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Impact of Alkyne Functionalization on Photophysical and Electrochemical Properties of 1,10-Phenanthrolines and Their Ru(II) Complexes

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Abstract: Three differently substituted alkyne phenanthrolines have been synthesized in high yields and the molecular structure in the solid state is confirmed by X-ray diffraction. Synthesis of the corresponding ruthenium polypyridine complexes is feasible without metal carbonyl formation. The photophysical and electrochemical properties of the compounds reveal that substitution of the phenanthroline in the 5-position leads to a pronounced effect in the absorption properties of the uncomplexed ligands as well as a significant shift of the redox potentials of the complexes. However, no effect on the energy of the MLCT transition and emission could be detected. This rather contradictory behavior is further analyzed by TD-DFT calculations.

Introduction

The investigation of the interplay between the substitution pattern of a molecule and the impact on the resulting photophysical and electrochemical characteristics is an essential topic in chemical sciences. In this respect, 1,10-phenanthroline (phen) is an important bidentate ligand for many transition metal complexes, which has served as a potent model compound due to the accessibility of differently functionalized derivatives and, probably most importantly, the possibility to investigate the impact of functionalization on the corresponding characteristics of the metal complexes.^[1]

In this context, 5- or 5,6-substituted 1,10-phenanthrolines have been used for designing supramolecular entities for various applications such as artificial photosynthetic systems,^[2] photodynamic therapy^[3] or DNA-binding.^[4] The development of complex molecular compounds with regard to their stability and function require sophisticated synthetic strategies in order to build up functional multicomponent systems. Ideally, the integration of the components should be accessible under mild conditions and allow for follow-up synthetic manipulations at the integrated system stage.^[5]

In this regard, alkynes serve as highly attractive functionalities for various transformations such as for CLICK reactions, which can be used for further manipulations without placing chemical strain on the architecture upon integration. Several reports have shown

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that this approach is highly rewarding as complex molecular ensembles could be efficiently generated. $^{\rm [6,7]}$

However, it was shown that alkyne functionalities at similar architectures are normally part of the π and π^* orbital set which could be involved in the formation of the ¹MLCT state or the stabilization of the long lived ³MLCT state.^[8] Therefore, significant changes in the UV-vis and emission properties upon transformation of the alkyne cannot be excluded.^[9] Synthetic access to such alkyne functionalized ruthenium polypyridine complexes is synthetically very challenging as the formation of significant amounts of side products may lead to a significant loss of the desired pure product.^[10]

It is therefore crucial to develop robust synthetic methods to access ruthenium complexes with alkyne substitution patterns and understand their photophysical properties in detail.

Several phenanthroline based complexes exhibiting pendant alkyne functionalities are already known in literature.^[2,3,8,11–22] In this study, we focused on establishing different synthetic routes towards the ruthenium complexes **C1** - **C3**, which contain different alkyne substituents at the 5-position of 1,10-phenanthrolines, as synthetic access to 5-bromo-phenanthroline is the most facile up to date. Detailed photophysical and electrochemical properties are presented and compared to the unsubstituted Ru(II) complex **C0** with 1,10-phenanthroline (phen) ligand. The molecular structure of the ligand **L1** along with the corresponding complex **C1** in the solid state have been further analyzed. The experimental results are accompanied by TD-DFT (timedependent density functional theory) calculations in order to analyze similarities of the absorption properties of the complexes with the corresponding ligands in detail.

Results and Discussion

Synthesis and Structural Characterization

The synthesis of alkyne substituted phenanthrolines was performed according to literature by submitting 5-bromo-1,10phenanthroline (5Br-phen) to standard Sonogashira-Hagihara reaction conditions.^[23] Usually, molecules bearing metal binding sites tend to coordinate the catalysts such as copper during the cross-coupling reactions. A common way to eliminate the complexed copper from the phenanthroline moiety is the use of aqueous KCN solutions.^[24] Surprisingly, submitting the reaction product to an aqueous KCN solution led to partial deprotection of the trimethylsilyl (TMS) group, when the solution was sonicated. Heating the reaction mixture in sonication bath led even to full deprotection of the TMS group resulting in 5-ethinyl-1,10-phenanthroline **L1** as the product. In contrast, tri-*iso*-propylsilyl (TIPS) groups showed similar yields in synthesis, provided higher

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Scheme 1. Overview of the different reaction pathways to the alkyne substituted complexes C1-C3 (L = ,4'-di-tert-butyl-2,2'-bipyridine (tbbpy)).

stabilities and were not cleaved off during the decomplexation process.

