



# Homoleptic and heteroleptic Ru<sup>II</sup> complexes with extended phenanthroline-based ligands



F. Monti<sup>a</sup>, U. Hahn<sup>b</sup>, E. Pavoni<sup>a</sup>, B. Delavaux-Nicot<sup>c,\*</sup>, J.-F. Nierengarten<sup>b,\*</sup>, N. Armaroli<sup>a,\*</sup>

<sup>a</sup>Istituto per la Sintesi Organica e la Fotoreattività, CNR, Via Gobetti 101, 40129 Bologna, Italy

<sup>b</sup>Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (UMR 7509), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

<sup>c</sup>Laboratoire de Chimie de Coordination du CNRS (UPR 8241), Université de Toulouse (UPS, INPT), 205 Route de Narbonne, 31077 Toulouse, France

## ARTICLE INFO

### Article history:

Received 16 April 2014

Accepted 14 May 2014

Available online 23 May 2014

### Keywords:

Ru(II) complexes

Extended phenanthrolines

NIR luminescence

Photophysics

Solar energy conversion

## ABSTRACT

Four Ru<sup>II</sup> complexes of general formula  $[\text{Ru}(\text{PT})_3]^{2+}$ ,  $[\text{Ru}(\text{NT})_3]^{2+}$ ,  $[\text{Ru}(\text{PT})(\text{bpy})_2]^{2+}$ , and  $[\text{Ru}(\text{NT})(\text{bpy})_2]^{2+}$ , where **PT** = 10,13-bis((triisopropylsilyl)ethynyl)dipyrido[3,2-*a*:2',3'-*c*]phenazine, **NT** = 10,15-bis((triisopropylsilyl)ethynyl)benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine and **bpy** = 2,2'-bipyridine have been synthesized. Their electrochemical and photophysical properties have been studied, with the aid of DFT and TD-DFT theoretical methods. The extended phenanthroline ligand **PT** exhibits two reduction processes at  $-0.98$  and  $-1.55$  (versus SCE) and no clearly detectable oxidation processes; the more extended analogue **NT** is substantially easier to reduce by about 300 mV. In the four complexes, the two first reduction processes are centered on the extended phenanthroline ligands, and, according to DFT calculations, also oxidations are likely to be located on such moieties. **PT** and **NT** exhibit green-yellow fluorescence at 298 and 77 K with photoluminescence quantum yields of 3.4% and 62.1%, respectively, at room temperature. At 77 K, a strong and long-lived phosphorescence is detected only for **PT** ( $\lambda_{\text{max}} = 658$  nm,  $\tau = 29$  ms). In oxygen-free solution at 298 K  $[\text{Ru}(\text{PT})_3]^{2+}$  and  $[\text{Ru}(\text{PT})(\text{bpy})_2]^{2+}$  exhibit a very weak emission band with  $\lambda_{\text{max}}$  at about 700 nm, which extends towards the near infrared region and is unambiguously attributed to emission from the lowest triplet level centered on the **PT** ligand; its emission intensity is strongly enhanced at 77 K where lifetimes of 724 and 767 ns are measured for  $[\text{Ru}(\text{PT})_3]^{2+}$  and  $[\text{Ru}(\text{PT})(\text{bpy})_2]^{2+}$ , respectively. The two complexes with the **NT** ligand show no triplet emission as observed for the **PT** analogues, but only a faint fluorescence signal attributable to negligible amounts of free ligand in solution. Photophysical data are fully rationalized with DFT methods, which always predict that the lowest triplet excited state is centered on the extended phenanthroline ligand in all of the investigated Ru<sup>II</sup> complexes. The estimated energy of the lowest triplet level of the PT-based compounds is in good agreement with the experimental value determined from the phosphorescence spectra. Moreover, the theoretical model rationalizes the lack of phosphorescence for the NT series, because the lowest triplet is estimated to be at 0.97 eV above the ground state ( $\approx 1280$  nm), where non-radiative deactivations prevail.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

