Carbon-Rich Ruthenium Complexes and Photochromic Units: Luminescence and Conductivity Modulations

Thèse soutenue à Rennes le 1er Juillet 2015
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ACKNOWLEDGEMENT

I would like to express my gratitude to all those who gave me the possibility to complete this degree.

First and foremost I offer my sincerest gratitude to Prof. Stéphane Rigaut, my PhD director, who welcomed me in his group for three years. I thank him for his patience and for the time he spent in developing new ideas, discussions, teaching me the art of writing and explaining different concepts related to our project. Special thanks to Dr. Lucie Norel for her patience and profundity of her knowledge to help me solve many problems, for all the time she donated me in discussing new ideas and results and for her persistent encouragement and help when I was in difficult situation.

Second, I would like to thank also Prof. Guy Royal and Dr. Phillippe Blanchard for accepting to examine and judge my work as reporters. Equally, thank to Prof. Elena Ishow for coming to Rennes to be one jury for my defense and Prof. Stephane Rigaut and Dr. Lucie Norel for accepting to be part of the jury.

A part of my PhD work is concerned with luminescence switching, which was successfully performed thanks to Dr. Olivier Maury (Ecole normale supérieure de Lyon) for the nice collaboration in his laboratory. I would equally thank Prof. Rainer Winter (University of Konstanz in Germany) for welcoming me in his laboratory for one month; I appreciate his nice reception, discussion and allowing me to do experiments and use the equipments of his laboratory and two of his PHD students, Fabian Geist and Stefan Scheerer, for their useful suggestions and nice help during my stay. Then I would also equally thank Prof. Elena Ishow and Florian Charrier for sending us their beautiful ligand and nice discussion about our results and her great absorption and luminescent studies. Futhermore, I would also like to equally thank Prof. Xuefeng GUO and his post-doc Huimin WEN for their solid knowledge and nice conductivity measurement. Last but not least, equal thanks also go to Chengshuo
SHEN and Prof. Jeanne Crassous for their smart idea, nice discussion and all the efficient synthesis and characterization.

This manuscript and the publications would not been done without analysis, thanks to the members of CRMPO Rennes, namely Mlle Muriel Escadeillas for elemental analysis, M Philippe Jéhan for the mass spectrometry. And thanks also go to our secretary Cécile Peron, that prepared me a lot of mission orders, sent and received my letters, and printed all the colored papers I needed.

Coming back to our group, I would like to thank all the members of group “Organometallics and Molecular Materials” and the members of “Organometallics for Optics”: permanent staff: Véronique, Hubert, Jean Luc, Lucie, Huriye, Julien and Muriel once and once again for the nice environment they supported for us which made research easier, I would like to thank every one of you for the notes and comments you gave during the group meetings. To my office mates Paul, Moussa, Yves-Marie, Mickaële, Pramila, Andrea and Claus, thank you.

Since I have spent three years in France, I cannot forget to thank Prof. Carpentier, Prof. Xianghua Zhang, Dr. Hongli Ma, Lingfang Wang, Bo Fan, Bai Xue, Yang Xu, Shui Cui, Gang Zhou, Shuo Cui, Jixing Meng, Kun Han for all their assistance or teaching. I would like to thank Jianxia Zheng, Fan Jiang, Liqin Zhao, Kedong Yuan, Min Feng, Hanyu Zhang for all their help.

Finally I would especially like to thank my husband Guang Yang, for his encouragement, friendship and love; my lovely son Luoyu Yang for his born; my parents and my parents in law for their love and support over years. Thank you very much for your unending love and support!
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General introduction

In light of the rapid development of semiconductor technologies, the feature size of electronic devices is gradually approaching the miniaturization limits of silicon technology. At the same time, molecules are attracting more attention due to their remarkable properties, which could bring some new elements to continue this race towards miniaturization and bring multifunctionality. In that direction, fundamental research of individual molecule-based devices such as molecular switches, molecular wires, molecular diodes, molecular transistors, and molecular charge storage have been recently reported.

The objective of our laboratory focuses on the design, the synthesis and the study of new molecules that can perform the functions of switches or of organometallic molecular wires. To that end, the mostly used building blocks in our laboratory and in the whole thesis are ruthenium acetylide moieties. These ruthenium acetylide compounds are prepared in a reaction between an organic ligand having a free alkyne function and the metal precursor [RuCl₂(dppe)₂] (dppe = diphenylphosphinoethane), in the presence of a noncoordinating salt.

![Scheme 1. Ruthenium acetylide complexes](image)

Importantly, these compounds can be reversibly oxidized at low potential. During the redox process, the ligands are widely involved. Indeed, theoretical calculations have shown the presence of spin density on the entire conjugated path in the first oxidation state. In addition, it is possible to modulate the electronic contribution of the various components of these complexes (metal, ligand) by changing the type of groups (electron donors or acceptors) on their phenyl acetylene ligands. Indeed, for complex trans-[ClRu(dppe)₂-C≡C₆H₄-R] (R = NO₂, H, OMe, NMe₂) shown in Figure 1, the electron spin resonance studies (ESR) and
General introduction

Theoretical calculations (DFT) have shown that the density of spin on ruthenium atom varies depending on the groups R (electron donor or acceptor) from 0.4 e⁻ (X = NO₂) to 0.2 e⁻ (X = NMe₂).¹⁴

![Figure 1. Representation of the oxidation of a ruthenium acetylide complex.](image)

Thus, this type of complex has been used to modulate, via a redox stimulus, a number of properties such as the magnetic property¹⁶ or more recently the luminescence of a lanthanide ion¹⁷,¹⁸. They were also used to achieve molecular wires since they allow a very good electronic delocalization on long distances.¹⁹,²⁰

The goal of this work is precisely to achieve new original molecular wires and switches:

In order to ultimately electro-switch luminescence of triarylamines in the solid state at low potential, in chapter 2 we will describe an association between redox active ruthenium acetylide complexes and triarylamine units for their peculiar properties which will be described in chapter 2.

In our group, the Ytterbium (Yb) NIR emitter has been successfully sensitized using a ruthenium based redox-active ligand that further allowed the redox perturbations of the NIR emission (Scheme 2). However, the disadvantage of this system is the limited reversibility of the switching event.¹⁷ Therefore, in chapter 3 we aim to describe the switching of Yb and also of Eu luminescence by taking advantage of the redox communication of one or two new vinyl ruthenium antennae which are more stable than Ru acetylide moieties in their oxidized state (Scheme 3).²¹
Another interesting way for luminescence modulation of lanthanide(III) complexes is to use photochromic moieties as switching unit. Photochromic DTEs display high potential as molecular photomemory and photoactive switching materials via subsequent modulation of a given properties.\textsuperscript{22} Therefore, in chapter 4 we will focus on the combination of a Ln(III) (Eu, Yb) complex with a DTE unit, which makes luminescence of lanthanide ion capable to be modulated through the photochromic reaction of the DTE unit upon irradiation of UV or visible light. Furthermore, the perspective is to make a new complex with a ruthenium acetylide moiety bearing the photochromic DTE unit and a lanthanide ion to provide a compound whose luminescence may be sensitized at lower energies (through the MLCT transition) and switched by means of both electrochemical and optical stimuli.

Wires incorporating metal complexes are also particularly interesting for molecular electronics because they offer multiple redox and spin states that can lead to unusual current-voltage (I-V) characteristics as well as efficient charge conduction.\textsuperscript{20} For example, in collaboration with Prof. Frisbie, our group, has examined a series of organometallic wires in CP-AFM and X-wire junctions (Figure 2).\textsuperscript{19} Room-temperature CP-AFM measurements revealed minimal length dependence illustrating that charge transport through the ruthenium σ-arylacetylide bridges is extremely efficient.
We will, in chapter 5, address the synthesis of similar redox-active organometallic compounds containing or not a photochromic unit to produce new switchable molecular electrical devices based on graphene. Indeed, the production of devices containing molecular switches could play an important role in obtaining systems with unique electronic performances in the near future with this new material. Thus, our interest is not only on the examination of charge transport mechanisms as a function of electrochemically controlled oxidation states of a series of ruthenium (II) bis(σ-arylacetylide) complexes, but also on the optical modulation of the electrical properties (UV-visible absorption) on modified surface, this to achieve new multifunctional devices.

More details about molecular switches and wires will be presented in chapter 1 (bibliography chapter). In that chapter, we will explain the concept of molecular switches and wires and some examples will be described to illustrate them.
References:

(2) Sense Jan van der, M.; Peter, L. *Journal of Physics: Condensed Matter* 2010, 22, 133001.
(22) Irie, M. *Chemical Reviews* 2000, 100, 1685-1716.
Chapter 1:
Molecular switches and wires,
a bibliographic survey
Chapter 1: Molecular switches and wires, a bibliographic survey

This chapter has been classified into four sections. In the first section we are going to describe the concept of molecular switches and to give examples of molecular switches using several kinds of external stimulus to modulate various properties such as luminescence, magnetism, chemical reactivity or photomechanical response. The second section will specifically focus on luminescence molecular switches. In the third section, we will give an introduction on molecular wires for molecular electronics with relevant examples including molecular switches for molecular electronics.

1. Molecular switches

1.1 Definition

The large family of components of molecular electronics, which will be mentioned in this part, and in which we are particularly interested in, is molecular switches. These are systems which are inter-convertible between two stable states under the influence of one or more stimuli. These stimuli can be light, electrical current, mechanical action, or a chemical reaction (Figure 1). As their macroscopic counterparts, they are able to control a number of functions and properties of materials because each state displays specific optical, magnetic, electronic or conduction properties.  

![Figure 1. Schematic representation of a molecular switch](image)

Through chosen examples, we will present in this chapter the different types of molecular switches, and we will present them according to the stimuli used to modify the properties. Thus, we will briefly summarize systems switched by electrochemical, chemical, mechanical and optical stimuli (photochromism). Afterwards, we will focus our attention on systems in which optical properties are switched with light or electrochemical stimulus, two orthogonal stimuli relevant for molecular electronics.
1.2 Molecular switches using an electrochemical stimulus

Ji and coworkers reported that a new ruthenium(II) polypyridine complex, [Ru(bpy)$_2$(PAIDH)]$^{2+}$ (2) (bpy = 2,20-bipyridine; PAIDH = 2-pyridyl-1H-anthra[1,2–d]imidazole-6,11-dione) (Figure 2) displays electrochemically “off - on” luminescent switch through exchanging two protons and two electrons between the quinine/hydroquinone redox couple at room temperature.$^2$

In aqueous CH$_3$CN (5% H$_2$O) solutions containing 0.1 M TBAClO$_4$, complex 2 shows one oxidation event (+ 1.35 V) and three reduction waves (- 0.46, - 1.36 and - 1.61 V). Exhaustive coulometric reduction of complex 2 (10 µM) at 0.5 V generated complex 3 (Figure 2a) that was identified by UV–visible and NMR spectroscopies. In the emission spectra, the electrochemically generated complex 3 with hydroquinone form exhibited strong MLCT luminescence at 600 nm ($\Phi = 0.03$, $\tau = 0.83 \mu$s), while complex 2 with the quinone form was found to be almost non-luminescent (Figure 2b). The solution containing complex 3 showed an oxidation wave at + 0.93 V, and the bulk exhaustive coulometry conducted at + 1.1 V was seen to regenerate complex 2 (Figure 2). This process was thus totally reversible and repeatable. These findings suggest that “off–on” redox switching of the emission properties of the Ru(II) complexes was achieved by the redox control of the quinone/hydroquinone redox couple.
Figure 2. (a) Reversible redox conversion between 2 and 3; (b) Luminescence spectra (CH$_3$CN/5% H$_2$O, 0.1 M TBAClO$_4$, $\lambda_{\text{exc}} = 460$ nm) of 2 and 3 as obtained by exhaustive electrolysis at the indicated applied potentials in each case. The arrows refer to the reversible changes observed upon electrochemical interconversion of these complexes.\(^2\)

1.3 Molecular switches using a chemical stimulus

\textit{Jeong} and \textit{Lah},\(^3\) for the first time, have prepared the new chiral indolocarbazole dimers 1 that shows complete inversion of the helical sense upon anion addition, and that can function as a new class of chiroptical molecular switches based on a helical foldamer.\(^3\) Chiral indolocarbazole dimers 1 can fold into a helical confirmation by virtue of intramolecular hydrogen bonds (Figure 3). The optical properties of dimmers were found to be extremely sensitive to the nature of solvent, depending on whether they are folded or not. The helical sense of the dimmers can be reversibly switched by binding sulfate ion, which gives rise to complete inversion of the CD spectra (Figure 3).
Figure 3. Molecular structures of 1 and 4. (a) Schematic representation of the reversible switching of the helical sense of 1 upon addition and removal of sulfate ion. (b) CD spectra of unbound 1 (green) and its sulfate complex (blue) and (inset) a repetitive CD cycle upon addition of sulfate or the sulfate-sequestering agent 4.3

1.4 Molecular switches using a mechanical stimulus

The term "tribochromism" was first introduced by Heller et al. in 2000 to describe the color change of the crystals of the compound represented in Figure 4 after a mechanical friction.4 The colored form obtained is stable and does not undergo reversible change of state, when stored in the dark after heating.

Figure 4. First compound presented with tribochromism properties.4

“Writing” and “erasing” of a letter with scratching and heating, respectively, were reported by
Koga\textsuperscript{5} by taking advantage of the differences in the emission intensity of \textbf{5} depending on its state, that is super cooled liquid (SCL) or solid. The SCL of \textbf{5} emitted weakly, whereas the crystalline state is a strong emitter. In the SCL state, molecules were amorphous and were quickly crystallized by a mechanical stimulus such as scratching. Then, when the letter \textit{P} was written by scratching several times with a tiny wire, the letter \textit{P} rapidly appeared under black light due to the crystallization at the stimulation point. With time, the letter \textit{P} became blurred. Subsequently, when the temperature was raised to 100 °C and cooled to room temperature, the letter \textit{P} disappeared and the sample returned to the SCL state. A different letter, \textit{L}, was then further written. The emission behavior of \textbf{5} in the cycle of heating and cooling is shown in Figure 5.

![Figure 5](image_url)

\textbf{Figure 5.} Photographs for \textbf{5} in the cycle of heating at 100 °C, cooling at 25 °C, and scratching. The letters “\textit{P}” and “\textit{L}” were written by scratching with a tiny wire. The white scale bar indicates 5 mm.\textsuperscript{5}

1.5 Molecular switches using an optical stimulus: the particular case of photochromism

Among the possible stimuli, photon is the most convenient because of its easy and rapid on/off switching operation with remote control. First of all, in this part, we will introduce and define the concept of photochromism, (Greek light "photo" and color "chrome"). Basically, photochromic compounds are able to change their colors with an optical stimulus. We will further present the structures of the most commonly used families of photochromic compounds and the structural changes they undergo during light irradiation. Then, we will see that these compounds may also be used to modify properties of associated units with their conjugation change, for example, magnetism or luminescence properties and so on.\textsuperscript{6}
In fact, photochromism expanded during the 1960s, when photochromic glasses became available at that period and further stimulated research:

“Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra”.

Figure 6. UV-visible absorption spectra of a photochromic compound in its original form A (solid line) and form B obtained after irradiation (dotted line).

The thermodynamically stable form A is transformed by irradiation into form B. The latter is metastable and depending on its stability, the back reaction can occur thermally (Photochromism of T type) or not. On the other hand, the B form can be converted back to A photochemically (Photochromism of P type).

Scheme 1. Typical examples of photochromic molecules
Typical examples of photochromic molecules are shown in Scheme 1. Upon irradiation with ultraviolet light (UV), the upper two molecules, azobenzene 6a and spiropyran 7a, can be converted from the left-side isomers to the right-side ones, and their color changes from pale yellow and colorless to orange and blue, respectively. The photo generated right-side isomers are thermally unstable, and the colors disappear in the dark at room temperature. These traditional molecules are classified into T type (thermally reversible) photochromic molecules. On the other hand, more recently invented, the lower two molecules, furyfulgide 8 and diarylethene 9, both of which change color from colorless to red, are classified into P type (thermally irreversible, but photochemically reversible), because the photogenerated right-side isomers are thermally stable and hardly return to the left-side isomers in the dark at room temperature. Although vast numbers of photochromic molecules have been so far reported, molecules that undergo the otherwise thermally irreversible photochromic back-reaction are limited within a few families of compounds. The thermal irreversibility is an essential and indispensable property for the use of photochromic molecules in optical memories, switches, and actuators.8

Among all the photochromic compounds, diarylethene derivatives that we will mainly described in this chapter are interesting compounds due to their performance summarized as follows by Irie.8

“(1) Both isomers are thermally stable: well-designed derivatives have a half-life time at room temperature longer than 400 000 years.
(2) Coloration/decoloration cycles can be repeated more than 10 000 times.
(3) The quantum yield of coloration is close to 1 (100%).
(4) Both coloration and decoloration reactions take place in a picosecond time region.
(5) Many diarylethenes undergo photochromic reactions in the single crystalline phase.”

Photoinduced cyclization and cycloreversion reactions of diarylethenes belong to electrocyclic reactions between hexatriene and cyclohexadiene structures, as described above (Scheme 1). The open-ring isomer having a hexatriene structure is colorless in most cases, while the closed-ring isomer having a cyclohexadiene structure has a yellow, red, or blue color, depending on the molecular structure. Not only the color but also various physical properties are different between the open- and the closed-ring isomers because of the difference in the electronic and geometrical structures. A striking feature of this molecular system is that while the π-systems of the two aryl rings are discontinued in the open-ring isomer, the closed-ring isomer has a planar structure and its π-electrons are delocalized throughout the molecule. Thus, the difference in the two electronic structures brings about the
physical property changes, which have been widely used to switch the physical and chemical functions of molecular systems. In this section, the switching of magnetism, chemical reactivity, NLO (Non-Linear Optic) property, chiral property and photomechanical response will be presented. In addition, switching of optical properties with the diarylethene molecular systems will be more detailed in section 2 that deals about luminescence molecular switches. Switching of molecular conductivity using diarylethene molecular systems will be discussed later in section 3 that deals with molecular electronics.

### 1.5.1 Switching of magnetism

Two radicals were connected to a diarylethene unit, as shown in compound 11 (Scheme 2), in which 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene 14 is employed as a photochromic spin coupler and nitronylnitroxides as spinsources. The measurement of the magnetic susceptibilities revealed that the spins of 11b have a remarkable antiferromagnetic interaction \(2J/k_B = -11.6 \text{ K}\), whereas the interaction between the two spins is small in the open-ring isomer 11a \(2J/k_B = -2.2 \text{ K}\). The photoinduced change in magnetism agrees well with the prediction that the open-ring isomer has an “OFF” state and the closed-ring isomer has an “ON” state.

![Scheme 2. Molecule 14 and diarylethene diradicals showing photoswitching of magnetic interaction.](image)

Thus, in the above example Irie and coworkers have demonstrated that the exchange interaction between two nitronyl nitroxide radicals, which are located at both ends of a diarylethene, is photoswitched reversibly by alternate irradiation with ultraviolet and visible light. It was found that the change in the exchange interaction between the two switching states is more than 30-fold. When a diarylethene dimer is used as a switching unit (Figure 7), there are three photochromic states; open-open (OO), closed-open (CO), and closed-closed (CC). From the analogy to electric circuit, it is inferred that the dimer has two switching units
in series. The ESR spectra of 15(OO) and 15(OC) are 5-line spectra, suggesting that the exchange interaction between the two nitronylnitroxide radicals is much weaker than the hyperfine coupling constant. Yet, the spectrum of 15(CC) has a clear 9-line spectrum, indicating that the exchange interaction between the two spins is much stronger than the hyperfine coupling constant. The result indicates that each diarylethene photochromic unit serves as a switching unit to control the magnetic interaction.\textsuperscript{10}

![Figure 7. Diarylethene dimer 15 that shows photoswitching of magnetic interaction. X-band ESR spectra measured at room temperature in benzene (9.32 GHz): (a) 15(OO), (b) 15(CO), and (c) 15(CC).\textsuperscript{10} Red line indicates the connection of the bond alternation.]

1.5.2 Switching of chemical reactivity

Chemical reactivity and catalytic activity can also be photoswitched using the photoisomerization of diarylenes.\textsuperscript{12,13,14} One example is the incorporation of an aromatic imidazolium moiety into the bridge position of diarylethene 16o reported by Kawai and coworkers (Scheme 3).\textsuperscript{12} Due to its aromatic stabilization, the imidazolium ion is not prone to nucleophilic addition of methoxide. However, upon photocyclization to 16c, the bridge moiety is transformed into animidazolinium ion, removing the crucial double bond as well as the aromatic stabilization. The closed-form switch can then react to yield the methanol adduct 17.
Scheme 3. Photo-controlled addition of methanol to imidazol(in)ium ions embedded in a diarylethene framework.\textsuperscript{12}

Photo modulation of nucleophilicity could be achieved by Branda and coworkers, who reported diarylethene 18 incorporating a pyridyl substituent into one aryl moiety and an electron withdrawing pyridinium group into the other (Scheme 4).\textsuperscript{13} In the open ring form 18\textit{o}, the two aryl moieties are not conjugated and thus the nucleophilicity of the pyridyl-lone pair is unbiased in a reaction with p-bromobenzyl bromide to 19\textit{o}. However, upon UV-induced photocyclization of 18\textit{o} to 18\textit{c}, a conjugation pathway between the two aryl-moieties is opened up and electron density is removed from the pyridyl-lone pair lowering its nucleophilic character and hampering the reaction with p-bromobenzyl bromide to 19\textit{c} severely.

Scheme 4. Photomodulation of nucleophilicity by switchable coupling to an acceptor moiety through a diarylethene bridge.\textsuperscript{13}

Electronic effects can significantly influence the active site and hence electronic fine-tuning constitutes one of the main strategies in catalyst design. Therefore, it is no surprise the efforts were put into photo modulation of the electronic properties of a catalyst. The basic concept is
founded on breaking or forming a conjugated system between the active site and an electronically activating group. Recently, Bielawski and Neilson used this concept to control the activity of a catalyst.\textsuperscript{14} An N-heterocyclic carbene (NHC) functionality was incorporated into the backbone of a dithienylethene (DTE) 20 (Scheme 5). The length of the conjugated $\pi$-system modulates the electronic properties of the NHC-functionality. In the presence of visible light and a base, the NHC 20o catalyzes transesterification and amidation reactions. Upon irradiation with UV-light to the ring-closed derivative 20c the rate of a transesterification and anamidation reaction was significantly decreased.

\begin{center}
\begin{tikzpicture}
\begin{scope}[scale=0.5]
\begin{scope}[rotate=90]
\node (a) at (0,0) {$R^2\text{OR}^2$};
\node (b) at (2,0) {$R^1\text{XH}$};
\node (c) at (4,0) {$R^2\text{XR}^1$};
\node (d) at (4,2) {$R^2\text{OR}^2$};
\node (e) at (2,2) {$R^1\text{XH}$};
\node (f) at (4,2) {$R^2\text{XR}^1$};
\draw (a) -- (b);
\draw (b) -- (c);
\draw (c) -- (d);
\draw (d) -- (e);
\draw (e) -- (f);
\end{scope}
\end{scope}
\node at (3,1) {$(X = O, N)$};
\node at (4.5,1) {313 nm};
\node at (7,1) {500 nm};
\end{tikzpicture}
\end{center}

\textit{Scheme 5.} Ring-open N-heterocyclic carbene (NHC) 20o catalyzes transesterification, amidation as well as ring-opening polymerization reactions yet upon irradiation its corresponding ring-closed isomer 20c exhibits significantly reduced catalytic activity.\textsuperscript{14}

### 1.5.3 Switching of chiral properties

Photochromic dithienylethenes (DTEs) have also been used with success in chiroptic applications.\textsuperscript{15,16} Recently, Branda and co-workers reported a photo-responsive DTE derivative bearing chiral pinene-based arms 22 (Scheme 6), which underwent a stereo-selective photoinduced cyclization reaction to produce 98\% of a single diastereomer (M-23).\textsuperscript{17} This is supported by molecular modeling, which predicts that this isomer is more stable than its counterpart P-23. This system satisfies the requirements of a successful chiroptical photoswitch. It is thermally stable in both states: it displays high stereo-selectivity in its photocyclization reactions, and it exhibits large changes in circular dichroism (CD) (Figure 8). This is because this kind of helicene (M-23) is created upon isomerisation and helicene are known for their great CD properties which is different from that of compound 22.
Figure 8. Changes in UV-vis absorption spectra of a solution of 22 (2×10^{-5} M) in benzene upon irradiation with 400 nm light for a total of 240 s. The inset shows the CD spectra measured on a solution of 22 (2×10^{-4} M) in benzene (black trace) and the photostationary state (red trace) generated with 400 nm light.\textsuperscript{17}

1.5.4 Switching of NLO properties

Photochromic compounds seem to be also promising candidates for the design of photoswitchable NLO materials.\textsuperscript{18,19} In order to carry out the photoswitching of the NLO properties, a new type of 4,4’-bis(ethenyl)-2,2’-bipyridine ligands functionalized by a dimethylaminophenyl–dithienylethene (DTE) group and the corresponding zinc(II) complex have been designed by Le Bozec.\textsuperscript{20} This molecule undergoes an efficient reversible interconversion between a non-conjugated open form and a π-conjugated closed form when irradiated at 365 and 588 nm, respectively (Scheme 7). The NLO properties have been evaluated by Electric Field Induced Second Harmonic Generation (EFISH) measurement for the open and PSS closed forms: the \(\mu\beta_0\) value for the open form is very small, in agreement with the absence of π-conjugation between the two thiophene rings of the DTE fragment. Upon conversion to the closed form in the photostationary state, the NLO activity dramatically increased, from 160×10^{-48} esu to 1800×10^{-48} esu. Thus, the huge enhancement of
µβ₀ clearly reflects the efficient delocalization of the π-electron system in the closed form and demonstrates an efficient ON/OFF switching of the NLO responses.

Scheme 7. Photoswitching of the quadratic NLO response by using a photochromic metal complex\textsuperscript{20}

1.5.5 Photomechanical response

One of the most spectacular use of DTE concerns crystal actuators. For practical applications, the crystal actuators should have sufficient durability and substantial mechanical properties. To improve the mechanical property, multi component crystals were prepared. The two-component cocrystal composed of a diarylethene derivative, 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)-perfluorocyclopentene (24), and perfluoronaphthalene (Np\textsuperscript{F}) exhibited light-driven bending upon irradiation with UV and visible light.\textsuperscript{21} The rectangular plate-like crystal turned its color from colorless to blue and bent moving away from the light source. The bending ceased when the illumination light was switched off, and the crystal kept the bent shape in the dark. Upon visible light irradiation, the blue color disappeared, and the crystal returned to the initial straight shape. The rectangular plate-like cocrystal 24-Np\textsuperscript{F} was fixed at the edge of a glass plate as a cantilever arm, and a lead ball was loaded onto the crystal, as shown in Figure 9.\textsuperscript{21} The crystal and the ball weigh 0.17 and 46.77 mg, respectively. Upon irradiation with UV light, the heavy ball is lifted as high as 0.95 mm. The cantilever arm performs lifting work, and the amount of the work is as large as 0.43 µJ. The photo generated maximum stress was estimated to be 44 MPa.
Figure 9. Photomechanical work of a molecular crystal cantilever made of the cocrystal (24-NpF). Illumination of light was carried out below the crystal. The weight of the lead ball and the crystal cantilever were 46.77 and 0.17 mg, respectively.~

2. Luminescence molecular switches

In this section, we will focus on the switching of a specific property: luminescence. Among outputs, luminescence emission is considered to be one of the most attractive, owing to the ease of detection and the cheap fabrication of devices in which it is detected. We will focus in the first part on the use of pH, light or metal ions as stimuli.~

2.1 General examples of luminescent molecular switches.

2.1.1 Metal ion sensors

Many examples of such switches have been described.~ As an example, Sachleben and coworkers have synthesized 1,3-alternate di-deoxygenatedcalix[4](9-cyano-10-anthrylmethyl)benzocrown-6 (25) and1,3-alternatealox[4](9-cyano-10-anthrylmethyl)benzocrown-6 (26) as cesium selective fluorescent probes using the concept of fluorescence turn-on as a platform for its detection. Probe 25 shows 54-fold fluorescence enhancement upon cesium complexation, while 26 exhibits only 8-fold enhancement; the selectivity ratios for 25 to complex cesium ion over potassium and rubidium (KCs/KK and KCs/KRb) are ca. 10 fold higher than those of 26 for the same ions; the observed selectivity ratios are due to different interactions (weak or strong) between these ions and 25 or 26 (Figure 10).~
Figure 10. The structure 25 and 26 (left) and changes in the emission intensity of 25 (10^{-6} M) in CH_2Cl_2-MeOH (1:1) upon addition of alkali metal ions (as acetate salts) (right). λ_ex = 376 nm. Each data point represents the integrated total area under the emission curve (λ_em = 400 – 600 nm).^2^4

2.1.2 A luminescent pH sensor

Complex [(bpy)_2Ru(bpibH_2)Ru(bpy)_2](ClO_4)_4P_3H_2O (27) (bpy = 2,2'-bipyridine and bpibH_2 = 1,4-bis([1,10]phenanthroline[5,6-d]- imidazol–2-yl)benzene), which contains two metallo-luminophores and a two receptors system, acts as an ‘off–on–off’ luminescent pH sensor through protonation and deprotonation in MeOH–H_2O (1:1 v/v) solution at room temperature (Figure 11).^2^5 Luminescence is off for complex 27^6^+ at low pH (1-5.9) and complex 27^2^+ at high pH (8.5-12), while luminescence is on for complex 27^4^+ at mid pH. Complex 27 acts as an ‘off–on–off’ luminescent switch depending on the pH through two different mechanisms, one involving luminescence quenching arising from the positive charge and the other originating from rapid radiationless decay.
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Figure 11. Representation of complex 27 through protonation and deprotonation and the pH dependence of the luminescence intensity ($I$) of complex 27 in MeOH-H$_2$O (1:1 v/v) solution at $\lambda_{ex} = 469$ nm at room temperature.$^{25}$

2.1.3. Luminescence commutation with light

In this part, we mainly want to describe selected examples about the photochromic luminescent switches containing DTE units.

Many examples of fluorescence photo regulation with photochromic molecules have been published by combining a DTE unit with an organic fluorophore.$^{26}$ Moreover, the access to triplet states by incorporation of the DTE fragment into the ligands of transition-metal complexes allows the photo-regulation of phosphorescence.

Tao Yi has designed and synthesized an amphiphilic diarylethene (terpy-DTE) as a photoswitchable probe for imaging living cells, by combining diarylethene and terpyridine units (Scheme 8). The compound terpy-DTE exhibits several clearly different and reversible fluorescence states that can be controlled by varying light frequency and metal ion concentration. As expected, terpy-DTE shows reversible absorption and fluorescence intensity changes with DTE as a switching unit upon irradiation with UV and visible light. In addition, the fluorescence intensity can be reversibly controlled by Zn/ethylenediaminetetracetic acid (EDTA): Zn$^{2+}$ acts as a trigger for fluorescence switch-OFF while EDTA acts as a trigger for fluorescence switch-ON.$^{27}$
Scheme 8. The complexation and photoirradiation of terpy-DTE$^{27}$

The second example deals with a photochromic Ir complex published by Tian in which the thiophene ring of the DTE fragment is directly linked to the metal center (Scheme 9). Complex (py-DTE)$_2$Ir(acac) showed excellent near-infrared photochromic behavior accompanied by efficient quenching of phosphorescence emission$^{28}$.

Scheme 9. Photo isomerization and luminescence change with light irradiation$^{28}$

Note that from the two examples above, triplet reaction pathways have been demonstrated, allowing the extension of the excitation wavelengths to lower energies, which are less destructive. Also, these metal systems allow photo modulation of phosphorescence, for which the presence of the organometallic fragment is crucial for the mentioned properties.
2.2 Luminescence modulation with redox-active units

Molecular switches for fluorescence have been attracting considerable attention, especially because of high sensitivity of luminescence signals. Redox-dependency of fluorescence has been studied by using metal-centered redox couples, where the communication between the redox-active site (transition metal complex) and the light-emitting-fragment (fluorophore) plays an important role for the ON/OFF mechanism. Pure organic switches without metal ions are scarcer. Herein, in the 2.2 section, we will discuss several examples with luminescence modulation with an organic redox-active unit that might be the fluorophore itself, and with a metal-centered redox unit.

2.2.1 Organic redox-active fluorophores

![Diagram of the cell](image)

**Figure 12. Diagram of the cell**

An electrofluorescent switch was prepared by Audebert and coworkers with an electroactive fluorescent tetrazine blended in a polymer electrolyte; the cells contain four layers: the tetrazine polymer film, a photocured polymer electrolyte film, and two indium-tin oxide plates as the two contact electrodes (Figure 12). Unlike electrochromism, this is the first example where direct fluorescence switching can be monitored by electrochemical potential in an all solid state cell in which the fluorescent tetrazine molecules are in contact with the solid polymer electrolyte. Figure 13 displays a series of pictures showing the fluorescence of the device as a function of the applied electrochemical potential. It demonstrates that this device, which is fluorescent at the start (A), becomes less emissive when a negative potential is applied (B) and the emission is almost extinguished when the applied potential is -3 V (C). Then, most of the fluorescence is restored on the return sweep (D). This process is reversible. The tetrazines are very promising candidates to examine electrochemical fluorescence switching, in which the fluorescence of the neutral state could be reversibly switched on and off by converting the molecules successively to their reduced form (non fluorescent) and back to the neutral (fluorescent) state.
Figure 13. Successive images of the cell fluorescence recorded at different potentials, A: 0 V; B: -1.25 V; C: -3 V; and D: +1 V.\(^{37}\)

The compound 28 prepared by Tsuji and coworkers has a very long C-C bond [1.635(2) Å], which was readily cleaved upon oxidation to give dication 29\(^{2+}\) containing two 10-methylacridinium chromophores.\(^{38}\) The colorless donor 28 (\(E^\text{ox} = +0.18\) V) is non-fluorescent whereas the orange dication 29\(^{2+}\) (\(E^\text{red} = -0.27\) V) emits strong green fluorescence, so that, this pair can be considered as a novel redox switch for fluorescence with high electrochemical bistability (Figure 14).

Figure 14. Representation of 28 and 29\(^{2+}\) (left). Changes in the fluorescence spectrum of 28 (7.43×10\(^{-6}\) M in MeCN) upon constant-current electrochemical oxidation (25 µA at 2 min interval) to 29\(^{2+}\) (right).\(^{38}\)
Figure 15. The fluorescence spectra of 2-MT, 2-MT$^+$ and 2-MT$^{2+}$ in CH$_2$Cl$_2$. $\lambda_{ex} = 350$ nm.$^{39}$

Another organic system 2-MT was synthesized with tetrathiafulvalene (TTF) and 5-methoxy-2-pyridylthiazoles coupled directly and rigidly. The fluorescent emission of 2-MT can be reversibly switched on/off depending on the oxidation states of the TTF unit, due to the peculiar property of TTF being oxidized reversibly and selectively. Fluorescence spectra were recorded in the visible region as shown in Figure 15. The neutral 2-MT show a negligible fluorescence, while the dicationic 2-MT$^{2+}$ display a very strong emission at 465 nm for 2-MT upon excitation at 350 nm.$^{39}$ The redox characteristic of the TTF unit can induce quenching of the above emission via a photoinduced electron transfer (PET) process.$^{40}$

Becher reported that incorporation of one TTF unit directly to a porphyrin chromophore produces an almost non-fluorescent species which can be transformed into a fluorescent species by oxidation of the TTF unit (Figure 16).$^{41}$ A preliminary experiment was carried out to test the potential of the mono-TTF-porphyrin TTF4 as a fluorescence switch by adding increasing amounts of the chemical oxidant FeCl$_3$ to a solution of TTF4. Absorption spectra recorded on this solution displayed the characteristic band ($\sim$ 810 nm) of a TTF radical cation. The emission spectra (Figure 16) showed that the fluorescence intensity increased upon addition of increasing amounts of FeCl$_3$, clearly indicating that TTF4 has the potential to act as a fluorescence switch. This observation could be explained with an electron transfer from the TTF donor to the porphyrin chromophore that occurs in the emitting excited state of TTF4. Removal of one electron from the TTF unit (TTF$\rightarrow$TTF$^{2+}$) in the mono-TTF-porphyrin TTF4 would prevent the TTF unit from acting as an electron donor and subsequent quenching of the porphyrin emission. The outcome is a fluorescence switch with the non-fluorescent
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mono-TTF-porphyrin and the fluorescent mono-TTF\(^{+}\)-porphyrin species, activated by oxidation of the TTF unit.

