectra of **C1** and **C2**, the different charge states ions were derived from losing different numbers of  $\text{PF}_6^-$ . **C1** was measured at a normal condition; **C2** was measured at the high source temperature and capillary voltage.

surprise, the  $\text{Ph-H}_c$  and  $\text{Ph-H}_d$  in **C1** displayed the unexpected upfield shifts due to the shielding effect produced by the mid-(tpy-Ru-tpy) unit [11].  $\text{Ph-H}_c$  in **C1** which is closer to the mid-(tpy-Ru-tpy) displayed a larger upfield shift ( $\Delta\delta = 1.99$  ppm) compared to **L1** ( $\text{Ph-H}_c$  in **C2**:  $\Delta\delta = 0.09$  ppm compared to **L2**). Likewise, a similar upfield shift happened for the  $\text{Ph-H}_d$  of **C1** which was  $\Delta\delta = 0.47$  ppm, while there is a downfield shielding effect in **C2** for  $\text{Ph-H}_d$ , which indicated a sufficient distance between the  $\text{Ph-H}_d$  and mid-(tpy-Ru-tpy).

ESI-MS also validated the proposed structures for these complexes. For complex **C1** (Fig. 3), the peaks at  $m/z$  ( $Z = 4^+$ ) 593.37,  $m/z$  ( $Z = 3^+$ ) 839.48 and  $m/z$  1331.71 ( $Z = 2^+$ ) suitably correspond to the structures of  $[\text{M}-4\text{PF}_6]^{4+}$  (calcd  $m/z = 593.36$ ),  $[\text{M}-3\text{PF}_6]^{3+}$  (calcd  $m/z = 839.47$ ), and  $[\text{M}-2\text{PF}_6]^{2+}$  (calcd  $m/z = 1331.68$ ), respectively. The peaks in complex **C2** (Fig. 3) at  $m/z$  ( $Z = 6^+$ ) 348.25,  $m/z$  ( $Z = 5^+$ ) 446.89,  $m/z$  ( $Z = 4^+$ ) 594.86,  $m/z$  ( $Z = 3^+$ )



Scheme 1. Synthetic routes to complexes **C1** and **C2**.

Download English Version:

<https://daneshyari.com/en/article/1305401>

Download Persian Version:

<https://daneshyari.com/article/1305401>

[Daneshyari.com](https://daneshyari.com)