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Anton S. Abel, Ilya S Zenkov, Alexei Averin, Andrey V Cheprakov, Alla Bessmertnykh-Lemeune, et al.. Tuning of emissive properties of Ru (II) complexes with amino-1,10-phenanthrolines by varying the position of the amino group in the heterocycle. *ChemPlusChem*, 2019, 84 (5), pp.498-503. 10.1002/cplu.201900206 . hal-02380660

HAL Id: hal-02380660

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Submitted on 26 Nov 2019

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Tuning of emissive properties of Ru (II) complexes with amino-1,10-phenanthrolines by varying the position of the amino group in the heterocycle

Anton S. Abel,^[a] Ilya S. Zenkov,^[a] Alexei D. Averin,^[a,b] Andrey V. Cheprakov,^[a] Alla G. Bessmertnykh-Lemeune,^[c] Boris S. Orlinson,^[d] and Irina P. Beletskaya^{*,[a,b]}

Abstract: Eight 1,10-phenanthrolines bearing one or two 2-(1-adamantyloxy)ethylamino substituents attached to different positions of the heterocyclic core were prepared according to S_NAr or palladium-catalyzed amination reactions. Their reaction with *cis*-Ru(bpy)₂Cl₂ (bpy = 2,2'-bipyridine) was investigated and Ru(bpy)₂(L)(PF₆)₂ (L = amino-substituted 1,10-phenanthroline) complexes were obtained in good yields. The electronic structure and emissive properties of these complexes are strongly dependent on the position of the amino substituent in the heterocycle. Emission bands of the complexes bearing 2- and 4-substituted 1,10-phenanthroline ligands are red-shifted (up to 56 nm) and less intense compared to that of the parent [Ru(phen)(bpy)₂](PF₆)₂ (phen=1,10-phenanthroline). In contrast, the introduction of the substituent in 3- or 5-position of 1,10-phenanthroline ring induces only small decrease of luminescence and the brightness of the complex with the 3-substituted ligand is comparable to that of the parent complex.

Design and synthesis of molecular optical sensors for analysis of environmentally and biologically relevant analytes in aqueous media have been attracting growing interest due to the rapid development of biological researches and the increase of societal problems related to the environmental pollution causing serious human deceases.^[1] The list of analytes that should be controlled in environmental and biological samples is ample and includes gaseous molecules, anions, toxic metal cations and small organic molecules. To achieve long-term goals in this multidisciplinary field a serious contradiction between a hydrophobic nature of the most of organic chromophores and

necessity to conduct the analyses in aqueous media should be overcome. Large aromatic molecules exhibit a tendency to aggregate in aqueous solutions. The aggregation strongly decreases their luminescence and can generate faults in electronic absorption analyses. From this point of view, luminescent complexes of some heavy metal (Re(I), Rh(I), Cu(I), Ru(II), Ir(III), Pt(II), Os(II)) with 2,2'-bipyridine and 1,10-phenanthroline ligands are of particular interest because they are highly emissive in aquatic media in part due to electrostatic repulsive interactions which prevent the aggregation of these charged species.^[2] These complexes may bind various biomolecules and are used as enzyme inhibitors, biomarkers and biosensors.^[3] Synthetic chemistry of 1,10-phenanthrolines is rich and provides various routes to fluorescent chemosensors and chemodosimeters.^[4] Varying structural features of the ligands and the complexes, such as the nature, the number and position of substituents in the phenanthroline ring, the number of the phenanthroline ligands at metal centers, the selectivity and sensitivity of sensing can be finely turned.^[5,6]

In this series of luminophores, Ru(II) complexes are widely studied because they have several specific features such as intensive absorption and emission in the visible region of electromagnetic spectrum, relatively long-living luminescence, large Stokes shifts, low cytotoxicity and high chemical, thermal and photostability.^[2a,7] These complexes have been widely explored as biomarkers^[8] but also have attracted growing interest as molecular probes for detection of small molecules and ions.^[2a] They are of particular interest for sensing different anions because the anion binding by such compounds are supported by additional electrostatic interactions with positively charged Ru(II)-bpy signalling unit.^[9] These complexes also display specific advantages for sensing gases (oxygen,^[10] nitric oxide,^[11] and carbon monoxide^[12]), metal cations^[13] and biologically relevant molecules such as methylglyoxal,^[14] cysteine and homocysteine.^[15] However, this field is still underdeveloped. Most of the reported chemosensors are based on very simple and may be not optimal receptor units because the chemical modification of Ru(II)-bpy complexes is much more complicated compared to that of classical organic luminophores. Moreover, photophysics of these derivatives is very complex^[16] and their sensing properties are difficult to predict and rationalize. The studies of model compounds and development of theoretical methods are needed to better understand the influence of structural parameters on spectroscopic properties of these compounds.