![Image of TTF4 molecule]

**Figure 16.** Emission (THF, 298 K) spectra of the mono-TTF-porphyrin TTF4 upon addition of increasing amounts of the oxidant FeCl\(_3\). Excitation was performed at 425 nm (Soret band).\(^{31}\)

### 2.2.2 Metal complex unit as redox-active centers

Three-component molecular systems (redox active subunit)-spacer-(light-emitting fragment) can operate as fluorescence switches, following the alternate addition of an oxidizing agent and a reducing agent (or the adjustment of the potential of the working electrode in an electrolysis experiment). The redox active subunit typically consists of a metal centered redox couple (M\(^{\text{Ⅱ}+1}\)/M\(^{\text{Ⅰ}+}\)), encircled by a macrocyclic receptor. The switching efficiency requires that one of the two oxidation states quenches the proximate fluorophore and the other does not.

Two ON/OFF systems, based on either the Cu\(^{\text{Ⅱ}+1}\)/Cu\(^{\text{Ⅰ}+}\) or Ni\(^{\text{Ⅲ}+1}\)/Ni\(^{\text{Ⅱ}+1}\) couple, will be discussed here. The nature of the quenching process responsible for the OFF state, either electron transfer or energy transfer, is related to the length and to the flexibility or rigidity of the spacer. A metal ion can quench an excited fluorophore via an energy transfer ET mechanism, either by a bimolecular or an intramolecular process, if it possesses empty or half-filled d orbitals of appropriate energy.\(^{31}\)
In particular, the case of a d⁹ cation like Cu²⁺ in an elongated-octahedral environment is sketched in the Figure 17. The excited fluorophore is deactivated through a double electron exchange (ET process of the Dexter type) involving the highest occupied d orbitals of the metal center M, dz² and dx²−y². The excited state M* which results from the ET process then undergoes rapid non-radiative decay.³¹

Figure 18. Sketch of the fluorescence switching activity of the [Cu²⁺(30)]²⁺⁺ system. The Cu²⁺ centre promotes an ET process causing fluorescence quenching. Reduction to the photophysically inactive Cu⁺ species makes fluorescence revive.⁴²

An intramolecular ET process of this type has been observed as shown in Figure 18 which gives a bistable system, the blue [Cu²⁺(30)]²⁺ complex, in an MeCN solution, undergoing quasi-reversible one-electron reduction at a moderately negative potential (− 0.14 V versus Fe⁺/Fe). An MeCN solution of [Cu²⁺(30)]²⁺ form is not fluorescent. On addition of the reducing agent 2,5-di-tert-butylhydroquinone, the blue solution decolorizes, due to the formation of the [Cu⁺(30)]⁺ species, and the naphthalene emission is revived. Addition of an oxidizing agent, NOBF₄, restores the blue color and quenches the fluorescence almost completely.⁴²
Figure 19. Details of an electron transfer process (double-electron exchange mechanism) involving an excited fluorophore and a d\textsuperscript{9} metal ion in an octahedrally elongated coordinative arrangement.\textsuperscript{31}

Before going to the second example, let’s first describe what electron transfer (eT) is and the difference with ET. The choice of a metal centered redox couple for a molecular switch operating through an eT mechanism is not related to a particular change of the electronic configuration, but can, in principle, range over the entire d block of the Periodic Table. The only requirement is that one of the oxidation states induces an intramolecular electron transfer process from/to the proximate excited fluorophore and the other oxidation state does not (Figure 19).\textsuperscript{31}

Figure 20. Sketch of the fluorescence switching activity of the [Ni\textsuperscript{III,II}(31)]\textsuperscript{3+,2+} system. The Ni\textsuperscript{II} center promotes a fluorophore-to-metal electron transfer and quenches dansyl fluorescence. The Ni\textsuperscript{III}-to-Ni\textsuperscript{II} reduction restores fluorescence.\textsuperscript{43}

An OFF/ON switch based on the eT mechanism is given by the three-component system 31
The fluorophore is a dansyl subunit and the switch is the Ni$^{	ext{III}}$/Ni$^{	ext{II}}$ couple within an azacyclam receptor. The Ni$^{	ext{II}}$ form, in an MeCN solution, displays the typical dansylamide fluorescence in the visible region, which originates from a charge-transfer excited state. On anodic oxidation, in a controlled potential electrolysis experiment (working electrode potential: 0.23 V versus Fc$^+$/Fc), the fluorescent emission is completely quenched. Then, if the potential is set at −0.07 V, the emission is revived. The fluorescence can be switched ON/OFF at will, by adjusting the potential of the working electrode. Fluorescence quenching/enhancement can be realized chemically in an ethanolic solution using sodium peroxydisulphate as an oxidizing agent and sodium nitrite as a reducing agent. Interestingly, freezing of the ethanolic solution of the Ni$^{	ext{III}}$ form makes fluorescence revive, which indicates that room temperature quenching is due to a genuine eT mechanism (from the excited fluorophore to the metal).

Another example has been presented by Lapinte and coworkers. Unlike the related luminescent rhenium(I)-alkynylcomplex [Re(bpy)(CO)$_3$(C≡C-C$_6$H$_4$-C≡C-H)], complex 32 (Scheme 10) is found to be non-emissive, and such a phenomenon is attributed to an intramolecular quenching of the emissive d$_{\pi}$(Re)$\rightarrow$d$_{\pi}$(bpy) $^3$MLCT state by the low-lying MLCT and LF (ligand field) excited states of the iron moiety. Interestingly, switching on of the luminescence property derived from the d$_{\pi}$(Re)$\rightarrow$d$_{\pi}$(bpy) $^3$MLCT state can be demonstrated in the oxidized species 33 (Scheme 10) due to the absence of the quenching pathway.
2.3 Luminescence modulation of Lanthanide complexes

Lanthanides are the 15 elements from lanthanum to lutetium, with a general electronic configuration \([\text{Xe}]4f^{n}5d^{1}6s^{2}\), and a stable oxidation state \(\text{Ln}(\text{III})\) ([Xe]4f\(^n\)). They usually have high coordination numbers, owning to their large size, and have diverse coordination geometry, due to the weak interaction between the deep buried \(f\) orbitals and the ligands.\(^{45}\)

Concerning the photophysical properties, lanthanide ions display luminescence from the Laporte forbidden \(f-f\) transitions which is a long live, sharp, easy recognizable, and almost ligand independent emission.\(^{46}\) In the case of NIR emitters (Yb), it can be applied for in vivo labeling. Because \(f-f\) transition is forbidden, the introduction of a chromophore as ligand of the lanthanide ion is necessary in order to take advantage of these interesting luminescent properties. The chromophore absorbs a suitable wavelength of radiation strongly (acts as an antenna) and then transfers to the lanthanide and excites it to the emissive state. This is so called sensitization or antenna effect (Figure 21).\(^{47}\)

![Figure 21. The sensitization or antenna effect\(^{47}\)](image)

Sensitized luminescence from lanthanide complexes has been of interest for many years\(^{22}\) and has begun to be widely applied in bioassays and microscopy. The long-lived luminescence associated with lanthanide ions is readily separated from fluorescence and scattered light using time-gated techniques, meaning that very low concentrations of lanthanide probes can be observed in biological media.\(^{48}\) Within the past decade or so, a number of important breakthroughs have been made in the development of lanthanide complexes that respond to changes in the concentration of a range of analytes.\(^{49}\) These systems have been developed as ratiometric probes of ionic concentration,\(^{50}\) and some show considerable promise as clinical agents for the early stage diagnosis of tumor markers.\(^{51}\)

Early studies on luminescent lanthanide complexes focused on the development and utilization of europium and terbium complexes, which emit visible light, but over the past decade or so the approach has been extended to exploit the long-wavelength emission from
lanthanides such as neodymium, ytterbium, and erbium.\textsuperscript{52,53,54} The low-lying emissive states of these ions can be populated using a much wider range of chromophores, and much has been made of the use of transition metal complexes or organic compounds as antennae.

Figure 22. Highly coordinated complexes between ligand 34 and Eu(FOD)\textsubscript{3} (left). And electro chemical switching of luminescence at 615 nm of 34·Eu(FOD)\textsubscript{3} (1 mM) in deaerated acetonitrile containing NBuPF\textsubscript{6} (0.1 M) with alternate oxidation at 0.5 V vs Fc/Fc\textsuperscript{+} and reduction at – 0.50 V(right). Excitation at 290 nm.\textsuperscript{55}

Triarylamine units can be used as redox-active unit to tune the luminescence of a system. Tsukube and coworkers have successfully developed ‘‘ON–OFF’’ switching of the luminescent europium complex, in which triarylamine-linked terpyridine ligand 34 directly coordinated to Eu(FOD)\textsubscript{3} (Figure 22). The redox active triarylamine unit provided a unique way to switch the luminescence from Eu\textsuperscript{3+} via intramolecular energy transfer from the diketonate moiety to the oxidized triarylamine radical cation moiety.\textsuperscript{55} Specifically, luminescence turned off upon oxidation because low lying energy levels of oxidized triarylamine trap the energy from the sensitizer (the diketonate moiety) which was used to populate the Eu ion when the triarylamine unit was in neutral state.

~ 34 ~
Higuchi presented that based on the different coordination properties of a lanthanide metal ion and a transition metal ion, a heterometallo-supramolecular polymer with Eu(III) and Fe(II) ions introduced alternately (polyEuFe) was precisely prepared via stepwise complexation of the metal ions to a new unsymmetrical ligand with both a dicarboxylate-substituted terpyridine and an unsubstituted terpyridine. PolyEuFe showed reversible “on–off” switching of the Eu(III) luminescence by the electrochemical oxidation/reduction of the Fe(II) ions in the solid-state (Figure 23). In this case, the MLCT of Fe and the blue ligand in Figure 23 can behave as sensitizers.

Figure 24. Monitoring of the emission spectra ($\lambda_{ex} = 440$ nm) upon the first oxidation of 2Yb (right) in an OTTLE cell (CH$_2$Cl$_2$, 0.2 M Bu$_4$NPF$_6$): initial emission spectrum in CH$_2$Cl$_2$ (black), after oxidation at 0.8 V vs Ag/Ag$^+$ (red), and after reduction at 0 V (blue). The asterisk shows a cell artifact.
In our group, we built new original d–f heterometallic complexes with the help of associations between Yb$^{3+}$ and Nd$^{3+}$ ions and low-potential redox-active ruthenium carbon-rich complexes bearing a bipyridine chelating unit of the type trans-[Ph–C≡C–(dppe)$_2$Ru–C$_6$H$_4$]n–C≡C–bipy–κ$^2$N,N’–Ln(TTA)$_3$] (Ln = Yb, or Nd; n = 1 or 0) (Figure 24). Efficient sensitization of the Ln$^{3+}$ near infrared emitter was achieved by the metal–acetylide antenna. The redox properties of this group further allowed for low-potential redox modulation of the Ln$^{3+}$ ion. More details and other relevant examples about redox modulation of lanthanide luminescence will be presented in Chapter 3.

Recently, photo-switching modulation of the emission of lanthanide ions has also been achieved.

![Figure 25. Structures of diarylethene 35, Eu$^{3+}$ complex 36, and reference compound 37 without DB24C8](image)

![Scheme 11. Schematic illustration of the light-modulated molecular switch](image)
Liu and coworkers have designed and synthesized the host–guest partners 35 and 36 with perfect spectral overlap between the host emission and the guest absorption. The [36]pseudorotaxane 35⊂36 was readily constructed from Eu$^{3+}$ complex 36, bearing a tpy-DB24C8 moiety (a dibenzo-24-crown-8 (DB24C8) derivative bearing terpyridine unit) as the host, and the photochromic DTE 35 containing a dialkylammonium moiety as the guest through complexation of the ammonium moiety of 35 with the DB24C8 moiety of 36. This assembly facilitates the resonant energy transfer (RET) process upon the ring-closing reaction of 35 under UV irradiation (Scheme 11). Control of the RET process by the alternating UV and visible-light irradiation enabled the reversible on/off switching of the lanthanide luminescence (Figure 26). Furthermore, the reversible luminescence behavior of the [36]pseudorotaxane system could be manipulated by the successive addition of K$^+$ as a competitive guest and 18-crown-6 as a competitive host (Figure 25). This dual-stimuli-driven luminescent lanthanide molecular switch possesses two distinctive features: (1) the combination of RET with photochromic switching can provide a highly efficient luminescence switch, and (2) the self-assembled supramolecular scaffold can be disassembled and reassembled non-covalently to function as a molecular switch (Scheme 11). The present results may provide a novel perspective for the design of multistimulus-driven molecular machines and logic gates. More examples about luminescence modulation of lanthanide complexes associated with photochromic units will be presented in chapter 4.
Chapter 1 | Molecular switches and wires

3. Molecular electronics: molecular devices

The creation of efficient (opto)electronic devices based on individual functional molecules often termed “molecular electronics” is one of the ultimate goals in nanotechnology. Molecular electronics aroused considerable interests over the past decade since molecular compound have both small dimensions and an overwhelming degree of diversity and functionality. In relation to applications, the development of molecular wires and switches is a central goal for the field of molecular electronics, where the aim is to fully exploit the properties of molecules.

3.1 Molecular wires and technics

A molecular wire should consist in a molecular chain connected between two electrodes attached to its chain ends, in order to promote electron transfer through this bridge forming a “molecular junction” (Figure 27).

![Figure 27. Molecular wires connected between metal electrodes in a molecular junction.](image)

Different types of conductivity measurements are shown in Figure 28. Normally, measurement of molecular junctions can be divided in two broad categories: single-molecule and molecular ensemble strategies. Single-molecule approaches include Scanning Tunneling Microscopy (STM) (A) and break junctions (B). Other junctions include probe such as conduction probe AFM (CP-AFM) (C), crossed wire junction (D), and other bulk and nano electrodes that sandwich molecular films (E, F) (Figure 28).
Figure 28. Representative examples of formed metal/wire/metal junctions formed by (A) scanning tunneling microscopy (STM); (B) break junction; (C) CP-AFM; (D) crossed-wire junction; (E) mercury drop junction; (F) conducting polymer top contact.

An important goal is to understand the charge transport mechanism through the molecular junctions. In a simple understanding, a large difference between the vacant orbital of molecules and the Fermi level of the metal electrode leads to simple tunneling of electron through the molecule orbitals in a single step. When the energy difference is smaller and molecules-electrodes coupling higher, coulomb blockade behavior can occur in which charges transport occurs in two steps: metal to molecule, molecule to metal.

In general, molecular junction involving conjugated molecules with alternating double and single bonds or delocalized π electrons are better candidates for long-distance charge transport. These molecules have much smaller HOMO-LUMO gaps compared to saturated molecular junctions (alkanes) and therefore transport charge more efficiently, thanks to the lower tunneling barrier. 63

To date, the majority of molecular systems investigated for molecular electronics purposes have been purely organic in composition. 65,66,67,68,69,70 One example considering organic molecular wires was presented by Wang and coworkers. 64 The system was studied in order to observe the evolution of the conduction mechanism, depending on the length of molecular wires inserted in devices. The authors prepared seven compounds (OPE1-7) (Scheme 12). The current-voltage curves of each of the seven compounds were measured by a scanning tunneling microscopy technique (STM) in a range of potential between 0 V and 0.4 V (Figure...
29a). The results (Figure 29b) indicate that the charge transport mechanism occurring in the devices containing OPE1-3 (tunneling) is different from those containing OPE4-7 (hopping). This example demonstrates the evolution of the transport mechanism of molecular wires depending on their length.

Scheme 12. Structures of seven amine-terminated OPE molecular wires

Figure 29. (e) Current−voltage characteristics for the seven diamine-terminated molecules. The lines are the linear fits, which could yield the most probable single molecular resistance. (f) Semilog plot of single molecular resistance versus molecular length for all of the Au_molecular wire_Au junctions. The inset is a linear plot of resistance against length, demonstrating the linear scaling of resistance with length for longer OPE molecules.

Metal complexes, which combine organic and inorganic (metal centers and clusters) components with exquisite atomic-level control of structure afforded by synthetic chemistry, coupled with the electronic and magnetic diversity of such species, has received far less
attention for molecular electronics applications than organic compounds.\textsuperscript{71}

One example of organic porphyrin molecular wires was reported by Nichols and coworkers.\textsuperscript{72}

Single molecular bridges are formed with P\textsubscript{1}-P\textsubscript{4} between a gold substrate surface and a gold STM tip. Current plateau values ($I(s)$ technique) or current-jumps ($I(t)$ technique) are then analyzed statistically to determine the single molecule conductance. Single molecule conductance for molecules P\textsubscript{1}-P\textsubscript{4} are plotted logarithmically against the calculated sulfur-sulfur distance ($S\cdots S$ distance) in Figure 30b, giving a very low attenuation factor of the tunneling current, $\beta$) ($0.04 \pm 0.006$) Å\textsuperscript{-1}. This is considerably lower than generally observed for $\pi$-conjugated organic bridges, which typically give values in the range 0.1 - 0.6 Å\textsuperscript{-1}.\textsuperscript{73}

Figure 30. (a) Porphyrin oligomers P\textsubscript{1} – P\textsubscript{3} and reference compound P\textsubscript{4}. (b) Dependence of the single molecule conductance (at $V_{bias} = 0.6$ V) as determined by the $I(t)$ (blue square) and $I(s)$ (red circle) methods on the molecular length for wires P\textsubscript{1}-P\textsubscript{4}. In the $I(s)$ technique current is monitored as molecular wires are stretched in the STM gap, while in the $I(t)$ technique the stochastic formation of molecular bridges is followed by monitoring current jumps overtime.\textsuperscript{72}
In collaboration with Frisbie, our group has reported the electrical transport characteristics of two series of linear ruthenium(II) bis(σ-arylacetylide) molecular wires, RunM and RunH (n = 1, 2, 3) (Figure 31), consisting of multiple redox-active Ru(II) centers and different saturated side chains (M = -CH₂-, and H = -O(CH₂)₆-) with lengths up to 6.0 nm. The self-assembled monolayers of these molecular wires on Au surfaces display interesting features. Both series of molecular wires exhibited very weak length dependence of the wire resistance, the β value of RunM being 1.02 nm⁻¹, and that of RunH being 1.64 nm⁻¹, indicating a high degree of electronic coupling between the redox centers. Further analysis of I-V characteristics revealed that the charge transport in RunM junctions was direct tunneling, but in RunH (n = 2, 3) junctions with the long chains the mechanism was thermally activated hopping, consistent with the temperature-dependent conduction measurement.

Another example was reported by Venkatesan and coworkers. They studied the influence of molecule–metal coupling on charge transport of dinuclear X(PP)₂FeC≡CC≡CFe(PP)₂X molecular wires (PP = Et₂PCH₂CH₂PxEt₂); X = NCS (42) and C₄SnMe₃ (44) (Figure 32) under ultrahigh vacuum and variable temperature conditions. Compound 44 formed a Au–C≡CC≡C₄FeC≡CC≡C₄FeC≡CC≡C₄–Au junction (Au-43-Au) after SnMe₃ extrusion, which revealed a conductance of 8.9 × 10⁻³ G₀, 3 orders of magnitude higher than for Au-42-Au (7.9 × 10⁻⁶ G₀). Density functional theory (DFT) confirmed the experimental trend in the conductance for the various anchoring motifs. The strong hybridization of
molecular and metal states found in the C–Au coupling case enables the delocalized electronic system of the organometallic Fe2 backbone to be extended over the molecule–metal interfaces to the metal electrodes to establish high-conductive molecular wires.

Figure 32. (A) Compounds 42 with corresponding reaction schemes upon coupling to Au electrodes. In contrast to compounds 42, the SnMe3 end groups of 44 cleave off and direct C–Au bonds are formed yielding the Au–43–Au (B). Schematic representations of the Au–42–Au (C) and the Au–43–Au junctions (D). The strong hybridization of metal and molecular states in the case of Au–43–Au as evidenced by the difference in the HOMO’s amplitude on the bonding site as obtained from DFT (gray circles), leads to the formation of a strong molecule–metal bond and enables to extend the delocalized electronic system between the two Fe centers over the molecule–electrode interfaces, in contrast to the weakly bonded Au–42–Au system. 

~ 43 ~
3.2 Molecular switches (for molecular electronics)

Compounds with switching functionality sandwiched between two conductive electrodes were used to modulate conductivity properties.\textsuperscript{76,77} Conductivity modulation of junctions incorporating, organic redox-active molecules, photochromic compounds or cation-binding molecules will be discussed in this part. Decurtins and coworkers reported that when molecular junctions incorporating TTF type units are treated with an oxidizing agent, such as iron chloride, the TTF units are oxidized to form its second oxidation state with a rearrangement of the TTF molecular orbitals, which leads to an order of magnitude increase of the conductance. When treated with a reducing agent, such as ferrocene, the oxidized TTF unit is reduced to its original neutral state. Correspondingly, the conductance switches back to the initial state (Figure 33).\textsuperscript{78}

![Figure 33. Structure of the redox-active dithiolated tetrathiafulvalene (TTFdT) studied. In presence of iron chloride or ferrocene, the TTFdT compounds can be oxidized or reduced in situ.\textsuperscript{78}}

Concerning the photochromic switching, as a first example, Nuckolls and coworkers have compared the device conductance when the constituent molecule, a modified diarylethene, switch between its two states of conjugation. More precisely, when the diarylethene molecule was immobilized inside a gap of SWNT through covalent amide linkages (Figure 34), the thiophene-based molecular (DTE) bridge can be switched from the open form to the closed form but not back again. In contrast, the pyrrole-based photoswitch can be cycled reversibly between the open and closed states.\textsuperscript{79}
Figure 34. (a) Molecular bridges between the ends of an individual SWNT electrode. (b) Switching between conjugated and non-conjugated molecular structures.  

Also, the conductance properties of a photoswitchable dimethyldihydropyrene (DHP) derivative have been investigated by Royal and coworkers for the first time in single-molecule junctions, using the mechanically controllable break junction technique. DHP (47) is a polycyclic π – conjugated unit, which can be optically converted into a less π – conjugated unit and colorless cyclophanediene (CPD) (48) isomer, while CPD reversibly reverts both photochemically and thermally into the colored and more stable isomer (DHP). Single-molecule conductance experiments clearly reveal distinct changes in conductance between the fully conjugated ON state (47, closed form) and the broken conjugated OFF state (48, open form) (Figure 35). The photothermally triggered conductance switching between these two isomers is fully reversible and stable over more than five sequential cycles, which reveals an excellent ON/OFF ratio approaching $10^4$. 
Figure 35. (A) Representation of isomerization between 47 (DHP) and 48 (CPD) in molecular junctions. (B) Five sequential, fully reversible cycles of the in situ photothermally triggered conductance switching between DHP (47) and CPD (48). The blue circles represent the most probable middle single junction conductance of the ON state 47, and the red circles symbolize the upper limit of the OFF state 48.\(^{80}\)

Concerning chemical switching, Blanchard and Roncali presented that the Pb\(^{2+}\) complexation by a crown-ether quarterthiophene (49) (Figure 36a) can move one of the oligomer molecular orbitals close to the Fermi energy of the electrodes, inducing a significant increase (up to \(1.6 \times 10^3\)) of the current at low bias (Figure 36b).\(^{81}\) The current-voltage (I-V) are measured on Au-molecule-metal junctions by contacting the top surface of the monolayer with an eutectic gallium-indium (eGaIn) drop. This type of junction could be useful to build simple sensors.

Figure 36. (a) Crown-ether quarterthiophene 49. (b) Typical I-V curves (averaged over 5 measurements) for the Au/molecules/eGain junction before and after Pb\(^{2+}\) complexation.\(^{81}\)
From the examples described above, we can see that, in particular, the compounds containing redox active units or photochromic units could be used for simple conductance switching in molecular junctions. Further examples dealing with compounds including both organometallic redox active units and DTE units in molecular junctions for conductance switching, among other relevant examples, will be discussed in chapter 5.

4. Conclusion

At the beginning of this chapter, we presented some representative works dealing with molecules displaying switching properties with various stimulus, and particularly photochromic compounds which could be used for switching of magnetism, chemical reactivity and photomechanical response.

Then, we focused on luminescent molecular switches with different kinds of switching mechanism before emphasizing luminescence modulation with redox-active units. In this section, luminescence modulations of triarylamine derivatives and lanthanide complexes were highlighted.

Finally, through the presentation of characteristics of molecular wires, we have shown the potential of these molecules for the preparation of conductive devices. We also showed that conductivity of such junctions could be modulated with molecules including ion sensors, redox-active units or photochromic units.

In the following chapters, we will present different combinations between ruthenium metal acetylide moieties, vinyl ruthenium moieties, triarylamine moieties, DTE units and lanthanide ions to achieve new molecular switches:

In chapter 2, combination of ruthenium acetylide moieties and luminescent triarylamine cores will be designed to try to realize the luminescence switching of triarylamine by changing the oxidation states of ruthenium acetylide moieties.

In chapter 3, ruthenium vinyl bipyridine complexes will be used to coordinate lanthanide ions, since those organometallic ruthenium vinyl moieties are redox active. This association was designed to achieve improved redox switching of luminescence of lanthanide complexes.

In chapter 4, association of a DTE unit with a lanthanide ion will also be used for luminescence modulation via the photochromic isomerization of the DTE unit.

Finally, in chapter 5, we will use redox-active molecular wires incorporating ruthenium bis(σ-arylacetylide) complexes to prepare graphene molecular junctions featuring an electrochemical gate for conductivity switching by changing the redox state of the ruthenium
acetylide moieties. Further incorporation of a photochromic DTE unit will be also attempted to add the photo-manipulation of conductance to these devices.
References

(1) Feringa, B. L. In Molecular Switches; Wiley-VCH Verlag GmbH: 2001, p i-xii.
(22) Bunzl, J.-C. G.; Piquet, C. Chemical Society Reviews 2005, 34, 1048-1077.
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(36) Sato, T.; Higuchi, M. Chemical Communications 2013, 49, 5256-5258.
(37) Kim, Y.; Kim, E.; Clavier, G.; Audebert, P. Chemical Communications 2006, 3612-3614.
(70) Livingston, R. C.; Cox, L. R.; Gramlich, V.; Diederich, F. Angewandte Chemie International Edition 2001, 40, 2334-2337.
Chapter 2:
Luminescent triarylamine cores associated with redox active units
Chapter 2: Luminescent triarylamine cores associated with redox active units

1 Introduction

Controllable luminescence switching materials have attracted significant attention for their potential applications including sensors,\(^1\) especially optical memory devices,\(^2\) logic gates,\(^3\) in vivo imaging,\(^4\) and displays.\(^5\) As presented in chapter one, the changes of fluorescent intensity can be triggered by different types of external conditions, such as voltage,\(^6\) temperature,\(^7\) pH,\(^8\) and light.\(^9\) Among them, electrical control is a facile approach to achieve the demand. Electrofluorochromism (EFC) deals with the reversible optical switching between high (ON) and low (OFF) fluorescence intensity states via redox-driven electric potentials. The electrofluorochromism behavior could be attributed to two kind of mechanism. One deals with redox active fluorophore switched from an emissive state to a non-emissive one via intrinsic electron transfer during the redox process, such as in tetrazine\(^10\) and triphenylamine (TPA).\(^11\) The other consists in the introduction of a redox active moiety as a quencher to induce deactivation of the fluorophore in one redox state.\(^12\) A high-performance electrofluorochromism device should include the following characteristics: high photoluminescent (PL) efficiency, high contrast, long-term stability, and rapid response time. Therefore, the design of materials with appropriate molecular structures is essential for modern optoelectronic applications. Since 2006, several electrofluorochromism devices have been fabricated and investigated including small organic molecules,\(^13\) inorganic materials,\(^14\) conjugated polymers,\(^12\) high-performance polymers,\(^15\) and hybrids.\(^16\) However, emerged materials could not comprise all the characteristics mentioned above yet to achieve a high-performance EFC device.

Triarylamine derivatives are promising materials for optoelectronic applications such as hole-transporters, light-emitters, photovoltaic, electrochromic, and memory devices due to their outstanding photo- and redox-active properties.\(^17\) In light of the importance of these properties, we believe that it could be of interest to modulate their luminescence by introducing a redox-switchable building block into these luminescent molecular systems in order to obtain convenient electro-generated molecular devices that could be easily modulated by electric current at low potential with good reversibility and rapid response time. One type of attractive building blocks for redox switches are group 8 metal complexes, and especially Ruthenium (Ru) acetylides, which display strong ligand-mediated electronic effects.\(^18\)
1.1 Triaryamine

The triaryamine unit is well-known for its easy oxidation of the nitrogen center and the ability to transport charge carriers via the radical cation species with high stability.\textsuperscript{19} It is widely investigated and applied in various electro-optical materials such as organic light emitting diodes (OLEDs),\textsuperscript{20} organic field-effect transistors,\textsuperscript{21} non-linear optic materials,\textsuperscript{22} and xerography.\textsuperscript{23} In recent years, it was found that the excellent photoelectric function of triarylamine was desirable for organic sensitizers, and a substantial number of dyes with triarylamine as electron donor were developed for organic solar cells.\textsuperscript{24}

![Figure 1. Structures of compounds 1 – 5](image)

In particular, triarylamine derivatives are promising luminescent materials.\textsuperscript{17} For example, a series of emitting push–pull triarylamine derivatives were well investigated by Prof. Elena Ishow (2-5 in Figure 1).\textsuperscript{25} All compounds (1-5) display strong absorption in the UV range, and compound 3, 4 and 5 show an additional band in the visible range ascribed to a CT band from the central amino group to the X group (Figure 2). Besides, their structural originality stems from the sole change of the electron-withdrawing substituent X (–H: 1, –CN: 2, CHO: 3,

![Figure 2. Normalized UV-vis absorption (left) and emission spectra (λ\textsubscript{ex} = 343 nm) (right) of 100 nm thick evaporated films of molecules 1 - 5.](image)
–NO2: 4, –CH(CN)2: 5) that gives rise to efficient emission tuning from blue to red upon increasing the X electron-withdrawing character. All these compounds are highly fluorescent in alkanes solvent 26 and solid state under single UV wavelength excitation.

1.2 Luminescent switching of triarylamine derivatives

As stated above, reversible luminescence switching by electrochemistry or electrofluorochromism is an attractive field. Emission of triarylamine derivatives is susceptible to be switched by changing its redox state as triphenylamine species display most of the time extremely stable cation-radicals which can be formed at moderate oxidizing potential. The first example about redox-controlled fluorescence modulation in triarylamine derivatives was described in 2014 by Audebert and coworkers,27 after we started this work. They have realized a straightforward fluorescence modulation with this organic dye acting both as the light emitter and the redox switch. They synthesized six triphenylamine derivatives bearing different groups in para positions (S1- S6, Scheme 1). These triphenylamine derivatives are fluorescent in the blue to the green region in their neutral state. The fluorescence intensity is quenched upon oxidation due to the formation of non-fluorescent cation-radical. The fluorescence can be thus electrochemically switched between the strongly fluorescent (neutral) state and the non-fluorescent (oxidized) state (Scheme 1 and Figure 3). Therefore triarylamine derivatives constitute a family of very promising candidates for applications in electrofluorochromism.

Scheme 1. The two redox states of triphenylamine derivatives S1-S6 with different fluorescence properties.27
Figure 3. Fluorescence emission spectra recorded upon oxidation of S₆ by Cu(ClO₄)₂ in CH₃CN as a function of R = [Cu]/[S₆]. [S₆] = 4.8 × 10⁻⁶ mol • L⁻¹. λₑₓc = 307 nm.²⁷

1.3 Application of polymers based on triphenylamine—successful materials for electrochemical fluorescence switching

In 2014, Wu and coworkers created a novel electrochromic and photoluminescent (PL)-active poly(4-cyanotriphenylamine) (CN-PTPA) by oxidative coupling polymerization from 4-cyanotriphenylamine (CN-TPA) using FeCl₃ as an oxidant (Figure 4).²⁸ The high-performance electrofluorochromic devices using CN-PTPA thin film with photoluminescent quantum yield of 21.9 % as active layer were readily fabricated and revealed the highest fluorescent contrast ratio (Iₜ₉₉ / Iₜ₉₉) of 242 between the fluorescent (neutral) state and the non-fluorescent (oxidized) state, rapid response time shorter than 0.4 s, and excellent electrofluorochromic stability longer than 9000 s. Furthermore, by introducing viologen into the electrolyte as a counter layer for charge balance, the resulting electrofluorochromic device exhibits notable improvement in reducing oxidation potential (from 2.30 V to 1.55 V) and switching recovery time (from 78 to 38 s) with enhanced fluorescent contrast ratio during pulse on/off multi-cyclic scanning. These results demonstrate that incorporation of the electrochromism and PL-active CN-PTPA is a facile and feasible approach to prepare highly efficient electrofluorochromic devices.
1.4 Association of carbon-rich complexes with triaryl-amines.

Several associations of ruthenium redox active complexes with triarylamines have been achieved to study the nature of the electronic interactions between such different redox-active units.\textsuperscript{29,30,31} Rainer F. Winter reported the triarylamine-derived styryl ruthenium complexes 1–3 where one (1), two (2) or three (3) vinyl ruthenium moieties are appended to a triphenylamine core.\textsuperscript{29} The near equivalency of the styryl ruthenium and the triarylamine redox systems leads to strong interactions between these moieties and strong mixing of the respective frontier orbitals. This results, \textit{inter alia}, in the observation of two to four consecutive reversible one-electron redox couples with potential splittings of 185 – 435 mV. The associated radical cations and higher oxidized forms show strong absorptions whose positions vary from deep in the near-infrared (NIR) to the border region between the Vis and NIR regimes as a function of the oxidation state. Absorption coefficients and oscillator strengths reach rather impressive values of up to 90000 L.mol$^{-1}$.cm$^{-1}$ and $\geq 1.0$. 
Scheme 2. The vinyl ruthenium complexes

From the three examples listed above, we can see that triarylamine derivatives are very interesting molecules, which can not only be employed as luminescence switches and in electrofluorochromic devices, but also coordinate with ruthenium moieties to generate new interesting complexes which absorptions could be tuned in the visible and NIR region as a function of the oxidation states.

1.5 Objective

In order to ultimately electro-switch fluorescence of triarylamines in the solid state at low potential, we choose an association with redox active ruthenium acetylide complexes for their peculiar properties. The investigated units will consist in push-pull triarylamine derivatives with two ruthenium acetylides as electron donors, while substituent X (NO$_2$ or CHO) will act as the acceptor group (Scheme 3). The need of π-electron conjugation to ensure emission in the solid state, prompts us to choose the phenyl linker introducing some degree of non-planarity. The presence of the bulky metal complexes unit in the periphery will also help the formation of amorphous phase required for electro-optical studies in thin films, ie. to avoid deleterious light scattering.
1.6 Working strategy

The introduction of electron-withdrawing groups (NO$_2$ or CHO) of varying strengths will target a twofold objective: (i) the wavelength (color) tuning of emission, expected from blue to red, originating from the energy modulation of the radiative excited state; (ii) the modulation of the oxidation potential of the conjugated triphenylamino moiety which could be used as an additional electrochemical trigger input.

