Universitat de Girona

Facultat de Ciències | Memòria del Treball Final de Grau

Synthesis of a chromophore-catalyst dyad ruthenium complex for oxidation reactions

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AGRAÏMENTS

Ha arribat el moment després de tantes hores de treball al laboratori i després de passar unes tantes més escrivint la memòria del meu treball de final de grau , de parar un moment per reflexionar i pensar en tants bons moments viscuts en aquesta experiència sintètica.

He de donar les gràcies a la meva tutora de treball, Maria Isabel Romero, pel seu suport, per tot el que m´ha ensenyat i jo he après , i sobretot perquè em va fer creure en mi mateixa per aconseguir els meus objectius . També he d´agraïr el suport donat per la meva cap d´estudis, Montse Rodríguez , perquè em va ensenyar, donar suport i ajudar en el meu dia a dia al laboratori. També agrair a Ester Manrique, el seu suport , ajuda i paciència , com a companya al laboratori. Gràcies a vosaltres, sempre he trobat alguna solució a cada problema.

I finalment, però no menys important, dono les gràcies al meu home, perquè en va recolçar sempre en la lluita per aconseguir els meus somnis, i a les meves filles per la seva paciència infinita .

Gràcies de tot cor.

RESUM

En aquests treball final de grau es presenta la síntesi , caracterització espectroscòpica i redox d´una diada de compostos de ruteni (cromòfor-catalitzador), (Ru_p-Ru_c-Cl), units per un lligand pont polipiridílic, (trpy-ph-trpy). També es presenta un estudi preliminar del seu comportament catalític en la fotooxidació de l´alcohol 1-feniletanol en medi aquós.

El sistema està format per un catalitzador basat en un clorocomplex de Ruteni (Ru^{II}-Cl, Ru_c) $[RuCl(R\text{-}trpy)(bpy)]^{2+}$ i un cromòfor (Ru_p) que és un compost un compost de ruteni que absorbeix el llum en el visible, $[Ru(trpy)(R\text{-}trpy)]^{2+}$. Ambdós compostos comparteixen el lligand pont (trpy-ph-trpy).

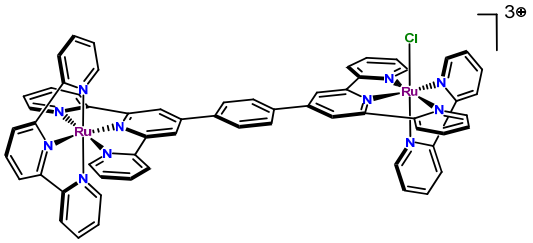
Dos rutes sintétiques s´han portat a terme per l´obtenció d´aquest compost: 1) En primer lloc , s´ha dut a terme la síntesi del catalitzador $[Ru^{II}Cl(trpy\text{-}ph\text{-}trpy)(bpy)]^{+}$ (Ru_c-Cl) **[3]** a partir de la reacció del lligand pont trpy-ph-trpy amb el complex cis (Cl),cis (S)-$[RuCl_2(DMSO\text{-}S)_2]$ **[2]** . Seguidament el complex Ru_c^{II}-Cl **[3]** reacciona amb $[Ru^{III}(trpy)Cl_3]$ **[4]** , per obtenir finalment el complex diada Ru_p-Ru_c-Cl **[5]** .

En una altra ruta de síntesis,2), en primer lloc es duu a terme la síntesis del cromòfor $[Ru^{II}(trpy)(trpy\text{-}ph\text{-}trpy)]^{2+}$($Ru_p$) [7] mitjançant la reacció de $[Ru^{II}(trpy)(DMSO)Cl_2]$ **[6]**, amb el lligand pont (trpy-ph-trpy). Seguidament el compost **[7]** es fa reaccionar amb el complex cis(Cl),cis(S)-$[Ru^{II}Cl_2(bpy)(DMSO\text{-}S)_2]$ **[2]** per obtenir finalment el complex Ru_p-Ru_c-Cl **[5] .**

La caracterització dels complexos s'ha dut a terme en estat sòlid mitjançant anàlisi elemental i espectroscòpia infraroja (IR), i en dissolució mitjançant tècniques espectroscòpiques com ressonància magnètica nuclear (NMR), ultraviolat visible (UV-Vis) i voltametria cíclica (CV).