As a part of our ongoing research on the catalytic amination reaction of heteroaromatic halides, we recently focused our interest on the molecular engineering of water soluble detectors in which polyamino-based receptor groups directly attached to

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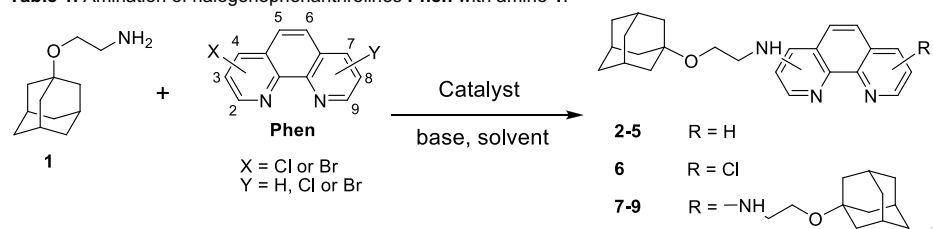
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Table 1. Amination of halogenophenanthrolines **Phen** with amine **1**.

Entry	Phen		1 /equiv.	Catalyst (mol %)	Base (equiv.)	Solvent	T /°C	t/h	Product (yield/%)
	X	Y							
1	2-Cl	H	1	-	K ₂ CO ₃ (4)	DMF	140	24	2 (50)
2	4-Cl	H	1	-	K ₂ CO ₃ (4)	DMF	140	24	3 (37)
3	4-Cl	H	1	Pd(dba) ₂ /BINAP ^[a] (4/4.5)	Cs ₂ CO ₃ (2)	Dioxane	100	8	3 (49)
4	3-Br	H	1	Pd(dba) ₂ /BINAP (8/9)	<i>t</i> -BuONa(1.5)	Dioxane	100	8	4 (20)
5	3-Br	H	1	Pd(dba) ₂ /Josiphos ^[b] (8/9)	<i>t</i> -BuONa(1.5)	Dioxane	100	8	4 (60)
6	5-Br	H	1	Pd(dba) ₂ /BINAP (8/9)	<i>t</i> -BuONa(1.5)	Dioxane	100	8	5 (30)
7	5-Br	H	1	Pd(dba) ₂ /Josiphos (8/9)	<i>t</i> -BuONa(1.5)	Dioxane	100	8	5 (63)
8	2-Cl	9-Cl	4	-	K ₂ CO ₃ (8)	DMF	140	24	6 (32)
									+ 7 (29)
9 ^[c]	2-Cl	9-Cl	4	-	K ₂ CO ₃ (8)	DMF	155 ^[c]	30	7 (47)
10	4-Br	7-Br	4	Pd(dba) ₂ /BINAP (8/9)	<i>t</i> -BuONa(3)	Dioxane	100	24	8 (37)
11	4-Br	7-Br	4	Pd(dba) ₂ /BINAP (8/9)	Cs ₂ CO ₃ (4)	Dioxane	100	24	8 (58)
12	3-Br	8-Br	4	Pd(dba) ₂ /Josiphos (8/9)	<i>t</i> -BuONa(3)	Dioxane	100	24	9 (50)

[a] BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. [b] Josiphos = (R)-1-[(SP)-2-(Diphenylphosphino)-ferrocenyl]ethyl-di-*tert*-butylphosphine. [c] The reaction was conducted in Microwave reactor Monowave 300 (Anton Paar).

aromatic signaling units that allow better management of optical responses of the chemosensors.^[17] To increase the scope of our synthetic methodology to luminescent Ru(II)-bpy complexes, in this article we report the synthetic procedures to prepare isomeric amino-1,10-phenanthrolines and their Ru(II)-bpy complexes. All compounds obtained were investigated by spectroscopic methods to assess how the number and position of amino groups affect the photophysical properties of the luminescent complexes. This data is of interest for the synthesis of biomarkers or multimodal molecules composed of signaling and receptor units. 2-(1-Adamantyloxy)ethylamine **1** was chosen as a model amine in these studies because adamantyl derivatives are known by their good solubility in most of organic solvents. Moreover, this specific substituent is of interest for biochemistry related to DNA studies.^[18]