Depending on the redox wave separations (in part due to the electronic coupling) and the number of electro-active units ($E^{\circ}[\text{Ru}^{+}/0] \sim 0.3-0.4$ V vs saturated calomel electrode (SCE) and $E^{\circ}[\text{triarylamine}^{+}/0] \sim 1-1.6$ V vs SCE as a function of electron-withdrawing groups (X = NO$_2$ or CHO), different redox states are anticipated. Chemical oxidation or electrolysis of the solution at potentials defined previously will be performed to generate the oxidized or reduced species, expected to possess a charge transfer character dramatically distinct from that of the neutral compounds. These experiments will be coupled to simultaneous absorption and emission detection to follow the electro-induced change in the electronic energy of the ground and excited states. Variation of the emission energy (Scheme 4, case 1) and/or of intensity (case 2) are expected, and will provide information on the mechanisms involved, i.e. energy (de)stabilization of the intramolecular charge transfer emitter state, photoinduced energy transfer.
Scheme 4. Working strategy
2 Synthesis

2.1 Synthesis of target complexes $\text{trans-}[(\text{dppe})_2\text{ClRu(C} \equiv \text{C-4-C}_6\text{H}_4\text{-C}_6\text{H}_4)]_2\text{N-C}_6\text{H}_4\text{-X}]$ $(X = \text{NO}_2, \text{CHO})$

Scheme 5. Retrosynthesis of target complexes

The synthesis of desired complexes will be accomplished by using terminal alkyne functions of a functionalized triarylamine to achieve activation of ruthenium complexes$^{33}$, thereby
providing selective formation of vinylidene complexes that are the key intermediates for the formation of mono-alkynyl after deprotonation.

### 2.2 Synthesis of the organic precursors [(HC≡C-4-C₆H₄-C₆H₄)₂N-C₆H₄-X] (X = NO₂, CHO)

The synthesis of triisopropylsilyl (Tips) protected organic compounds (2-CHO and 2-NO₂) were achieved by Florian Charrier under the supervision of Prof. Eléna Ishow in the University of Nantes in France. Then, the deprotection reactions were achieved with the help of Florian Charrier in the presence of tetrabutylammonium fluoride (TBAF) and tetrahydrofuran (THF) in our lab to obtain the organic precursors {H-C≡CH-4-C₆H₄-C₆H₄}₂N-C₆H₄-X (X = NO₂, CHO) (3-NO₂ or 3-CHO) in a good yield, i.e. 69 % for the compound with the aldehyde substituent group and 75 % for the NO₂ group.

![Scheme 6. Synthesis of the organic precursor](image-url)
2.3 Synthesis of the ruthenium precursor [RuCl(dppe)_2][PF_6]

Here, we describe the route to synthesize the 16-electron species 1.\textsuperscript{34} Ruthenium trichloride trihydrate and 1,2-bis(diphenylphosphino)ethane (dppe) were mixed with ethanol and water to get \textit{trans}-[RuCl_2(dppe)_2] (80 \%) (\textbf{Scheme 7}). In this reaction, Ru(III) is reduced to Ru(II), with keeping the remaining chloride atoms in a \textit{trans} position. The \textit{trans}-[RuCl_2(dppe)_2] was converted into \textit{cis}-[RuCl_2(dppe)_2] by elution on a silica column with dichloromethane as eluent. The 16-electron species [RuCl(dppe)_2][PF_6] was generated from \textit{cis}-[RuCl_2(dppe)_2] by chloride abstraction using NaPF_6.

2.4 Synthesis of desired complexes

The conditions used for the synthesis are similar to that previously reported.\textsuperscript{31} Compound 3 and complex 1 were dissolved in dichloromethane, and the reaction mixture heated to 40 °C for 6 hours. Vinylidene complexes \textit{trans}-[[((dppe)_2ClRu(C=CH-4-C_6H_4-C_6H_4)_2N-C_6H_4- X][PF_6]) (X = NO_2, CHO) (4) (with yield of 71 \% for 4-NO_2 and 75 \% for 4-CHO) were obtained as green powders unambiguously identified by \textsuperscript{31}P-NMR spectroscopy with a characteristic peak of vinylidene units at 39.29 and 39.26 ppm, respectively, and readily used in the next step.
Our desired final complexes (5-NO2 and 5-CHO) were obtained with yields of 18% and 21%, respectively, from deprotonation of the vinylidene complexes trans-[(dppe)2ClRu(C=CH-4-C6H4-C6H4)]2N-C6H4-X][PF6]2 (X = NO2, CHO) (4-NO2, 4-CHO) in the presence of triethylamine for 5 minutes in dichloromethane.

Note that due to the limited quantity of organic precursors (30 – 50 mg), the two steps of the synthesis (complexation and deprotonation) were performed without isolating the intermediate vinylidene.

3 Characterizations

The targeted complexes (5-NO2 and 5-CHO) were characterized by IR, 1H, 31P NMR spectroscopy, high-resolution mass spectrometry, and satisfactory microanalysis.

3.1 NMR spectroscopy

The 31P NMR spectra of each complex show a sharp singlet (δ = 49.53 ppm for 5-NO2, 48.76 ppm for 5-CHO), which is consistent with ruthenium acetylides with a trans arrangement of the dppe ligands around the ruthenium atom.
The interpretation of the $^1$H NMR spectrum of complex 5-CHO has been completed with the help of a COSY spectrum and chemical shifts are listed in Table 1. This $^1$H NMR spectrum of complex 5-CHO in CD$_2$Cl$_2$ is presented in Figure 6 and Table 1.

![Figure 5. $^{31}$P-NMR spectrum of complex 5-CHO in CD$_2$Cl$_2$](image)

5-CHO
Figure 6. $^{1}$H-NMR spectrum of complex 5-CHO in CD$_2$Cl$_2$

Table 1. $^{1}$H-NMR data of complex 5-CHO

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
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<tr>
<td>9.84</td>
<td>s</td>
<td></td>
<td>1</td>
<td>CHO</td>
</tr>
<tr>
<td>7.73</td>
<td>d</td>
<td>8.8</td>
<td>2</td>
<td>H$_6$</td>
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<td>d</td>
<td>8.6</td>
<td>4</td>
<td>H$_3$</td>
</tr>
<tr>
<td>7.45-7.40</td>
<td>m</td>
<td></td>
<td>36</td>
<td>o-PPh$_2$ and H$_2$</td>
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<tr>
<td>7.28</td>
<td>d</td>
<td>8.6</td>
<td>4</td>
<td>H$_4$</td>
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<tr>
<td>7.26-7.19</td>
<td>m</td>
<td></td>
<td>16</td>
<td>p-PPh$_2$</td>
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<td>d</td>
<td>8.8</td>
<td>2</td>
<td>H$_5$</td>
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<tr>
<td>7.08-6.96</td>
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<td>32</td>
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<td>6.73</td>
<td>d</td>
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<td>m</td>
<td></td>
<td>16</td>
<td>PCH$_2$CH$_2$P</td>
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</table>
The $^1$H NMR spectrum of complex 5-CHO in CD$_2$Cl$_2$ presents a singlet at 9.84 ppm corresponding to H$_{CHO}$ and a doublet at 7.73 ppm ($J = 8.8$ Hz) corresponding to H$_6$ coupled with H$_5$. Another doublet appears at 7.64 ppm ($J = 8.6$ Hz), corresponding to H$_1$ coupled with H$_4$. Protons on o-PPh$_2$ and H$_2$ give rise to multiplets from 7.45 - 7.40 ppm. Another doublet appears at 7.28 ppm ($J = 8.6$ Hz) corresponding to H$_4$ coupled with H$_3$. Protons on p-PPh$_2$ give rise to multiplets from 7.26 - 7.19 ppm. Protons on m-PPh$_2$ and H$_5$ give rise to multiplets from 7.08 - 6.96 ppm. Another doublet appears at 6.73 ppm ($J = 8.2$ Hz) corresponding to H$_1$ coupled with H$_2$. The protons on PCH$_2$CH$_2$P give rise to a multiplet at 2.72 ppm.

Similar results were found for 5-NO$_2$. These data for both 5-CHO and 5-NO$_2$, as well as interpretation of $^{13}$C NMR of complexes 5-CHO and 5-NO$_2$, are reported in the appendix 1 of the experimental part.

**3.2 IR spectroscopy and Mass spectrometry**

The infrared measurements of complexes 5-NO$_2$ and 5-CHO were performed in KBr pellets. The data are summarized in Table 2.

In the IR spectrum of complex 5-NO$_2$, a band at 2058 cm$^{-1}$ is observed and corresponds to the C≡C stretching vibration. For complex 5-CHO, this band is observed at 2062 cm$^{-1}$, while another band at 1689 cm$^{-1}$ corresponds to the stretching vibration of the C=O of the aldehyde group.

Data obtained with mass spectrometry were also included in Table 2, which also confirm the successful synthesis of the desired complexes 5-NO$_2$ and 5-CHO.
Table 2. Data obtained by IR spectroscopy and mass spectrometry

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR ((\text{cm}^{-1}))</th>
<th>Mass (m/z)</th>
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</thead>
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<tr>
<td>5-NO₂</td>
<td>2058 (C≡C)</td>
<td>[M⁺] 2354.4465 (2354.4396)</td>
</tr>
<tr>
<td>5-CHO</td>
<td>2062 (C≡C), 1689 (C=O)</td>
<td>[M⁺] 2337.4553 (2337.4495)</td>
</tr>
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</table>

3.3 UV-vis absorption studies

![Normalized UV/Vis absorption spectra of 2-CHO, 3-CHO, 2NO₂ and 3-NO₂ in toluene at 25 °C](image)

Figure 7. Normalized UV/Vis absorption spectra of 2-CHO, 3-CHO, 2NO₂ and 3-NO₂ in toluene at 25 °C

The absorption measurements of compound 3-CHO, 3-NO₂, 2-CHO and 2-NO₂ were completed in toluene solutions by the group of Eléna Ishow. Their absorption data are summarized in Table 3, and absorption spectra are shown in Figure 7. Compound 3-NO₂ displays two strong absorption bands, one centered at 403 nm which corresponds to an intramolecular charge transfer (ICT) from the triphenylamino core (TPA) to the NO₂ group, while the other band centered at 348 nm can be assigned to π-π* transition from TPA to the biphenyl groups (BPh). The absorption spectrum of 2-NO₂ is very similar to that of 3-NO₂. There is only one strong absorption bands in the absorption spectrum of 3-CHO which is centered at 360 nm, and that is probably a combination of the ICT from TPA to CHO group.
and of the $\pi-\pi^*$ transition from TPA to BPh groups.\textsuperscript{26} The absorption spectrum of 2-CHO is almost the same as that of 3-CHO.

Table 3. Normalized UV/vis absorption data of 2-CHO, 3-CHO, 2NO\textsubscript{2} and 3-NO\textsubscript{2} at 25°C in toluene

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (absorption) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-CHO</td>
<td>360</td>
</tr>
<tr>
<td>2-CHO</td>
<td>360</td>
</tr>
<tr>
<td>3-NO\textsubscript{2}</td>
<td>348, 403</td>
</tr>
<tr>
<td>2-NO\textsubscript{2}</td>
<td>345, 403</td>
</tr>
</tbody>
</table>

The absorption measurements of complexes 5-NO\textsubscript{2} and 5-CHO were achieved in dichloromethane solutions with concentrations in the range of $10^{-5}$ and $10^{-6}$ mol.L\textsuperscript{-1} (Figure 8). Their absorption data are summarized in Table 4.

![Absorption spectra of complexes 5-CHO and 5-NO\textsubscript{2} (CH\textsubscript{2}Cl\textsubscript{2}, 298 K).](image)

Figure 8. Absorption spectra of complexes 5-CHO and 5-NO\textsubscript{2} (CH\textsubscript{2}Cl\textsubscript{2}, 298 K).
Table 4. UV-visible spectral data obtained on absorption of complexes 5-NO₂ and 5-CHO at 25 °C in CH₂Cl₂ ([C] = 3~4*10⁻⁶ M)

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-visible λmax nm (Ɛ in M⁻¹.cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-NO₂</td>
<td>383 (68100)</td>
</tr>
<tr>
<td>5-CHO</td>
<td>386 (52800)</td>
</tr>
</tbody>
</table>

For complex 5-CHO, the intense absorption band centered at 386 nm can be tentatively assigned to the metal-to-ligand charge transfer (MLCT) excitations, corresponding to transitions from the two Ru(dπ)/ankynyl-based orbitals to a carbon-rich ligand antibonding orbitals, overlaping with those originating from the triarylamine core (vide supra). Similarly, for complex 5-NO₂, a band centered at 383 nm can be ascribed to the MLCT transition also overlapping with those originating from the triarylamine core, with a shoulder at around 450 nm that could account for the ICT from the triphenylamino core to the NO₂ group.
3.4 Electrochemical studies

Figure 9. Cyclic voltammograms of 5-CHO and 5-NO₂ in CH₂Cl₂ with 0.2 M [N₄Bu₄][PF₆], SCE as the reference, Pt as working and auxiliary electrodes. v = 0.1 V·s⁻¹.

Cyclic voltammetry (CV) data for 5-CHO and 5-NO₂ are collected in Table 5 and typical CV traces are displayed in Figure 9. Two distinct oxidation waves are observed for each bimetallic complexes 5-CHO and 5-NO₂. With the help of square wave voltammetry, we observed two one-electron processes for the first event (shown on Figure 9), therefore attributed to the concomitant oxidation of the two Ru-acetylide carbon-rich units, while the other oxidation (1e⁻) is rather ascribed to the triarylamine core. These assumption are
enforced by the fact that for 5-NO₂, the first oxidation wave is very similar to that of 5-CHO, while there is 70 mV difference in second oxidation wave, probably related to the more electron withdrawing character of the NO₂ group. Both the triarylamine unit and ruthenium acetylide oxidation are chemically reversible.

Table 5. Cyclic voltammetric data of complexes 5-NO₂ and 5-CHO at 25 °C in CH₂Cl₂

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_{1/2}, (\Delta E_p) ) [mV] vs FeCp₂/FeCp₂⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-NO₂</td>
<td>( E_{\text{ox}1} = -29 ) (71) ( E_{\text{ox}2} = 560 ) (114)</td>
</tr>
<tr>
<td>5-CHO</td>
<td>( E_{\text{ox}1} = -22 ) (88) ( E_{\text{ox}2} = 488 ) (130)</td>
</tr>
</tbody>
</table>

3.5 Study of the first oxidation state by UV-visible-NIR spectroscopy (spectroelectrochemical study - SEC).

Figure 10. UV/Vis/NIR spectra of 5-CHO upon oxidation, obtained by in situ electrolysis of 5-CHO in an OTTLE cell at 25 °C in 1,2-C₂H₄Cl₂ (0.2 M nBu₄NPF₆).

To record the changes in the absorption spectra of 5-NO₂ and 5-CHO across the possible redox states, both complexes were electrolyzed in situ by using an optically transparent thin-layer electrochemical (OTTLE) cell at 25 °C. Results are collected in Table 6 and typical spectra shown in Figure 10 - 12. Sequential application of the appropriate potentials [0, 500, 550, 570, 600, 650, 700 mV vs Ag wire (pseudo reference)] to a solution of 5-CHO in
Cl\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Cl that contained 0.2 M [N\textsubscript{n}Bu\textsubscript{4}][PF\textsubscript{6}] as the supporting electrolyte cleanly afforded the two e\textsuperscript{-} oxidation process to [5-CHO]\textsuperscript{2+}. More specifically, at 0 mV (5-CHO), the maximum of the absorption band is centered at 386 nm. Then, oxidation of the compound begins and a decay of the absorption band is observed while applying potential increase from 0 mV to 700 mV. At the same time, the intensities of two bands centered at 489 nm (shoulder) and at 1088 nm increase and reach their maximum at 700 mV. On the basis of the absorption intensity of the initial band, upon application of a reduction potential, the reversibility of the process is estimated to be 97 %. For 5-NO\textsubscript{2}, the trend is quite similar to that of 5-CHO. The spectrum of [5-NO\textsubscript{2}]\textsuperscript{2+} shows the same dramatic changes compared to that of 5-NO\textsubscript{2}. The band at 383 nm in the neutral complex (5-NO\textsubscript{2}) is replaced by two strong bands at 413 nm and 945 nm in the spectrum of [5-NO\textsubscript{2}]\textsuperscript{2+}. Following the decrease in the MLCT bands, the appearance of a new broad near infrared (NIR) bands is probably due to multiple transitions from HOMO-n to the SOMO for both compounds resulting from the depopulation of the HOMO d\textsubscript{π}/π orbital, a behavior which is usually observed for Ru acetylide.\textsuperscript{36} The NIR bands seem to be composed of at least two main transitions, which relative intensity change when comparing [5-CHO]\textsuperscript{2+} and [5-NO\textsubscript{2}]\textsuperscript{2+}. The similarity of spectral signature of [5-CHO]\textsuperscript{2+} and [5-NO\textsubscript{2}]\textsuperscript{2+} is again an indication that probably the first two oxidations are localized on the Ru-acetylide parts, without significant participation of the triarylamine part.

The third oxidation process at ca. 500 mV involving the triarylamine core was also investigated for both compounds. Although the process is reversible on the CV timescale, it leads to decomposition of the compounds on the timescale of the SEC experiments in both cases. Therefore, this process was not further studied.
Figure 11. UV/Vis/NIR spectra of 5-CHO (starting) and [5-CHO]$^{2+}$ (first two oxidation), obtained upon in situ electrolysis of 5-CHO in an OTTLE cell at 25 °C in 1,2-C$_2$H$_4$Cl$_2$ (0.2 M nBu$_4$NPF$_6$).

Figure 12. UV/Vis/NIR spectra of 5-NO$_2$ (starting) and [5-NO$_2$]$^{2+}$ (first two oxidation), obtained upon in situ electrolysis of 5-NO$_2$ in an OTTLE cell at 25 °C in 1,2-C$_2$H$_4$Cl$_2$ (0.2M nBu$_4$NPF$_6$).
Table 6. UV/Vis/NIR spectral data obtained upon electrolysis of complexes 5-NO₂ and 5-CHO at 25 °C in OTTLE cell in 1,2-C₂H₄Cl₂ (0.2 M nBu₄NPF₆).

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-visible λmax nm (Ɛ in M⁻¹.cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-NO₂</td>
<td>383(67271); 465(sh)</td>
</tr>
<tr>
<td>[5-NO₂]²⁺</td>
<td>413 (42629); 504 (shoulder); 945 (16877); 1078 (shoulder)</td>
</tr>
<tr>
<td>5-CHO</td>
<td>386 (50225)</td>
</tr>
<tr>
<td>[5-CHO]²⁺</td>
<td>375 (29447); 489 (shoulder); 951 (shoulder); 1088 (11948)</td>
</tr>
</tbody>
</table>

3.6 Emission studies

The emission measurements of the organic precursors were performed in degassed dichloromethane and toluene solutions at room temperature in Nantes. The absorption and emission spectra were recorded both in toluene and in chloroform solutions at a concentration between 5x10⁻⁵ and 5x10⁻⁴ mol.L⁻¹.

The data resulting from the emission in toluene are summarized in Table 7 and typical emission spectra are shown in Figure 13. The data resulting from the emission in chloroform are summarized in Table 8. Compounds 3-CHO and 2-CHO showed similar emission spectra, with maximum emission at 454 nm for 3-CHO and 456 nm for 2-CHO, after excitation at

![Normalized emission spectra of 3-CHO, 3-NO₂, 2-CHO and 2-NO₂ in toluene at 25 °C (λex = 360 nm for 2-CHO and 3-CHO; 345 nm for 2-NO₂ and 348 nm for 3-NO₂).](image)
336 nm. Quantum yield for 3-CHO is 0.25 while that of 2-CHO is 0.26. Compounds 3-NO₂ and 2-NO₂ showed similar emission spectra, with maximum emission at 559 nm for 3-CHO and 562 nm for 2-NO₂, after excitation at 450 nm. Quantum yield for 3-NO₂ is 0.17 while that of 2-NO₂ is 0.11. The red shift of emission band of NO₂ derivatives compared with CHO derivatives is probably due to the more electron withdrawing character of NO₂ group compared with the CHO group. The quantum yields of our organic precursors are quite similar with that of similar compounds synthesized by Prof. Ishow.

Table 7. Normalized UV/vis absorption and emission data of 2-CHO, 2-NO₂, 5-CHO and 5-NO₂ at 25 °C in toluene (λₐₓ = 385 nm for 5-NO₂ and 5-CHO; 345 nm for 2-NO₂, 348 nm for 3-NO₂, 360 nm for 2-CHO and 3-CHO).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λₐₓ(absorption) /nm</th>
<th>λₐₓ(emission) /nm</th>
<th>Φₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-CHO*</td>
<td>385</td>
<td>453</td>
<td>0.01</td>
</tr>
<tr>
<td>3-CHO</td>
<td>360</td>
<td>454</td>
<td>0.25</td>
</tr>
<tr>
<td>2-CHO</td>
<td>360</td>
<td>456</td>
<td>0.26</td>
</tr>
<tr>
<td>5-NO₂</td>
<td>385, 462 (sh)</td>
<td>569</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>3-NO₂</td>
<td>348, 403</td>
<td>559</td>
<td>0.17</td>
</tr>
<tr>
<td>2-NO₂</td>
<td>345, 403</td>
<td>562</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Figure 14. Normalized emission spectra of 5-CHO and 5-NO₂ in toluene and in chloroform at 25 °C (λₐₓ = 385 nm).
The emission measurements of the two complexes 5-CHO and 5-NO₂ were performed in degassed toluene and chloroform solutions at room temperature. Their emission data are summarized in Table 7 and Table 8, and emission spectra are shown in Figure 14. Compound 5-CHO in toluene presents an emission band at 453 nm with a quantum yield of 0.01 after excitation at 385 nm, while there is a 58 nm red shift for that of 5-CHO in chloroform solution to compare with the 76 nm red shift observed with the organic precursor 2-CHO. Compound 5-NO₂ in toluene presents an emission band at 569 nm with a quantum yield lower than 0.001 after excitation at 385 nm, which is almost the same as that of 5-NO₂ in chloroform solution. Compared with 5-CHO, there is a red shift in the emission band of 5-NO₂ in both toluene and chloroform solutions probably due to enhanced electron withdrawing capability since NO₂ is more electron withdrawing than the aldehyde group as observed with the organic precursors. Although the luminescence observed with 5-CHO is weak, it is attributable to the complex because of the shift observed in chloroform is different to that of the precursors. In the case of 5-NO₂, it is highly possible that the very weak observed luminescence is due to the presence of traces of the organic precursors.

Why our target complexes are poorly luminescent is still under investigation with the help of theoretical simulation. However we can tentatively state that the deactivation of the excited state of the triarylamine cores occurs via low-lying energy levels located on the ruthenium fragment.

### Table 8. Normalized UV/vis absorption and emission data of 2-CHO, 2-NO₂, 5-CHO and 5-NO₂ at 25 °C in chloroform (λ<sub>ex</sub> = 336 nm for 2-CHO and 5-CHO; 450 nm for 2-NO₂ and 5-NO₂).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;(absorption) /nm</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;(emission) /nm</th>
<th>Φ&lt;sub&gt;f&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-CHO</td>
<td>385</td>
<td>511</td>
<td>0.01</td>
</tr>
<tr>
<td>2-CHO</td>
<td>357, 383 (sh)</td>
<td>532</td>
<td>0.22</td>
</tr>
<tr>
<td>5-NO₂</td>
<td>385, 462 (sh)</td>
<td>569</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>2-NO₂</td>
<td>338, 415</td>
<td>non emissive</td>
<td>--</td>
</tr>
</tbody>
</table>

### 3.7 Redox-controlled luminescence modulation

Since our target complexes are poor emitters, luminescence switching is difficult to be obtained and our working strategy needs to be revised. Despite this fact, we have tried several
times to achieve redox-control of the luminescence of 5-CHO. Unfortunately, no satisfactory emission was observed in home made electrochemical cell. We are still trying to reobtain the emission with a modified cell.

4 Conclusion and perspectives.

In this chapter, we have reported the synthesis of two ruthenium complexes incorporating triarylamine units and their photophysical and electrochemical properties. The two complexes Trans-[(dppe)₂ClRu(C≡C-4-C₆H₄-C₆H₄)₂N-C₆H₄-X] (X = NO₂, CHO) (5-CHO, 5-NO₂) were obtained and characterized by IR, NMR, UV-vis, CV, spectroelectrochemistry, and photoluminescence. Unfortunately, complexes 5-CHO and 5-NO₂ are poorly luminescent and their luminescence was not successfully modulated by changing their oxidation states.

One reason of this poor/non-emissive behavior can be the deactivation of the excited state of the triarylamine cores via low-lying energy levels located on the ruthenium fragment. In order to try to avoid this, we seek to use another ligand (TIPS-C≡C(CN)₂) with a lower lying excited state that might lie bellow the ruthenium state responsible of the quenching. This triaryl ligand (TIPS-C≡C(CN)₂ in Scheme 9) bearing a stronger electron withdrawing group (-C≡C-CN₂), which absorption and emission bands are significantly red shifted by comparison to that of 2-NO₂ and 2-CHO to 452 nm (absorption) and 581 nm (emission) according to Prof. Ishow’s measurements, is currently under study.

Scheme 9. New organic ligand TIPS-C≡C(CN)₂

~ 80 ~
Chapter 2  
Luminescent triarylamine cores associated with redox active units

References.

(6) Audebert, P.; Miomandre, F. Chemical Science 2013, 4, 575-584.
(11) Yen, H.-J.; Liou, G.-S. Chemical Communications 2013, 49, 9797-9799.


Chapter 3:
New associations of luminescent lanthanide ions with organometallic ruthenium complexes
Chapter 3: New associations of luminescent lanthanide ions with organometallic ruthenium complexes

1 Introduction

Much attention has been focused on the switching of luminescence by using appropriate stimuli such as change of pH, variation of redox potential, light, addition of ions and molecules.\(^1\) We believe that it is of high interest to modulate luminescence by introducing one or several redox-switchable building blocks into luminescent molecular systems in order to obtain convenient electro-generated molecular switches, because their luminescence can be easily modulated by a simple electric current (see chapter 1).

In this chapter we will try to achieve luminescent redox switches based on lanthanides ions and organometallic ruthenium complexes.

1.1 Lanthanides

The 15 elements from lanthanum (atomic number 58) to lutetium (atomic number 71) are termed lanthanides; they correspond to the gradual filling of the 4f electron shell, which is shielded by the outer 5s\(^2\)5p\(^6\) subshells. All of the elements in the group have a close chemical resemblance, which rendered their separation and characterization quite difficult. Their discovery extended over more than a century (Ce, 1803; Lu, 1907; artificial Pm, 1947), and identification was very often primarily made by spectroscopy. Lanthanides have the general electronic configuration [Xe]4f\(^n\)5d\(^1\)6s\(^2\) with \(n\) from 0 (La) to 14 (Lu), and their most stable oxidation state, particularly in water, is + 3 with a [Xe]4f\(^n\) configuration, although a rich chemistry of their divalent state is now developing in nonaqueous solvents.\(^2\)

Here we will focus on the luminescence properties of these lanthanide ions, which intensity is low. This is due to f-f transitions, which are theoretically prohibited by the rules of electric dipole selection (Laporte rule and rule of spin). Thus, the Ln\(^{3+}\) ions possess low molar absorption coefficients (between 1 and 10 L. mol\(^{-1}\). cm\(^{-1}\)). The antenna effect can be used to enhance their emission intensity and consists of the coordination of an organic or organometallic ligand, playing the role of sensitizer in the environment of the lanthanide ion. So, after excitation in the UV-visible region, wherein the sensitizer generally has a strong absorption, an energy transfer mechanism leads to the population the lanthanide ion excited state. This results in intense luminescence (Figure 1).\(^3\)
Figure 1. Representation a lanthanide ion with a sensitizing ligand.\(^4\)

Figure 2. Partial energy diagram of lanthanide trivalent ions (except La, Ce, Pm, and Lu) showing the ground state and one of the most luminescent excited states.\(^2\)

For example, we can note that Europium with the energy level about 27,000 cm\(^{-1}\) (Figure 2) is almost two times higher than the energy level of Ytterbium (around 10,000 cm\(^{-1}\)) (Figure 2). Thus, Europium complexes are luminescent in the visible region while Ytterbium complexes are usually emissive in the near infrared region. Herein, different types of antennae for Eu and Yb complexes will be developed.

1.2 Lanthanide luminescence switches

Two relevant examples of lanthanide luminescence switches reported in literature are presented in this part.
Tropiano and coworkers synthesized the Eu.2 complex and demonstrated that the redox characteristic of a ferrocene antennae could be used in the reversible switching of the luminescence of the lanthanide center (Figure 3).<sup>5</sup> This switching event leads to the modulation of the luminescence intensity of 40 % in the present case. More specifically, electrolytic oxidation of the ferrocene chromophore results in a significant reduction of the intensity of the lanthanide-centered emission. While ferrocene has been used several times as a sensitizer for lanthanide emission, this is the rare case in which its electrochemistry has been exploited for such a switching purpose.

![Emission spectrum of Eu.2](image)

**Figure 3.** Emission spectrum of Eu.2 in its reduced state (black line) and after electrochemical oxidation (red line) ($\lambda_{ex} = 340$ nm).<sup>5</sup>

**Scheme 1.** Redox modulation of emission of Yb2
Figure 4. (a) Initial emission spectrum of Yb2 in CH$_2$Cl$_2$ (black), after in situ oxidation with acetylferricinium (red), and after reduction with decamethylferrocene (blue) ($\lambda_{\text{ex}}$ = 450 nm). (b) Monitoring of the absorption spectra during the first oxidation of Yb2 in an OTTLE cell (CH$_2$Cl$_2$, 0.2 M Bu$_4$NPF$_6$).

Attractive building blocks to achieve for redox switches are group 8 metal complexes, and especially Ruthenium metal-acetylides, which display strong ligand-mediated electronic effects. Di piazza in our group synthesized the Yb2 complex and described the straightforward switching of ytterbium luminescence by taking advantage of the redox commutation of a carbon rich ruthenium antenna and via the use of its MLCT bands. As shown in Figure 4, when Yb2 was excited at 450 nm, it displays a characteristic band shown in black curve in Figure 4a. When Yb2 has been oxidized to Yb 2$^+$, its luminescence has been fully quenched as shown with the red curve of Figure 4a. When Yb 2$^+$ is reduced back to Yb 2, Yb NIR luminescence recovered 53 % of its original intensity (blue trace in Figure 4a). This concept could be extended to other Ln (Nd), and to the electrochemical switching with an increase of reversibility up to 85 %. However, those ruthenium acetylide complexes are not efficient for the sensitization of Eu emission. Its emissive state is too high in energy. We would like to highlight here that although the reversibility has been improved electrochemically (see chapter 1), the stability of the both redox states need to be improved. Indeed, the disadvantage of this system is the well-known hydrolysis of the acetylide ligand to a carbonyl adduct in the oxidized state, under the experimental luminescence conditions (high dilution: OD < 0.1, C < 10$^{-6}$ mol·L$^{-1}$, addition of reactants) that led to a limited reversibility of the switching event.

1.3 Objective

As mentioned before, lanthanide ions which luminescence is ranging from the visible up the near-IR (NIR), are one of the most popular luminescent elements for practical applications
such as luminescent display, imaging, laser and optical devices.\textsuperscript{12} Herein, we aim to achieve
the switching of Yb and also of Eu luminescence by taking advantage of the redox
communication of one or two new vinyl ruthenium antennae. Indeed, vinyl ruthenium
complexes are more stable than Ru acetylide moieties in their oxidized state.\textsuperscript{13} In order to
reach this goal, owing to their different energy levels, the Yb complexes will be able to use
new vinyl ruthenium moiety as the antennae (MLCT), while the Eu complexes will use TTA
as the sensitizer units. It would be then interesting to check if redox switching is possible for
both sensitization pathways, as low lying state will be available to quench the emission in
both case after oxidation, as observed for $\text{Yb2}$ (see Figure 4b).\textsuperscript{6}

The syntheses of complex $\text{KRu-Eu}$, $\text{KRu-Yb}$, $\text{KRu}_2$-$\text{Eu}$ and $\text{KRu}_2$-$\text{Yb}$ are planned to be
achieved by coordination of the precursor $\text{[(CO)(Cl)(iPr}_3\text{P)}_2\text{Ru(vinylbipyridinyl)]}$ and
$\text{[(CO)(Cl)(iPr}_3\text{P)}_2\text{Ru(divinyl{bipyridinyl})Ru(PiPr}_3\text{)(Cl)(CO)]}$ to $\text{[Yb(TTA)]}_3\cdot2\text{H}_2\text{O}$ or
$\text{[Eu(TTA)]}_3\cdot2\text{H}_2\text{O}$ (Scheme 2). This work was accomplished in collaboration with Stefan
Scheerer and Fanbian Geist of Prof. Winter’s group in Konstanz.

\begin{center}
\includegraphics[width=\textwidth]{scheme2.png}
\end{center}

\textbf{Scheme 2. The target molecules}
2. Synthesis of the molecules

Two types of ruthenium (II) complexes will be synthesized; one type is a bimetallic one of the
type Ru^{II} - Ln^{III}, while the other type is a trimetallic one Ru^{II} - Ln^{III} - Ru^{II} (Ln = Yb, Eu)
(Scheme 2).

2.1 Synthesis of organometallic precursors

The precursors complexes Ln(TTA)₃·2H₂O (Ln = Yb or Eu) (K₇ and K₈) were easily
synthesized following an existing procedure (Scheme 3).

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H₂} & \quad \text{O} \\
\text{CF₃} & \quad \text{S}
\end{align*}
\]
YbCl₃, 6(H₂O)

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H₂} & \quad \text{O} \\
\text{CF₃} & \quad \text{S}
\end{align*}
\]
H₂O, 60 °C
NH₄OH

\text{Yb} \cdot \text{TTA} \cdot 2 \cdot \text{H₂O}_2

\text{K₇}

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H₂} & \quad \text{O} \\
\text{CF₃} & \quad \text{S}
\end{align*}
\]
 EuCl₃

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H₂} & \quad \text{O} \\
\text{CF₃} & \quad \text{S}
\end{align*}
\]
H₂O, 60 °C
NH₄OH

\text{Eu} \cdot \text{TTA} \cdot 2 \cdot \text{H₂O}_2

\text{K₈}

Scheme 3. Synthesis of inorganic precursors

2.2 Synthesis of target complexes

The complexes K₉Ru-Eu, K₉Ru-Yb, K₉Ru₂-Eu and K₉Ru₂-Yb were synthesized as shown in
Scheme 4 and Scheme 5.

Free alkynes K₂, K₅ were generated from the deprotection of the protected alkynes K₁
or K₄ in the presence of KF. Complexes K₆ and K₇ were obtained by the regio- and
stereoselective addition of the hydrido complex RuHCl(CO)(P^Pr₃)₂ to the corresponding free
alkyne in isolated yields of 73 to 78 %, respectively. In particular, we checked by the
occurrence of the two doublets with a J coupling constant of 13.6 Hz that only the \textit{trans}
isomer is obtained. K₉Ru-Yb and K₉Ru-Eu complexes were obtained from the coordination
reactions between K₆ and Ln(TTA)₃(H₂O)₂ (Ln = Yb, Eu) with yields of 47 % and 61 %, respectively (Scheme 4).
Finally, KRu₂-Yb and KRu₂-Eu were obtained from the coordination reactions between K6 and Ln(TTA)₃(H₂O)₂ (Ln = Yb, Eu) with yields of 54 % and 65 %, respectively (Scheme 5).

### 3 Characterization

The targeted complexes (K₃, K₆, KRu-Eu, KRu-Yb, KRu₂-Eu, KRu₂-Yb) were characterized by IR, ¹H, ³¹P NMR spectroscopy, cyclic voltammetry (CV), UV-vis absorption, high-resolution mass spectrometry, and satisfactory microanalysis.

#### 3.1 NMR spectroscopy of diamagnetic the complexes K₃ and K₆

For complex K₃, particularly informative is the single resonance peak in the ³¹P NMR spectrum at δ = 38.53 ppm, a typical value for the phosphine in this Ru-vinyl moiety.¹⁷ Datas
Luminescent redox switches based on Lanthanide ions and organometallic ruthenium complexes obtained from the $^1$H-NMR spectrum of K3 in CD$_2$Cl$_2$ are showed in detail in Table 1. Assignments are based on a cosy spectrum.