Finalment , s´ha avaluat la capacitat catalítica del compost Ru_p-Ru_c-Cl **[5]**, en la reacció de fotooxidació de 1-feniletanol en medi aquós.

L'estructura del nou complex **[5]** sintetitzat es mostra a continuació:



RESUMEN

En este trabajo final de grado se presenta la síntesis, caracterización espectroscópica y redox de una diada de compuestos de rutenio (cromóforo-catalizador),(Ru_p-Ru_c-Cl), unidos por un ligando puente polipiridílico,(trpy-ph-trpy). También se presenta un estudio preliminar de su comportamiento catalítico en la fotooxidación del alcohol 1-feniletanol en medio acuoso.

El sistema está formado por un catalizador basado en un clorocomplejo de Rutenio [RuCl(R-trpy)(bpy)]$^{2+}$ (Ru^{II}-Cl, Ru_c) y un cromóforo que es un compuesto de rutenio que absorbe la luz en el visible, [Ru(trpy)(R-trpy)]$^{2+}$ (Ru_p). Ambos compuestos comparten el ligando puente (trpy-ph-trpy).

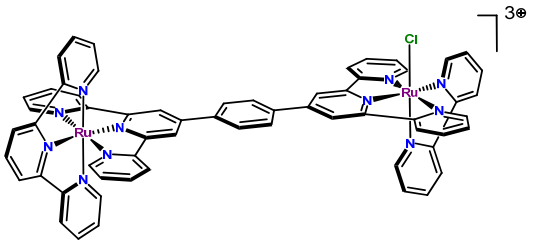
Dos rutas sintéticas se han llevado a cabo para la obtención de este compuesto: 1) Síntesis preliminar del catalizador [Ru^{II}Cl(trpy-ph-trpy)(bpy)]$^{+}$ (Ru_c-Cl) **[3]** a partir de la reacción del ligando puente trpy-ph-trpy con el complejo cis-(Cl)-cis-(S)-[$RuCl_2$(bpy)DMSO-S)$_2$] **[2].** Seguidamente, el complejo Ru_c^{II}-Cl **[3]** reacciona con [Ru^{III}(trpy)Cl_3] **[4]**, para obtener finalmente el complejo Ru_p-Ru_c-Cl **[5]** .

En otra ruta de síntesis, 2), en primer lugar se lleva a cabo la síntesis del cromóforo [Ru^{II}(trpy)(trpy-ph-trpy)]$^{2+}$(Ru_p) **[7]** mediante la reacción de [Ru^{II}(trpy)(DMSO)Cl_2] **[6]**, con el ligando puente (trpy-ph-trpy). Seguidamente el compuesto **[7]** se hace reaccionar con el complejo cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$] **[2]** para obtener finalmente el complejo Ru_p-Ru_c-Cl **[5] .**

La caracterización de los complejos se ha llevado a cabo en estado sólido mediante análisis elemental y espectroscopia infraroja (IR), y en disolución mediante técnicas espectroscópicas como resonancia magnética nuclear (NMR) y ultravioleta visible (UV-Vis). La caracterización redox se ha llevado a cabo mediante voltametría cíclica (CV) .

Finalmente, se ha evaluado la actividad catalítica del compuesto Ru_p-Ru_c-Cl **[5]**, en la reacción de fotooxidación de 1-feniletanol en medio acuoso.

La estructura del nuevo complejo **[5]** sintetizado se muestra a continuación:



ABSTRACT

In this work, we present the synthesis, spectroscopic and redox characterization of a new chromophore-catalyst dyad ruthenium compound, (Ru_p-Ru_c-Cl), linked by a bridging polypiridyl ligand (trpy-ph-trpy). A preliminary study of it catalytic behaviour in the photo-oxidation of 1-phenylethanol in aqueous medium is also presented.

The system consists of a catalyst based on a ruthenium chlorocomplex [RuCl (R-trpy)(bpy)] $^{2+}$ (Ru^{II}-Cl, Ru_c) and a chromophore which absorbs light in the visible spectrum, [Ru (trpy)(R-trpy)] $^{2+}$(Ru_p). Both compounds share the bridging ligand (trpy-ph-trpy).