In order to obtain access to the TMS protected ruthenium complex Sonogashira-Hagihara reaction was performed directly on the respective complex [(tbbpy)₂Ru(5Br-Phen)]²⁺ CO, as well. Using identical conditions as for the free ligands, comparable yields of approximately 70 % were obtained. Protodesilylation of C2 (after complexation of L2 with Ru(tbbpy)₂Cl₂ and C3 were performed using tetrabutylammonium fluoride (C2) and K_2CO_3 (C3), respectively, while the presence of wet MeOH was necessary in both cases. Comparison of the yields of the three routes towards target complex C1 gave no significant differences, although Sonogashira coupling reaction at the already complexed species prevents tedious purification steps. An alternative procedure in order to circumvent the challenge of removing copper impurities is the use of copper-free coupling synthesis, [3,25,26] although more reactive iodine functionalized phenanthrolines might be necessary. After complexation of L1 to form C1, surprisingly no evidence for Ru-CO formation could be found, although formation of this species were observed in the past with the similar substituted 4-ethynyl-2,2'-bipyridine complex.^[10]

All ligands and complexes were characterized by ¹H and ¹³C NMR spectroscopy as well as high resolution mass spectrometry. Additionally, all three complexes were characterized by H,H-COSY (see Supporting Information, Fig. S7, S10, S13). Evaporation of acetone/water solutions of L1 provided crystals suitable for X-ray diffraction. The solid state structure of ligand L1 (Fig. 1, left, CCDC 1866244) contains phenanthroline, together with two molecules of water per ligand, forming a layered hydrogen bonding network (Fig. 1, right). Herein, the alkynyl substituted phenanthrolines form two rows of stacked aromatic molecules, bridged by two water molecules alternatively oriented to one of the two phenanthroline piles at the NN-coordination sphere. Comparison of L1 with crystals of L2 obtained by slow evaporation of a hexane/acetone solution of L2 (solid state structure see Supporting Information, Fig. S15, CCDC 1866245) revealed that L2 forms no short contacts between the molecules.

Additionally, the alkyne bond in **L2** between the carbon atoms C13 and C14 is slightly elongated from 1.187(2) Å to 1.206(2) Å compared to **L1**.



Fig. 1. Solid state structure of **L1** (left). Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms were omitted for clarity. Right: Packing behavior of **L1** in the solid state. Here, most of the hydrogen atoms were omitted for clarity (thermal ellipsoids are drawn at the 50% probability level).

Crystallization of **C1** (CCDC 1866243) from an acetone-water mixture provided crystals suitable for X-ray diffraction, as well; a procedure that allowed for purification of the compound on a preparative scale. The complex **C1** exhibits an octahedral coordination environment (Fig. 2) with expected N-Ru-N angles of 78.22° and 79.05° for the two 4,4'-di-*tert*-butyl-2,2'-bipyridine (tbbpy) ligands and 79.79° for the alkynylated phenanthroline ligand **L1**. Crystal structures of similar coordination compounds have already been published using 5,6-dialkynylated 1,10phenenthrolines featuring comparable alkyne C-C distances of 1.203(9) Å in an Ir-based system^[27] or 1.189(6) Å using Zn as central metal.^[28] This is in accordance to the alkyne C-C distance of **C1** with 1.17(4) Å.

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Fig. 2. Molecular structure of C1 in the solid state (hydrogen atoms and solvent molecules were omitted for clarity, thermal ellipsoids are drawn at the 50% probability level).