Table 1. $^1$H NMR of K3 in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.02</td>
<td>d</td>
<td>13.6</td>
<td>1</td>
<td>H$_1$</td>
</tr>
<tr>
<td>8.59</td>
<td>d</td>
<td>5.0</td>
<td>1</td>
<td>H$_9$</td>
</tr>
<tr>
<td>8.31</td>
<td>d</td>
<td>7.8</td>
<td>1</td>
<td>H$_6$</td>
</tr>
<tr>
<td>8.30</td>
<td>d</td>
<td>2.1</td>
<td>1</td>
<td>H$_3$</td>
</tr>
<tr>
<td>8.21</td>
<td>d</td>
<td>8.3</td>
<td>1</td>
<td>H$_5$</td>
</tr>
<tr>
<td>7.75</td>
<td>td</td>
<td>$^{3}$J$<em>{HH} = 7.8$, $^{4}$J$</em>{HH} = 1.7$</td>
<td>1</td>
<td>H$_7$</td>
</tr>
<tr>
<td>7.47</td>
<td>dd</td>
<td>$^{3}$J$<em>{HH} = 8.3$, $^{4}$J$</em>{HH} = 2.1$</td>
<td>1</td>
<td>H$_4$</td>
</tr>
<tr>
<td>7.22</td>
<td>dd</td>
<td>$^{3}$J$_{HH} = 7.8$, 5.0</td>
<td>1</td>
<td>H$_8$</td>
</tr>
<tr>
<td>6.09</td>
<td>dt</td>
<td>$^{3}$J$_{HH} = 13.6$</td>
<td>1</td>
<td>H$_2$</td>
</tr>
<tr>
<td>2.84 - 2.67</td>
<td>m</td>
<td></td>
<td>6</td>
<td>PCH/CH$_3$</td>
</tr>
<tr>
<td>1.34 – 1.23</td>
<td>m</td>
<td></td>
<td>36</td>
<td>PCH/CH$_3$</td>
</tr>
</tbody>
</table>
Table 2. $^1$H NMR data of K6 in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.92</td>
<td>d</td>
<td>13.6</td>
<td>2</td>
<td>H$_1$</td>
</tr>
<tr>
<td>8.24</td>
<td>d</td>
<td>1.6</td>
<td>2</td>
<td>H$_3$</td>
</tr>
<tr>
<td>8.11</td>
<td>d</td>
<td>8.2</td>
<td>2</td>
<td>H$_4$</td>
</tr>
<tr>
<td>7.42</td>
<td>d</td>
<td>8.2</td>
<td>2</td>
<td>H$_5$</td>
</tr>
<tr>
<td>6.06</td>
<td>d</td>
<td>13.6</td>
<td>2</td>
<td>H$_2$</td>
</tr>
<tr>
<td>2.84 - 2.67</td>
<td>m</td>
<td></td>
<td>12</td>
<td>PCH$\text{CH}_3$</td>
</tr>
<tr>
<td>1.34 – 1.23</td>
<td>m</td>
<td></td>
<td>72</td>
<td>PCH$\text{CH}_2$</td>
</tr>
</tbody>
</table>

For complex K6, particularly informative is the single resonance peak in the $^{31}$P NMR spectra at $\delta = 38.49$ ppm. As shown in Table 2, the trans double bonds show two doublets at 8.92 and 6.06 ppm (J = 13.6 Hz). Assignments are based on a cosy spectrum.


Figure 5. $^1$H-NMR spectrum of complex KRu-Eu in CD$_2$Cl$_2$
Table 3. $^1$H NMR data of KRu-Eu in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.14</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$_{12}$ or H$_7$</td>
</tr>
<tr>
<td>13.72</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$<em>7$ or H$</em>{12}$</td>
</tr>
<tr>
<td>10.53</td>
<td>d</td>
<td>13.6</td>
<td>1</td>
<td>H$_1$</td>
</tr>
<tr>
<td>9.32 - 9.28</td>
<td>m</td>
<td></td>
<td>1</td>
<td>H$_{11}$</td>
</tr>
<tr>
<td>9.00 - 8.98</td>
<td>m</td>
<td></td>
<td>2</td>
<td>H$<em>4$ and H$</em>{10}$</td>
</tr>
<tr>
<td>8.53 – 8.50</td>
<td>m</td>
<td></td>
<td>2</td>
<td>H$_5$ and H$_9$</td>
</tr>
<tr>
<td>7.82</td>
<td>d</td>
<td>13.6</td>
<td>1</td>
<td>H$_2$</td>
</tr>
<tr>
<td>7.04</td>
<td>d</td>
<td>4.95</td>
<td>3</td>
<td>H$<em>{20}$ or H$</em>{18}$</td>
</tr>
<tr>
<td>6.49 – 6.47</td>
<td>m</td>
<td></td>
<td>3</td>
<td>H$_{19}$</td>
</tr>
<tr>
<td>6.03</td>
<td>d</td>
<td>2.68</td>
<td>3</td>
<td>H$<em>{18}$ or H$</em>{20}$</td>
</tr>
<tr>
<td>3.26</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$_{15}$</td>
</tr>
<tr>
<td>3.00 – 2.93</td>
<td>m</td>
<td></td>
<td>6</td>
<td>H$_{21}$</td>
</tr>
<tr>
<td>1.52 – 1.38</td>
<td>m</td>
<td></td>
<td>36</td>
<td>H$_{22}$</td>
</tr>
</tbody>
</table>

In the NMR spectra of 4f complexes (paramagnetic complexes), a paramagnetic shift is produced by an interaction between the nuclear magnetic moment of the diamagnetic nuclei and the magnetic moment produced by the unpaired f-electrons of the lanthanide ions. This interaction occur mainly in a through-space dipole-dipole manner (psedo-contact shift), or by delocalization of f-electron density towards the resonating nucleus through the bonds (contact
shift).\textsuperscript{18} This paramagnetic shift depend on the anisotropy of the Ln and is therefore larger for Yb than for Eu.

For KRu-Eu, we can observe a single resonance peak in the $^{31}$P NMR spectra at $\delta = 38.96$ ppm. The details of the $^1$H NMR spectrum, shown in Figure 5, of complex KRu-Eu in CD$_2$Cl$_2$ are well described in table 3 with the help of integration and COSY NMR. As expected, compared with diamagnetic complex K3, this $^1$H-NMR spectrum of KRu-Eu shows chemical shifts and broadening signals due to coordination effect. First, H$_1$ and H$_2$ are identified by the J constant (trans) of 13.6 Hz.\textsuperscript{17} Second, the integration can be used to assign the H of the TTA ligand, the H$_{15}$ being the only signal with 3H integration and showing no correlation peak in the cosy experiment. Third, based on the fact that paramagnetic shifts are higher when the H-Eu distance is smaller, the different signals for H$_7$ and H$_{12}$ of the bipyridine can be assigned. Fourth, the remaining protons of the byridine unit are assigned with the help of cosy experiments.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure6.png}
\caption{\textsuperscript{1}H-NMR spectrum of complex KRu$_2$-Eu in CD$_2$Cl$_2$}
\end{figure}
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![Diagram of KRu2-Eu](image)

Table 4. $^1$H NMR data of KRu2-Eu in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.82</td>
<td>s</td>
<td></td>
<td>2</td>
<td>H$_7$</td>
</tr>
<tr>
<td>10.43</td>
<td>d</td>
<td>13.3</td>
<td>2</td>
<td>H$_1$</td>
</tr>
<tr>
<td>8.89</td>
<td>d</td>
<td>7.4</td>
<td>2</td>
<td>H$_5$ or H$_4$</td>
</tr>
<tr>
<td>8.07</td>
<td>d</td>
<td>13.2</td>
<td>2</td>
<td>H$_2$</td>
</tr>
<tr>
<td>8.00</td>
<td>d</td>
<td>7.5</td>
<td>2</td>
<td>H$_4$ or H$_5$</td>
</tr>
<tr>
<td>7.04</td>
<td>d</td>
<td>4.5</td>
<td>2</td>
<td>H$<em>{15}$ or H$</em>{13}$</td>
</tr>
<tr>
<td>6.46</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$_{14}$</td>
</tr>
<tr>
<td>5.98</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$<em>{13}$ or H$</em>{15}$</td>
</tr>
<tr>
<td>3.31</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$_{10}$</td>
</tr>
<tr>
<td>3.03 - 2.98</td>
<td>m</td>
<td></td>
<td>12</td>
<td>H$_{16}$</td>
</tr>
<tr>
<td>1.55 – 1.43</td>
<td>m</td>
<td></td>
<td>72</td>
<td>H$_{17}$</td>
</tr>
</tbody>
</table>

For KRu2-Eu, the expected single resonance peak in the $^{31}$P NMR spectrum is observed at $\delta = 38.84$ ppm.

The details of the $^1$H NMR spectrum of complex KRu2-Eu in CD$_2$Cl$_2$ are well described in Table 4, also with the help of integrations and of a COSY NMR experiments. They are shown in Figure 6.

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Figure 7. $^1$H-NMR spectrum of complex KRu-Yb in CD$_2$Cl$_2$
Table 5. $^1$H NMR data of KRu-Yb in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.39</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$_9$</td>
</tr>
<tr>
<td>23.02</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$_5$</td>
</tr>
<tr>
<td>20.41</td>
<td>d</td>
<td></td>
<td>1</td>
<td>H$_{12}$ or H$_7$</td>
</tr>
<tr>
<td>17.61</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$<em>7$ or H$</em>{12}$</td>
</tr>
<tr>
<td>15.64</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$_{10}$</td>
</tr>
<tr>
<td>14.86</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$_4$</td>
</tr>
<tr>
<td>13.42</td>
<td>s</td>
<td></td>
<td>1</td>
<td>H$_{11}$</td>
</tr>
<tr>
<td>12.43</td>
<td>d</td>
<td>10.98</td>
<td>1</td>
<td>H$_1$</td>
</tr>
<tr>
<td>7.87</td>
<td>d</td>
<td>10.67</td>
<td>1</td>
<td>H$_2$</td>
</tr>
<tr>
<td>6.82</td>
<td>d</td>
<td>3.64</td>
<td>3</td>
<td>TTA</td>
</tr>
<tr>
<td>5.61</td>
<td>s</td>
<td></td>
<td>3</td>
<td>TTA</td>
</tr>
<tr>
<td>2.90</td>
<td>m</td>
<td></td>
<td>12</td>
<td>H$_{21}$+TTA</td>
</tr>
<tr>
<td>1.43–1.24</td>
<td>m</td>
<td></td>
<td>36</td>
<td>H$_{22}$</td>
</tr>
<tr>
<td>-9.69</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$_{15}$</td>
</tr>
</tbody>
</table>

For **KRu-Yb**, we can observe the single resonance peak in the $^{31}$P NMR spectrum at $\delta=39.31$ ppm.

The details of the $^1$H NMR spectrum of complex **KRu-Yb** in CD$_2$Cl$_2$ are described in Table 5 and shown in Figure 7. Compared with **KRu-Eu** complexes, some signals of **KRu-Yb** has larger chemical shift in $^1$H-NMR spectrum due to a stronger paramagnetic effect of Yb complexes than Eu complexes.
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Figure 8. $^1$H-NMR spectra of complex KRu$_2$-Yb in CD$_2$Cl$_2$

![1H-NMR spectra of complex KRu$_2$-Yb in CD$_2$Cl$_2$](image)
Table 6. $^1$H NMR data of KRu$_2$-Yb in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.64</td>
<td>s</td>
<td></td>
<td>2</td>
<td>H$_5$ or H$_4$</td>
</tr>
<tr>
<td>20.28</td>
<td>s</td>
<td></td>
<td>2</td>
<td>H$_7$</td>
</tr>
<tr>
<td>14.53</td>
<td>s</td>
<td></td>
<td>2</td>
<td>H$_4$ or H$_5$</td>
</tr>
<tr>
<td>12.28</td>
<td>d</td>
<td>10.9</td>
<td>2</td>
<td>H$_1$</td>
</tr>
<tr>
<td>8.42</td>
<td>d</td>
<td>8.26</td>
<td>2</td>
<td>H$_2$</td>
</tr>
<tr>
<td>6.70</td>
<td>m</td>
<td></td>
<td>3</td>
<td>H$_{14}$ (TTA)</td>
</tr>
<tr>
<td>5.53</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$<em>{13}$ or H$</em>{15}$ (TTA)</td>
</tr>
<tr>
<td>3.01</td>
<td>s</td>
<td></td>
<td>12</td>
<td>H$_{16}$</td>
</tr>
<tr>
<td>2.80</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$<em>{15}$ or H$</em>{13}$ (TTA)</td>
</tr>
<tr>
<td>1.52 – 1.37</td>
<td>m</td>
<td></td>
<td>72</td>
<td>H$_{17}$</td>
</tr>
<tr>
<td>-8.98</td>
<td>s</td>
<td></td>
<td>3</td>
<td>H$_{10}$</td>
</tr>
</tbody>
</table>

For KRu$_2$-Yb, there is the single resonance peak in the $^{31}$P NMR spectrum at $\delta$ = 39.25 ppm.

The details of the $^1$H NMR spectrum of complex KRu$_2$-Yb in CD$_2$Cl$_2$ are described in Table 6 and shown in Figure 8. As mentioned above for the bimetallic complex, compared with KRu$_2$-Eu complexes, some signals of KRu$_2$-Yb display larger chemical shifts in its $^1$H-NMR spectrum due to a stronger paramagnetic effect of Yb complexes than Eu complexes.

### 3.3 IR spectroscopy

The infrared measurements of complexes K3, K6, KRu-Eu, KRu$_2$-Eu, KRu-Yb and KRu$_2$-Yb were performed both by ATR and in 1,2-dichloroethane solutions. The data are summarized in Table 7.

In the IR spectra of K3 and K6, a band around 1900 cm$^{-1}$ is observed and corresponds to the C≡O stretching vibrations which in fact probes the Ru electronic density (vide infra).$^{17}$ These value of the C≡O stretching for K3 and K6 are expected values for neutral Ru vinyl complexes.$^{17}$ For KRu-Eu and KRu-Yb, there is a blue shift because of the coordination of the electron withdrawing Ln(TTA)$_3$ (Ln = Eu or Yb) moieties, further enhancing charge transfer from the peripheral electron-rich {Ru}-CH=CH moieties to the bipyridine bridge. So far we are not sure about why KRu$_2$-Eu and KRu$_2$-Yb show two bands for C≡O stretching vibration by ATR by comparison with solution measurements.
Table 7. Datas obtained by IR spectroscopy

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR(cm(^{-1})) by ATR</th>
<th>IR(cm(^{-1})) in 1,2-C(_2)H(_4)Cl(_2) solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>K3</td>
<td>(\nu) (C≡O) = 1903</td>
<td>(\nu) (C≡O) = 1916</td>
</tr>
<tr>
<td>K6</td>
<td>(\nu) (C≡O) = 1900</td>
<td>(\nu) (C≡O) = 1908(^b)</td>
</tr>
<tr>
<td>KRu-Eu</td>
<td>(\nu) (C≡O) = 1919</td>
<td>(\nu) (C≡O) = 1918</td>
</tr>
<tr>
<td>KRu-Yb</td>
<td>(\nu) (C≡O) = 1921</td>
<td>(\nu) (C≡O) = 1919</td>
</tr>
<tr>
<td>KRu(_2)-Eu</td>
<td>(\nu) (C≡O) = 1917, 1907</td>
<td>(\nu) (C≡O) = 1917</td>
</tr>
<tr>
<td>KRu(_2)-Yb</td>
<td>(\nu) (C≡O) = 1917, 1909</td>
<td>(\nu) (C≡O) = 1918</td>
</tr>
</tbody>
</table>

\(^a\): in 1,2-C\(_2\)H\(_4\)Cl\(_2\) solutions pertain to 0.2 M NBu\(_4\)\(^+\)PF\(_6\)\(^-\) solutions in 1,2-C\(_2\)H\(_4\)Cl\(_2\).\(^b\): in CH\(_2\)Cl\(_2\)/NBu\(_4\)\(^+\) [B\(_{C_6H_3(CF_3)_2-3,5}\)]\(_4\). data obtained from publication\(^17\).

3.4 UV-vis absorption studies

The absorption measurements in the UV-Vis range of K3, KRu-Eu and KRu-Yb were performed in dichloromethane solutions (Figure 9). The data are summarized in Table 8. Complex K3 in dichloromethane shows intense short-wavelength absorption band at 266 nm for the transition corresponding to \(\pi \rightarrow \pi^*\) transitions of bipyridyl moieties. The complex shows also an absorption band at 377 nm with an extinction coefficient of 28500 L.mol\(^{-1}\).cm\(^{-1}\). This band results from a transition mixing the Ru(d\(\pi\)) orbitals with alkenyl orbitals, and with contribution from bipyridine orbitals as proven by DFT calculations achieved by Prof.Záliš.\(^17\) Indeed the HOMO of Ru-bpy moieties has higher contribution from the electron-rich alkenyl ruthenium moiety, while the LUMO is more heavily centered on the bpy moiety. This adds some metal-to ligand (MLCT) and intraligand (ILCT) charge transfer components to the overall \(\pi \rightarrow \pi^*\) transition. Because of the electron accepting properties of the bpy constituent, the LUMO is more stabilized than the HOMO, resulting in the lowering of the HOMO-LUMO gap. For KRu-Eu in dichloromethane, in addition to the short-wavelength absorption band at 290 nm for transition corresponding to \(\pi \rightarrow \pi^*\) transitions of bipyridyl moieties, the complex KRu-Eu shows a band at 340 nm with an extinction coefficient of 77200 L.mol\(^{-1}\).cm\(^{-1}\) corresponding to \(\pi \rightarrow \pi^*\) transitions of TTA, and a band corresponding to MLCT.

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transitions at 427 nm with an extinction coefficient of 28100 L·mol⁻¹·cm⁻¹. The absorptions of the complex \( \text{KRu-Yb} \) is very similar to those of \( \text{KRu-Eu} \). We note a 50 nm red shift of MLCT bands after \( K3 \) was coordinated with \( \text{Ln(TTA)}_3(\text{H}_2\text{O})_2 \) (Ln = Eu, Yb), due to the electron withdrawing character of the lanthanide ions after coordination.\(^6\)

Figure 9. Absorption spectra of complexes \( K3, \text{KRu-Eu} \) and \( \text{KRu-Yb} \) (CH\(_2\)Cl\(_2\), 298 K).

The absorption measurements of \( K6, \text{KRu}_2\text{-Eu} \) and \( \text{KRu}_2\text{-Yb} \) were also measured in dichloromethane solution (Figure 10). Their absorption data are summarized in Table 8. \( K6 \) in dichloromethane presents an absorption band at 266 nm for transition corresponding to \( \pi \rightarrow \pi^* \) transitions of bipyridyl moieties and an absorption band at 403 nm with an extinction coefficient of 57200 L·mol⁻¹·cm⁻¹ ascribed to the MLCT.\(^{17}\) Four absorption bands were observed for \( \text{KRu}_2\text{-Eu} \) in dichloromethane. They are two absorption bands at 277 nm, 290 nm for transitions corresponding to \( \pi \rightarrow \pi^* \) transitions of bipyridyl moieties, a band at 342 nm with an extinction coefficient of 77500 L·mol⁻¹·cm⁻¹ corresponding to \( \pi \rightarrow \pi^* \) transitions of the TTA ligands, and a band corresponding to the MLCT transitions at 457 nm with an extinction coefficient of 48100 L·mol⁻¹·cm⁻¹. The absorptions of the complex \( \text{KRu}_2\text{-Yb} \) is almost the same as those of \( \text{KRu}_2\text{-Eu} \). A 54 nm red shift of the MLCT band was noted after coordination of \( K6 \) with \( \text{Ln(TTA)}_3(\text{H}_2\text{O})_2 \) (Ln = Eu, Yb) due to electron withdrawing character of the lanthanide ions after coordination, as expected.\(^6\)

Note that charge transfer from the ruthenium alkenyl donors to the bipy or (bipy)Ln(TTA)\(_3\) (Ln = Yb or Eu) acceptors of complexes \( K6 \) to \( \text{KRu}_2\text{-Yb} \) (or \( \text{KRu}_2\text{-Eu} \)) can be optically...
excited as attested by the electronic spectra and from quantum chemical calculations. Given the presence of only one conjugated alkenyl ruthenium donor substituent in K3 as opposed to two in K6, it is not surprising that the main MLCT band of K3 is blue shifted by 26 nm with respect to that of complex K6, while the absorptivity is decreased by a factor of almost 2. Similar results are also found when comparing KRu-Ln with KRu2-Ln (Ln = Yb, Eu).

![Absorption spectra of complexes K6, KRu2-Eu and KRu2-Yb (CH2Cl2, 298 K).](image)

**Figure 10.** Absorption spectra of complexes K6, KRu2-Eu and KRu2-Yb (CH2Cl2, 298 K).

**Table 8.** UV-visible data obtained for absorption of complexes K3, K6, KRu-Eu, KRu-Yb, KRu2-Eu and KRu2-Yb in CH2Cl2 at 25 °C (C = 1〜13*10^{-5} M)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}1} \text{ nm (}\varepsilon \text{ in M}^{-1}.\text{cm}^{-1}))</th>
<th>(\lambda_{\text{max}2} \text{ nm (}\varepsilon \text{ in M}^{-1}.\text{cm}^{-1}))</th>
<th>(\lambda_{\text{max}3} \text{ nm (}\varepsilon \text{ in M}^{-1}.\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>K3</td>
<td>266 (20100) (\pi-\pi^*) of bipyridine</td>
<td>377 (28500) (\pi-\pi^*) of TTA</td>
<td>377 (28500) (\pi-\pi^*) of TTA</td>
</tr>
<tr>
<td>K6</td>
<td>266 (24300) (\pi-\pi^*) of bipyridine</td>
<td>403 (57200) (\pi-\pi^*) of TTA</td>
<td>403 (57200) (\pi-\pi^*) of TTA</td>
</tr>
<tr>
<td>KRu-Eu</td>
<td>290 (44900) (\pi-\pi^*) of TTA</td>
<td>340 (77200) (\pi-\pi^*) of TTA</td>
<td>340 (77200) (\pi-\pi^*) of TTA</td>
</tr>
<tr>
<td>KRu-Yb</td>
<td>289 (40600) (\pi-\pi^*) of TTA</td>
<td>339 (69500) (\pi-\pi^*) of TTA</td>
<td>339 (69500) (\pi-\pi^*) of TTA</td>
</tr>
<tr>
<td>KRu2-Eu</td>
<td>277 (42100) (\pi-\pi^*) of TTA</td>
<td>342 (77500) (\pi-\pi^*) of TTA</td>
<td>342 (77500) (\pi-\pi^*) of TTA</td>
</tr>
<tr>
<td>KRu2-Yb</td>
<td>276 (43100) (\pi-\pi^*) of TTA</td>
<td>338 (75600) (\pi-\pi^*) of TTA</td>
<td>338 (75600) (\pi-\pi^*) of TTA</td>
</tr>
</tbody>
</table>
3.5 Electrochemical studies

Cyclic voltammetry (CV) was used to study the electrochemical behavior of all complexes (CH<sub>2</sub>Cl<sub>2</sub>, 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>). CV data for K<sub>3</sub>, KRu-Eu and KRu-Yb are collected in Table 9, and typical CV traces are displayed in Figure 11. We can observe that complex K<sub>3</sub> undergoes one reversible one-electron oxidation at E<sub>1/2</sub> = 808 mV vs SCE, as one alkenyl ruthenium moieties is present. This value is typical for such complexes.17 Similarly, KRu-Eu and KRu-Yb complexes display a reversible one-electron oxidation at E<sub>1/2</sub> = 911 and E<sub>1/2</sub> = 909 mV vs SCE, respectively. The half-wave potential for the oxidation of the bipy-substituted monoruthenium complex KRu-Eu or KRu-Yb is around 100 mV higher than that of K<sub>3</sub>. This is expected owing to the enhanced electron withdrawing character of the bipyridine moieties upon coordination with Ln(TTA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> ions (Ln = Eu, Yb).
Figure 11. Cyclic voltammogram of K3, KRu-Eu and KRu-Yb. In CH2Cl2 with 0.2 M [NnBu4][PF6], FeCp2/FeCp2⁺ as the reference, Pt as working and auxiliary electrodes. v = 0.1 V·s⁻¹.
Figure 12. Cyclic voltammogram of K6, KRu2-Eu and KRu2-Yb. In CH2Cl2 with 0.2 M [NnBu4][PF6], FeCp2/FeCp2+ as the reference, Pt as working and auxiliary electrodes. v = 0.1 V·s⁻¹.

CV data for K6, KRu2-Eu and KRu2-Yb are collected in Table 9 and typical CV traces are displayed in Figure 12. As two alkenyl ruthenium moieties are present, complex K6 undergoes two reversible consecutive one-electron oxidations at E₁/₂ = 737 and E₁/₂ = 817 mV vs SCE. Similarly, KRu2-Eu displays two consecutive reversible one-electron oxidations at E₁/₂ = 814 and E₁/₂ = 930 mV vs SCE, while KRu2-Yb also displays a two consecutive reversible one-electron oxidation at E₁/₂ = 806 and E₁/₂ = 932 mV vs SCE. Also here, the first half-wave potential for the oxidation of KRu2-Eu or KRu2-Yb is around 80 mV higher than that of K6 due to the enhanced electron withdrawing character of the bipy moiety upon coordination with Ln(TTA)3(H2O)2 (Ln = Eu, Yb).

<table>
<thead>
<tr>
<th></th>
<th>E₁/₂⁺ (ΔEp) (mv vs FeCp2/FeCp2⁺ or SCE)</th>
<th>E₁/₂²⁺ (ΔEp) (mv vs FeCp2/FeCp2⁺ or SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K3</td>
<td>348/ 808 (77)</td>
<td>-</td>
</tr>
<tr>
<td>KRu-Eu</td>
<td>451/ 911 (79)</td>
<td>-</td>
</tr>
<tr>
<td>KRu-Yb</td>
<td>449/ 909 (88)</td>
<td>-</td>
</tr>
<tr>
<td>K6</td>
<td>277/ 737 (76)</td>
<td>357/ 817 (98)</td>
</tr>
<tr>
<td>KRu2-Eu</td>
<td>354/ 814 (104)</td>
<td>470/ 930 (76)</td>
</tr>
<tr>
<td>KRu2-Yb</td>
<td>346/ 806 (110)</td>
<td>472/ 932 (114)</td>
</tr>
</tbody>
</table>
3.6 Spectroelectrochemical studies

The spectroelectrochemical studies have been performed by Stefan Scheerer, Fabian Geist in our collaboration with the group of Konstanz University, and by me as well. Spectroscopic investigation of \( \text{K6} \) has been done in \( \text{CH}_2\text{Cl}_2 \) solutions containing \( \text{NBu}_4^+ \text{[B(C}_6\text{H}_3(\text{CF}_3)_{2-3,5}]_4^-} \), while \( \text{K3}, \text{KRu-Eu}, \text{KRu-Yb}, \text{KRu}_2-\text{Eu} \) and \( \text{KRu}_2-\text{Yb} \) have been done in 0.2 M \( \text{NBu}_4^+\text{PF}_6^- \) solutions in 1,2-\( \text{C}_2\text{H}_4\text{Cl}_2 \). The data are summarized in Table 10.

A characteristic asset of complexes \( \text{Ru(CO)}\text{Cl(P}^3\text{Pr}_3)_2(\text{CH}=\text{CHR}) \) is the strong IR band of the \( \text{Ru(CO)} \) stretching vibration, whose position mirrors the electron richness of the metal center(s). This allows assessing the nature of the oxidations, i.e. to evaluate the participation of the metal and of the ligand. The \( \text{C}=\text{O} \) stretching for \( \text{K3} \) is found at 1916 cm\(^{-1}\), while upon oxidation it moves to 1960 cm\(^{-1}\). This is the usual behavior of such complexes because the oxidation has a significant impact on electron richness of the ruthenium center. On the contrary, the \( \nu(\text{CO}) \) band for \( \text{K6} \) is found at 1908 cm\(^{-1}\), while upon oxidation it moves to 1921 cm\(^{-1}\) with a shoulder at 1941 cm\(^{-1}\). This reflects the much weaker participation of the ruthenium vinyl moieties in the oxidation process. The Winter group has been able to show that this first oxidization process of \( \text{K6} \) has actually a main contribution from the bipyridine ligand.

Table 10. IR and UV/vis/NIR data of the complexes \( \text{K3}, \text{K6}, \text{KRu-Eu}, \text{KRu-Yb}, \text{KRu}_2-\text{Eu} \) and \( \text{KRu}_2-\text{Yb} \) in their various oxidation states

<table>
<thead>
<tr>
<th></th>
<th>( \nu(\text{CO}) ) [cm(^{-1})]</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>( \epsilon ) [M(^{-1})cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{K3} )</td>
<td>1916(^a)</td>
<td>266(17300), 288 (sh, 14600), 377 (20300), 438 (sh, 7200)(^a)</td>
<td></td>
</tr>
<tr>
<td>( \text{K3}^+ )</td>
<td>1960(^a)</td>
<td>No result</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu-Eu} )</td>
<td>1918</td>
<td>290, 340, 427</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu-Eu}^+ )</td>
<td>1982</td>
<td>274, 341, 430</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu-Yb} )</td>
<td>1919</td>
<td>289, 337, 427</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu-Yb}^+ )</td>
<td>1985</td>
<td>275, 337, 430</td>
<td></td>
</tr>
<tr>
<td>( \text{K6} )</td>
<td>1908(^a)</td>
<td>267, 405</td>
<td></td>
</tr>
<tr>
<td>( \text{K6}^+ )</td>
<td>1921, 1941(sh)(^a)</td>
<td>263, 418, 473</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu}_2-\text{Eu} )</td>
<td>1917</td>
<td>281, 340, 458</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu}_2-\text{Eu}^+ )</td>
<td>1923</td>
<td>273, 340, 468, 705</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu}_2-\text{Yb} )</td>
<td>1918</td>
<td>280, 337, 458</td>
<td></td>
</tr>
<tr>
<td>( \text{KRu}_2-\text{Yb}^+ )</td>
<td>1922</td>
<td>273, 338, 463</td>
<td></td>
</tr>
</tbody>
</table>

\( \text{a: data obtained from publication}^{17} \)

The oxidation of the \( \text{KRu-Eu} \) complex was found to be reversible in IR and UV/Vis spectroelectrochemical experiments. The shift of the Ru(CO) band from 1918 to 1982 cm\(^{-1}\)
indicates that the first oxidation involves the Ru-alkenyl unit (Figure 13). This shift upon oxidation is different from that of the precursor K3, meaning that no decoordination occurs upon oxidation. In the UV/Vis Spec-EC, the band near 427 nm, MLCT in nature, bleaches while there are only minor effects on the UV bands (Figure 14). As expected, the change of the Ru(CO) vibration and UV/Vis bands upon Spec-EC of KRu-Yb are similar as that of KRu-Eu. Note that they are also similar to a related Ru—Re complex that has been synthesized in Prof. Winter’s group in Konstanz.17

![Figure 13](image13.png)

**Figure 13.** Changes in the IR spectrum on stepwise oxidation of KRu-Eu to [KRu-Eu]⁺ (0.2 M 1,2-C₂H₄Cl₂/NBu₄PF₆).

![Figure 14](image14.png)

**Figure 14.** Changes in the UV/Vis spectrum on oxidation of KRu-Eu to [KRu-Eu]⁺ (0.2 M 1,2-C₂H₄Cl₂/NBu₄PF₆).
Chapter 3

Luminescent redox switches based on Lanthanide ions and organometallic ruthenium complexes

The spectroscopic behaviors of KRu$_2$-Yb and KRu$_2$-Eu complexes upon oxidation are different from those of KRu-Yb and KRu-Eu. The KRu$_2$-Eu complex shows two closely spaced one-electron oxidation waves at 814 mV and 930 mV vs SCE, and the KRu$_2$-Yb complex displays similar oxidations at 806 mV and 932 mV. Note that this makes difficult the separation of the first and second oxidation states. In a first attempt, in IR-SpecEc, only partial first oxidation has been studied. In the case of KRu$_2$-Yb (Figure 15), the Ru(CO) band shifts from 1918 to 1922 cm$^{-1}$, which is quite similar to what is observed for KRu$_2$-Eu. That new Ru(CO) band observed for the first oxidation of KRu$_2$-Yb or KRu$_2$-Eu is very similar to that for [K6]$^+$. This indicates that decoordination might unfortunately happen. In the UV/Vis Spec-EC of KRu$_2$-Eu (Figure 17), the first oxidation state shows that the band centered at 458 nm, MLCT in nature, shifts to 468 nm. This shift at lower energy could be related with the formation of [K6]$^+$ which maximum is located at 473 nm (Figure 16). Upon further oxidation, a new band appears at 705 nm which might correspond to the band observed in second oxidation process of K6 (Figure 16), which definitively indicates that the first oxidation of KRu$_2$-Eu is likely to induce decoordination, probably because the oxidation mainly occurs on the bipyridine unit.$^{17}$

This suspected decoordination upon oxidation is probably the reason why the behavior of KRu$_2$-Eu and KRu$_2$-Yb could not be fully studied, since decomposition ensued when trying to reach the first and then second oxidation states.

Figure 15. Changes in the IR spectra on stepwise oxidation of KRu$_2$-Yb (0.2 M 1,2-C$_2$H$_4$Cl$_2$/NBu$_4$PF$_6$).
Figure 16. Changes in the UV/Vis spectra on stepwise oxidations of K6 to [K6]$^+$ and [K6]$^+$ to [K6]$^{2+}$ (0.2 M 1,2-C$_2$H$_4$Cl$_2$/NBu$_4$PF$_6$).

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Figure 17. Changes in the UV/Vis spectra on oxidation of KRu₂-Eu (0.2 M 1,2-C₂H₄Cl₂/NBu₄PF₆).

Figure 18. Changes in the UV/Vis spectra on stepwise oxidation of KRu₂-Yb (0.2 M 1,2-C₂H₄Cl₂/NBu₄PF₆).
3.7 Emission studies

The emission measurements were performed in dichloromethane solutions at room temperature. The emission data are summarized in Table 11. As expected, after the excitation in the MLCT band with a wavelength of 430 or 460 nm ($\lambda_{ex} = 430$ or 460 nm), no emission of KRu-Eu or KRu$_2$-Eu, respectively, was observed because this MLCT transition is not strong enough to populate the Eu excited state. After the excitation of the $\pi\rightarrow\pi^*$ transition of the TTA ligand ($\lambda_{ex} = 330$ nm), the emission spectra of KRu-Eu presents five emission bands at 586, 598, 618, 660, 710 nm corresponding to the $^5D_0 \rightarrow ^7F_J$ transitions ($J = 0 \rightarrow 4$) (Figure 19). Similarly, the emission bands of KRu$_2$-Eu upon excitation at 330 nm were observed at 550, 592, 612, 652 and 704 nm, also corresponding to the $^5D_0 \rightarrow ^7F_J$ transitions ($J = 0 \rightarrow 4$) (Figure 19).

Figure 19. Emission spectra of KRu-Eu and KRu$_2$-Eu in CH$_2$Cl$_2$ at 25 °C ($\lambda_{ex} = 330$ nm) C = 5~7 *10$^{-6}$ mol/L

Concerning the Yb complexes, upon excitation in the aforementioned MLCT transition ($\lambda_{ex} = 430$ nm for KRu-Yb and 450 nm for KRu$_2$-Yb), the $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission of ytterbium having
a characteristic line shape was observed in the NIR spectral range at 976 nm for **KRu-Yb**, and at 977 nm for **KRu2-Yb**, respectively (**Figure 20**). Note that the emission intensity of **KRu2-Yb** is higher than that of **KRu-Yb**, due to the absorption intensity of MLCT band for **KRu2-Yb** that is around twice that of **KRu-Yb**. However, emission intensity of both complexes remains low.