1,10-Phenanthroline exhibits a fortunate combination of structural and chemical properties [1]. Therefore, along with its many derivatives, it constitutes an extensively investigated class of molecules both in the area of organic and inorganic chemistry [2]. Pristine 1,10-phenanthroline is poorly luminescent but,

through rational functionalization at specific ring positions or by extension of  $\pi$ -delocalization, a large number of highly luminescent phenanthroline derivatives have been prepared, which may emit across the UV–Vis–NIR spectral window [2–5]. Such a remarkable versatility in preparing luminescent materials is further enhanced when combined with its chelating character. In fact, 1,10-phenanthroline has been utilized to prepare a huge number of luminescent complexes with transition metal (e.g. Zn<sup>2+</sup>, Cu<sup>+</sup>, Re<sup>+</sup>, Ru<sup>2+</sup>, Os<sup>2+</sup>, Ir<sup>3+</sup>) and lanthanide ions (e.g. Eu<sup>3+</sup>, Tb<sup>3+</sup>) [6,7]. A further possibility is provided by the simple protonation of phenanthroline ligands in solution, which enables facile, reversible and extensive tuning of luminescence [3,8,9].

\* Corresponding authors. Tel.: +39 51 6399820; fax: +39 51 6399844 (N. Armaroli).

E-mail addresses: [beatrice.delavaux-nicot@cc-toulouse.fr](mailto:beatrice.delavaux-nicot@cc-toulouse.fr) (B. Delavaux-Nicot), [nierengarten@unistra.fr](mailto:nierengarten@unistra.fr) (J.-F. Nierengarten), [nicola.armaroli@isof.cnr.it](mailto:nicola.armaroli@isof.cnr.it) (N. Armaroli).

The study of phenanthroline and its organic and inorganic derivatives has been always at the core of our research activity [2,9–14]. Recently, we have undertaken a research program targeting extended phenanthroline ligands to be used as tunable organic luminophores and/or chelating agents for transition metal complexes. For the latter compounds, we aim at preparing systems with extended absorption in the Vis region and long-lived excited states [15], which can be exploited as light harvesting units in artificial photosynthetic systems or solar cells [16,17].

In this paper, we present four Ru<sup>II</sup> complexes of general formula [Ru(PT)<sub>3</sub>]<sup>2+</sup>, [Ru(NT)<sub>3</sub>]<sup>2+</sup>, [Ru(PT)(bpy)<sub>2</sub>]<sup>2+</sup>, and [Ru(NT)(bpy)<sub>2</sub>]<sup>2+</sup>, where **PT** = 10,13-bis((triisopropylsilyl)ethynyl)dipyrido[3,2-*a*:2',3'-*c*]phenazine, **NT** = 10,15-bis((triisopropylsilyl)ethynyl)benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine and **bpy** = 2,2'-bipyridine. **PT** and **NT** are alkynyl derivatives [18] of dipyrido[3,2-*a*:2',3'-*c*]phenazine (**dppz**) and benzo[*i*]dipyrido[3,2-*a*:20,30-*c*]phenazine (**dppn**), respectively, two extended phenanthroline ligands that have been already utilized for the synthesis of Ru<sup>II</sup> complexes, to be typically used for establishing  $\pi$ -stacking interaction with DNA [19–25] and even carbon nanotubes [26]. Such complexes were found to exhibit low-lying electronic levels of both metal-to-ligand charge transfer (MLCT) and ligand-centered nature (LC) [27]. They are normally poor emitters, but literature luminescence data are scattered [22,23]. The purpose of this paper is (i) to illustrate the photophysical properties of Ru<sup>II</sup> complexes involving extended phenanthroline ligands with the extensive support of DFT and TD-DFT calculations; (ii) to provide exhaustive photophysical data for Ru<sup>II</sup> homoleptic complexes with such ligands, a relatively elusive topic in current literature; (iii) to evaluate the suitability of these complexes for applications related to solar energy conversion.