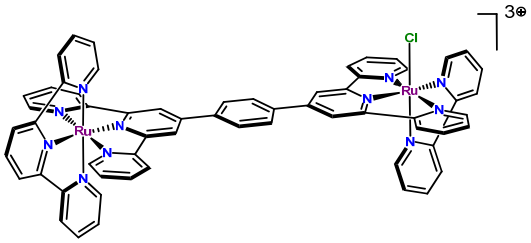
Two synthetic pathways have been carried out to obtain this compound : 1) First, it has been carried out the synthesis of catalyst $[Ru^{II}Cl(trpy\text{-}ph\text{-}trpy)(bpy)]^+$ (Ru_c-Cl) **[3]** by the reaction of bridging ligand (trpy-ph-trpy) with cis (Cl),cis (S)-$[RuCl_2(DMSO\text{-}S)_2]$ **[2].** Then, the complex Ru_c^{II}-Cl **[3]** reacts with $[Ru^{III}(trpy)Cl_3]$ **[4]**, to obtain the final complex Ru_p-Ru_c-Cl **[5]**.

In another synthetic patway, 2), first, it is carried out the synthesis of chromophore $[Ru^{II}(trpy)(trpy\text{-}ph\text{-}trpy)]^{2+}$($Ru_p$) **[7]** by the reaction of $[Ru^{II}(trpy)(DMSO)Cl_2]$ **[6]** with the bridging (trpy-ph-trpy) ligand. Then, compound **[7]** reacts with cis(Cl),cis(S)-$[Ru^{II}Cl_2(bpy)(DMSO\text{-}S)_2]$ **[2]** to obtain the final complex Ru_p-Ru_c-Cl **[5]**.

The characterization of complexes have been carried out in solid state through elemental analysis and infrared spectroscopy (IR) and in solution by spectroscopic techniques such as nuclear magnetic resonance (NMR) and ultraviolet visible (UV-Vis).The redox characterization has been done by cyclic voltammetry (CV).

Finally, it has been evaluated the catalytic activity of the compound Ru_p-Ru_c-Cl **[5]**, in the photooxidation reaction of 1-phenylethanol in aqueous medium.

The structure of the new complex **[5]** synthesized is shown below:



GLOSSARY OF TERMS AND ABBREVIATIONS

Abs	Absorbance
A∞	Absorbance at infinite time
A_t	Absorbance at determinate time
abs.	absolute
acetone-d_6	Deuterated acetone
atm.	atmosphere
Anal. Found (Calc.)	Analysis found (analysis calculated)
μ-trpy-ph-trpy	4´,4´´-(1,4 – phenylene) bis (2,2´:6´,2´´-terpyridine)
trpy	2,2';6',2''-terpyridine
bpy	2,2'-bipyridine
ca.	Approximately
Cl	Chlorido
$CDCl_3$	Deuterated chloroform
CD_3CN	Deuterated acetonitrile
CV	Cyclic voltammetry
d	Doblet
DMSO	Dimethyl sulfoxide
DMF	*N,N*-Dimethylformamide
ε	Extinction coefficient
E	Potential
$E_{1/2}$	Half-wave potential
E_{pa}	Anodic pic potential
E_{pc}	Cathodic pic potential
ESI-MS	Electrospray ionization mass spectrometry
ET	Electron transfer
h	Hours
IR	Infrared
J	Coupling constant
M	Metal
m	Multiplet
MHz	Megahertz
MLCT	Metal to ligand charge transfer
MeOH	Methanol
m/z	Mass-to-charge ratio
NMR	Nuclear magnetic resonance
PCET	Proton-coupled-electron transfer
Ru_p	Crhromophore unit
Ru_c	Catalyst unit
ppm	Parts per million
S	Sulfur
s	Singlet
Ru	Ruthenium
T	Temperature
TMS	Tetramethylsilane
t	Triplet
TBAH	Tetra(n-butyl)ammonium hexafluorophosphate
TON	Turnover number

UV-Vis	Ultraviolet-visible spectroscopy
vs	Versus
λ	Wavelength
δ	Chemical shift
W	watt

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CHAPTER 1. INTRODUCTION

1.1 Ruthenium complexes properties

Ruthenium is a metal situated in the d group of the periodic table. The electronic configuration of ruthenium ([Kr] $4d^7\,5s^1$) makes this metal, together with osmium, unique among most of the elements in displaying the widest range of oxidation states in their complexes. The oxidation state of ruthenium takes place from -2 as in $[Ru(CO)_2]^{2+}$ (d^0) to +8 as in RuO_4 (d^{10}). The synthetic versatility and the kinetic stability of ruthenium complexes in different oxidation states make these complexes particularly interesting. Other characteristics of ruthenium's coordination compounds are their high electron transfer capacity,[1] a robust character of their coordination sphere, their redox-active capacity, their easily available high oxidation states and their applications as redox reagents in many different chemical reactions.