**Figure 20.** Emission spectra of KRu-Yb and KRu2-Yb in CH2Cl2 at 25 °C (\(\lambda_{ex} = 450 \text{ nm}\)). C = 1 ~ 2 * 10^{-5} \text{ mol/L}. 

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max} (emission) /nm (relative emission intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRu-Eu (λ_{ex} = 330 nm)</td>
<td>586 (79), 598 (137), 618 (3735), 660 (97), 710 (161)</td>
</tr>
<tr>
<td>KRu₂-Eu (λ_{ex} = 330 nm)</td>
<td>550 (16793), 592 (85611), 612 (1782988), 652 (64234), 704 (35056)</td>
</tr>
<tr>
<td>KRu-Yb (λ_{ex} = 430 nm)</td>
<td>976 (63934), 1004 (61983), 1032 (59016)</td>
</tr>
<tr>
<td>KRu₂-Yb (λ_{ex} = 450 nm)</td>
<td>977 (192274), 1005 (178235), 1032 (169593)</td>
</tr>
</tbody>
</table>

3.8 Redox-controlled luminescence modulation

We tried several times to modulate the luminescence of KRu-Yb, KRu-Eu, KRu₂-Yb and KRu₂-Eu. Unfortunately, no successful redox modulation could be achieved in an electrochemical cell. As we discussed before, KRu₂-Eu and KRu₂-Yb go through decoordination during oxidation process, which makes our luminescence modulation meaningless to be done.

Since KRu-Yb is a poor emitter, luminescence observation and switching is difficult to achieve in an electrochemical device, no satisfactory spectra could be recorded yet. For KRu-Eu, we will try in the future to see if any modulation could happen upon oxidation.

4 Conclusion and perspective

In this chapter, we have reported the synthesis of six ruthenium complexes K3, K6, KRu-Eu, KRu-Yb, KRu₂-Eu and KRu₂-Yb and their photophysical and electrochemical properties. KRu-Eu and KRu-Yb are luminescent and reversibly oxidized on the time scale of optical experiments, but their luminescence was not successfully modulated by changing their oxidation states because KRu-Yb is a poor emitter while luminescence modulation of KRu-
Eu is underway. Although emission intensity of KRu$_2$-Eu and KRu$_2$-Yb are stronger than that of KRu-Eu and KRRu-Yb, luminescence modulation could not be successfully realized due to the lanthanide decoordination upon oxidation. From the previous work in our group, the emission of ruthenium acetylides after coordination with Yb(TTA)$_3$ are electrochemically better modulated.
References

Chapter 3

Luminescent redox switches based on Lanthanide ions and organometallic ruthenium complexes
Chapter 4:
Lanthanide luminescence switches with a dithienylethene (DTE) unit
Chapter 4: Lanthanide luminescence switches with a dithienylethene (DTE) unit

1 Introduction

Lanthanide metal complexes display unique properties that attract considerable interests for molecular materials as discussed in chapter 1. In chapter 3, we have introduced the redox-active ruthenium vinyl moieties as switching unit to modulate their luminescence, and we met some difficulties due to decoordination upon oxidation or because some complexes appear to be poor emitters. As discussed in chapter 1, photochromic DTE unit is very promising and has received wide application as switching unit for modulation of optical property, magnetic property, reactivity, mechanical response and so on. Herein, in this chapter, we would like to use light to modulate luminescence of Ln complexes by exploiting photochromic DTE unit as the switching unit. Indeed, DTEs can serve as a non-fluorescent switch to modulate the fluorescence of a neighboring fluorophore through energy transfer. Combinations of DTE and metal centers have also opened up new perspectives for the design of metal based photoswitchable fluorescent materials, but also for the modulation of other properties such as NIR absorption, stability enhancement and catalysis. Few examples of intramolecular Förster resonance energy transfer were very recently reported with lanthanide complexes containing an organic photochromic unit or embedded in a pseudo-rotaxane supramolecular assembly controlled by a DTE unit (see chapter 1).

1.1 Examples of lanthanide luminescence switches

Two selected examples of lanthanide luminescence switches reported in literature are presented in this part.

Figure 1. Photochromic unit (phenyl thiazole) coordinated to an europium complex Eu(hfac)$_3$ for luminescence modulation through the modification of its coordination environment (left) and modification of the emission spectrum of the Eu$^{3+}$ ion ($\lambda_{em} = 619$ nm) upon excitation at $\lambda_{exc} = 465$ nm (right).

In the first example reported by Kawai et al., diarylethene type ligands comprise two terthiazole membered units directly coordinated to europium ions carrying hfac ligands
Lanthanide luminescence switches with dithienylethene (DTE) unit (hexafluoroacetylacetonate). The modulation of the luminescence of the lanthanide ion is generated during the photoisomerization process of the ligand (Figure 1). Indeed, the intensity of the emission band of the europium ion located at $\lambda_{em} = 619$ nm is being sensitive to the environment (its ligand field). Thus, isomerization of the DTE unit causes a change in the europium centered luminescence although the modulation is only 30 % of the initial intensity.

Figure 2. Luminescence modulation of Eu ion by changing coordination environment by isomerization of a DTE ligand (left). Modulation of the emission spectrum of the Eu$^{3+}$ ion ($\lambda_{em} = 619$ nm) at excitation $\lambda_{exc} = 465$ nm (center), absorption and emission spectra (right).

The second example reported also by Kawai et al. highlights a photochromic system in which it is possible to read the luminescence intensity of the emission band of the Eu$^{3+}$ ion located at $\lambda_{em} = 619$ nm, without changing the state of the photochromic compound (nondestructive reading) as shown in Figure 2.

Indeed, the authors have developed a system with four characteristic wavelengths for information storage. Both open and cyclized forms of dithienylethene unit obtained after light irradiation at $\lambda = 313$ and 420 nm are not affected during the luminescence measurement of europium ion ($\lambda_{exc} = 526$ nm, Figure 2, right). Similar to the previous example (Figure 1), the intensity of the emission band of the lanthanide center is sensitive to its environment ($\lambda_{em} = 619$ nm) and is therefore different between open and closed form of the DTE ligand (Figure 2, middle).

1.2 Objective

Dipicolinic acid is a widely used building block in coordination and supramolecular chemistry. The corresponding bis-amide (DPAM) derivatives behave as tridentate ligands, which efficiently coordinate to transition metals or lanthanides. Recently, the use of such ligands was extended to the formation of complexes featuring interesting luminescence, nonlinear...
optical\textsuperscript{12} or magnetic properties,\textsuperscript{13} in solution as well as in the crystalline state.\textsuperscript{14}

Herein, we will focus on the combination of a lanthanide (III) (Eu, Yb) complex with a DTE unit, with 2,6-pyridine dicarboxamide as the spacer and Ln binding unit. This assembly should allow the modulation of luminescence of Lanthanide ions through the photochromic reaction of the DTE unit upon irradiation with UV or visible light. The molecules that we synthesized are shown in Scheme 1. A representation of the expected relative energy levels of the component chromophores are shown in Scheme 1. Compound 1a should be converted to 1b upon irradiation with UV light (350 nm), and 1b returns to 1a upon irradiation with visible light (580 nm). When the DTE unit is in its open form, the energy after excitation of the TTA antenna can be transferred to sensitize the lanthanide ion, and, hence, strong emission should be observed. In the case of the closed DTE, luminescence could be quenched since the energy from the sensitizer is expected to be trapped by the closed DTE form of 1b. The choice of lanthanide ions with very different energy of the emissive state should allow us to evaluate the influence of the match or mismatch of closed DTE excited state and Ln emissive state.

Scheme1. Strategy to obtain luminescence switches.

2 Synthesis

Two types of ruthenium (II) complexes will be synthesized; one type is DTE- Eu type, while the other one is DTE- Yb.
2.1 Synthesis of organometallic precursors

Complexes \[ \text{Ln(TTA)}_3 \cdot 2\text{H}_2\text{O} \quad (\text{Ln} = \text{Yb} \text{ or } \text{Eu}) \quad (6 \text{ and } 7) \] were synthesized following the existing procedure (scheme 2) which has been presented in chapter 3.\textsuperscript{15}

\[
\begin{align*}
&\text{CoCl}_3, 6(\text{H}_2\text{O}) \\
\text{H}_2\text{O}, 60 \degree \text{C} & \quad \text{NH}_4\text{OH} \\
\text{Yb(TTA)}_3(\text{H}_2\text{O})_2 \\
\end{align*}
\]

\[
\begin{align*}
&\text{EuCl}_3 \\
\text{H}_2\text{O}, 60 \degree \text{C} & \quad \text{NH}_4\text{OH} \\
\text{Eu(TTA)}_3(\text{H}_2\text{O})_2 \\
\end{align*}
\]

Scheme 2. Synthesis of organometallic precursors

2.2 Synthesis of organic precursors

The organic precursor 10 was synthesized as previously reported.\textsuperscript{16} Compound 10 was prepared after five steps as shown in scheme 3. The first reaction was a Sonogashira coupling reaction between 3,5-dibromo-2-methylthiophene (8) and trimethylsilylacetylene (TMSA) to generate compound 9. Compound 8 could further react with bromobenzene to generate compound 10 with a yield of 66 % via a Suzuki coupling reaction. Compound 11 could be obtained after two stages with a yield of 82 % as shown in Scheme 3. Lithiation using n-butyllithium at -78 °C of the brominated derivative 10, followed by a nucleophilic attack on the sp\(^2\) atoms of the fluorocyclopentene of compound 11 can form the DTE unit 12, with a yield of 27 %. This species bears an alkyne fonction protected with a trimethylsilyl group which is then deprotected with K\(_2\)CO\(_3\) to form the compound 10. The formation of this species is observed, by \(^1\)H-NMR spectroscopy, with the disappearance of the signal of the protons of the trimethylsilyl group at \(\delta = 0.25 \) ppm and the appearance of the signal of the proton of the free alkyne \(\delta = 3.38 \) ppm, as shown in Figure 3. The signals of the methyl groups of the DTE unit can also be observed at \(\delta = 3.38 \) ppm.
Scheme 3. Synthesis pathway for organic precursor 1o.

Figure 3. $^1$H-NMR of compound 1o in CDCl$_3$
The organic precursor 4-iodo-2,6-bis (diethylcarbamoyl) pyridine (2) (Scheme 4) was provided by Dr. Oliver Maury (ENS Lyon).17

2.3 Synthesis of target complexes

Compound 3o was synthesized via Sonogashira cross-coupling reaction between 1o and 2 with a yield of 76 %. Target complexes 4o and 5o were further generated by reaction, respectively, between 3o and Eu(TTA)₃(H₂O)₂ or Yb(TTA)₃(H₂O)₂ with a yield of 95 % for 4o and 90 % for 5o, as shown in Scheme 4.

Scheme 4. Synthetic pathways for 4o and 5o complexes.

3 Characterization

The targeted complexes (3o, 4o, and 5o) were characterized by ¹H NMR spectroscopy, UV-vis, high-resolution mass spectrometry, and satisfactory microanalysis as shown in this section.

3.1 NMR spectroscopy

The ¹H-NMR spectrum of 3o is shown in Figure 4. Data of this ¹H-NMR spectrum of 3o in CD₂Cl₂ are presented in details in Table 1.
Figure 4. $^1$H-NMR spectrum of compound 3o in CD$_2$Cl$_2$

Table 1. $^1$H NMR data of 3o in CD$_2$Cl$_2$

<table>
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<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
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<tr>
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<td>$^3$J = 7.0</td>
<td>6</td>
<td>NCH$_2$CH$_3$</td>
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</table>

The $^1$H-NMR spectrum of 3o in CD$_2$Cl$_2$ was well interpreted with the help of COSY NMR. There are two quartets for the protons on NCH$_2$ and two triplets for protons on the methyl group of NCH$_2$CH$_3$. This is because the protons on the two different NCH$_2$ and on the methyl
group of NCH₂CH₃ cannot rotate freely due to the resonance structure of the dipicolinate moieties, ie. the two ethyl groups on each amide moiety are not equivalent due to the restricted rotation around N-C Sp² partial double bond.

Figure 5. ¹H-NMR spectrum of compound 4o in CD₂Cl₂

¹H-NMR spectrum of 4o is shown in Figure 5. The Datas of this ¹H-NMR spectrum CD₂Cl₂ are shown in details in Table 2.

For the two lanthanide complexes 4o and 5o, paramagnetic shifts are observed due to the through space interactions between the observed nuclei and the 4f unpaired electrons (pseudo-contact shifts) which depends on the magnetic anisotropy of the lanthanide ion (Figures 5 and 6). The assignment of the TTA proton is based on integration and a COSY experiment, and comparison with similar complexes. We assign the broad and deshielded signal at 9.58 to the pyridine ring proton. DTE moiety signals show limited paramagnetic shifts and their assignment is confirmed after isomerization studies (Section 3.5). Finally, the ethyl groups experience a large paramagnetic shift and broadening of their signals which are not the same for 4 and 4’ and 5 and 5’ since their distance to the Eu ion are different. We observed for 4o, that the pyridine ring and N-ethyl protons are deshielded compared to 3o, whereas the DTE protons (thiophene and methyl groups) are shielded.
Table 2. $^1$H NMR data of 4o in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
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<td>3</td>
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$^1$H-NMR spectrum of 5o in CD$_2$Cl$_2$ is shown in Figure 6, and the datas are displayed in Table 3. It occurs that coordination to the more anisotropic Yb ion in 5o lead to similar changes compared with 4o, but with a greater amplitude. The protons of the pyridinedicarboxamide ligand are found as very broad deshielded peaks and cannot be identified easily. The TTA protons are found with similar shifts as in similar complexes. The ones of the DTE are shielded to 6.33 and 4.63 ppm (thiophene), and 0.58 and 0.28 ppm (methyl groups).
3.2 Photophysical properties of ligand 3 (3o and 3c)

The absorption measurements of 3o and 3c were completed in dichloromethane solution (Figure 7). The absorption spectrum of 3o shows several intense transitions in the UV range.
A qualitative assignment of these bands can be proposed based on the comparison with the absorption spectra of the building blocks of 3 (1o and 2 in Figure 8). The more energetic transition at 272 nm is probably DTE centered when the 317 nm and 341 nm bands must have a significant contribution from the pyridine-dicarboxamide unit. These are red-shifted compared with 2 ($\lambda_{\text{max}} = 282$ nm), because of the substitution of the iodine by an acetylide unit, which increases the conjugation.

Upon irradiation at 350 nm, a decrease of absorption is observed at 272 nm while two new bands appear at 383 and 610 nm. This is consistent with the previous assignment of the 272 nm band to an open-DTE centered process. As well, the pyridine-dicarboxamide based transitions are barely affected by the isomerization process, showing that the participation of the DTE moiety to these transitions is probably low. It is also consistent with the usual photochromic behavior of DTE, the lower energy band (610 nm) being attributed to IL transitions centered on the closed DTE moiety. By comparing with the behavior of 1o/1c, it is clear that the position of the visible absorption of the closed DTE unit does not seem to depend much on the triple bond substituent (584 nm for 1c / 610 nm for 3c), so that we can assume that this intra ligand transition is centered on the DTE-CC fragment with a small participation from the dipicolinic amide moiety. This result is consistent with previous work from Branda and co-workers on a platinium complex of 1c in which the visible absorption band is located at 600 nm, with the corresponding HOMO localized on the DTE-CC fragment and only a small contribution of the Pt to the LUMO.

Figure 7. Absorption changes of 3o in CH$_2$Cl$_2$ solution upon UV light irradiation ($\lambda = 350$ nm) to PSS (50 min). The initial spectrum was recovered after bleaching at 580 nm (40 min). c = 2.2×10$^{-5}$mol•L$^{-1}$ for 3o
Figure 8. Comparison of absorption spectra of 1o, 2 and 3o and absorption spectra of 1c, 2 and 3c. Absorption changes of 1o in CH₂Cl₂ solution upon UV light irradiation (λ = 254 nm) to PSS (3 min). The initial spectrum was recovered after bleaching at 580 nm (210 min). c = 1.5×10⁻⁵ mol·L⁻¹ for 1o

3.3 ¹H-NMR photo-isomerization study of 3

The isomerization was also studied by ¹H NMR (Figure 9 and table 4). The ¹H-NMR spectrum of 3c in CD₂Cl₂ is assigned with the help of a COSY NMR. There are two quartets for the protons on the NCH₂ group and two triplets for the protons on the methyl group of NCH₂CH₃. The isomerization study proved that a high photoisomerization conversion (93 % of 3c) can be reached in the photo stationary state, which was obtained by calculating integration of H₃ in 3o and 3c.
Figure 9. $^1$H-NMR spectrum of compound 3c in CD$_2$Cl$_2$

Table 4. $^1$H NMR data of 3c in CD$_2$Cl$_2$

<table>
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<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
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</table>
3.4 Absorption and photochromism of 4o and 5o

The absorption spectra of the two complexes 4o and 5o are identical (Figure 10). They show two broad bands at 280 nm (ε ≈ 53500 L.mol⁻¹.cm⁻¹) and 342 nm (ε ≈ 90 000 L.mol⁻¹.cm⁻¹). The high energy part of this spectrum can be reproduced well by addition of the contributions from the [Ln(TTA)₃.2H₂O] (Ln = Eu, Yb) precursors and from 3o. The strong absorption bands at λ_max = 342 nm is assigned to the TTA ligand absorption that could overlap with transitions of the DTE or pyridine-dicarboxamide. Typically, upon irradiation in this band (at 350 nm) of 4o and 5o solutions, a broad absorption assigned to the deep blue closed isomers 4c and 5c appears at λ_max = 614 and 611 nm, respectively and a shoulder at 380 nm is also observed. The fact that the 342 nm transition does not change much upon isomerization show that the relative contribution of open DTE based transition to TTA based transition is small. As shown in Figure 10, the bands at 380 nm and 611 nm display exactly the same energy in both 5c and 3c so that we can conclude that the pyridine-dicarboxamide must be weakly involved in the corresponding transitions (see section 3.2) or weakly impacted by coordination. Another hypothesis is that the coordination equilibrium between 3c and the Ln(TTA)₃ moiety could be shifted by high dilution so that the observed absorption spectra are a mere superposition of the contribution of 3c and Ln(TTA)₃. However, absorption measurements have been carried out on spin-coated films of 4o (obtained from dichloroethane solutions). In these experiments, no change is observed between the solid state absorption and the solution absorption spectra. It means that the hypothesis of decoordination cannot be checked through absorption studies. As well, the absorption study was made at concentrations ranking from 3.3×10⁻⁴ M to 2.0×10⁻⁵ M with no detectable change in the spectra of both the open and closed forms of the complexes. The solutions of 4c and 5c can be further bleached to the pure open forms under visible light (580 nm), with quantitative recovering of the initial spectra.
Figure 10. Absorption spectra of 3o, 5o and the \([\text{Yb(TTA)}_3 \cdot 2\text{H}_2\text{O}]\) precursor in CH$_2$Cl$_2$ solutions (left). Absorption spectrum of 5c obtained upon UV light irradiation ($\lambda = 350$ nm) of 5o and its comparison with 3c (right). The Europium complex 4o show identical behavior.

Scheme 5. Photochromic behavior of complexes 4 and 5.

3.5 $^1$H-NMR isomerization studies of 4o and 5o

$^1$H NMR monitoring of the isomerization process in CD$_2$Cl$_2$ ([C] $\approx 5 \times 10^{-3}$ - $1 \times 10^{-2}$ mol.L$^{-1}$) has been done on complexes 4 and 5. In Figure 11, for DTE-Eu complexes we can see that H$_2$, H$_2'$ and H$_3$ shifted around 0.5 – 1 ppm, which is normal because the cyclization reaction occurs on DTE unit. Besides, H$_1$ was deshielded upon closing of DTE unit since they are closed to the DTE unit. The closing also has some impact on H$_4$ and H$_5$, which are deshielded as well. Protons on TTA display minor change during the isomerization studies. In Figure 12, For DTE-Yb complex, similar results are obtained to that of DTE-Eu complex upon closing the DTE unit. Protons H$_2$ and H$_2'$ on 5c are shielded around 0.5 – 1 ppm, while H$_1$ and H$_3$ are deshielded around 0.5 ppm upon cyclization reaction of 5o. Assignment and integration of the
CH₃ and CH proton signals on the DTE unit unambiguously shows that the photochromic process upon UV irradiation is almost complete with the reaching a photostationary state composed of ca. 95 % of closed isomers, consistent with a value of 93 % for 3. In both the open and closed state, the NMR signals from uncoordinated 3o or 3c are not detected and well resolved signal are observed (Figure 11 and 12). Therefore, the stability of 4o, 4c, 5o and 5c against decoordination or light-induced decoordination is established in this concentration range.

Figure 11. ¹H NMR spectrum of 4o (dark purple line) and of PSS (97 % of 4c, light purple line) obtained from irradiation of 4o in CD₂Cl₂ (λ = 350 nm, 45 h, ([c] ≈ 1 × 10⁻³ mol.L⁻¹). The numbering refers to Figure 5.
Finally, the quantum yields for the cyclization have been measured by Rémi Métivier in ENS Cachan. Those of 4o ($\phi_{334} = 0.177$) and 5o ($\phi_{334} = 0.142$) are much higher than those for cycloreversion (4c: ($\phi_{575} = 0.008$) and 5c: ($\phi_{575} = 0.007$)), and are in the classical values for diarylperfluorocyclopentene compounds, and consistent with the photostationary state at ca. 95 % of closed isomers.

### 3.6 Emission studies
First, the emission properties of the two complexes europium complexes (4o and 4c) have been studied, in conditions in which no photo-isomerization occurs, as checked by the absorption spectra recorded after each luminescence measurement. For 4o, upon excitation at 350 nm, the emission features the $^5D_0 \rightarrow ^7F_J$ ($J = 0$ - 4) transitions, characteristic of Eu(III) luminescence is observed (Figure 13). The luminescence decay time of the $^5D_0$ state was measured to be 260 $\mu$s (using the $^7F_2$ transition), and the single exponential decay curve indicates that only one emitting specie is present in solution. This value is in the classical range for this type of Eu(III) complexes. With a 340 nm excitation, the emission spectrum of 4c is very similar whereas an excitation in the closed DTE centered transitions (at 550 nm) does not induce any luminescence from the Eu(III) center. Indeed the excitation spectrum of 4c is composed of a single broad band centered at 345 nm. Finally a luminescence decay time of the $^5D_0$ state of 250 $\mu$s was measured for 4c. At this stage, we can conclude that the sensitization occurs in both open and closed state through the $\pi-\pi^*$ transitions centered on the $\beta$-diketonate ligand with a possible additional participation from a dipicolinic amide or DTE centered transition overlapping the former. The fact that sensitization cannot occur by excitation in the visible absorption of 4c (at 550-580 nm ie 17000-18000 cm$^{-1}$) indicates that this level is too close in energy from the europium accepting and emissive levels ($^5D_2$ at 21300 cm$^{-1}$, $^5D_1$ at 19000 cm$^{-1}$ and $^5D_0$ at 17400 cm$^{-1}$) so that the transfer is not efficient or compete with fast back transfer leading to non-radiative processes.

Figure 13. Emission spectrum of 4o and 4c, $\lambda_{ex} = 340$ nm in CH$_2$Cl$_2$ at room temperature.
Figure 14. Emission spectra of 5c in CH$_2$Cl$_2$, at room temperature with $\lambda_{ex} = 350$ nm (black) and $\lambda_{ex} = 580$ nm (red).

As far as the ytterbium complexes are concerned, measuring the full luminescence spectrum of the open isomer 5o with excitation in the absorption band ($\lambda_{ex} = 350$ nm) was not possible owing to the concomitant rapid closing to 5c. This detection in the NIR range is less sensitive so that higher excitation beam power is needed to obtain measurable luminescence in this range. With high excitation beam power, the closing of the system is obviously much faster. In contrast, the luminescence spectra of 5c could be measured, and it displays the characteristic ytterbium ($^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$) transitions in the NIR spectral range at around 980 nm (Figure 14), indicating also for this complex a straightforward sensitization mechanism from the TTA ligand and maybe from the dipicolinic amide or DTE units. Unexpectedly, we also found out that 5c is also emissive upon irradiation at $\lambda_{ex} = 580$ nm, in the absorption band of the closed DTE unit. The emission is weak but characteristic of Yb(III) (Figure 14). In contrast, 5o is not emissive upon irradiation at this wavelength where no absorption band is detected. Therefore, it occurs that the closed DTE unit can sensitize Yb (III) luminescence, the emissive level of Yb (III) (at around 9500 cm$^{-1}$) being situated well below the one of closed DTE unit (singlet state at 17-18000 cm$^{-1}$).

3.7 Modulation of the luminescence response under irradiation

Continuous irradiation in the large absorption band of the open form of 4o ($\lambda_{ex} = 350$ nm) led to the gradual formation of the closed form during which the decay of the luminescence emission was followed at $\lambda = 610$ nm ($^{7}F_{2}$ transition). This decay of the emission process
follows a mono-exponential law with a characteristic time of 10 s, an approximation in which back reaction is neglected. At the photostationary state, the emission is 70 % of its initial value while the optical density measured at 600 nm is consistent with that of the above described absorption spectrum, and thus with the conversion of 4o to 4c (ca. 95 %). Upon further irradiation of 4c at $\lambda = 560$ nm, the compound being not emissive at this wavelength, 4o is fully regenerated on the basis of the absorption spectrum and the initial luminescence intensity is fully recovered. Note that the closing process (75 s) is faster than the opening one (300 s). Four opening closing processes are depicted on Figure 14 showing that the process is fully reversible and occurs without notable alteration. Therefore the total closing of the DTE unit in this europium complex results in a decrease of its luminescence intensity of 30 %. Given that 4o and 4c have similar absorptivity at 350 nm, this decrease can be assigned either to the suppression one of the sensitization pathways (through the open DTE transitions) or to the quenching of the europium excited state by an energy transfer to the lower energy state of the closed DTE system. Because of the good spectral overlap of the emission of Eu(III) (at 610 nm) and the absorption of the colored photochromic unit (which is maximum at 610 nm), this process would be expected to be more efficient. Quenching as large as 80 % of the emission intensity have been observed in a supramolecular combination of Eu(TTA)$_3$(tpy) (tpy = terpyridine) and DAE units when a tpy centered transition is used for sensitization ($\lambda_{\text{irr}} = 390$ nm). In our case, the N-donor based sensitization process also probably competes with the TTA centered one, the latter being more efficient. Further experiment is planned in order to understand why the quenching is only 30 %. In particular, the role of dilution will be studied since we cannot rule out a possible decoordination issue.
Figure 15. Evolution of the emission of 4 at $\lambda = 610$ nm upon irradiation at $\lambda = 350$ nm observed at room temperature with conversion of 4o to 4c, and the mono-exponential fit (red line) with $\tau = 10$ s. (bottom) Representation of four opening-closing cycles: emission at $\lambda = 610$ nm upon irradiation at $\lambda = 560$ nm (blue) and at $\lambda = 350$ nm (red) successively.

In the case of the ytterbium complexes, the question whether luminescence quenching occurs upon DTE closing cannot be addressed upon excitation at 350 nm because the isomerization process is too fast to be studied. However, we can benefit from the alternative sensitization pathway through the closed DTE units in order to photo-modulate the NIR emission of the ytterbium center. Continuous irradiation in the large absorption band of 5c ($\lambda_{ex} = 580$ nm) gradually leads to the formation of the open form, and the decay of the luminescence emission at $\lambda = 1000$ nm (Figure 15) can be monitored. At the photostationary state, the optical density measured at 580 nm in this experiment is virtually zero, consistent with the total conversion of 5c to 5o, and the luminescence is turned off. Upon further irradiation of 5o at $\lambda = 350$ nm, complex 5c is fully regenerated on the basis of the absorption spectrum, and the previous luminescence intensity is also fully regenerated. The closing process (600 s) is faster than the opening one (293 s). Three opening closing processes are depicted on Figure 16 showing that the process is reversible and occurs without notable alteration.
4 Conclusion and perspective

In this chapter, we have reported the synthesis of three compounds $3o$, $4o$, and $5o$ and their photophysical and isomerization studies.

Complex $4o$ and $5o$ are luminescent, and their luminescences were successfully modulated by photo irradiation. However, only $30\%$ of emission of $4o$ could be modulated and the mechanism is still under investigation. We also found that it is possible to modulate Yb(III) ($5o$) luminescence using the ubiquitous DTE photochromic unit although emission is weak.
To sum up, we showed in this work that the ligand 3 can act as a versatile sensitizer of lanthanide luminescence, depending on its status, on the lanthanide ion used and on the excitation wavelength. Furthermore, this work show that it is possible to modulate Yb(III) luminescence using the ubiquitous DTE photochromic unit, and further chemical engineering should allow further adjustment of the energy level of this DTE unit in order to perform a more efficient process. In the future, a new complex with a ruthenium acetylide moiety between the photochromic DTE unit and the lanthanide ion (Scheme 6) could provide a compound whose luminescence may be sensitized at lower energies (through the MLCT transition) and switched by means of both electrochemical type of stimulus and optical stimulus.

Scheme 6. Photoisomerization of future target molecule
References

Chapter 5:
Synthesis of redox-active molecular wires incorporating ruthenium bis(σ-arylacetylide) complexes for incorporation in graphene junctions
Chapter 5: Synthesis of redox-active molecular wires incorporating ruthenium bis(σ-arylacetylide) complexes for incorporation in graphene junctions

1 Introduction

We will, in this section, address the grafting of redox-active organometallic compounds containing or not photochromic on surfaces in order to produce switchable molecular electrical devices. Indeed, the production of devices containing molecular switches could play an important role in obtaining systems with unique electronic performances in the near future. Thus, we will focus our interest not only on the examination of charge transport mechanisms as a function of electrochemically controlled oxidation states of a series of ruthenium (II) bis(σ-arylacetylide) complexes, but also on the optical modulation of the electrical properties (UV-visible absorption) on modified surface. More specifically, after the presentation of the synthesis of these compounds, we will present an application of the conductivity modulation with a device containing a series of ruthenium (II) bis(σ-arylacetylide) complexes disposed between two graphene electrodes. This work was realized in collaboration with the group of Prof. Guo in Perking University.

Selected examples complementary to those given in chapter one of molecular wires and molecular junctions reported in the literature are first presented in this part, their synthesis and physical properties are discussed as well.

1.1 Study of charge transport in redox-active molecular wires incorporating ruthenium(II) bis(-acetylide) complexes

As already mentioned in the first chapter, Frisbie and Rigaut reported the electrical transport behavior of a series of redox-active conjugated molecular wires as a function of temperature and molecular length. In one study, the wires consist in covalently coupled ruthenium (II) bis(σ-arylacetylide) complexes (R1-R3) (Figure 1) and range in length from 2.4 to 4.9 nm. The molecules are unique in that they contain multiple metal-redox centers that are well-coupled by conjugated ligands. The molecules were self-assembled and their films were extensively characterized using ellipsometry, X-ray photoelectron spectroscopy, reflection absorption infrared spectroscopy, and cyclic voltammetry. They probed their electrical properties using conducting probe atomic force microscopy and crossed-wire junctions. At room temperature, they found a very weak dependence of the wire resistance with molecular length, consistent with a high degree of electronic communication along the molecular backbone. At low-temperature (5 K) experiments, Coulomb blockade like behavior was
observed in junctions incorporating R3; direct tunneling appears to be the dominant transport mechanism in R1 and R2 junctions.

![Molecular structures](image)

**Figure 1.** Molecular structures (a) and schematic representations of the CP-AFM (b) and the X-wire (c) junction test structures. In both test structures, the top Au electrode was brought into contact with a SAM of ruthenium complexes formed on the bottom Au electrode.

1.2 Photo-modulable molecular transport junctions based on organometallic molecular wires

Chen and Rigaut have reported a photo-controllable molecular transport junction (MTJ) nanodevice based on the association of a ruthenium-based organometallic molecular wire including a DTE unit using on-wire lithography (OWL) - generated nanogap. The obtained devices perform bidirectional conductive switching upon irradiation with UV and visible light. The theoretical calculations performed on 1 (Figure 2) reveal (i) that the ruthenium acetylide moieties decrease judiciously the electronic coupling of the DTE fragment with the metal electrodes, allowing the system to switch upon irradiation by preventing quenching of excited state by the electrodes, and (ii) that the the HOMO of the closed isomer is lying near the Fermi level of the junction to lead to an efficient conductivity. The switching in conductivity is explained by a weak delocalization in the photochromic part in the open form in addition to the polarization of its HOMO level lying near the Fermi level. Therefore, such a photo-controllable device not only shows a potential application in functional nanocircuits, but also provides a promising platform to clarify the nature of charge transport across single molecules.
1.3 Orthogonally modulated molecular transport junctions for resettable electronic logic gates

In a further study of Chen and Rigaut, they reported for the first time the photo- and electro-commutation of MTJs based on OWL generated nanogaps modified with two Ru/DTE complexes. The reversible and repeatable conductivity switching can be achieved upon orthogonal optical and/or electrochemical triggering of the molecular isomerization of \( \text{1o} \) (Figure 3a), thanks to the remarkable low potential for electrochemical cyclization (Figure 4) allowing the maintenance of stable thiol linking bonds at electrode interface. In order to apply optical and electrochemical stimuli to the functional molecules, the nanogap devices are incorporated in a fluidic cell to achieve an electrochemical environment for device modulation, as shown in Figure 5a. Electrochemical processes were carried out using a gold nanorod on one side of nanogap as the working electrode with a diameter of \( \sim 300 \) nm, a Pt wire as counter electrode and a homemade AgCl coated Ag wire as reference electrode (Figure 5a). In a typical experiment, complex \( \text{1c} \) was covalently bonded onto the two sides of OWL-generated \( \sim 3 \) nm gaps (Figure 5b, inset) after deprotection of the thiol, to ensure the accurate electronic coupling between the molecule and electrodes. As expected, a photo-triggered conductive switching from low resistance state (LRS, Figure 5b black curve) to high resistance state is observed (HRS, Figure 5b, red curve) upon 700 nm irradiation, leading to the photochemical isomerization of the \( \pi \)-conjugated \( \text{1c} \) to the non-conjugated \( \text{1o} \). The reverse process switches back the device to LRS via the photochemical closure upon UV light...
irradiation (365 nm) (Figure 5b, blue curve).

Subsequently, the electrochemical ring closure was successfully realized (Figure 5b, yellow curve). After applying a potential of 450 mV, it is anticipated that 1o within the nanogap is oxidized to 1o^{2+}. Then, 1o^{2+} undergoes radical coupling to form the more stable isomer 1c^{2+}, which is further reduced to 1c by the slightly negative potential (-50 mV) applied successively (Figure 4). Moreover, this electrochemically obtained LRS state could be switched back to the initial HRS state (open state) upon visible light irradiation as described above.

Based on its unique orthogonally modulable property, the 1- functionalized MTJs can be viewed as an electronic gate. Then, this functionalized logic gate is also resettable with the help of 700 nm irradiation. Therefore, as shown in Figure 6 (a, b), both photo- and electro-triggered conductive switching could be repeatedly operated. This is the very first and only example of a junction modulated with two different stimuli.

Figure 3. Orthogonally modulated isomerization of 1. (a) Chemical structure of 1o. (b) Scheme of molecular isomerization of 1 under external controls. E: electrolysis; UV: UV irradiation; Vis: visible light irradiation.\textsuperscript{5}
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![Diagram of electro-cyclization of 1o and 1c](image)

**Figure 4.** Schematic electro-cyclization of 1o.\(^5\)

![Diagram of 1c-functionalized nanogap devices](image)

**Figure 5.** 1c-functionalized nanogap devices. (a) Diagram of the functionalized nanogap devices. Inset: SEM image of a device fabricated by OWL-generated nanowire (scale bar: 1 μm). (b) I-V characteristics of ~ 3 nm gap devices loaded with 1c device. Red curve: after 700 nm irradiation of 1c device for 2h to 1o device. Yellow curve: after subsequent electrolysis of 1o at 450 mV versus Ag/AgCl for 10 min followed by -50 mV for 10 min in CH\(_2\)Cl\(_2\) to return to 1c device. Blue curve: after 365 nm irradiation of 1o device for 30 min to obtain the 1c device. Inset: SEM image of a ~ 3 nm gap (scale bar: 10 nm).\(^5\)
Figure 6. (a,b) Endurance performance: current response of a 1c-based nanodevice under alternate modulation of visible light irradiation (700 nm for 2 h) and (a) UV irradiation (365 nm for 30 min) or (b) Electrochemical cycles (oxidation at 450 mV and reduction at -50 mV for 10 min). The current values were recorded at 0.6 V bias in vacuum.