The most convenient synthetic pathway to isomeric amino-1,10-phenanthrolines seems to be the substitution reaction (Table 1) because all the starting halogenophenanthrolines (Phen) can be easily prepared in good yields according to the literature procedures.^[19]

The substitution of the halogen atom at 2 and 4 positions (see labelling scheme in Table 1) of electron-deficient 1,10-phenanthrolines can be achieved under catalyst-free conditions.^[20] In accordance with this data, 2-chlorophenanthroline reacted with equimolar amount of amine **1** in DMF in the presence of K₂CO₃ at 140 °C in 24 h affording the target product **2** in 50% yield (Table 1, entry 1). 4-Chloro-1,10-phenanthroline has been also completely consumed under these

conditions but amine **3** was isolated in only 37% yield (entry 2). To increase the product yield, the Pd-catalyzed amination reaction which was widely studied from synthetic and mechanistic aspects during last 25 years was applied.^[21] It was recognized that the catalytic cross-coupling reactions are difficult to perform in the case of *N*-chelators and heterocycles which readily coordinate transition metal ions removing them from the catalytic cycle.^[22] Nevertheless, the yield of the product **3** slightly increased (49%) when 4-chloro-1,10-phenanthroline was reacted with amine **1** in the presence of the Pd(dba)₂/BINAP and caesium carbonate in refluxing dioxane compared to that of the catalyst-free reaction (entry 3). This indicated that competing coordination of *N*-chelate to the palladium centre does not significantly influence on the reaction course.

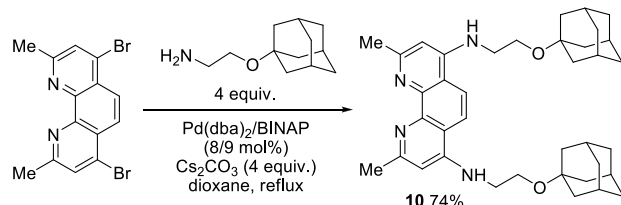
The amination of less reactive 3-bromo- and 5-bromophenanthrolines proceeds only in the presence of palladium catalyst. When the reactions were performed employing Pd(dba)₂/BINAP and sodium *tert*-butylate, the yields of aminophenanthrolines **4** and **5** were as low as 20% and 30%, respectively (entries 4 and 6). A competing hydrodebromination reaction^[22] also occurs under these conditions leading to 1,10-phenanthroline. The screening of catalysts revealed that Pd(dba)₂/Josiphos is the most efficient in both cases (entries 5 and 7). Using this catalytic system, the product **4** and **5** were obtained in 60 and 63% yields, respectively.

Diamino-substituted 1,10-phenanthrolines were prepared by the amination of dihalogeno-phenanthrolines using 4 equiv. of amine **1** according to the procedures developed for analogous mono-substituted derivatives. 2,9-Dichloro-1,10-phenanthroline afforded the target product **7** under the catalyst-free conditions (entry 8) as 2-chloro-1,10-phenanthroline (entry 1). However, the product yield decreased from 50% up to 29% due to a low reactivity of the monoaminated intermediate compound. The mono-substituted compound **6** was also isolated in the reaction in 32% yield. A complete conversion of **6** was achieved only when the reaction of 2,9-dichloro-1,10-phenanthroline with amine **1** was carried out in microwave reactor at 155 °C for 30 h. Under these conditions the product **7** was isolated in 47% yield (entry 9).