## 2. Experimental

### 2.1. Materials for synthesis and general methods

Chemicals were purchased as reagent grade and used without further purification. Absolute THF was obtained from Sigma Aldrich and was also used without further purification. Compounds PhTIPS [28], NQTIPS [29], PhenDione [30], and dichlorotetrakis(dimethyl sulfoxide) ruthenium(II) (RuDMSO<sub>4</sub>Cl<sub>2</sub>) [31] were prepared according to literature procedures. All reactions were performed in standard glassware under an inert argon atmosphere. Evaporation and concentration were done using a Vacuubrand Vacuum Pumping Unit PC 101 NT, drying in vacuo at 10<sup>-2</sup> Torr. Column chromatography: silica gel 60 (70–230 mesh, 0.063–0.200 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F<sub>254</sub> obtained from E. Merck, visualization was made by UV light. IR spectra (cm<sup>-1</sup>) were recorded on an ATI Mattson Genesis Series FTIR apparatus. NMR spectra were recorded on a Bruker Avance 300 spectrometer with solvent peaks as reference (H<sub>tips</sub>: triisopropylsilyl protons, H<sub>dppz</sub>: dipyridophenazine protons, H<sub>dppn</sub>: benzodipyridophenazine protons, H<sub>bpy</sub>: bipyridine protons). Mass spectra were obtained with an UltraflexTM matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) equipped with SCOUT™ High Resolution Optics, a X–Y multi-sample probe, and a gridless reflector. The instrument was used at a maximum accelerating potential of 25 kV in positive mode and was operated in reflector mode at 26 kV with a matrix suppression deflection (cut off) set to 500 *m/z*. A saturated solution of 1,8-dihydroxy-9,10-dihydroanthracen-9-one (dithranol, ALDRICH) in CH<sub>2</sub>Cl<sub>2</sub> was used as matrix. Elemental analyses were performed by the analytical service at the *Institut de Chimie* of the University of Strasbourg, France.

### 2.2. Synthesis of Ligands **PT** and **NT**

**PT**: A solution of **PhTIPS** (680 mg, 1.45 mmol) and **PhenDione** (290 mg, 1.38 mmol) in EtOH (15 mL) was heated at gentle reflux for 4 h. After cooling to rt, a yellow precipitate appeared and the flask was left in the fridge overnight. The solid was filtered, washed with a small quantity of cold EtOH and dried under vacuum to give **PT** (586 mg, 66%) as a bright yellow solid. IR:  $\nu = 2153$  (C≡C) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 1.29$  (m, 42H, H<sub>tips</sub>), 7.79 (dd, *J* = 5 Hz, 8 Hz, 2H, H<sub>dppz</sub>), 8.04 (s, 2H, H<sub>dppz</sub>), 9.32 (dd, *J* = 2 Hz, 5 Hz, 2H, H<sub>dppz</sub>), 9.77 ppm (dd, *J* = 2 Hz, 8 Hz, 2H, H<sub>dppz</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 11.7, 19.0, 100.6, 103.4, 124.2, 124.4, 127.7, 134.4, 134.6, 141.5, 142.7, 148.7, 153.0$  ppm. MALDI-TOF-MS: *m/z* = 643.3 ([M+H]<sup>+</sup>, calcd for C<sub>40</sub>H<sub>51</sub>N<sub>4</sub>Si<sub>2</sub>: 643.4). *Anal. Calc.* for C<sub>40</sub>H<sub>50</sub>N<sub>4</sub>Si<sub>2</sub>: C, 74.71; H, 7.84; N, 8.71. Found: C, 74.44; H, 7.44; N, 8.71%.

**NT**: A solution of **NQTIPS** (400 mg, 0.77 mmol) and **PhenDione** (162 mg, 0.77 mmol) in EtOH (15 mL) was heated at gentle reflux for 2 d. After cooling to rt, a red solid precipitated. The solvent was evaporated under reduced pressure to half volume and the flask was left in the fridge overnight. The solid was filtered, washed with a small quantity of cold EtOH and dried under vacuum to give **NT** (438 mg, 82%) as a bright red solid. IR:  $\nu = 2139$  (C≡C) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 1.35$  (m, 42H, H<sub>tips</sub>), 7.75 (m, 4H, H<sub>dppn</sub>), 8.82 (AA'BB', 2H, H<sub>dppn</sub>), 9.26 (dd, *J* = 2 Hz, 5 Hz, 2H, H<sub>dppn</sub>), 9.78 ppm (dd, *J* = 2 Hz, 8 Hz, 2H, H<sub>dppn</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 11.8, 19.1, 102.6, 107.8, 121.1, 124.3, 127.8, 128.0, 128.5, 134.6, 135.4, 140.2, 142.4, 149.2, 153.1$  ppm. MALDI-TOF-MS: *m/z* = 693.3 ([M+H]<sup>+</sup>, calcd for C<sub>44</sub>H<sub>53</sub>N<sub>4</sub>Si<sub>2</sub>: 693.4). *Anal. Calc.* for C<sub>44</sub>H<sub>52</sub>N<sub>4</sub>Si<sub>2</sub>: C, 76.25; H, 7.56; N, 8.08. Found: C, 75.98; H, 7.48; N, 8.02%.