1.4 Conductance switching and mechanisms in single-molecule graphene junctions

Guo and coworkers also demonstrated the ability to integrate electronic functions based on molecules into electronic nanocircuits, but in another testbed. They achieved optoelectronic switching from the off state to the on state when individual photochromic diarylenes sandwiched between graphene contacts can isomerize between the two states of conjugation (Figure 7). The theoretical calculation supports the experimental observation of the photogated tunneling transition in molecular junctions. This demonstration also provides insight into the design of new types of molecule-based devices for revealing the relationship between charge-transport mechanisms and the electronic structures of molecular junctions.

Figure 7. Switching of graphene–diarylene junctions
1.5 Building high-throughput molecular junctions using indented graphene point contacts

Guo and coworkers also reported a coordination compound bridging single graphene electrode. They used a simple terpyridyl ligands with single amine functionality (4 in Figure 8a) being able to connect covalently to only a single electrode, and they ensured that this species does not conduct. In fact none of such devices showed any detectable current. The contacts made by covalent amide bond formation are quite robust and tolerate broad chemical treatments, thus offering the chance to study the reversibility of coordination reactions with a metal ion (Figure 8). Figure 8b shows the cycles of decomplexation and complexation with cobalt ions for a device connected by molecule 3. After they immersed the connected device in a solution of ethylenediamine tetraaceticacid (EDTA), it became an open circuit (red curve in Figure 8b). When they introduced Co(OAc)₂ again, the device nearly returned to its original conductive state (blue curve in Figure 8b). Moreover, after several cycles of alternate treatments of EDTA and Co(OAc)₂, the device still showed good conductance switching (Figure 8b inset).

Figure 8. a) Strategy for studying the reversibility of coordination reactions. b) S-D current (I_{SD}) versus gate voltage (V_G) data of a rejoined device by molecule 3 under sequential treatments of EDTA and cobalt ions. Inset: three representative switching cycles for the same device when alternately treated with EDTA and cobalt ions. S-D voltage (V_{SD}) = -50 mV.⁹
1.6 Objective

With these few examples, we have seen that molecular wires incorporating ruthenium(II) bis(σ-arylacetylide) complexes can particularly interesting for molecular electronic studies because they offer multiple redox and spin states that can lead to unusual current-voltage (I-V) characteristics, efficient charge conduction, as well as original switching devices. On the other hand, among carbon materials, graphene holds a set of remarkable electronic and physical properties, such as high electrical conductivity stemming from its high-quality tight two-dimensional crystallographic lattice, the ease of device fabrication and the good device stability. These properties make them ideal candidates for use in plastic electronics, and its discovery has led to a deluge of worldwide research interest. However, the ability to control the conductance of molecules at the molecular level by an external mode is still a formidable challenge in this field. Therefore, in collaboration with Prof. Guo in Beijing University (China), we decided to examine the charge transport mechanisms of a series of ruthenium(II) bis(σ-arylacetylide) complexes bridging graphene electrodes, as a function of their electrochemically controlled oxidation states, including a wire bearing a photoswitchable photochromic unit.

\[
\begin{align*}
&\text{GRu 1-GRu 3 (} n = 1, 2, 3) \\
&\text{H}_2\text{N} \quad \text{Ph}_2\text{P} \quad \text{PPh}_2 \quad \text{PPh}_2 \\
&\quad \text{Ru} \quad \text{Ph}_2\text{P} \quad \text{PPh}_2 \\
&\quad \text{NH}_2 \\
&\quad n
\end{align*}
\]
Therefore, in this work, we will report the synthesis of a series of redox-active molecular wires, which are ruthenium(II) bis(σ-arylacetylide) complexes terminated with amine functional groups, one including a photochromic bimetallic complex based on diarylethylene (see Figure 9). These molecules will be used to covalently bridge a gap between graphene electrodes by amide bonds formation between the terminal amine groups on the ruthenium complexes and the carboxylic acid functions that terminate the graphene electrodes. This will lead to novel molecular transport junctions (Figure 10) in which we will examine transport properties (i) as a function of electrochemically controlled oxidation states of the simple GRu 1 – GRu 3 complexes, and (ii) with photo- and electro-switching of the DTE unit in the GRu2-DTE complex.
2 Synthesis of the complexes

Two types of ruthenium(II) bis(σ-arylacetylide) complexes (Figure 9) will be considered; the first type includes monometallic, bimetallic or trimetallic complexes where the ruthenium(II) metal centers are linked via a conjugated bridging ligand, while in the second type, the photochromic bimetallic complexes, two ruthenium(II) metal centers are linked via a photochromic unit: the dithenylethene.

2.1 Synthesis of organic precursors

In order to synthesize the organic precursor 4-ethynylaniline (G1) for further coordination reactions with ruthenium complexes, we started from the 4-iodo-aniline precursor and ethynyltrimethylsilane to get 4-(2-(trimethylsilyl)ethynyl)aniline (82%) by Sonogashira coupling reaction (Scheme 1). Then, the TMS group of 4-(2-(trimethylsilyl)ethynyl)aniline was cleaved by sodium carbonate in THF and methanol to produce 4-ethynylanbenzenamine (G1) (90%) (Scheme 1).

\[
\text{I-} \begin{array}{c} \text{NH}_2 \\
\end{array} + \begin{array}{c} \text{H-} \text{Si} \\
\end{array} \xrightarrow{\text{PdCl}_2(\text{PPh}_3)_4, \text{CuI, Et}_3\text{N, THF, 40°C, 12h}} \begin{array}{c} \text{Si} \\
\end{array} \begin{array}{c} \text{NH}_2 \\
\end{array} \xrightarrow{\text{K}_2\text{CO}_3, \text{THF, MeOH, RT, 12h}} \begin{array}{c} \text{NH}_2 \\
\end{array}
\]

Scheme 1. Synthesis of the organic precursor

2.2 Synthesis of organometallic precursors

Complex G3 has been previously synthesized in our laboratory. Treatment of [RuCl(dppe)_2]PF_6 with an excess of a 1-alkyne (G2) and DBU in CH_2Cl_2 led to the alkylnyl complexes trans-RuCl(C=CC_6H_4-C≡C-TMS)(dppe)_2 (G3).
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Scheme 2. Synthesis of the organometallic precursors

2.3 Synthesis of target complexes

The reactions leading to GRu 1 is displayed on Scheme 3. According to the general procedure previously developed in the laboratory to obtain bis(σ-arylacetylide) complexes, the preparation of GRu 1 was readily achieved with the use of cis-[(dppe)2RuCl2] and of the alkyne G1, in the presence of non-coordinating salt (NaPF6) and a base (Et3N), to afford GRu 1. Since the solubility of GRu 1 and NEt3PF6 are very similar, the impurities (NEt3PF6) are difficult to removed. After many tries, GRu 1 is polluted (vide infra).

Scheme 3. Synthesis of target complex GRu 1

As shown in Scheme 4, the corresponding bimetallic complexes GRu 2 was obtained from the 16-electron species [(dppe)2RuCl][PF6] and diethynylbenzene, through the
known bis(vinylidene) G4. The latter was not isolated owing to its insolubility and its sensitivity to deprotonation. Thus, it was directly reacted with the terminal alkyne G1 bearing the linking group using classical reaction consisting in the substitution of the chlorine atoms in the presence of NaPF₆, after deprotonation of G4 with Et₃N, to afford GRu 2 with a yield of 56 %.

As shown in Scheme 5, the corresponding trimetallic complex GRu 3 was obtained with a yield of 90 % by using cis-[(dppe)₂RuCl₂] as a central core to react with G6 in the presence of non-coordinating salt, NaPF₆, and a base (Et₃N). G6 was generated after the deprotection of the TMS group of G5 in the presence of fluorine (TBAF), while G5 was obtained from the coordination reaction of G3 and G1 in the presence of NaPF₆ and Et₃N.
As shown in Scheme 6, the target complex GRu\textsubscript{2}-DTE bearing the photochromic unit was obtained from the reaction between G1 and G7 as the central core, in the presence of NaPF\textsubscript{6} and Et\textsubscript{3}N as previously described for analogous complexes\textsuperscript{3,16}. Complex G7 was generated from the reaction between the diethynyl-substituted dithienylethene and the 16-electron species [(dppe)\textsubscript{2}RuCl][PF\textsubscript{6}]\textsuperscript{17}. For the moment complex GRu\textsubscript{2}-DTE is still not completely pure after several recrystallizations (vide infra).
3. Characterization

The targeted complexes (GRu 1, GRu 2, GRu 3, GRu 2-DTE) were characterized by IR, $^1$H, $^{31}$P NMR spectroscopy.

3.1 NMR spectroscopy

For the mono wire GRu 1, particularly informative is the single resonance peak in the $^{31}$P NMR spectrum at $\delta = 51.5$ ppm (Figure 11). This singlet is characteristic of bis(σ-arylacetylide) species and of the trans disposition of two carbon-rich chains on the ruthenium, thus showing the full substitution process. Apart from this peak at 51.5 ppm, a small spetuplet appears at around 144.2, which correspond to a residual PF$_6$-salt. Due to the similar solubility of GRu 1 and NEt$_3$HPF$_6$ salt in almost all the organic solvent, it was not possible to get pure GRu 1.
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Figure 11. $^{31}$P-NMR spectrum of complex GRu 1 in DMSO-d6

Figure 12. $^1$H-NMR spectrum of complex GRu 1 in DMSO-d6
Table 1. $^1$H NMR data of GRu 1 in DMSO-d6

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.44</td>
<td>d</td>
<td>6.9</td>
<td>16</td>
<td>H$_3$</td>
</tr>
<tr>
<td>7.21 - 7.17</td>
<td>M</td>
<td></td>
<td>8</td>
<td>H$_5$</td>
</tr>
<tr>
<td>6.96 - 6.92</td>
<td>M</td>
<td></td>
<td>16</td>
<td>H$_4$</td>
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<td>6.54</td>
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<td>H$_1$</td>
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<td>6.37</td>
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<td>H$_2$</td>
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<tr>
<td>4.75</td>
<td>S</td>
<td></td>
<td>4</td>
<td>NH$_2$</td>
</tr>
<tr>
<td>2.61</td>
<td>M</td>
<td></td>
<td>8</td>
<td>H$_6$</td>
</tr>
</tbody>
</table>

As shown in Figure 12 and Table 1, the $^1$H NMR spectrum of complex GRu 1 in DMSO-d6 presents a doublet at 7.44 ppm ($J = 6.9$ Hz) corresponding to the H$_3$. Protons on H$_5$ and H$_4$ give rise to multiplet at 7.21-7.17 ppm and 6.96 - 6.92 ppm, respectively. Another doublet appears at 6.54 ppm ($J = 8.4$ Hz) corresponding to H$_1$. Another doublet appears at 6.37 ppm ($J = 8.4$ Hz) corresponding to H$_2$. Both protons on NH$_2$ give rise to a singlet at 4.75 ppm. Protons on PCH$_2$CH$_2$P give rise to a multiplet at 2.61 ppm. All the interpretation has been done with the help of integrations and 2D NMR. Peaks around 4.09 ppm and 3.16 ppm correspond to the impurities (NEt$_3$HPF$_6$). $^{13}$C-NMR of GRu 1 has not been successfully obtained due to the low solubility of GRu 1 in most of the normal deuterated reagents. HRMS has comforted the fact that the major product is indeed GRu 1.
For the bimetallic complex \( \text{GRu} \, 2 \), there is a single resonance peak in the \( ^{31}\text{P} \) NMR spectrum at \( \delta = 53.2 \) ppm (Figure 13). Like \( \text{GRu} \, 1 \), this singlet is characteristic of bis(\( \sigma \)-arylacetylide) species and of the trans disposition of two carbon-rich chains on each ruthenium, thus showing the full substitution process.
Table 2. $^1$H NMR data of GRu 2 in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.56</td>
<td>m</td>
<td></td>
<td>32</td>
<td>$H_1$, $H_1'$</td>
</tr>
<tr>
<td>7.25 - 7.17</td>
<td>m</td>
<td></td>
<td>16</td>
<td>$H_6$, $H_6'$</td>
</tr>
<tr>
<td>7.03 - 6.96</td>
<td>m</td>
<td></td>
<td>32</td>
<td>$H_2$, $H_2'$</td>
</tr>
<tr>
<td>6.64</td>
<td>d</td>
<td>6.3</td>
<td>8</td>
<td>$H_4$ or $H_3$ and $H_5$</td>
</tr>
<tr>
<td>6.50</td>
<td>d</td>
<td>8.0</td>
<td>4</td>
<td>$H_3$ or $H_4$</td>
</tr>
<tr>
<td>3.55</td>
<td>s</td>
<td></td>
<td>4</td>
<td>NH$_2$</td>
</tr>
<tr>
<td>2.68</td>
<td>m</td>
<td></td>
<td>16</td>
<td>PCH$_2$CH$_2$P</td>
</tr>
</tbody>
</table>

As shown in Figure 13 and Table 2, the $^1$H NMR spectrum of complex GRu 2 in CD$_2$Cl$_2$ presents a doublet at 7.56 ppm ($J = 3.9$ Hz) corresponding to $H_1$. Protons on $H_6$ and $H_2$ give rise to multiplet at 7.25 - 7.17 ppm and 7.03 - 6.96 ppm, respectively. Another doublet appears at 6.64 ppm ($J = 6.3$ Hz) corresponding to $H_4$ or $H_3$ and $H_5$. One more doublet appears at 6.50 ppm ($J = 8.0$ Hz) corresponding to $H_3$ or $H_4$. Protons on NH$_2$ give rise to a singlet at 3.55 ppm. Protons on PCH$_2$CH$_2$P give rise to multiplet at 2.68 ppm.

Figure 14. $^{31}$P-NMR spectrum of GRu 3 in Benzene-d$_6$
For the trimetallic complex \( \text{GRu} \text{ 3} \), two peaks at \( \delta = 53.7 \) and 53.9 ppm with a 2:1 intensity ratio appear in the \(^{31}\text{P}\) NMR spectra and fully support the structure with one central ruthenium unit and two peripheral units (Figure 14).

![NMR Spectrum](image)

**Figure 15.** \(^1\text{H}\)-NMR spectrum of \( \text{GRu} \text{ 3} \) in Benzene-d6

As shown in Figure 15 and Table 3, the \(^1\text{H}\) NMR spectrum of complex \( \text{GRu} \text{ 3} \) in benzene-d6 presents multiplet from 7.80 – 6.94 ppm corresponding to the protons on the aromatic ring. Protons on \( \text{NH}_2 \) give rise to a singlet at 2.81 ppm. Protons on \( \text{PCH}_2\text{CH}_2\text{P} \) give rise to multiplet at 2.66 ppm.

![Structural Diagram](image)

\( \text{GRu} \text{ 3} \)
Table 3. $^1$H NMR data of GRu 3 in Benzene-d6

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Coupling constant (Hz)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.80 - 6.94</td>
<td>m</td>
<td></td>
<td>132</td>
<td>H$_{Ar}$</td>
</tr>
<tr>
<td>6.45</td>
<td>d</td>
<td>8.4</td>
<td>4</td>
<td>H$_{C6H4}$</td>
</tr>
<tr>
<td>2.81</td>
<td>s</td>
<td></td>
<td>4</td>
<td>NH$_2$</td>
</tr>
<tr>
<td>2.66</td>
<td>m</td>
<td></td>
<td>24</td>
<td>PCH$_2$CH$_2$P</td>
</tr>
</tbody>
</table>

As shown in Figure 16, for the photochromic bimetallic wire GRu$_2$-DTE, a single resonance peak in the $^{31}$P NMR spectrum is observed at $\delta = 53.8$ ppm. Like for GRu 2, this singlet is characteristic of bis($\sigma$-arylacetylide) species and of the $trans$ disposition of two carbon-rich chains on each ruthenium atoms. There is another single resonance peak at $\delta = 49.0$ ppm with 7 % intensity corresponding to an unknown impurity for now. We have tried several
recrystallization of the mixture with different solvents. However, no pure product could be obtained. Although we measured the mass of complex \( \text{GRu}_2\text{-DTE} \), we still cannot make sure what the impurity at 49.0 ppm in \( ^{31}\text{P} \) NMR is.

### 3.2 IR spectroscopy and Mass spectrometry

The infrared measurements of complexes \( \text{GRu 1, GRu 2 and GRu 3} \) were performed in KBr pellets. Their data are summarized in Table 4.

For all of them, a \( \text{C≡C} \) stretching band is observed. For \( \text{GRu 1} \), a band at 850 cm\(^{-1}\) corresponding to the impurities (NEt\(_3\)HPF\(_6\)) is also observed. The interpretation was done with the help of previous literature.\(^{17}\)

Datas obtained with mass spectrometry were also included in Table 4, which also confirm the successful synthesis of desired complexes \( \text{GRu 1, GRu 2 and GRu 3} \).

Since complex \( \text{GRu}_2\text{-DTE} \) is still not pure, we did not measure its IR spectrum for the moment.

#### Table 4. Data obtained by IR spectroscopy and Mass spectrometry

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (cm(^{-1}))</th>
<th>Mass (m/z) Found (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{GRu 1} )</td>
<td>( \nu (\text{C≡C}) = 2064 ) ( \nu (\text{PF}_6^-) = 850 ) (NEt(_3)HPF(_6))</td>
<td>[M(^+)]1130.2753 (1130.2745)</td>
</tr>
<tr>
<td>( \text{GRu 2} )</td>
<td>( \nu (\text{C≡C}) = 2061 )</td>
<td>[M(^+)]2151.4812 (2152.4808)</td>
</tr>
<tr>
<td>( \text{GRu 3} )</td>
<td>( \nu (\text{C≡C}) = 2058 )</td>
<td>[M(^+)]3174.6905 (3174.6871)</td>
</tr>
</tbody>
</table>

### 3.3 UV-vis absorption studies

The absorption measurements of \( \text{GRu 2} \) were performed in dichloromethane solution (Figure 17) and of \( \text{GRu 3} \) in toluene solution (Figure 18). Due to the very low solubility of \( \text{GRu 3} \) in dichloromethane, we made the measurement in toluene. Their absorption data are summarized in Table 5. For \( \text{GRu 2} \) in dichloromethane, in addition to the intense short-wavelength absorption band at high energy for transition involving the dppe ligand (intra ligand transitions), a broad absorption band is seen at 375 nm with an extinction coefficient of 72400 L \( \cdot \) mol\(^{-1} \) \( \cdot \) cm\(^{-1}\). This band at 375 nm could result from a transition mixing of Ru(d\(\pi\)) orbitals.
with alkynyl orbitals, more precisely it can be discussed as a MLCT (\(\text{Ru}^{II}(d\pi) \rightarrow L(\pi^*)\)) character and mixed with a IL (\(\pi \rightarrow \pi^*\)) nature.\(^{15}\)

Figure 17. Absorption spectrum of complexe GRu 2 (CH\(_2\)Cl\(_2\), 298 K) in CH\(_2\)Cl\(_2\).

For GRu 3 in toluene, in addition to the intense short-wavelength absorption band for transition involving the dppe ligand (intra ligand transitions), the bis-acetylide complex GRu3 shows a broad absorption band at 383 nm similar nature to that of the transition described for GRu 2.

Figure 18. Absorption spectrum of complexes GRu 3 (toluene, 298 K).
Table 5. UV-visible spectral data obtained on absorption of complexes GRu 2 in CH$_2$Cl$_2$ and GRu 3 in toluene at 25 °C in dichloromethane (C = 4–5*10$^{-6}$ M)

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-visible λ$_{max}$ nm (Ɛ in M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRu 2 in CH$_2$Cl$_2$</td>
<td>375(72400)</td>
</tr>
<tr>
<td>GRu 3 in toluene</td>
<td>383(129200)</td>
</tr>
</tbody>
</table>

3.4 Electrochemical studies

Cyclic voltammetric (CV) data for GRu 1, GRu 2 and GRu 3 are collected in table 6 and table 7, and typical CV traces are displayed in Figure 19 and Figure 20. The monometallic complex GRu 1 undergoes three consecutive one-electron oxidations at 109 mV, 549 mV and 938 mV vs SCE (Figure 19, Table 6), which could be viewed as essentially involving the Ru atom and the carbon-rich ligand, and the two terminal amine groups.$^{16}$ Similarly, bimetallic complex GRu 2 undergoes four consecutive one-electron oxidations at 78 mV, 228 mV, 646 mV and 1307 mV vs SCE (Figure 19, Table 6), which could be viewed as essentially involving the ruthenium atoms and the carbon rich ligand and the two terminal amine groups, similar to the monometallic compound GRu 1.

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~ 169 ~
Figure 19. Cyclic voltammograms of GRu 1 (up) and GRu 2 (bottom) in CH₂Cl₂ with 0.2 M [N₄Bu₄][PF₆], SCE reference, Pt working and auxiliary electrodes. \( v = 0.1 \text{ V} \cdot \text{s}^{-1} \).

Figure 20. Cyclic voltammogram of GRu 3 in Benzonitrile with 0.2 M [N₄Bu₄][PF₆], SCE reference, Pt working and auxiliary electrodes. \( v = 0.1 \text{ V} \cdot \text{s}^{-1} \).

Due to the low solubility of GRu 3 in dichloromethane, CV measurement of GRu 3 was performed in benzonitrile. This trimetallic complex GRu 3 undergoes three consecutive oxidations at 179 mV (two-electron oxidation), 411 mV (one-electron oxidation) and 691 mV.
Synthesis of redox-active molecular wires incorporating ruthenium bis(σ-arylacetylide) complexes for graphene junctions

(two-electron oxidation) vs SCE (Figure 20, Table 7), which could be viewed as essentially involving the ruthenium atoms and the carbon rich ligand and the two terminal amine groups,

<table>
<thead>
<tr>
<th></th>
<th>$E_1^0$ ($\Delta Ep$) (mv vs SCE)</th>
<th>$E_2^0$ ($\Delta Ep$) (mv vs SCE)</th>
<th>$E_3^0$ ($\Delta Ep$) (mv vs SCE)</th>
<th>$E_4^0$ ($\Delta Ep$) (mv vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRu 1</td>
<td>109 (64)</td>
<td>549 (63)</td>
<td>938 (59)</td>
<td></td>
</tr>
<tr>
<td>GRu 2</td>
<td>78 (64)</td>
<td>228 (76)</td>
<td>646 (110)</td>
<td>1307 (72)</td>
</tr>
</tbody>
</table>

Table 6. Cyclic voltammetric datas for complexes GRu 1 and GRu 2 at 25 °C in CH$_2$Cl$_2$ with 0.2 M [N$_n$Bu$_4$][PF$_6$], SCE reference, Pt working and auxiliary electrodes. $v = 0.1$ V·s$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>($E_1^0 + E_2^0$)/2 ($\Delta Ep$) (mv vs SCE)</th>
<th>$E_3^0$ ($\Delta Ep$) (mv vs SCE)</th>
<th>($E_4^0 + E_5^0$)/2 ($\Delta Ep$) (mv vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRu 3</td>
<td>179 (112)</td>
<td>411 (69)</td>
<td>691 (107)</td>
</tr>
</tbody>
</table>

Table 7. Cyclic voltammetric datas for complexes GRu 3 at 25 °C in benzonitrile with 0.2 M [N$_n$Bu$_4$][PF$_6$], SCE reference, Pt working and auxiliary electrodes. $v = 0.1$ V·s$^{-1}$.

3.5 Molecular junctions: preliminary results

Our target molecules are now currently used in Prof. Guo’s group to covalently bridge a gap between graphene electrodes by amide bonds formation between the terminal amine groups on the complexes and the carboxylic acid functions that terminate the graphene electrodes. This will lead to novel molecular electronic devices in which we will examine transport properties as a function of electrochemically controlled oxidation states (Figure 21).
Figure 21. Switching of targeted graphene junctions

Figure 22. Diagram of the device for electrochemically controlled conductance measurements

The device used for electrochemically controlled conductance measurements is shown in Figure 22. After successfully bridging the target molecules we synthesized onto graphene junctions, our coworkers in the group of Xuefeng Guo’s group in Beijing university will try to tune the conductivity by changing oxidation states of ruthenium complexes.
Some preliminary results were collected by our coworker in Xuefeng Guo’s group on the analogous complex G8 previously synthetized in their group. After many tries, the complex G8 was successfully linked on the graphene junction by the formation of amide bonds as shown in two I-V curves of Figure 23. Similarly, GRu 2 was also successfully linked on the graphene junction by the formation of amide bonds as shown in two I-V curves of Figure 24. The observed symmetry of the I-V curves indicates that the G8 or GRu 2 molecules were covalently bound to each of the graphene electrodes on opposite sides of the gap respectively. If the molecules were bound only to one contact (and adsorbed on the other), the I–V curves would display an asymmetric shape due to different injection barriers. This I–V characteristic explicitly suggests a successful fabrication of G8 or GRu 2-based transport junctions.
4. Conclusion and perspective

In this chapter we have shown the synthesis of a novel series of ruthenium carbon-rich compounds \textbf{GRu 1, GRu 2, GRu 3} as well as the photochromic bimetallic complex \textbf{GRu$_2$-DTE} for molecular electronics. These ruthenium(II) $\sigma$-arylacetylide complexes thanks to the terminal linking functions and the structurally rigid conjugated carbon rich pathway were designed for the building of new molecular graphene junctions including one, two or three metal centers and the probing of electrochemical gating via oxidation of the molecules. Furthermore, the photochromic bimetallic complex \textbf{GRu$_2$-DTE} could probably realize combined optical and electrochemical conductance switching in single molecule graphene junctions (\textbf{Figure 25}).

Preliminary results of conductance measurements show that bimetallic complex \textbf{GRu 2} could be successfully bridged into graphene junctions.

In the future, we need to find a new way to purify \textbf{GRu 1} and complex \textbf{GRu$_2$-DTE} and to achieve all their characterizations. This will include isomerization study of complex \textbf{GRu$_2$-DTE} that also needs to be finished before bridging \textbf{GRu$_2$-DTE} in graphene junctions.
Figure 25. Switching of graphene–Ru-diarylethene junctions
Chapter 5

Synthesis of redox-active molecular wires incorporating ruthenium bis(σ-arylacetylide) complexes for graphene junctions

References

(12) Tian, Y.-J.; Meijer, E. W.; Wang, F. Chemical Communications 2013, 49, 9197-9199.
General conclusion

At the beginning of this work we had a total of four different objectives:

(1) We wanted at first to use two ruthenium acetylide moieties in combination with one triarylamine core to modulate the luminescence of triarylamine units. The study of the influence of different electron withdrawing groups (CHO and NO$_2$) on the physical properties of our target complexes was also targeted.

We have therefore, in chapter 2, reported the synthesis of two ruthenium complexes incorporating triarylamine units and their photophysical and electrochemical properties.

The two complexes $\text{Trans-} \{(\text{dppe})_2\text{ClRu(C≡C-4-C}_6\text{H}_4\text{-C}_6\text{H}_4)\}_2\text{N-C}_6\text{H}_4\text{-X} \}$ ($X = \text{NO}_2, \text{CHO}$) (5-CHO, 5-NO$_2$) were obtained and characterized by IR, NMR, UV-vis, CV, spectroelectrochemistry, and photoluminescence. Complexes 5-CHO and 5-NO$_2$ show expected reversible redox behaviors at low potential. Unfortunately, they are poorly luminescent and their luminescence was not successfully modulated by changing their oxidation states. One reason of this poor/non-emissive behavior can be the deactivation of the excited state of the triarylamine cores via low-lying energy levels located on the ruthenium fragment. In order to try to avoid this, we seek to use another ligand (TIPS-X-C=C(CN)$_2$) with a lower lying excited state that might lie below the ruthenium state responsible of the quenching. The TIPS-X-C=C(CN)$_2$ ligand (Scheme 1) bears a stronger electron withdrawing group (-C=C(CN)$_2$) compared with CHO and NO$_2$, which absorption and emission bands are significantly red shifted by comparison to the previously used ligands. In the future, the luminescence properties of the ruthenium complex of TIPS-X-C=C(CN)$_2$ will be studied.

![Scheme 1. The structure of TIPS-X-C=C(CN)$_2$](image-url)
(2) Secondly, we wanted to associate ruthenium vinyl moieties bearing pyridine units to a Ytterbium or Europium ion (Scheme 2) in order to modulate the luminescence by a redox stimulus. Then, the effect of changing the number of ruthenium vinyl moieties on the physical properties was also questioned.


Thus, in chapter 3, we have reported the synthesis of six ruthenium complexes K3, K6, KRu-Eu, KRu-Yb, KRu2-Eu and KRu2-Yb and their photophysical and electrochemical properties. KRu-Eu and KRu-Yb are luminescent and reversibly oxidized on the time scale of optical experiments. The luminescence of KRu-Yb was not successfully modulated by changing the oxidation states because it is a poor emitter. Luminescence modulation of KRu-Eu is still under investigation. Although emission intensity of KRu2-Eu and KRu2-Yb are stronger than that of KRu-Eu and KRu-Yb, luminescence modulation could not be successfully realized due to the lanthanide decoordination upon oxidation. From the previous work in our group, it occurs that the ruthenium acetylides coordinated with Yb(TTA)3 are better candidates for the electrochemical modulation of luminescence.

(3) The third objective we had was the preparation of photochromic lanthanide complexes made by the association of a DTE unit and a Ytterbium or Europium ion, and their luminescence modulation via photo isomerization of the DTE unit (Scheme 3).
**Scheme 3. Molecular structures of DTE-Ln (Ln = Yb, Eu) and the presentation of their photo isomerization**

In chapter 4, we then prepared one 4-iodo-2,6-bis(diethylcarbamoyl) pyridine ligand with a DTE unit (3o). We have studied the behavior of this photochromic compound and found that photochromic cyclization reaction could be completed by 93 % using UV light irradiation. We then carried out the complexation of 3o with a Eu$^{3+}$ or Yb$^{3+}$ precursors to obtain 4o and 5o. Photo isomerization studies of 4o (resp. 5o) showed that 97 % (resp. 91 %) have been converted to closed isomers and that this transformation is reversible. Complexes 4o and 5o are luminescent and their luminescence was successfully modulated by photo irradiation. However, for the europium ion, the luminescence quenching is only of 30 % of its initial value and the mechanism is still under investigation. We also found that it is possible to modulate ytterbium luminescence using the closed state of DTE to sensitize Ytterbium emission, although the emission is weak.

In the future, a new complex with a ruthenium acetylide moiety bearing the photochromic DTE unit and a lanthanide ion (Scheme 4) could provide a compound whose luminescence may be sensitized at lower energies (through the MLCT transition) and switched by means of both electrochemical and optical stimuli.
(4) The last goal we wanted to achieve was the adaptation of organometallic wires (Scheme 5) and photochromic redox switches between graphene electrodes to build molecular junctions whose conductivity can be modulated by means of light and electrochemical stimuli.
In chapter 5, we have shown the synthesis of a novel series of ruthenium carbon-rich compounds GRu 1, GRu 2, GRu 3, as well as that of a photochromic bimetallic complex GRu2-DTE for molecular electronics. They have been characterized by NMR, UV-vis, CV and emission studies. Preliminary results of conductance measurements showed that bimetallic complex GRu 2 could be successfully bridged into graphene junctions. In the future, we need to find a new way to purify GRu 1 and complex GRu2-DTE, and to complete their characterizations. In addition, isomerization study of complex GRu2-DTE also needs to be finished before bridging GRu2-DTE in graphene junctions. These ruthenium(II) σ-arylacetylide complexes with terminal linking functions and with a rigid conjugated carbon-rich pathway will allow for the building of new molecular graphene junctions including one, two or three metal centers and the probing of electrochemical gating via oxidation of the molecules. Furthermore, the photochromic bimetallic complex GRu2-DTE could probably realize combined optical and electrochemical conductance switching in single molecule graphene junctions (Figure 1)

![Diagram of switching of a graphene–Ru-diarylethene junction](image)

*Figure 1. Switching of a graphene–Ru-diarylethene junction*
Experimental part
Appendix 1: Experimental part

General comments

1 Solvents and reagents

All reactions were carried out under an inert atmosphere (Argon), using the Schlenk techniques. Commercial products were purchased from Acros, Alfa Aesar and Sigma Aldrich and were used without further purification. Solvents used for washing and extraction were purchased from Sigma Aldrich and were used without further purification, while those used in reactions and crystallization were dried and distilled under argon atmosphere following the standard procedures: sodium/benzophenone for tetrahydrofurane and diethylether, and calcium hydride for pentane, dichlromethane, 1,2-dichloroethane, triethylamine (NEt₃) and diisopropylamine, and Magnesium for methanol. Sometimes these solvents mentioned above were alternatively dried in a solvent purification system (M Brown).

2 Characterization of the products

2.1 Nuclear Magnetic Resonance

The following spectrometers were used:
- Bruker AVANCE I 500 MHz spectrometer (500 MHz for the $^1$H and 126 MHz for $^{13}$C).
- Bruker AVANCE III 400 MHz spectrometer (400 MHz for $^1$H and 101 MHz for $^{13}$C).
$^1$H and $^{13}$C chemical shifts are given versus SiMe₄ and were determined by reference to residual $^1$H and $^{13}$C solvent signals. Attribution of carbon atoms signals was based on HMBC, HMQC and COSY experiments.

2.2 Elemental analysis and mass spectrometry

The elemental analysis was performed in the laboratory of CNRS for microanalysis; Centre régional de mesures physiques de l'Ouest (CRMPO-Rennes). High resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l’Ouest) on a ZabSpecTOF (LSIMS at 4 kV) spectrometer Bruker MicroTOF-Q II.

2.3 Infrared spectroscopy

IR spectra were recorded on a IFS 28 Brucker spectrometer, and sample were measured in KBr pellets and by ATR.
2.4 UV-Visible spectroscopy

UV/vis absorption spectra were recorded using a UVIKON 9413, analytic jena SPECORD 205 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm path length and a CARY 5000 apparatus.

2.5 UV-Visible irradiation

UV-vis irradiations were performed with a LS series Light Source of ABET technologies, Inc (150W xenon lamp), with single wavelength light filters “350FS 10-25”, “580FS 40-25” in a caped UV cell in toluene or CH₂Cl₂.

2.6 Cyclic Voltammetry measurement

All electrochemical experiments were performed in a home-built cylindrical vacuum tight one compartment cell. A Pt disk and a SCE electrode were used as the counter and reference electrodes. They were introduced like the working electrode (Pt disk polished with 0.25 μm diamond paste before each experiment) via a Teflon screw cap with a suitable fitting. The cell may be attached to a conventional Schlenk line via two side arms equipped with Teflon screw valves and allows experiments to be performed under an atmosphere of argon with approximately 5.0 mL of analyte solution. Solvents for electrochemistry were obtained in the highest available purity from commercial sources (CH₂Cl₂ from Fluka (Burdick&Jackson brand)) or freshly distilled from CaH₂ (CH₂Cl₂) before use. NBu₄PF₆ (0.2 M) was used as the supporting electrolyte. Ferrocene or decamethylferrocene was used as an internal standard. Electrochemical data were acquired with a computer-controlled Eco Chemie Autolab PGSAT 30 potentiostat using the GPES 4.9 software package.

2.7 UV-Vis-NIR spectroscopy

UV-Visible-NIR Spectroelectrochemical experiments were performed in 1,2-C₂H₄Cl₂ at 298 K, under argon, with a Optically Transparent Thin-Layer Electrosynthetic (OTTLE) cell and a EG&G PAR model 362 potentiostat. The OTTLE cell comprises a Pt-mesh working and counter electrode, and a thin silver wire as a pseudo-reference electrode sandwiched between the two CaF₂ windows of a conventional liquid IR cell. The working electrode is positioned in the center of the spectrometer beam. The solvents used for the tests are obtained in the highest available purity from commercial sources (1,2-C₂H₄Cl₂ from Fluka (Burdick & Jackson brand)) and freshly distilled from CaH₂ before use, freeze-pump-thaw degassed, and transferred into the cell under argon. The electrolyte concentration is 0.2 M Bu₄NPF₆ in 1,2-
C_2H_4Cl_2.