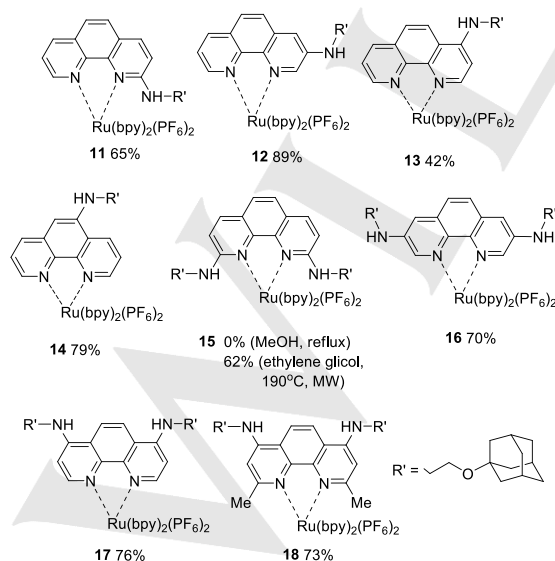
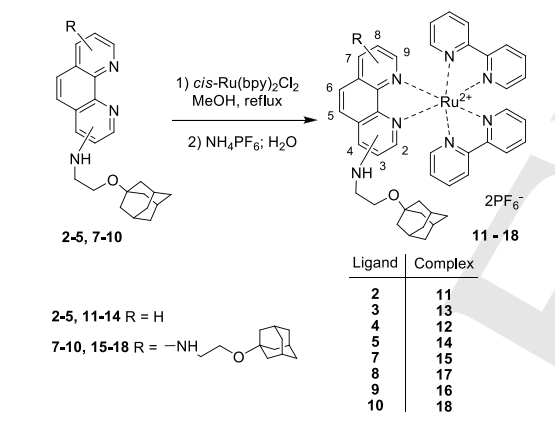
The palladium catalyst is needed for the substitution of the halogen atoms in 4,7- and 3,8-dibromophenanthrolines like in 3-bromo- and 5-bromophenanthrolines. The reaction of a more reactive 4,7-isomer was performed using Pd(dba)₂/BINAP as a catalyst (entries 10 and 11). Interestingly, the nature of the base is a key parameter influencing the product yield under these conditions. The higher yield of the diamine **8** (58%) was

obtained when sodium *tert*-butylate was replaced by a less nucleophilic caesium carboxylate to suppress a competing substitution of halogen by *tert*-butylate anion. The amination of less reactive 3,8-dibromo-1,10-phenanthroline by amine **1** smoothly proceeds under conditions developed for 3-bromophenanthroline (Pd(dba)₂/Josiphos, *t*-BuONa) and the product **9** was isolated in 50% yield (entry 12).

Finally, compound **10**, which is 2,9-dimethyl-substituted analogue of compound **8**, was obtained reacting 4,7-dibromo-2,9-dimethylphenanthroline with amine **1** (Scheme 1). The steric hindrances at the 1,10-phenanthroline *N,N*-chelating site has positive effect on the catalytic reaction. When the amination was conducted as the reaction of 4,7-dibromophenanthroline (Pd(dba)₂/BINAP, Cs₂CO₃, entry 11) the product yield increased up to 74%.



Scheme 1.



Scheme 2. Synthesis of Ru(II) complexes.

Thus, the amino group can be installed in all positions of heterocycle using substitution reactions. Assistance of palladium catalysts is often required to prepare the products in acceptable yields.

The substituted 1,10-phenanthrolines **2–5** and **7–10** were involved in the synthesis of [Ru(bpy)₂(L)](PF₆)₂ complexes (Scheme 2). For this purpose, the ligand and *cis*-Ru(bpy)₂Cl₂ were refluxed in methanol following by precipitation of the target complex by the addition of saturated aqueous solution of NH₄PF₆. The complexes were isolated in good yields (42–89%) in most of the studied reactions. However, the bulky ligand **7** forms a target complex **15** in 62% yield only under more harsh conditions (ethylene glycol, 190 °C, microwave reactor).

Electronic absorption and luminescence spectra of complexes **11–18** in acetonitrile solution saturated with argon at room temperature are shown on Figure 1 and the most important results are summarized in Table 2 where the data for the parent complex [Ru(bpy)₂(phen)](PF₆)₂ (**Ru(Phen)**) are also reported for the comparison.