Electrochemical Properties

The electrochemical properties of complexes C1, C2 and C3 in solutions of acetonitrile were investigated by cyclic voltammetry (Fig. 3, Table 1). Literature known analyses of similar compounds report two irreversible redox processes in the cathodic region,^[3] while others measured only one reduction process.^[12] In our hands, the cyclic voltammograms of all complexes show three reduction processes in the cathodic region, and one oxidation in the anodic area. The electrochemical processes occur for all complexes at almost identical potentials. In the cathodic region, the first reduction wave is observed at -1.63 V (C1 and C3) and -1.66 V (C2), respectively, which can be assigned to the reduction of the phenanthroline moieties within each molecule. Remarkably, the reduction potentials of the phenanthroline moiety of C1-C3 are influenced by the alkyne units. Compared to the unsubstituted C0 as well as the bromo substituted [(tbbpy)2Ru(5-Br-phen)]²⁺ an anodic shift of almost 120-150 mV is observed for complexes C1-C3. Interestingly, this first reduction process loses reversibility if potentials lower than -2.1 V are applied (compare second CV of C1, Fig. 3 grey). In case of the second reduction process, reversible waves are observed at around -1.96 V which can be attributed to the reduction of one bipyridine moiety. A second redox wave due to the reduction of another bipyridine moiety is observed at potentials around -2.21 V while only C2 shows a fully reversible redox process. In case of C1 and C3 the process is quasi reversible. Additionally, functionalization at the 5-position of the phenanthroline unit seems to affect the oxidation potential of the Ru center. Here, an anodic shift of 30-50 mV is observed for alkyne containing complexes C1-C3 and [(tbbpy)₂Ru(5Br-phen)]²⁺ compared to the unsubstituted phen ligand in CO.

Table 1. Cyclic voltammetry data of **C1**, **C2** and **C3**. $E_{1/2red}$ = half-wave potential of the redox process. E_{0red}/E_{0ox} = reduction or oxidation potential of the redox process.

	E _{1/2} (LL) ³	E _{1/2} (LL) ²	E _{1/2} (LL) ¹	E _{1/2} (Ru ^{2+/3+})
	/V	/V	IN	N N
C0 ^[29]	-2.26	-1.99	-1.78	0.79
C1	-2.21	-1.95	-1.63	0.84
C2	-2.23	-1.98	-1.66	0.82
C3	-2.22	-1.96	-1.63	0.83
[(tbbpy) ₂ Ru (5Br- phen)] ^{2+[29]}	-2.23	-1.98	-1.78	0.83



Fig. 3. Cyclic voltammograms of separate 1 mM MeCN solutions of **C1** (black, grey for CVs scanned to less negative voltages), **C2** (blue), and **C3** (red) at room temperature with "Bu₄NPF₆ as supporting electrolyte (0.1 M). Ag/AgCl is used as reference electrode, Pt wire as the counter electrode and glassy carbon as the working electrode. All data referenced against Fc⁺/Fc; scan rate = 100 mV s⁻¹. For CVs to less negative voltages compare Fig. S28.

Photophysical Properties

The absorption and emission spectra of L1 and L2 as well as C1-C3 were measured at room temperature in dichloromethane and acetonitrile (Fig. 4, Table 2, Fig. S17, S18) The absorption of 1,10phenanthroline possesses an intensive band at 268 nm, which can be assigned to typical π - π * transitions as supported by TD-DFT calculations (see Supporting Information, Fig. S21) and known from several studies.^[1] This absorption feature is slightly red-shifted in case of L1 and L2, respectively. Additionally, the introduction of the ethynyl group introduces two more absorption bands at 305 and 318 nm (L1) and 297, 309 for the TIPSprotected ligand L2, respectively. This is due to the extension of the π -system by the ethynyl group, which is considerably involved in the π - π * transitions (compare density plots in Supporting Information, Fig. S22). This shift is more pronounced in L2 compared to L1 due to the electron donating nature of the TIPS group.

The absorption spectra of the complexes (Fig. 4) feature strong absorption bands in the UV region at around 280 nm, with distinct shoulders at around 320 nm. These shoulders are, similar to the bands obtained for the sole ligands L1 and L2, more pronounced for the TMS (C3) and TIPS (C2) protected complexes compared to C1. The reason is again the involvement of the alkynyl group

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evident from the contributed orbital LUMO+1 (Fig. S26, Table S5). This behavior is in agreement with the higher reduction potentials in electrochemical measurements for the complexes **C1-C3** compared to the parent **C0** complex.

Surprisingly, the metal-to-ligand charge transfer (MLCT) transitions of the ruthenium complexes at around 455 nm remain unaffected upon introduction of 5-ethynyl substituents. Even highly π -delocalized substituents at 5-position of phenanthrolines like pyrenyl-ethynyl^[3] and phenyl-ethynyl^[8] as well as gold-ethynyl substituted ruthenium complexes^[19] showed no major influence on the photophysical properties of phenanthrolines compared to unsubstituted counterparts. This is in contrast to substitution in 4-position of phenanthroline which resulted in broadened, red-shifted MLCT absorption properties and redshifted emission maximum by 40 nm.^[8]