### 2.3. Synthesis of heteroleptic complexes [Ru(PT)(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> and [Ru(NT)(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>

**[Ru(PT)(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>**: **Ru(bpy)<sub>2</sub>Cl<sub>2</sub>** (75 mg, 156  $\mu$ mol) was dissolved in a mixture of H<sub>2</sub>O (8 mL) and EtOH (8 mL) and **PT** (100 mg, 156  $\mu$ mol) was added in one portion. The solution was heated at gentle reflux for 24 h. After cooling to rt, the volatiles were removed under reduced pressure. The solid residue was dissolved in a minimum amount of DMF and the solution poured onto a semi-concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. The arising precipitate was filtered, washed with water and dried under vacuum. The crude was purified by flash column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 30:1 to 15:1) followed by gel permeation chromatography (Biorad, Biobeads SX-1, eluent CH<sub>2</sub>Cl<sub>2</sub>) to give **[Ru(PT)(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>** (128 mg, 61%) as orange-brown glassy solid. IR:  $\nu = 2157$  (C≡C) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 1.24$  (m, 42H, H<sub>tips</sub>), 7.33 (t, *J* = 6 Hz, 2H, H<sub>bpy</sub>), 7.54 (t, *J* = 6 Hz, 2H, H<sub>bpy</sub>), 7.72 (d, *J* = 5 Hz, 2H, H<sub>bpy</sub>), 7.89 (d, *J* = 5 Hz, 2H, H<sub>bpy</sub>), 7.97 (m, 4H, H<sub>bpy</sub>), 8.05 (t, *J* = 8 Hz, 2H, H<sub>bpy</sub>), 8.14 (s, 2H, H<sub>dppz</sub>), 8.27 (d, *J* = 5 Hz, 2H, H<sub>dppz</sub>), 8.45 (m, 4H, H<sub>dppz</sub>, H<sub>bpy</sub>), 9.75 ppm (d, *J* = 8 Hz, 2H, H<sub>dppz</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 11.5, 18.9, 102.0, 102.6, 124.58, 124.62, 128.1, 128.2, 128.6, 130.5, 134.3, 136.0, 138.5, 138.6, 139.7, 143.1, 150.2, 151.4, 152.0, 154.3, 156.7, 156.9$  ppm. MALDI-TOF-MS: *m/z* = 1201.4 ([M–PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>60</sub>H<sub>66</sub>F<sub>6</sub>N<sub>8</sub>PRuSi<sub>2</sub>: 1201.4), 1056.5 ([M–2PF<sub>6</sub>]<sup>+</sup>, calcd for C<sub>60</sub>H<sub>66</sub>N<sub>8</sub>RuSi<sub>2</sub>: 1056.4). *Anal. Calc.* for C<sub>60</sub>H<sub>66</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub>RuSi<sub>2</sub> ½ CH<sub>2</sub>Cl<sub>2</sub>: C, 52.32; H, 4.86; N, 8.07. Found: C, 52.32; H, 4.83; N, 8.04%.

**[Ru(NT)(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>**: **Ru(bpy)<sub>2</sub>Cl<sub>2</sub>** (84 mg, 173  $\mu$ mol) was dissolved in a mixture of H<sub>2</sub>O (5 mL) and EtOH (10 mL) and **NT** (120 mg, 173  $\mu$ mol) was added in one portion. The solution was heated at gentle reflux for 24 h. After cooling to rt, the volatiles were removed under reduced pressure. The solid residue was dissolved in a minimum amount of EtOH and the solution poured onto a semi-concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. The arising

Download English Version:

<https://daneshyari.com/en/article/1336446>

Download Persian Version:

<https://daneshyari.com/article/1336446>

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