The electronic absorption spectra of all compounds under investigation are typical for Ru–bpy complexes.^[8f, 23] It is well known that the intensive bands at 250–300 nm in their spectra correspond to π–π* ligand-ligand charge transfer transitions. The complexes also display characteristic wide absorption bands in the visible region which are attributed to the overlapping of

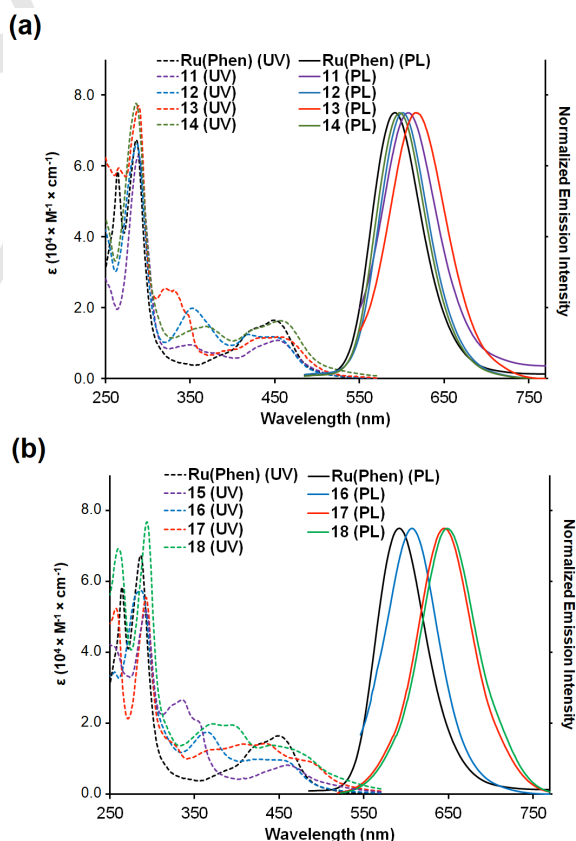


Figure 1. Normalized UV-vis (UV) and luminescence (PL, $\lambda_{\text{ex}} = 450$ nm) spectra of the complexes **11–14** and **Ru(Phen)** (a) and **15–17** and **Ru(Phen)** in acetonitrile saturated with argon at room temperature.

Table 2 Photophysical data for complexes **11–18** and **Ru(Phen)** obtained in acetonitrile saturated with Ar at room temperature.

Complex	$\lambda_{\text{abs}}^{[a]}$; nm	$\lg(\epsilon^{[b]})$	$\lambda_{\text{em}}^{[c]}$; nm	$\Phi_{\text{F}}^{[c]}$; %
Ru(Phen)	264	4.75(6)	593	9.1(6)
	286	4.81(2)		
	420	4.16(2)		
	448	4.25(1)		
11	289	4.76(1)	609	0.5(2)
	348	3.85(6)		
	453	3.95(4)		
12	289	4.83(4)	602	7.3(7)
	353	4.32(2)		
	419	4.11(3)		
	446	4.08(3)		
13	266	4.77(3)	622	1.1(1)
	289	4.86(5)		
	320	4.04(2)		
	330	4.03(3)		
	430–450	3.97(2)		
14	285	4.78(7)	600	6.2(6)
	369	4.15(6)		
	455	4.18(3)		
15	292	4.72(5)	– ^[d]	<0.01
	336	4.46(1)		
	460	3.96(1)		
16	286	4.76(1)	609	4.4(4)
	365	4.28(2)		
	425	4.04(2)		
	456	4.02(2)		
17	257	4.66(7)	646	0.3(1)
	293	4.72(7)		
	365	4.08(4)		
	408	4.15(3)		
	435	4.18(3)		
18	260	4.81(3)	649	0.2(1)
	294	4.89(1)		
	371	4.32(4)		
	397	4.32(4)		
	443	4.18(6)		

[a] Wavelength of the lowest energy absorption band. [b] ϵ ($\text{M}^{-1} \text{cm}^{-1}$) [c] $\lambda_{\text{ex}} = 450$ nm. The quantum yield was calculated with respect to $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ in acetonitrile ($\Phi_{\text{F}} = 9.4(4)\%$). [d] The complex was non-emissive.

the spin-allowed metal-ligand charge transfer (MLCT) and interligand bpy/Phen-based charge transfer (LLCT) transitions.^[9d] Because of their heteroleptic nature, **11–18** and **Ru(Phen)** are expected to exhibit two types of MLCT transitions. As a consequence, the shape of absorption curves in the visible region for these complexes is more complicated compared to that of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and additional absorption maxima appear at 300–350 nm region presumably due to ligand–ligand bpy/Phen-based $\pi\text{-}\pi^*$ transitions^[9d] involving aminated phenanthroline ligands.