UV-vis-NIR spectra were recorded with a Cary 5000 apparatus. For the photochromic compound, spectra were recorded every 2 minutes during \( \lambda_{\text{irr}} = 350 \) nm irradiations and every 10 min during \( \lambda_{\text{irr}} = 580 \) nm irradiations. The irradiations were stopped when two consecutive absorption spectra could be superimposed with a 5 % absorption difference at \( \lambda_{\text{max}} \).

### 2.8 Emission spectroscopy

The luminescence spectra were measured using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorimeter, equipped with a three-slit double grating excitation and emission monochromator with dispersions of 2.1 nm/mm (1200 grooves/mm). The steady-state luminescence was excited by unpolarized light from a 450W xenon CW lamp and detected at an angle of 90° for dilute solution measurements by a red-sensitive Hamamatsu R928 photomultiplier tube. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Uncorrected near-infrared spectra were recorded at an angle of 90° using a liquid nitrogen cooled, solid indium/gallium/arsenic detector (850–1600 nm) through a RG830 2 mm filter. The chemical oxidation–reduction experiments were carried out under a rigorously inert atmosphere directly in the luminescence cuvette using a homemade cell with Schlenk techniques. To that end, we used a homemade luminescence cell equipped with a Young valve and a connection to a vacuum line. Emission spectroelectrochemistry (SEC) experiments were performed at 20 °C, under argon, with homemade OTTLE cell, path length 1 mm, using an FLSP 920 spectrometer (Edinburgh Instruments) and an EG&G PAR Model 362 potentiostat. A Pt grid was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire as a pseudo reference electrode. The cell was disposed with a 45° angle relative to the excitation beam provided by a CW 450 W xenon Arc Lamp. Near infrared spectra were recorded at an angle of 90° using a liquid nitrogen cooled NIR PMT detector or a visible detector. Spectra were corrected from the Pt grid artifact.
Chapter 2:

The product 3-CHO and 3-NO₂ were prepared in Prof. Elena Ishow’s laboratory and the synthesis procedure are still not published, while ClRu(dppe)$_2$,\(^1\) were prepared as previously reported.

\textit{trans-}[(dppe)$_2$ClRu(C=CH-4-C$_6$H$_4$-C$_6$H$_4$)]$_2$N-C$_6$H$_4$-NO$_2$][PF$_6$]$_2$ (4-NO$_2$):

In a schlenk tube, Cl$_2$Ru(dppe)$_2$ (309 mg, 0.32 mmol) and NaPF$_6$ (65 mg, 0.39 mmol) were dissolved in dithloromethane (14 mL), and the solution was stirred for 20 h at room temperature in the dark. Compound 3-NO$_2$ (68 mg, 0.14 mmol) was added, and the reaction mixture heated to 40 $^\circ$C for 6 h. After cooling to room temperature, the suspension was filtered, washed with dichloromethane (2 $\times$ 5 mL), and the washings were concentrated to 5 mL under reduced pressure. Complex 4-NO$_2$ (260 mg, 71 %) was obtained as a green powder by addition of diethyl ether to the dichloromethane extract. After filtration, the process was repeated twice. The complex 4-NO$_2$ was used in next step just after the \textsuperscript{31}P-NMR measurement.

\textbf{\textsuperscript{31}P NMR} (161.99 MHz, CD$_2$Cl$_2$, 297 K): $\delta = 39.29$ (s, PPh$_2$).
trans-([(dppe)₂ClRu(C≡CH-4-C₆H₄-C₆H₄)]₂N-C₆H₄-NO₂) (5-NO₂):

In a schlenk tube, compound 4-NO₂ (260 mg, 0.0608 mmol) was dissolved in dichloromethane (20 mL), NEt₃ (0.4 mL, 2.86 mmol) was added, and the solution was stirred for 5 min. The reaction mixture was filtered and concentrated under reduced pressure to 2 mL. Methanol (10 mL) was slowly added to the mixture and the yellow complex 5-NO₂ (60 mg, 18%) was obtained by filtration, washed with pentane (3 × 5 mL) and dried under vacuum.

³¹P NMR (161.99 MHz, CD₂Cl₂, 297 K): δ = 49.53 (s, PPh₂).

¹H NMR (400.16 MHz, CD₂Cl₂, 297 K): δ = 8.10-8.08 (d, J = 9.3 Hz, 2H, H₆), 7.67 (d, J = 8.5 Hz, 4H, H₃), 7.56-7.40 (m, 36H, o-PPh₂ and H₂), 7.32 (d, J = 8.5 Hz, 4H, H₄), 7.27-7.19 (m, 16H, p-PPh₂), 7.08-6.97 (m 34H, m-PPh₂ and H₅), 6.74 (d, J = 8.3 Hz, 4H, H₁), 2.73 (m, 16H, P–CH₂).

¹³C NMR (100.62 MHz, CD₂Cl₂, 297K): δ = 153.86 (C₁₂ or C₁₁), 144.52 (C₁₀ or C₉), 140.58 (C₁₁ or C₁₂), 138.99 (C₉ or C₁₀), 137.08 (m, ipso-PPh₂), 136.39 (m, ipso-PPh₂), 134.98 (o-PPh₂), 134.53 (o-PPh₂), 134.24 (C₈ or C₇), 130.96 (C₁), 129.38 (p-PPh₂), 129.18 (p-PPh₂), 128.10 (C₃), 127.60 (m-PPh₂), 127.39 (m-PPh₂), 127.17 (C₄), 126.16 (C₂), 125.79 (C₆), 118.67 (C₅), 31.06 (m, PCH₂CH₂P).

IR (KBr): ν (cm⁻¹) = 2058 (νC≡C).

HR-MS ESI (m/z): 2354.4465 ([M⁺] calcd: 2354.4396).

Elemental analysis (%) for 2C₁₃₆H₁₁₈N₂O₂Cl₂P₈Ru₂·CH₂Cl₂: C, 69.17; H, 4.79; N, 1.08. (calcd: C, 69.32; H, 4.88; N, 1.17).

UV-vis [λₘₐₓ, (Ε, 10³ M⁻¹.cm⁻¹), CH₂Cl₂, nm]: 383 (68.100).

C.V. (CH₂Cl₂, 0.2 M n-Bu₄NPF₆, 20°C, 0.1 V.s⁻¹) E° in V vs. Fc (ΔEₚ in V): -0.29 (0.071), 0.560 (0.114).
trans-\{[(dppe)\(_2\)ClRu(C≡CH-\(\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\))\(_2\)N-\(\text{C}_6\text{H}_4\text{-CHO}\)]\([\text{PF}_6]\)\(_2\) (4-CHO):

In a schlenk tube, \(\text{Cl}_2\text{Ru(dppe)}\(_2\) (194 mg, 0.2 mmol) and NaPF\(_6\) (52 mg, 0.308 mmol) were dissolved in dichloromethane (10 mL), and the solution was stirred for 20 h at room temperature without light. Compound 3-CHO (38 mg, 0.08 mmol) was added, and the reaction mixture heated to 40 °C for 6 h. After cooling to room temperature, the suspension was filtered, washed with dichloromethane (3 × 5 mL), and the washings were concentrated to 10 mL under reduced pressure. Complex 4-CHO (160 mg, 75 %) was obtained as a green powder by addition of diethyl ether to the dichloromethane extract. The process was repeated twice.

\(^{31}\text{P NMR}\) (161.99 MHz, CD\(_2\text{Cl}_2\), 297 K): \(\delta = 39.26\) (s, PPh\(_2\)).

trans-\{[(dppe)\(_2\)ClRu(C≡CH-\(\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\))\(_2\)N-\(\text{C}_6\text{H}_4\text{-CHO}\)] (5-CHO):

In a schlenk tube, compound 4-CHO (160 mg, 0.0608 mmol) was dissolved in dichloromethane (10 mL), \(\text{NEt}_3\) (0.2 mL, 1.43 mmol) was added, and the solution was stirred for 5 min. The reaction mixture was filtered and concentrated under reduced pressure to 2 mL.
Methanol (10 mL) was slowly added to the mixture and yellow complex 5-CHO (30 mg, 21 %) was obtained after filtration, washing with pentane (3 × 5 mL) and drying in vacuum.

$^{31}$P NMR (161.99 MHz, CD$_2$Cl$_2$, 297 K): $\delta = 48.76$ (s, PPh$_2$).

$^1$H NMR (400.16 MHz, CD$_2$Cl$_2$, 297 K): $\delta = 9.84$ (s, 1H, CHO), 7.73 (d, J = 8.8 Hz, 2H, H$_6$), 7.64 (d, J = 8.6 Hz, 4H, H$_3$), 7.45 - 7.40 (m, 36H, $o$-PPh$_2$ and H$_2$), 7.30 (d, J = 8.6 Hz, 4H, H$_4$), 7.26 - 7.19 (m, 16H, $p$-PPh$_2$), 7.15 (d, J = 8.8 Hz, 2H, H$_5$), 7.08 - 6.96 (m, 32H, $m$-PPh$_2$), 6.73 (d, J = 8.2 Hz, 4H, H$_1$), 2.72 (m, 16H, P–CH$_2$).

$^{13}$C NMR (100.62 MHz, CD$_2$Cl$_2$, 297 K): $\delta = 190.54$ (CHO), 153.60 ($C_{12}$ or $C_{11}$), 145.11 ($C_{10}$ or $C_9$), 138.31 ($C_8$ or $C_{10}$), 137.09 (m, $ipso$-PPh$_2$), 136.41 (m, $ipso$-PPh$_2$), 134.99 ($o$-PPh$_2$), 134.54 ($o$-PPh$_2$), 134.43 ($C_7$ or $C_8$), 131.53 ($C_6$), 130.97 ($C_1$), 129.76 ($C_{11}$ or $C_{12}$), 129.38 ($p$-PPh$_2$), 129.18 ($p$-PPh$_2$), 127.95 ($C_3$), 127.61 ($m$-PPh$_2$), 127.39 ($m$-PPh$_2$), 126.92 ($C_4$), 126.07 ($C_2$), 119.96 ($C_3$), 31.06 (m, PCH$_2$CH$_2$P).

IR (KBr): $\nu$ (cm$^{-1}$) = 2062 ($\nu_{C=O}$), 1689 ($\nu_{C=C}$).

HR-MS ESI (m/z): 2337.4553 ([M+] calcd: 2337.4495).

Elemental analysis (%) for 2C$_{139}$H$_{117}$NOCl$_2$P$_3$Ru$_2$·CH$_2$Cl$_2$: C, 70.36; H, 5.20; N, 0.42. (calcd: C, 70.31; H, 4.96; N, 0.59).

UV-vis [$\lambda_{\text{max}}$, ($E$, 10$^3$ M$^{-1}$·cm$^{-1}$), CH$_2$Cl$_2$, nm]: 386 (50.200).

C.V. (CH$_2$Cl$_2$, 0.2 M $n$-Bu$_4$N$^+$PF$_6^-$, 20°C, 0.1 V·s$^{-1}$) $E^\circ$ in V vs. Fe (ΔEp in V): - 0.22 (0.088), 0.488 (0.13).
Chapter 3:

5-ethynyl-2-(pyridin-2-yl)pyridine, \(^2\) 5-ethynyl-2-(5-ethynylpyridin-2-yl)pyridine, \(^2\) RuClH(CO)(PiPr\(_3\))\(_2\), \(^3\) Eu(TTA)\(_3\)(H\(_2\)O)\(_2\), \(^4\) and Yb(TTA)\(_3\)(H\(_2\)O)\(_2\), \(^4\) were prepared as previously reported.

\[((CO)(Cl)(\textit{i}Pr\textit{P})\textit{2Ru(vinylbipyridinyl)})\] (K3):

In a schlenk tube, a solution of RuClH(CO)(PiPr\(_3\))\(_2\) (410 mg, 0.843 mmol) in 15 mL of degassed dichloromethane was slowly added to a solution of 5-ethynyl-2-(pyridin-2-yl)pyridine (152 mg, 0.843 mmol) in 15 mL of dichloromethane. The reaction mixture was stirred for 105 min at room temperature under a N\(_2\) atmosphere. The solvent was concentrated under reduced pressure, and then the product was washed with degassed n-hexane (4 × 15 mL), and dried under vacuum to obtain an orange powder (410 mg, 73%).

\(^{31}\)P NMR (162 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta = 38.53\)

\(^1\)H NMR (400.2 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta = 9.02\) (d, \(J = 13.6\) Hz, 1H, H\(_1\)), 8.59 (d, \(J = 4.8\) Hz, 1H, H\(_{12}\)), 8.32 (m, 1H, H\(_6\)), 8.30 (s, 1H, H\(_7\)), 8.22 (d, \(J = 8.4\) Hz, 1H, H\(_5\)), 7.75 (dt, \(^{3}\)J\(_{HH}\) = 7.7 Hz, \(^4\)J\(_{HH}\) = 1.6 Hz, 1H, H\(_{10}\)), 7.47 (dd, \(^3\)J\(_{HH}\) = 8.4 Hz, \(^4\)J\(_{HH}\) = 2.0 Hz, 1H, H\(_4\)), 7.22 (dd, \(^3\)J\(_{HH}\) = 7.0 Hz, \(^3\)J\(_{HH}\) = 4.8 Hz, 1H, H\(_{11}\)), 6.09 (dt, \(^3\)J\(_{HH}\) = 13.6 Hz, \(^3\)J\(_{PH}\) = 1.8 Hz, 1H, H\(_2\)), 2.76 (m, 6H, H\(_{13}\)), 1.29 (m, 36H, H\(_{14}\)).

\(^{13}\)CNMR (100.6 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta = 203.3\) (t, \(^2\)J\(_{PC}\) = 13.0 Hz, CO), 157.7 (t, \(^2\)J\(_{PC}\) = 10.7 Hz, C\(_1\)), 157.0 (s, C\(_8\)), 151.7 (s, C\(_6\)), 149.5 (s, C\(_{12}\)), 145.6 (s, C\(_7\)), 137.1 (s, C\(_{10}\)), 134.4 (t, \(^4\)J\(_{PC}\) = 2.0 Hz, C\(_3\)), 131.2 (s, C\(_4\)), 131.0 (t, \(^3\)J\(_{PC}\) = 3.3 Hz, C\(_2\)), 123.3 (s, C\(_{11}\)), 121.2 (s, C\(_9\)), 120.7 (s, C\(_5\)), 25.1 (t, \(^4\)J\(_{PC}\) = 9.9 Hz, C\(_{13}\)), 20.2 (d, \(^2\)J\(_{PC}\) = 30.1 Hz, C\(_{14}\)).

IR (ATR): \(v\) (cm\(^{-1}\)) = 1903 (\(\nu_{C=O}\))

Element analysis (%) for \(4C_3H_5ClN_2OP_2Ru\cdot CH_2Cl_2\): C, 54.59; H, 7.57; N, 4.05. (calcd: C, 54.60; H, 7.55; N, 4.07).

HR-MS ESI (m/z): 631.2520 ([M]\(^+\), calcd: 631.25146)
In Schlenk tube, \([(\text{CO})(\text{Cl})(\text{iPr}_3\text{P})_2\text{Ru(vinylbipyridinyl)})-\kappa^2-\text{N,N'}-\text{Eu(TTA)}_3\] (KRu-Eu):

In Schlenk tube, \([(\text{CO})(\text{Cl})(\text{iPr}_3\text{P})_2\text{Ru(vinylbipyridinyl)})] (70 mg, 105 mmol) and Eu(TTA)$_3$·2H$_2$O (89.3 mg, 105 mmol) were dissolved in 5 mL of methylene chloride. The red solution was stirred at room temperature for 24 h, after which the methylene chloride solution was layered with pentane. After 2 days, the orange precipitate was filtered off, washed with pentane (2 × 7 mL), and dried under vacuum, yielding the product (97 mg, 61%).

$^{31}$P NMR (162 MHz, CD$_2$Cl$_2$, 297 K): $\delta = 38.96$

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 297 K): $\delta = 15.14$ (s, 1H, H$_{12}$ or H$_7$), 13.72 (s, 1H, H$_7$ or H$_{12}$), 10.52 (d, $J = 13.6$ Hz, 1H, H$_1$), 9.28 (m, 1H, H$_{11}$), 8.98 (m, 2H, H$_4$ and H$_{10}$), 8.50 (m, 2H, H$_5$ and H$_6$), 7.81 (d, 1H, H$_2$), 7.04 (d, $^2$$J_{HH} = 4.95$ Hz, 3H, H$_{20}$ or H$_{18}$), 6.48 (m, 3H, H$_{19}$), 6.03 (d, $^3$$J_{HH} = 2.68$ Hz, 3H, H$_{18}$ or H$_{20}$), 3.26 (s, 3H, H$_{15}$), 2.96 (m, 6H, H$_{21}$), 1.38-1.52 (m, 36H, H$_{22}$).

IR (ATR): $\nu$ (cm$^{-1}$) = 1919 ($\nu$C=O); 1600 ($\nu$C=O).

Element analysis (%) for 2C$_{55}$H$_{53}$N$_2$O$_7$F$_9$ClP$_2$S$_3$RuEu·CH$_2$Cl$_2$: C, 43.63; H, 4.25; N, 1.87; S, 6.21. (calcd: C, 43.70; H, 4.24; N, 1.84; S, 6.31).

\([(\text{CO})(\text{Cl})(\text{iPr}_3\text{P})_2\text{Ru(vinylbipyridinyl)})-\kappa^2-\text{N,N'}-\text{Yb(TTA)}_3\] (KRu-Yb):

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In Schlenk tube, \([\text{(CO)}(\text{iPr}_3\text{P})_2\text{Ru(vinylbipyridinyl)}]\) (75 mg, 113 mmol) and \(\text{Yb(TTA)}_3 \cdot 2\text{H}_2\text{O}\) (98.2 mg, 113 mmol) were dissolved in 5 mL of methylene chloride. The reaction mixture was stirred for 24 h at room temperature, after which the methylene chloride solution was layered with pentane. After 5 days, the orange precipitate was filtered off and dried under vacuum, yielding to the product (80 mg, 47%).

\[^{31}\text{P NMR}\] (161 MHz, CD$_2$Cl$_2$, 297 K): \(\delta = 39.31\)

\[^{1}\text{H NMR}\] (500 MHz, CD$_2$Cl$_2$, 297 K): \(\delta = 23.39\) (s, 1H, H$_9$), 23.02 (s, 1H, H$_5$), 20.41 (s, 1H, H$_{12}$ or H$_7$), 17.61 (s, 1H, H$_7$ or H$_{12}$), 15.64 (s, 1H, H$_{10}$), 14.86 (s, 1H, H$_4$), 13.42 (s, 1H, H$_{11}$), 12.43 (d, \(^3\text{J}_{\text{HH}} = 10.98\) Hz, 1H, H$_1$), 7.87 (d, \(^3\text{J}_{\text{HH}} = 10.67\) Hz, 1H, H$_2$), 6.82 (d, J = 3.64 Hz, 3H, H$_{\text{TTA}}$), 5.61 (s, 3H, H$_{\text{TTA}}$), 2.90 (m, 12H, H$_{21}$+ H$_{\text{TTA}}$), 1.24-1.43 (m, 36H, H$_{22}$), - 9.70 (S, 3H, H$_{15}$).

**IR (ATR):** \(\nu\) (cm$^{-1}$) = 1921 (\nu$_{\text{C=O}}$); 1608 (\nu$_{\text{C=O}}$).

**Element analysis** (% for C$_{55}$H$_{63}$N$_2$O$_2$F$_7$ClP$_5$S$_3$RuYb•CH$_2$Cl$_2$: C, 42.61; H, 4.11; N, 1.76; S, 6.05. (calcd: C, 42.32; H, 4.09; N, 1.76; S, 6.05.)

\[\text{[(CO)}(\text{Cl})(\text{iPr}_3\text{P})_2\text{Ru(divinyl(bipyridinyl))Ru(P}_4\text{Pr}_3)(\text{Cl})(\text{CO})]\] (K6):

In a schlenk tube, a solution of Ru(Cl)H(CO)(P$_4$Pr$_3$)$_2$ (1125.5 mg, 2.316 mmol) in 23 mL of degassed dichloromethane was slowly added to a stirred solution of 5-ethylidene-2-(5-ethylidene-pyridin-2-yl) pyridine (236 mg, 1.155 mmol) in 16 mL of dichloromethane. The reaction mixture was stirred for 60 minutes at room temperature under Ar atmosphere. The solvent was concentrated under reduced pressure; the product was washed with degassed n-hexane (5x20 mL), and dried under vacuum to obtain a red powder (1.057 g, 78%).

\[^{31}\text{P NMR}\] (161 MHz, CD$_2$Cl$_2$, 297 K): \(\delta = 38.49\)

\[^{1}\text{H NMR}\] (400 MHz, CD$_2$Cl$_2$, 297 K): \(\delta = 8.89 - 8.93\) (d, \(^3\text{J}_{\text{HH}} = 13.59\) Hz, 2H, H$_1$), 8.23 (d, \(^4\text{J}_{\text{HH}} = 1.78\) Hz, 2H, H$_7$), 8.08 - 8.10 (d, \(^3\text{J}_{\text{HH}} = 8.30\) Hz , 2H, H$_3$), 7.40-7.42 (dd, \(^3\text{J}_{\text{HH}} = 8.26\) Hz, \(^4\text{J}_{\text{HH}} = 1.93\) Hz, 2H, H$_4$), 6.03- 6.06 (m, 2H, H$_2$), 2.72-2.78 (m, 12H, H$_{16}$), 1.24-1.32 (m, 72H, H$_{17}$).

**IR (ATR):** \(\nu\) (cm$^{-1}$) = 1900 (\nu$_{\text{C=O}}$)
Element analysis (%) for C_{52} H_{94} N_{2} O_{2} C_{4} Ru_{2}: C, 52.91; H, 7.88; N, 2.35. (calcd: C, 53.10; H, 8.06; N, 2.38).

[(CO)(Cl)(^{3}Pr_{3}P)_{2}Ru(divinyl{bipyridinyl})Ru(^{3}Pr_{3})(Cl)(CO)-κ^{2}-N,N’-Eu(TTA)_{3}] (KRu_{2}-Eu);

In a Schlenk tube [(CO)(Cl)(^{3}Pr_{3}P)_{2}Ru(divinyl{bipyridinyl})Ru(^{3}Pr_{3})(Cl)(CO)] and Eu(TTA)_{3}·2H_{2}O were dissolved in 5 mL of methylene chloride, and the dark red solution was stirred at room temperature for 24 h. The solvent was removed and the orange solid washed with pentane (2 x 6 mL). After washing with pentane, some impurities (^{31}P NMR: δ = 35.7 (s) and 35.0 (s)) still remained in the product. The product was then dissolved again in 3 mL of methylene chloride and layered with 7 mL of pentane. After 5 days, the precipitate was filtered off and dried under vacuum, yielding to the product (65 %).

^{31}PNMR (161 MHz, CDCl3, 297K): δ = 38.84

^{1}H NMR (600 MHz, CD_{2}Cl_{2}, 297K): δ = 14.82 (s, 2H, H7), 10.42 (d, ^{3}J_{HH} = 13.25 Hz, 2H, H1), 8.88 (d, ^{3}J_{HH} = 7.44 Hz, 2H, H5 or H4), 8.06 (d, ^{3}J_{HH} = 13.08 Hz, 2H, H2), 8.00 (d, ^{3}J_{HH} = 7.53 Hz, 2H, H4 or H5), 7.04 (d, 2H, H15 or H13), 6.46 (s, 3H, H14), 5.98 (s, 3H, H13 or H15), 3.31 (s, 3H, H10), 3.01 (m, 12H, H16), 1.43-1.55 (m, 72H, H17).

IR (ATR): ν (cm^{-1}) = 1907 (ν_{C≡O}), 1917 (ν_{C≡O}); 1597 (ν_{C≡O}).

Element analysis (%) for 4C_{76}H_{106}Cl_{2}EuF_{9}N_{2}O_{8}P_{4}Ru_{2}S_{3}·CH_{2}Cl_{2}: C, 45.47; H, 5.29; N, 1.39; S, 4.78 (calcd: C, 45.45; H, 5.29; N, 1.39; S, 4.78).
Appendix 1  |  Experimental part

\[
[(\text{CO})(\text{Cl})(\text{iPr}_3\text{P})_2\text{Ru(divinyl(bipyridinyl)})\text{Ru(P}^\text{t} \text{Pr}_3)(\text{Cl})(\text{CO})-\kappa^2-\text{N},\text{N'}-\text{Yb(TTA)}_3]\ (\text{KRU}_2-\text{Yb}): \]

In Schlenk tube, \([(\text{CO})(\text{Cl})(\text{iPr}_3\text{P})_2\text{Ru(divinyl(bipyridinyl)})\text{Ru(P}^\text{t} \text{Pr}_3)(\text{Cl})(\text{CO})-\kappa^2-\text{N},\text{N'}-\text{Yb(TTA)}_3)] (100 \text{ mg, 85 mmol}) and \text{Yb(TTA)}_3\cdot2\text{H}_2\text{O} (74.2 \text{ mg, 85 mmol}) were dissolved in 12 mL of methylene chloride. The reaction mixture was stirred for 24 h at room temperature after which the methylene chloride solution was layered with pentane. After 6 days, the red precipitate was filtered and dried under vacuum, yielding to the product (92 mg, 54 %).

\[^{31}\text{PNMR} (161\text{MHz, CDCl}_3, 297 \text{ K}): \delta = 39.25\]

\[^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2, 297 \text{ K}): \delta = 21.64 \text{ (s, 2H, H}_5 \text{ or H}_4), 20.28 \text{ (s, 2H, H}_7), 14.53 \text{ (s, 2H, H}_4 \text{ or H}_5), 12.28 \text{ (d, } {^3}\text{J}_{HH} = 10.91 \text{ Hz, 2H, H}_1), 8.42 \text{ (d, } {^3}\text{J}_{HH} = 8.26 \text{ Hz, H}_2), 6.70 \text{ (d, 3H, H}_14), 5.53 \text{ (s, 3H, H}_13 \text{ or H}_15), 3.01 \text{ (s, 12H, H}_16), 2.80 \text{ (s, 3H, H}_15 \text{ or H}_13), 1.37 - 1.52 \text{ (m, 72H, H}_17), - 8.98 \text{ (s, 3H, H}_10).\]

\[^\text{IR} (\text{ATR}) : v (\text{cm}^{-1}) = 1909 (\nu_{\text{C=O}}), 1917 (\nu_{\text{C=O}}); 1602 (\nu_{\text{C=O}}).\]

\text{Element analysis} (%) for \(4\text{C}_7\text{H}_{106}\text{Cl}_2\text{F}_9\text{O}_2\text{P}_2\text{Ru}_2\text{S}_3\text{Yb}\cdot3\text{CH}_2\text{Cl}_2: \text{C}, 44.38; \text{H}, 5.21; \text{N}, 1.15; \text{S}, 4.35(\text{calcd}: \text{C}, 44.35; \text{H}, 5.18; \text{N}, 1.35; \text{S}, 4.62).\)
Chapter 4:

4-iodo-2,6-bis (diethylcarbamoyl) pyridine,\(^{5}\) and compound \(1\) (ethenyl-DTE-C\(_6\)H\(_3\)),\(^{6}\) were prepared as previously reported. YbCl\(_3\).6H\(_2\)O and EuCl\(_3\) were purchased from ALDRICH (99.998 \%) and ALFA INORGANICS (99.99 \%), while Yb(TTA)\(_3\).2H\(_2\)O and Eu(TTA)\(_3\).2H\(_2\)O were prepared according to the literature.\(^{4}\) All the reactions and handling involving DTE compounds were carried out in the dark.

\[\text{[C}_6\text{H}_5-(\text{C}_5\text{S}_2\text{F}_8\text{H}_8)-\text{C=CC-}_m\text{m}(\text{C}(=\text{O})\text{N}(\text{CH}_2\text{CH}_3)_2)_2\text{-C}_3\text{H}_4\text{N}] (3o):\]

In a schlenk tube, compound \(1\) (ethenyl-DTE-C\(_6\)H\(_3\)) (394 mg, 0.84 mmol), 4-iodo-2,6-bis(diethylcarbamoyl)pyridine (2) (424 mg, 1.05 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (36.9 mg, 0.05 mmol) and CuI (20 mg, 0.11 mmol) were dried under vacuum for 30 minutes. Then, well degassed THF (100 mL) and diisopropylethylamine (0.29 mL, 1.68 mmol) were added. The reaction mixture was left under stirring at room temperature for 14 hours. Then, the solvents were evaporated to obtain a crude product that was purified by column chromatography using ethyl acetate and pentane (1/1) as eluent to obtain \(3\) as a yellow powder (480 mg, 76 \%).

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), 297 K): \(\delta = 7.61\) (s, 2H, H\(_1\)), 7.57 - 7.55 (m, 2H, o-C\(_6\)H\(_3\)), 7.41-7.38 (m, 3H, m-C\(_6\)H\(_5\)+H\(_2\)), 7.37 - 7.34 (m, 1H, p-C\(_6\)H\(_3\)), 7.28 (s, 1H, H\(_2\)), 3.53 (q, 4H, \(^3\)J = 7 Hz, NCH\(_2\)), 3.33 (q, 4H, \(^3\)J = 7 Hz, NCH\(_2\)), 2.00 (s, 3H, H\(_3\)), 1.98 (s, 3H, H\(_3\)), 1.23 (t, 6H, \(^3\)J = 7 Hz, NCH\(_2\)CH\(_3\)), 1.14 (t, 6H, \(^3\)J = 7 Hz, NCH\(_2\)CH\(_3\)).

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\textbf{\(^{13}\text{C NMR}\)} (125.76 MHz, \(\text{CD}_2\text{Cl}_2\), 297 K): \(\delta = 167.6\) (s, C\(_6\)), 154.7 (C\(_7\)), 146.1 (s, C\(_{13}\)), 143.0 (s, C\(_{17}\)), 142.1 (s, C\(_{16}\)), 137.6 (m), 135.6 (m), 133.7 (s, C\(_2\)), 133.6 (s, C\(_{19}\)), 133.1 (s), 129.4 (s, C\(_{21}\)), 128.4 (s, C\(_{22}\)), 126.0 (s, C\(_{20}\)), 125.7 (s, C\(_{12}\) or C\(_{18}\)), 124.9 (s, C\(_1\)), 122.6 (s, C\(_2\)), 120.5 (s, C\(_{11}\)), 116.5 (m), 111.5 (m), 91.0 (s, C\(_9\)), 87.7 (s, C\(_{10}\)), 43.6 (s, C\(_4\) or C\(_4'\)), 40.4 (s, C\(_4\) or C\(_4'\)), 14.8 (s, C\(_3\) or C\(_3'\)), 14.7 (s, C\(_3\) or C\(_3'\)), 14.5 (s, C\(_5\) or C\(_5'\)), 12.92 (s, C\(_5\) or C\(_5'\)).

\textbf{IR (KBr)}: \(\nu (\text{cm}^{-1}) = 2209\) (\(\nu\text{C≡C}\)), 1638 (\(\nu\text{C=O}\)).

\textbf{Element analysis (%) for 11[C\(_{38}\)H\(_{35}\)N\(_3\)O\(_2\)F\(_6\)S\(_2\)] \cdot \text{CH}_2\text{Cl}_2\): C 60.83, H 4.56, N 5.40, S 8.44 (Calcd: C 60.82, H 4.68, N 5.59, S 8.52).

\textbf{HR-MS ESI (m/z)}: 766.1968 ([M+Na]\(^+\), calcd: 766.19671); 744.2123 ([M+H]\(^+\), calcd: 744.21477).

\[\text{[C}_6\text{H}_5-(\text{C}_1\text{S}_2\text{F}_6\text{H}_8)\text{─C≡C─m,m-(C(=O)N(CH}_2\text{CH}_3)_2\text{)}\text{─C}_5\text{H}_4\text{N]} (3c):}\]

Upon irradiation with UV light (\(\lambda = 350\) nm) for 380 min, 3o in dichloromethane was converted to 3c with a yield of 93\%. ([c] \(\approx 2 \times 10^{-3}\) mol·L\(^{-1}\))

\textbf{\(^1\text{H NMR}\)} (400 MHz, \(\text{CD}_2\text{Cl}_2\), 297 K): \(\delta = 7.62-7.44\) (m, 7H, \(\text{C}_6\text{H}_5 + \text{H}_{\text{CH}_2\text{NAN}}\)), 6.72 (s, 1H, \(\text{H}_2\)), 6.58 (s, 1H, \(\text{H}_2\)), 3.50 (q, 4H, \(^3\text{J} = 7.1\) Hz, N\(\text{CH}_2\)), 3.30 (q, 4H, \(^3\text{J} = 7.1\) Hz, N\(\text{CH}_2\)), 2.21 (s, 6H, \(\text{CH}_3\text{DTE}\)), 2.20 (s, 6H, \(\text{CH}_3\text{DTE}\)), 1.21 (t, 6H, \(^3\text{J} = 7.2\) Hz, N\(\text{CH}_2\text{CH}_2\)), 1.12 (t, 6H, \(^3\text{J} = 7.2\) Hz, N\(\text{CH}_2\text{CH}_3\)).
Appendix 1
Experimental part

In a schlenk tube, compound 3o (51 mg, 0.069 mmol) and Eu(TTA)\(_3\)(H\(_2\)O\(_2\)) (58.4 mg, 0.069 mmol) were dried under vacuum for 30 min and dissolved in dichloromethane (5 mL). This solution was stirred at ambient temperature for 16 hours. The mixture was taken to dryness under vacuum to yield a green powder (106 mg, 95 %).

**\(^1\)HNMR** (400.16 MHz, CD\(_2\)Cl\(_2\), ppm): \(\delta = 9.58\) (s, 2H, H\(_{C5H2N}\)), 7.26-7.46 (m, 5H, C\(_6\)H\(_5\)), 7.14 (s, 1H, 2 or 2’), 7.09 (brs, 3H, CH\(_{Thio-TTA}\)), 6.82 (s, 1H, 2’or 2), 6.53 (brs, 3H, CH\(_{Thio-TTA}\)), 6.21 (brs, 3H, CH\(_{Thio-TTA}\)), 5.63 (brs, 4H, NCH\(_2\)), 3.84 (brs, 6H, NCH\(_2\)CH\(_3\)), 3.51 (brs, 4H, NCH\(_2\)), 2.53 (brs, 6H, NCH\(_2\)CH\(_3\)), 2.1 (s, 3H, CH\(_{TTA}\)), 1.79 (s, 3H, CH\(_3\)DTE), 1.69 (s, 3H, CH\(_3\)DTE).

**\(^{13}\)H NMR** (125.77 MHz, CD\(_2\)Cl\(_2\), 297 K): \(\delta = 167.86, 145.88, 142.91, 141.84, 135.10, 133.46, 129.35, 128.40, 127.31, 125.86, 125.57, 125.30, 124.41, 122.46, 119.88, 90.07, 46.43, 16.48, 14.58, 14.45, 1.18.

**IR** (KBr): \(\nu\) (cm\(^{-1}\)) = 2212 (\(\nu_{C≡C}\)), 1608 (\(\nu_{C=O}\)).

**Element analysis (%)** for \([10C\(_6\)H\(_{47}\)N\(_3\)O\(_8\)F\(_{15}\)S\(_5\)Eu]\cdot 6CH\(_2\)Cl\(_2\)): C 46.66, H 3.06, N 2.36, S 10.05 (calcd: C 46.66, H 2.99, N 2.61, S 9.94).