 Table 2. Photophysical data of complexes and ligands compared to the unsubstituted phen analogues in dichloromethane (DCM) and acetonitrile (MeCN). The emission lifetimes were obtained under deaerated conditions (Fig. S29).

	solvent	λ _{max,abs} / nm	$\lambda_{max, em} / nm$	τ/μs
phen	DCM	268	360	
L1	DCM	271, 297, 309	368	
L2	DCM	274, 305, 318	374	
C0	MeCN ^[30]	265 (53), 287 (63), 454 (16)	610	1.38
	DCM ^[29]	267 (64), 288 (69), 455 (19)	602	
C1	MeCN	275 (66), 286 (63), 452 (17)	625	2.12
	DCM	276 (71), 287 (66), 455 (17)	614	
C2	MeCN	277 (79), 286 (71), 453 (18)	624	1.97
	DCM	280 (79), 286 (71),456 (17)	611	
C3	MeCN	278 (83), 287 (73), 453 (18)	624	2.33
	DCM	281 (87), 287 (80), 456 (19)	611	



Fig. 4. Absorption spectra (top) of the ligands (dotted) phen (green), L1 (black), L2 (blue) and the complexes (solid) C1 (black), C2 (blue), and C3 (red) as well as the emission spectra (bottom) of complexes C1 (black), C2 (blue), and C3 (red) in aerated acetonitrile.

Detailed investigations with TD-DFT methods of these very surprising findings revealed for complex **C1** that the MLCT is mainly localized on the bipyridine ligand as well as the bipyridine part of the phenanthroline moiety, while the ethynyl group itself is not involved. The LUMO and LUMO+2 orbitals are located at the core of the phenanthroline ligand (Fig. S26). Accordingly, the contribution of LUMO+1 to the transitions in the visible region is negligible (Fig. S27), and the experimental (Fig. 4) and calculated (Fig. 5) absorption spectra are nearly unaffected despite the substitution in **C1-C3**.

Additionally, the emission from a triplet excited state appears for **C1-C3** at 624 nm in acetonitrile and no difference in the shapes are detectable. With about 2 μ s, the lifetime of the substituted complexes **C1-C3** are increased compared to **C0** or [Ru(tbbp)₃]^{2+,[31]} Subsequently, further investigation with ultrafast techniques and TD-DFT calculations of the triplet excited states should be subject of future work.



Fig. 5. Calculated absorption spectra of 1,10-phenanthroline (black, dashed) and **L1** (blue, solid) resulting from the deconvolution of the transitions above 240 nm. Compare with Table S3. The experimental absorption spectrum of **L1** in acetonitrile is depicted in black dotted for comparison.

Conclusions

Three novel Ru(II) complexes containing 5-ethynyl substituted phenanthrolines were made accessible using different synthetic strategies. As a potent building block for further functionalization, the complex [(tbbpy)₂Ru(5-ethynyl-1,10-phenanthroline)]²⁺ C1 and the alkynyl substituted derivatives C2 and C3 were used for detailed electrochemical and photophysical investigations. Cyclic voltammetry revealed that the first reduction of these complexes can be assigned to the reduction of the phenanthroline moiety, where the substitution at the 5-position caused an anodic shift of 150 mV compared to the non-substituted counterparts.

Photophysical characterizations of the ligands and metal complexes yielded very surprising results. Whereas a significant impact of the alkynyl substitution on UV-vis properties of the ligands were observed, no such effect could be found for the

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metal-to-ligand charge transfer transitions. This is due to the location of the π^* orbitals on the phenanthroline moiety revealing no or only weak contribution of the alkynyl group as underlined by TD-DFT calculations. Figure 6 summarizes these findings schematically.



Fig. 6. The red marked part of the structure indicates the location of the π^* -orbitals, which are involved concerning the MLCT transitions (R₁ being *tert*-butyl groups).

The emission properties of the substituted ruthenium complexes are similar within individual molecules with a remarkably long lifetime of $2 \mu s$.

The series of **C1-C3** present therefore close to ideal building blocks for functionalized molecular assemblies. On the one hand it possible to tune the chemical reactivity for appropriate choice of the protecting group. Furthermore, the terminal alkyne functionality is not part of the pi-system involved in the MLCT state. Therefore, structural incorporation into functional molecular devices will not affect important photochemical properties, enabling a precise pre-synthesis design of properties. Detailed insights into the photophysical properties of this class of compounds are under way using ultrafast photophysical techniques in combination with extended TD-DFT calculations.

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