The luminescence band is mostly due to MLCT transitions which involve the lowest energy spin-forbidden excited states.^[23] The shape of this band is similar for all complexes under

investigation but the introduction of amino substituent at the heterocycle induces a red-shift of the band which is the largest for complexes **17** and **18** bearing diaminated Phen ligands (53 and 57 nm, respectively). These shifts are likely to result from the electronic effects of amino substituents at the phenanthroline ring because they are larger for 2- and 4- substituted derivatives in both series of compounds (mono- and diaminated derivatives) (**11**, **13** and **17**, **18**, respectively). Moreover, the attachment of the second amino symmetrically located substituent leads to red shift of the luminescence maximum (24 nm) and the emission band of complex **17** appears at 646 nm.

Surprisingly, luminescence quantum yield (Φ_{F}) of studied complexes is also strongly dependent on the position of the amino substituents in Phen ligand. The complexes of the ligands possessing any substituent in positions 2 and 9 (**11**, **15** and **18**) showed typical low quantum yield ($\Phi_{\text{F}} = 0\text{--}0.5\%$) presumably due to the distortion of octahedral environment of ruthenium atom or their particular electronic structure.^[6] The emission was also rather weak for the compounds **13** and **17** bearing the 2-(1-adamantyloxy)ethylamino substituent at 4- and 7-positions ($\Phi_{\text{F}} = 0.3\text{--}1.1\%$). In contrast, the luminescence quantum yield of other compounds was in the range of 4.4–7.3%. These trends are in accordance with those observed for the series of $\text{Ru}(\text{II})$ complexes with 1,10-phenanthrolines bearing acetylene substituents.^[6a]

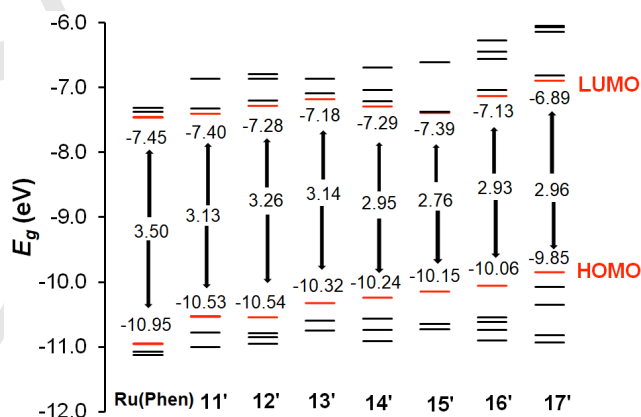


Figure 2. The schematic representation of the calculated energy levels in **Ru(Phen)** and complexes **11'–17'**.

To gain deeper insight into the structure of studied complexes and its electronic properties, basic DFT studies were performed. The structure of complexes was modelled using DFT calculations with Firefly quantum chemistry package,^[24] which is partially based on the GAMESS (US)^[25] source code. The calculations were performed using B3LYP functional with STO 6-31G(d,p) basis set for all elements except Ru, for which we have used the Stuttgart valence basis set and pseudopotential.^[26] 1-Adamantyloxy fragment was replaced by a smaller methoxy group, the corresponding complexes are labeled as **11'–17'**. The

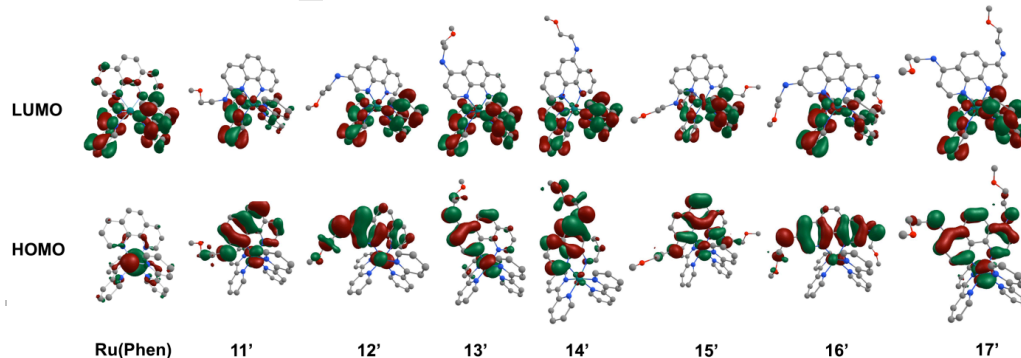


Figure 3. Isodensity plot of the HOMO and LUMO orbitals for complexes **11'–17'**.