**HR-MS** ESI(m/z): 1582.0837. ([M\(^+\)Na\(^+\)], calcd: 1582.08319).

\[C_6H_5-(C_{15}S_2F_6H_8)-C≡C-m-(C(=O)N(CH_2CH_3)_2)_2\cdot C_5H_4N-Eu(TTA)_3\] (4o):
\[ \text{[C}_6\text{H}_5-(\text{C}_15\text{S}_2\text{F}_6\text{H}_8)-\text{C}≡\text{C}-\text{m,m}-(\text{C}(=\text{O})\text{N(CH}_2\text{CH}_3)_2)_2\text{C}_5\text{H}_4\text{N}-\text{Eu(TTA)}_3)] (4c): \]

Upon irradiation with UV light (\(\lambda = 350 \text{ nm}\)) for 45 hours, 4o in dichloromethane was converted to 4c with a yield of 97\%. ([c] \approx 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1})

\(^1\text{HNMR} (400.16 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm}): \delta = 9.85 (s, 2\text{H, H}_{\text{C5H4N}}), 7.38-7.52 (m, 5\text{H, C}_6\text{H}_5), 7.11 (\text{brs}, 3\text{H, CH}_{\text{Thio-TTA}}), 6.62 (s, 1\text{H, 2}), 6.52 (\text{brs, 3H, CH}_{\text{Thio-TTA}}), 6.13 (\text{brs, 3H, CH}_{\text{Thio-TTA}}), 5.93 (s, 1\text{H, 2}), 5.66 (\text{brs, 4H, NCH}_2), 4.21 (\text{brs, 6H, NCH}_2\text{CH}_3), 3.66 (\text{brs, 4H, NCH}_2\text{CH}_3), 2.53 (\text{brs, 6H, NCH}_2\text{CH}_3), 1.98 - 1.91 (3\text{H, H}_6), 1.98 (s, 3\text{H, CH}_{3\text{DTE}}), 1.91 (s, 3\text{H, CH}_{3\text{DTE}}).

\(\text{IR (KBr): } \nu (\text{cm}^{-1}) = 2202 (\nu_{\text{C≡C}}), 1610 (\nu_{\text{C=O}}).\)

\[ \text{[C}_6\text{H}_5-(\text{C}_15\text{S}_2\text{F}_6\text{H}_8)-\text{C}≡\text{C}-\text{m,m}-(\text{C}(=\text{O})\text{N(CH}_2\text{CH}_3)_2)_2\text{C}_5\text{H}_4\text{N}-\text{Yb(TTA)}_3)] (5o): \]

In a schlenk tube, 3o (51.5 \text{ mg, 0.069 mmol}) and Yb(TTA)_3(H_2O)_2 (60.4 \text{ mg, 0.069 mmol}) were dried under vacuum for 30 min and dissolved in dichloromethane (5 mL). This solution was stirred at ambient temperature for 16 hours. The mixture was taken to dryness under vacuum to yield a light green powder (109 \text{ mg, 95%}).

\(^1\text{HNMR} (400.16 \text{ MHz, CD}_2\text{Cl}_2, \text{ppm}): \delta = 8.48 (s, 3\text{H, CH}_{\text{Thio-TTA}}), 7.12 (\text{brs, 3H, C}_6\text{H}_5), 6.92 (\text{brs, 2H, C}_6\text{H}_5), 6.79 (\text{brs, 3H, CH}_{\text{Thio-TTA}}), 4.92 (\text{brs, 3H, CH}_{\text{Thio-TTA}}), 0.58 (s, 3\text{H, CH}_3\text{DTE}), 0.28 (s, 3\text{H, CH}_3\text{DTE}), -14.61 (s, 3\text{H, CH}_{\text{TTA}}). \)
Appendix 1

Experimental part

$^{13}$C NMR (125.77 MHz, CD$_2$Cl$_2$, 297 K): $\delta$ 149.36, 143.34, 141.65, 140.26, 137.83, 135.80 (m), 134.30, 133.81, 132.38, 129.99, 128.56, 127.82, 127.66, 125.92, 124.88, 124.00, 122.79, 121.08, 116.29, 114.98, 114.43, 112.23, 109.98, 107.71, 90.66 (m), 87.69, 83.63, 46.86, 45.72, 22.46, 12.73, 12.59, 0.69.

IR (KBr): $\nu$ (cm$^{-1}$) = 2212 ($\nu$C≡C), 1606 ($\nu$C=O).

Element analysis (%) for [C$_{62}$H$_{47}$O$_3$N$_3$F$_{15}$S$_5$Yb]· CH$_2$Cl$_2$: C 45.35, H 2.95, N 2.48, S 9.99 (calcd: C 45.39, H 2.94, N 2.52, S 9.61).

HR-MS ESI(m/z): 1359.1227 ([M-TTA]$^+$, calcd: 1359.1226).

[C$_6$H$_5$-(C$_{15}$S$_2$F$_8$H)$_8$]-C≡C-m,m-(CON(CH$_2$CH$_3$)$_2$)$_2$-C$_5$H$_4$N-Yb(TTA)$_3$] (5c):

Upon irradiation with UV light ($\lambda$ = 350 nm) for 45 hours, 5o in dichloromethane was converted to 5c with a yield of 91 %. ([c] ≈ $1 \times 10^{-3}$ mol·L$^{-1}$)

$^1$HNMR (400.16 MHz, CD$_2$Cl$_2$, ppm): $\delta$ = 8.53 (brs, 3H, CH$_{\text{Thio}}$TTA), 7.01 - 7.22 (m, 5H, C$_6$H$_5$), 6.82 (brs, 3H, CH$_{\text{Thio}}$TTA), 4.93 (brs, 3H, CH$_{\text{Thio}}$TTA), 0.66 (s, 3H, CH$_{\text{3DTE}}$), 0.47 (s, 3H, CH$_{\text{3DTE}}$), -14.70 (s, 3H, CH$_{\text{TTA}}$).

IR (KBr): $\nu$ (cm$^{-1}$) = 2201 ($\nu$C≡C), 1605 ($\nu$C=O).
Appendix 1
Experimental part

Chapter 5:

\[((\text{dppe})_2\text{RuCl})\text{(OTf)}, \text{[HC≡C–p-C}_6\text{H}_4\text{–C≡CH]}, \text{trans-[ClRu(dppe)}_2\text{=C=CH–C}_6\text{H}_4\text–
\text{HC=C=Ru(dppe)}_2\text{Cl}]\text{[TfO]}_2\text{, G1}, \text{G3}^\text{10}\) were prepared as previously reported.

![G1](image)

*trans-[NH}_2\text{–C}_6\text{H}_4\text{–C≡C=Ru(dppe)}_2\text{=C=C=C}_6\text{H}_4\text{–NH}_2\] (GRu 1):

![GRu 1](image)

In a Schlenk tube, \textit{cis}-\text{RuCl}_2\text{(dppe)}_2\text{(300 mg, 0.31 mmol)}, \text{NaPF}_6\text{ (208 mg, 1.24 mmol)}, \text{G1}
\text{(91 mg, 0.777 mmol)} were introduced with \text{CH}_2\text{Cl}_2\text{ (40 mL)} and triethylamine
\text{(0.9 mL, 20 eq.). The reaction mixture was stirred for 4 days at room temperature. The solvent was reduced to 5
mL under vacuum and the product was precipitated with 12 mL methanol. Then, washing of
the precipitate with pentane was achieved three times, and a yellow solid (100 mg, 29 %) was
obtained upon evaporation of the residual solvent.}

\text{\textsuperscript{31}\text{P NMR}}\text{ (161.99 MHz, DMSO-d6, 297 K): }\delta = 51.51 \text{ (s, PPh}_2\).

\text{\textsuperscript{1}\text{H NMR}}\text{ (400.16 MHz, DMSO-d6, 297 K): }\delta = 7.44 \text{ (d, } J = 6.9 \text{ Hz, 16H, H}_3\text{), 7.19 \text{ (m, 8H, H}_5\text{), d} = 6.93 \text{ (m, 16H, H}_4\text{), 6.54 \text{ (d, } J = 8.4 \text{ Hz, 4H, H}_1\text{), 6.37 \text{ (d, } J = 8.4 \text{ Hz, 4H, H}_2\text{), 4.75 \text{ (s, 4H, NH}_2\text{), 2.61 \text{ (m, 8 H, H}_6\text{).}}}

\text{IR (KBr): }\nu \text{ (cm}^{-1}) = 2064 \text{ (v}_\text{C≡C).}

\text{HR-MS ESI (m/z): 1130.2753 ([M}^+\text{] calcd: 1130.2745).}

\text{Elemental analysis (}\%\text{) for 4C}_{68}\text{H}_{60}\text{N}_2\text{P}_4\text{Ru}\cdot\text{9CH}_2\text{Cl}_2:\text{ C, 63.85; H, 4.76; N, 2.14.(calcd: C, ~202 ~}
Appendix 1

Experimental part

C.V. ([CH₂Cl₂, 0.2 M n-Bu₄N⁺PF₆⁻, 20°C, 0.1 V.s⁻¹] E° in V vs. Fc (ΔEₚ in V): -0.31 (0.056), 0.126 (0.059), 0.515 (0.056).

trans-[NH₂–C₆H₄–C≡C–Ru(dppe)₂–C≡C–C₆H₄–C≡C–Ru(dppe)₂–C≡C–C₆H₄–NH₂]

(GRu 2):

In a Schlenk tube, G₄ (190 mg, 0.083 mmol), NaPF₆ (56 mg, 0.332 mmol), G₁ (29 mg, 0.249 mmol) were introduced with CH₂Cl₂ (25 mL) and triethylamine (0.6 mL, 50 eq.). The reaction mixture was stirred during 5 days at room temperature. The solvent was then pumped to dryness and the residue was washed with toluene (3 × 20 mL), and filtered off. The solid was recrystallized with dichloromethane and methanol. Then, washing of the precipitate with pentane three times yielded to a yellow precipitate (110 mg, 56 %) after evaporation of the residual solvent.

³¹P NMR (161.98 MHz, CD₂Cl₂, 297 K): δ = 53.15 (s, PPh₂).

¹H NMR (400.13 MHz, CD₂Cl₂, 297 K): δ = 7.56 (d, J=3.9, 32H, H₁), 7.17 - 7.25 (m, 16H, H₆), 6.96-7.03 (m, 32H, H₂), 6.64 (d, J = 6.33 Hz, 8H, H₄ or H₃ and H₅), 6.50 (d, J = 8.0 Hz, 4H, H₃ or H₄), 3.55 (s, 4H, NH₂), 2.68 (m, 16 H, P–CH₂).

¹³C NMR (100.62 MHz, CD₂Cl₂, 297K): δ = 142.94 (C₈ or C₉), 137.97 (C₇), 134.78 (C₁), 131.15 (C₄ or C₃), 129.59 (C₃), 128.88 (C₆), 127.35 (C₂), 126.09(C₁₀), 121.99 (C₉ or C₈), 117.56, 116.48, 114.95 (C₃ or C₄), 31.95 (m, PCH₂CH₂P).

IR (KBr): v (cm⁻¹) = 2061 (νC=C).

HR-MS FAB (m/z): 2152.4812 ([M+] calcd: 2152.4808).

Elemental analysis (%) for 10C₁₃₀H₁₁₂N₂P₈Ru₂·17CH₂Cl₂: C, 68.83; H, 4.92; N, 1.10.(calcd: C, 68.81; H, 5.02; N, 1.22).

UV-vis [λmax, (E, 10³ M⁻¹.cm⁻¹), CH₂Cl₂, nm]: 236 (180.200), 375 (72.400).

C.V. ([CH₂Cl₂, 0.2 M n-Bu₄N⁺PF₆⁻, 20°C, 0.1 V.s⁻¹] E° in V vs. Fc (ΔEₚ in V): -0.38 (0.06), -0.23 (0.07), 0.188 (0.11), 0.849 (0.07).
trans-[TMS-C≡C-C₆H₄-C≡C–Ru(dppe)₂–C≡C–C₆H₄–NH₂] (G5):

In a Schlenk tube, G₃ (380 mg, 0.336 mmol), NaPF₆ (169 mg, 1.008 mmol), G₁ (59 mg, 0.504 mmol) were introduced with CH₂Cl₂ (60 mL) and triethylamine (1.4 mL, 10.08 mmol). The reaction mixture was stirred for 5 days at room temperature. The solvent was then pumped to dryness and the residue was recrystallized with dichloromethane and methanol. Then, the precipitate was washed with pentane three times and a yellow precipitate (366 mg, 90 %) was obtained upon evaporation of the residual solvent.

³¹P NMR (161.99 MHz, CD₂Cl₂, 297 K): δ = 53.07 (s, PPh₂).

¹H NMR (400.16 MHz, CD₂Cl₂, 297 K): δ = 7.63 (d, J = 6.8 Hz, 8H, o-PPh₂), 7.37 (d, J = 6.9 Hz, 8H, o-PPh₂), 7.20-7.14 (m, 10H, p-PPh₂ and o-ph-TMSA), 7.00-6.91 (m, 16H, m-PPh₂), 6.66 (d, J = 8.4 Hz, 2H, Ph-NH₂), 6.59 (d, J = 8.2 Hz, 2H, m-Ph-TMSA), 6.50 (d, J = 8.5 Hz, 2H, Ph-NH₂), 3.56 (s, 2H, NH₂), 2.64 (m, 8 H, P–CH₂), 0.25 (s, 9H, Si-Me₃).

HR-MS ESI (m/z): 1211.3042 ([M⁺] calcd: 1211.3031).

trans-[H-C≡C-C₆H₄-C≡C–Ru(dppe)₂–C≡C–C₆H₄–NH₂] (G₆):

In a Schlenk tube, G₅ (366 mg, 0.308 mmol) and Bu₄NF (1 M in THF, 0.37 mL) were dissolved in dichloromethane (130 mL). The solution was stirred 1 h at room temperature and
Appendix 1  |  Experimental part

evaporated to dryness. The residue was washed with distilled methanol (3 × 20 mL), dried under vacuum. Then, a light yellow powder was obtained (200 mg, 58%).

$^{31}\text{P NMR}$ (161.99 MHz, CDCl$_3$, 297 K): $\delta = 53.73$ (s, PPh$_2$).

$^{1}\text{H NMR}$ (400.16 MHz, CDCl$_3$, 297 K): $\delta = 7.62$ (d, J = 6.6 Hz, 8H, -PPh$_2$), 7.39 (d, J = 6.5 Hz, 8H, -PPh$_2$), 7.24 (d, J = 8.2 Hz, 2H, -O-PPh$_2$), 7.18-7.13 (m, 8H, -P-PPh$_2$), 6.98-6.90 (m, 16H, -m-PPh$_2$), 6.67 (d, J = 8.4 Hz, 2H, -m-PH-NH$_2$), 6.57 (d, J = 8.2 Hz, 2H, -m-Ph-TMSA), 6.52 (d, J = 8.4 Hz, 2H, -o-PH-NH$_2$), 3.51 (s, 2H, NH$_2$), 2.61 (m, 8H, P-CH$_2$).

$^{13}\text{C NMR}$ (126 MHz, CD$_2$Cl$_2$, 297K) $\delta = 143.07$ (s, C$_8$ or C$_9$ or C$_{10}$), 140.24 (m, Ru-C), 140.12 (m, Ru-C), 137.77 (m, ipso-C$_6$H$_5$(PPh$_2$)), 137.50 (m, ipso-C$_6$H$_5$(PPh$_2$)), 134.81 (s, -o-C$_6$H$_5$(PPh$_2$)), 134.45 (s, -o-C$_6$H$_5$(PPh$_2$)), 134.67 (s, C$_1$), 131.07 (s, C$_3$), 130.23 (s, C$_2$), 129.05 (s, -p-C$_6$H$_5$(PPh$_2$)), 128.95 (s, -p-C$_6$H$_5$(PPh$_2$)), 127.38 (s, -m-C$_6$H$_5$(PPh$_2$)), 121.80 (s, C$_8$ or C$_9$ or C$_{10}$), 117.06 (s, C$_8$ or C$_9$ or C$_{10}$), 116.79 (s, C$_5$ or C$_6$ or C$_7$), 115.74 (s, C$_5$ or C$_6$ or C$_7$), 114.96 (s, C$_4$), 85.07 (s, C=CH$_2$), 77.04 (s, C=CH$_2$), 31.85 (m, PCH$_2$CH$_2$P).

IR (KBr): ν (cm$^{-1}$) = 2058 (υC=C).

HR-MS ESI (m/z): 1139.2641 ([M$^+$] calcd: 1139.2636).

Elemental analysis (%) for 2C$_{70}$H$_{59}$NP$_4$Ru$\cdot$CH$_2$Cl$_2$·C, 71.69; H, 5.15; N, 1.30 (calcd: C, 71.59; H, 5.08; N, 1.18).

UV-vis [$\lambda_{\text{max}}$ (ε, 10$^3$ M$^{-1}$.cm$^{-1}$), toluene, nm]: 234 (65.100), 368 (34.100).

C.V. (CH$_2$Cl$_2$, 0.2 M n-Bu$_4$N$^+$PF$_6^-$, 20°C, 0.1 V.s$^{-1}$) $E^\circ$ in V vs. Fc ($\Delta E_p$ in V): -0.218 (0.066), 0.245 (0.058).

$^{\text{trans-}}$[NH$_2$–C$_6$H$_4$–C≡C–Ru(dppe)$_2$–C≡C–C$_6$H$_4$–C≡C–Ru(dppe)$_2$–C≡C–C$_6$H$_4$–C≡C–Ru(dppe)$_2$–C≡C–C$_6$H$_4$–NH$_2$] (GrU 3):

In a schlenk tube, G6 (100 mg, 0.088 mmol), NaPF$_6$ (28.8 mg, 0.171 mmol), cis RuCl$_2$(dppe)$_2$ (41.4 mg, 0.0427 mmol), triethylamine (29 mg, 0.249 mmol) were introduced with CH$_2$Cl$_2$ (10 mL) and triethylamine (0.18 mL, 1.28 mmol.). The reaction mixture was stirred during 3
days at room temperature. The solvent was then pumped dryness, and the residue was recrystallized with dichloromethane and methanol. Then, washing of the precipitate with pentane three times yielded to a yellow precipitate (70 mg, 51 %) after evaporation of the residual solvent.

$^{31}$P NMR (161.99 MHz, Benzene-d$_6$, 297 K): $\delta = 53.92$ and 53.74 (s, PPh$_2$).

$^1$H NMR (400.16 MHz, Benzene-d$_6$, 297 K): $\delta = 7.80 - 6.94$ (m, 132H, H$_{Ar}$), 6.45 (d, J = 8.4 Hz, 4H), 2.81 (s, 4H, NH$_2$), 2.66 (m, 24 H, P–CH$_2$).

IR (KBr): $\nu$ (cm$^{-1}$) = 2058 ($\nu$C≡C).

HR-MS ESI (m/z): 3174.6905 ([M$^+$] calcd: 3174.68711).

Elemental analysis (%) for C$_{192}$H$_{164}$N$_2$P$_{12}$Ru$_3$·CH$_2$Cl$_2$: C, 70.97; H, 5.08; N, 0.84. (calcd: C, 71.06; H, 5.09; N, 0.86).

UV-vis [$\lambda_{\text{max}}$, (E, 10$^3$ M$^{-1}$.cm$^{-1}$), toluene, nm]: 286 (83.800), 383 (129.200).

C.V. (benzonitrile, 0.2 M $n$-Bu$_4$N$^+$PF$_6^-$, 20°C, 0.1 V.s$^{-1}$) $E^0$ in V vs. SCE ($\Delta E_p$ in V): 0.179 (0.112), 0.411 (0.069), 0.691(0.107).
References:

This work is devoted to the synthesis and characterization of novel molecular switches and wires that incorporate ruthenium organometallic moieties.

First, a bibliographic chapter presents the advantages and applications of the building blocks used in the following chapters and discuss the general context of molecular electronics.

The second part of this manuscript deals with preparation, electrochemical and photophysical studies of bimetallic ruthenium complexes bearing a triarylamine core. The goal is to modulate the luminescence of this core by changing the states of the redox-active ruthenium acetylide moieties.

In the third part, combinations of Ln (Ln = Eu or Yb) complexes and redox-active ruthenium vinyl bipyridine moieties were formed in order to tune the luminescence of Ln center via oxidation of the redox-active ruthenium vinyl moieties.

The fourth part describes an association of a Ln (Ln = Eu or Yb) precursor and a ligand bearing a dithienylethene (DTE) unit, in order to commute the light emission of the Ln center. These DTE-Ln compounds were successfully synthesized and their luminescence was reversibly modulated by photo irradiation.

In the last part, we report the synthesis of a series of redox-active molecular wires, which are ruthenium (II) bis(σ-arylacetylide) complexes terminated with amine functional groups, one of them including a photochromic DTE unit. These molecules are designed to covalently bridge a gap between graphene electrodes for probing the electrochemical gating of conductance via oxidation of the molecules. Furthermore, the photochromic complex should allow combined optical and electrochemical conductance switching in single molecule graphene junctions.

Résumé

Ce travail est consacré à la synthèse et à la caractérisation de commutateurs et de fils moléculaires.

La première partie, une étude bibliographique, présente les avantages et les applications des unités moléculaires utilisées dans le contexte de l’électronique moléculaire.

La deuxième partie de ce manuscrit traite de la préparation, des études électrochimiques et photophysiques de complexes de ruthénium bimétalliques portant un cœur triarylamine. Le but est ici de moduler la luminescence de ce cœur en changeant l’état redox des groupements acetylyde de ruthénium.

Dans la troisième partie, des combinaisons de précurseurs de complexes de Ln (Ln = Eu ou Yb) et de groupements vinyl-ruthénium redox-actifs ont été formées afin de moduler la luminescence des centres Ln via l’oxydation des groupements vinyl-ruthénium.

La quatrième partie décrit l'association d'un précurseur de complexe de Ln (Ln = Eu ou Yb) à un ligand portant une unité dithienylethène (DTE), afin de commuter l'émission de lumière du centre Ln. Ces composés ont été synthétisés avec succès et leur luminescence a été reversiblement modulée par irradiation lumineuse.

Dans la dernière partie, nous décrivons la synthèse d'une série de fils moléculaires composée de complexes bis(acetylure) de ruthénium (II) terminés par des groupes fonctionnels amine, et comprenant un complexe bimétallique photochrome avec une unité DTE. Ces molécules ont été conçues de manière à être insérées entre deux électrodes de graphène pour étudier leur conductance dans les différents états redox. En outre, le complexe photochrome doit pouvoir permettre la commutation de la conductance par voie optique et électrochimique dans des jonctions moléculaires de graphène.

Key words: ruthenium complexes, luminescence, photochromism, conductivity, switches
Moduler l’intensité de luminescence est l’un des objectifs les plus attrayants pour l’obtention
dephotocommutateurs moléculaires en raison de la haute sensibilité, la résolution, le contraste
et le temps de réponse rapide de la détection de la luminescence.1 Le développement des
mécanismes de contrôle des systèmes moléculaires luminescents offrirait un moyen commode
de moduler ces propriétés optiques polyvalentes.
Les triarylamine ont été largement utilisées dans les matériaux optoélectroniques et électro-
actifs, car ce sont de bons donneurs d’électrons2 avec une structure moléculaire
tridimensionnelle particulière. Elles sont largement étudiées et appliquées dans divers
matériaux électro-optiques tels que les diodes organiques electroluminescentes (OLED)3 ou les
transistors à effet de champ organiques.4 En particulier, les dérivés de triarylamidine sont
prometteurs pour obtenir des matériaux luminescents.2 Par exemple, une série de dérivés de
triarylamidine de type donneur-accepteur ont été bien étudiée par le Prof. Elena ISHOW (2-5
dans le schéma 1).6 Leur originalité structurale résulte de la variation du substituant électro-
attrayant X (-H: 1, -CN: 2, CHO: 3, -NO2: 4, -CHC(CN)2: 5) qui donne lieu à une modulation
de l’émission du bleu au rouge lors de l’augmentation du caractère électro-attracteur de X.

Schéma 1. Structures des composés 1 - 56

Les changements d’intensité de luminescence peuvent être déclenchées par différents types de
conditions externes, telles que la tension,7 la température,8 le pH9 et la lumière.10 Parmi eux,
la commande électrique est une approche facile à réaliser à la demande. En particulier, les
complexes acétylure de métaux du groupe 8 qui démontrent des effets électroniques
particuliers, sont d’attrayants blocs de construction pour la réalisation de commutateurs
redox11,12 de propriétés optique ou de conductivité. Par exemple, les acétylures de ruthénium
permettent la perturbation d’unités photochromes DTE (dithiénylethene), donnant lieu à des
composés multifonctionnels, contrôlés par la lumière et le stimulus redox.11,13 Par conséquent,
d’autres modèles avec des combinaisons appropriées de ce type de composés
organométalliques et d’unités fonctionnelles devraient conduire à des perturbations redox des
architectures résultant d'une manière plus efficace qu'avec le groupement ferrocène, pourtant omniprésent.\textsuperscript{12,14}

Dans le chapitre 2, nous avons choisi une association de triarylamines luminescentes avec des complexes de ruthénium acétylure actifs au niveau redox. Ces complexes sont composés de dérivés de triarylamines de type donneur-accepteur avec deux acétylures de ruthénium en tant que donneurs d'électrons,\textsuperscript{15} tandis que le substituant X (NO\textsubscript{2} ou CHO) agira comme groupe accepteur (schéma 2).

![Diagramme de structures moléculaires de 5-CHO et 5-NO\textsubscript{2}](image)

Schéma 2. Structures moléculaires de 5-CHO et 5-NO\textsubscript{2}

Les deux complexes \textit{trans}-[\{(dppe)\textsubscript{2}ClRu(C≡C-C\textsubscript{6}H\textsubscript{4}-C\textsubscript{6}H\textsubscript{4})\textsubscript{2}N-C\textsubscript{6}H\textsubscript{4}-X\}] (X = NO\textsubscript{2}, CHO) (5-CHO, 5-NO\textsubscript{2}) ont été obtenus et caractérisés par IR, RMN, UV-vis, CV, spectroélectrochimie et photoluminescence. Les complexes 5-CHO et 5-NO\textsubscript{2} montrent le comportement redox attendu avec plusieurs vagues d'oxydation réversibles. Malheureusement, ils sont faiblement émissifs et leur luminescence n'a pas été modulée avec succès en changeant leurs états d'oxydation. Une des raisons de ce comportement non-émissif peut être la désactivation de l'état excité des triarylamines via les niveaux de basse énergie situés sur le fragment organométallique. Pour tenter d'éviter cela, nous chercherons à utiliser un autre ligand (TIPS-C=C(CN)\textsubscript{2}) avec un état excité d'énergie inférieure qui pourraient se trouver plus bas que le niveau responsable de l'extinction de la luminescence. Les TIPS-C=C(CN)\textsubscript{2} (Schéma 3) portant un groupement très électroattracteur (-C=C-(CN)\textsubscript{2}) par rapport aux groupes CHO et NO\textsubscript{2}, avec des bandes d'absorption et d'émission nettement décalées dans le rouge à celle de la 2-NO\textsubscript{2} 2-CHO sont de bons candidats.
En dehors de ces dérivés de triarylamines, les complexes de lanthanides ont également suscité un vif intérêt car ils montrent une luminescence de longue durée de vie, avec des raies étroites allant du visible jusqu'à la plage spectrale infrarouge proche, avec une efficacité d'émission élevée et des déplacements de Stoke importants. Ces caractéristiques suscitent un intérêt considérable pour les matériaux moléculaires et des applications en imagerie. \(^{16,17}\) Par conséquent, la modulation réversible de cette luminescence est une cible attrayante. Cette modulation peut être obtenue chimiquement, c'est-à-dire avec un stimulus externe comme le pH, la présence d'ions ou de molécules, \(^{18}\) ou électrochimiquement. \(^{19,20}\) Il pourrait être intéressant pour moduler la luminescence d'ions lanthanides d'introduire des unités redox-actives dans les systèmes moléculaires luminescents afin d'obtenir une des interrupteurs moléculaires qui pourraient facilement être modulés par un courant électrique.

Dans notre groupe, l'ytterbium (Yb), émetteur proche IR, a été sensibilisé avec succès en utilisant un ligand à base de ruthénium. Ceci a permis une perturbation paroxydo-réduction de l'émission dans le proche IR (comme montré dans le schéma 4). Toutefois, l'inconvénient de ce système est l'hydrolyse bien connue de l'acétylure lors de l'oxydation dans les conditions expérimentales de luminescence (haute dilution: DO <0.1, C <10^{-6} • mol L^{-1}, l'addition des réactifs) qui ont conduit à une mauvaise réversibilité de l'événement de commutation (environ 53\%). \(^{19}\) Par conséquent, dans le chapitre 3, nous proposons de décrire la commutation de la luminescence de l'Ytterbium et aussi de l'ion Europium en profitant des propriétés d'oxydo-réduction d'une ou deux nouvelles antennes à base d'unités vinyl-ruthénium qui sont plus stables que les groupements acétylure dans leur état oxydé (schéma 5). \(^{21}\) Afin d'atteindre cet objectif, les complexes d'Ytterbium utiliseront une nouvelle antennes de type vinyl-ruthénium(MLCT) tandis que les complexes d'Europium utiliseront les TTA comme sensibilisateur. Il sera intéressant de vérifier si la commutation de redox est possible pour les deux voies de sensibilisation.
Dans le chapitre 3, nous avons rapporté la synthèse de six complexes de ruthénium K3, K6, Ru-Eu, Ru-Yb, 2Ru-Eu et 2Ru-Yb et leur étude photophysique et leurs propriétés électrochimiques. Ru-Eu et Ru-Yb sont luminescents et réversiblement oxydés à l'échelle de temps des expériences d'optique, mais leur luminescence n'a pas été modulée avec succès en changeant leurs états d'oxydation parce Ru-Yb est faiblement émissif alors que les propriétés de Ru-Eu sont toujours à l'étude. Bien que l'intensité d'émissions de 2Ru-Eu et 2Ru-Yb soit plus forte que celle de Ru-Eu et Ru-Yb, la modulation ne peut pas être réalisée avec succès en raison de la décoordination du lanthanide lors de l'oxydation. Au final, les systèmes étudiés donnent de moins bons résultats pour la modulation de la luminescence que les acétylure de ruthénium précédemment étudiés dans notre groupe.

Une autre manière intéressante de moduler la luminescence de complexes Ln est d'utiliser une entité photochrome communauté de commutation. Les photochromes de type DTE présentent un potentiel comme mémoire moléculaire ou comme matériaux de commutation photosensibles. Ils montrent une grande stabilité thermique dans les états colorés et incolores, une excellente résistance à la fatigue et une réactivité photochimique relativement élevée tel que décrit dans le chapitre 1. Par conséquent, dans le chapitre 4, nous sommes concentrés sur la combinaison d'un complexe de lanthanide (III) (Eu, Yb) avec un DTE, pour moduler la
luminescence par la réaction photochrome des DTE lors d'une irradiation UV ou de lumière visible. Les molécules cibles sont présentées dans le schéma 6. Les composés 4o ou 5o devraient être convertis en 4c ou 5c par irradiation avec de la lumière UV, et 4c et 5c doivent revenir à 4o et 5o par irradiation avec la lumière visible. Lorsque l'unité DTE se trouve dans sa forme ouverte, l'énergie peut être transférée après excitation de l'antenne TTA et sensibiliser l'ion lanthanide. Une forte émission doit donc être observée, alors que la luminescence peut être désactivée par la fermeture du DTE car la forme 4c ou 5c agit comme un piège par transfert d’énergie.

Schéma 6. Structures moléculaires de DTE-Ln (Ln = Yb, Eu) et présentation de leur photoisomerisation

Dans le chapitre 4, nous avons préparé avec succès le ligand 4-iodo-2,6-bis (diéthylcarbamoyle) pyridine avec une unité DTE (3o). Nous avons étudié le comportement de ce composé photochrome et constaté que la réaction d’isomérisation pouvait être complétée à 93% par irradiation de lumière UV. Nous avons ensuite réalisé une complexation initiale de 3o avec un complexe d’ions Eu³⁺ ou Yb³⁺ pour obtenir 4o et 5o. Les photoisomérisations de 4o et 5o sont totalement réversibles et montrent que 97% et 91% des composés ont été convertis en isomères fermés, respectivement. 4o et 5o sont luminescents et leur luminescence a été modulée avec succès par irradiation. Cependant, la modulation n’est que de 30% dans le cas du complexe d’europium et le mécanisme est encore à l’étude. Nous constatons également qu’il est possible de moduler la luminescence du complexe d’ytterbium en utilisant l’unité photochromique DTE en tant qu’antenne même si l’émission est faible.

Dans l’avenir, un nouveau complexe avec un centre acétylure de ruthénium entre l’unité photochrome DTE et l’ion lanthanides (Schéma 7) pourrait fournir des composés dont la luminescence peut être sensibilisés à des énergies inférieures et commutée au moyen de deux types de stimuli : électrochimique et optique.
Schéma 7. Photoisomérisation d'avenir molécule cible

La création de dispositifs optoélectroniques efficaces à base de molécules fonctionnelles individuelles souvent appelées "électronique moléculaire", est l'un des buts ultimes des nanotechnologies. Ainsi, l'électronique moléculaire a suscité un intérêt considérable au cours de la dernière décennie, car les composés organiques ou des molécules organométalliques ont de petites dimensions et un éclatant degré de diversité et de functionalité. En ce qui concerne les applications, le développement de fils moléculaires est l'un des objectifs centraux pour le domaine de l'électronique moléculaire.

Des fils incorporant des complexes métalliques sont particulièrement intéressants pour de telles études car ils offrent de multiples états redox qui peuvent conduire à des réponses courant-tension inhabituelles et à une meilleure efficacité de la conduction de charges. Dans notre groupe, le professeur Rigaut et ses collaborateurs ont examiné une série de fils organométalliques à l'aide de la microscopie AFM et de jonctions croisées (Figure 1). A température ambiante, les mesures CP-AFM ont révélé la dépendance du transport de charge à travers les ponts de ruthénium σ-arylacetylide en fonction de la longueur de la molécule, transport qui par ailleurs est extrêmement efficace. Les mesures sur jonctions à fils croisés à basse température sont compatibles avec un transport par effet tunnel direct à la fois pour R1 et R2 et avec injection de charge pour R3. En comparant les résultats courant-tension avec les données des expériences de l'électrochimie standard, ils ont conclu que les pics de conductance observés dans le spectre de la jonction R3 proviennent d'états électroniques discrets.
Nous allons, dans le chapitre 5, présenter la synthèse de composés organométalliques contenant ou non l'unité DTE afin de produire des dispositifs moléculaires commutables. En effet, la production de dispositifs contenant des interrupteurs moléculaires pourraient jouer un rôle important dans l'obtention de systèmes électroniques avec des performances uniques dans un proche avenir. Ainsi, nous avons concentré notre intérêt sur la synthèse de composés permettant non seulement l'examen des mécanismes de transport de charge en fonction de l'oxydation électrochimique contrôlée avec une série de complexes de ruthénium (II) bis (σ-arylacetylure) (Schéma 6), mais également sur un composé permettant la modulation optique des propriétés de la jonction. Après la présentation de la synthèse de ces composés, nous présentons un dispositif contenant une série de complexes de ruthénium disposées entre deux électrodes de graphène. Ce travail est réalisé en collaboration avec le groupe du professeur Guo à Pékin (Chine).
Les résultats préliminaires de mesure de conductance montrent que complexe bimétallique Ru peut être utilisé avec succès dans les jonctions de graphène. A l’avenir, nous devons trouver une nouvelle façon de purifier parfaitement composé Ru et complexe 2Ru-DTE et terminer leur caractérisation. En outre, l’étude d’isomérisation du complexe 2Ru-DTE doit également être terminée avant d’insérer 2Ru-DTE dans les jonctions à base de graphène (Figure 2).

Figure 2.Jonction commutable
References:

(2) Ning, Z.; Tian, H. Chemical Communications 2009, 5483-5495.
(7) Audebert, P.; Miomandre, F. Chemical Science 2013, 4, 575-584.
(22) Irie, M. Chemical Reviews 2000, 100, 1685-1716.