optimized geometries of model complexes **11'**–**17'** are depicted in Figures S2–S8 and the selected bond lengths and angles are summarized in Table S9. The metal atom has a distorted octahedral geometry and bonded to three chelate ligands. The key structural parameters of the studied complexes change only slightly when one or two 2-(1-methoxy)ethylamino substituents appears at different positions of the phenanthroline heterocycle. The calculated Ru–N_{phen} and Ru–N_{bpy} bond lengths are rather similar in all compounds (2.10–2.11 Å) except complexes **11'** and **15'** bearing bulky Phen ligands with 2-(1-methoxy)ethylamino groups located at the nearest to chelating site position (2 and 9). In these complexes, Ru–N_{phen} bond lengths are increased to 2.18 Å.

The diagram showing the energy levels in studied complexes is depicted in Figure 2. The frontier HOMO and LUMO molecular orbitals are presented in Figure 3. In addition, isodensity plots of HOMO_{0–3} and LUMO_{0–3} molecular orbitals of **11'**–**17'** and **Ru(Phen)** are given in Tables S2–S8. Comparing HOMO_{0–3} and LUMO_{0–3} of **11'**–**17'** to those of parent complex **Ru(Phen)**, one remarkable difference can be noted. All HOMO_{0–3} of **Ru(Phen)** are localized mainly on the Ru atom while HOMO₀ of **11'**–**17'** are constructed mainly from π orbitals of phenanthroline ligand. Accordingly, the energies of metal-ligand charge transfer (MLCT) and interligand bpy/Phen-based charge transfer (LLCT) transitions should be significantly different for the aminated complexes **11'**–**17'** compared to the parent compound **Ru(Phen)**. Correct modeling of excited states for Ru complexes of this type requires sophisticated methods beyond the popular TD-DFT approach, and therefore are beyond of scope of our work.

The energy gaps between HOMO and LUMO for **11'**–**17'** and **Ru(Phen)** are shown in Figure 2. The values obtained for the aminated complexes are smaller than that of parent **Ru(Phen)** due to electronic effects of the amino substituent. In the series of mono-substituted derivatives **11'**–**14'**, the smallest value is observed for 5-amino derivative **14'**. The introduction of the second amino group decreases the energy gap.

In conclusion, both palladium-catalysed and catalyst-free conditions were explored for developing a concise approach to 1,10-phenanthrolines bearing one or two amino substituents at the heterocyclic core. Catalyst free-amination appeared to be convenient for the synthesis of 2-amino- and 2,9-diamino-1,10-phenanthrolines. To introduce amino groups at less reactive 3, 4 and 5 positions, the palladium catalysis is needed. After optimization of the reaction conditions all isomeric amino and symmetrically located diamino derivatives were synthesized in acceptable yields. These compounds smoothly react with *cis*-Ru(bpy)₂Cl₂ affording Ru(bpy)₂(L)(PF₆)₂ complexes in good yields. The positions of absorption and emission maxima, luminescence quantum yield and brightness of the complexes are strongly dependent on the location of the amino substituent in the heterocyclic core. The largest red shifts of emission band (up to 56 nm) compared to parent [Ru(phen)(bpy)₂](PF₆)₂ are observed for the complexes bearing 4- and 7-substituted 1,10-phenanthroline ligands. Ru(II) complexes with 2- and 4-aminophenanthrolines exhibit very weak emission while those with 3- or 3,8-substituted ligands are emissive and the brightness of the first is comparable to that of the parent [Ru(phen)(bpy)₂](PF₆)₂. These features should be taken into

consideration in the development of chemosensors based on Ru–bpy signaling group.

Acknowledgements

This work was supported by Russian Foundation for Basic Research (grant no. 18-33-00279). This work was carried out in the frames of the International Associated French-Russian Laboratory of Macrocyclic systems and Related Materials (LIA LAMREM) of the Centre National de la Recherche Scientifique (CNRS) and the Russian Academy of Sciences (RAS). Dr. Alla Bessmertnykh-Lemeune thanks CNRS for financial support. We acknowledge A.D. Harlamova for providing [Ru(Phen)(bpy)₂](PF₆)₂ complex.

Keywords: 1,10-phenanthroline • ruthenium complexes • luminescence • amination • catalysis

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