Ruthenium complexes have experienced a large boost in the fields of catalysis,[2] photochemistry and photophysics,[3] and more recently in supramolecular[4] and bio-inorganic chemistry.[5]

The properties of ruthenium complexes are certainly correlated with the nature of the ligands coordinated to the central metal ion. Ruthenium complexes with N-donor ligands are studied due to their spectroscopic, photophysical and electrochemical properties.[6] On the other hand, ruthenium complexes with π-conjugate ligands or systems that enable electronic delocalization have shown specific properties in nonlinear optics, magnetism, molecular sensors and liquid crystals.[7] Moreover, sulfoxide complexes have been extensively studied due to their relevant usefulness in chemotherapy.[8]

1.2 Ruthenium complexes with DMSO ligand

After the first transition metal complexes with sulfoxide ligands were reported in the 1960s,[9] its chemistry has been quickly expanded. The interest of these compounds relays on their utility in medicinal chemistry as antitumor compounds[10] and antimetastatic agents.[11]

Since the introduction of $[Ru(Cl)_2(DMSO)_4]$ by Wilkinson *et al.* in 1973[12] a huge number of Ruthenium compounds containing DMSO ligands combined with a variety of auxiliary ligands have been described as potent antitumor compounds,[13] as precursors for the synthesis of a large variety of complexes[14] and also as catalysts for a variety of reactions including hydrogen-atom transfer and hydrogenation,[15] aerobic oxidation of alcohols,[16] oxidation of sulphides to sulfoxides[17] and nitrile hydration.

The properties of this kind of complexes are closely associated with the nature of the metal-sulfoxide bond. Ruthenium complexes have the capacity to been coordinate for both oxygen and sulfur atoms illustrating linkage isomerism. For this reason, the understanding of the

factors which affects the bond mode is important for the study of these complexes.

DMSO ligand coordinates through the sulfur atom with elements of the second and third transition series, such as Ru(II) d^6 low spin configuration, and with some metals from VI and VII group. The metal-oxygen bond is common in tough metals like Ru(III). According to the acid-base theory of Pearson, diffuse orbitals of soft metal ions overlap better with other orbitals also widespread like S donors. The M-S bond is favored if it exist π-retrodonation from metal orbitals to DMSO orbitals, as this ligand has π-acceptor properties. This happen to Ru(II), which stabilizes the Ru-S bond yielding π-electron density to the empty orbitals of the DMSO ligand. When it has an oxidation of Ru(II) to Ru(III), as it decreases the ability of π-retrodonation from metal orbitals to DMSO orbital, the distance between Ru-S increases. This trend has been confirmed in numerous complexes Ru-DMSO.[18]

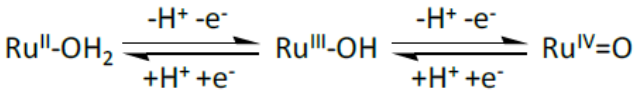
1.3 Ruthenium polypyridyl aqua complexes

In recent years, the study on ruthenium complexes with N-donor ligands have received much attention owing to their interesting uses in diverse areas such as photo sensitizers, as oxidation catalysis[19], for photochemical conversion of solar energy,[20] molecular electronic divides[21] and photoactive DNA cleavage agents for therapeutic purposes.[22]

Extensive coordination chemistry about hexacoordinated complexes containing polypyridyl ligands has been reported, due to these ligands stability against oxidation and their great coordinative capacity, increased by their chelating effect. These properties give a great stability to the formed complex.

The redox properties of these complexes become especially interesting when an aqua ligand is directly bound to the metal center. In this case, a proton-coupled-electron transfer (PCET) is possible, making the high oxidation states fairly accessible.[23]

The successive oxidation from Ru(II) to Ru(IV) are accompanied by a sequential loss of protons favored by the enhanced acidity of the bonded aqua ligand (*Scheme 1*). Therefore, the initial Ru^{II}-OH_2 is oxidized to Ru^{IV}=O, passing through a Ru^{III}-OH species.



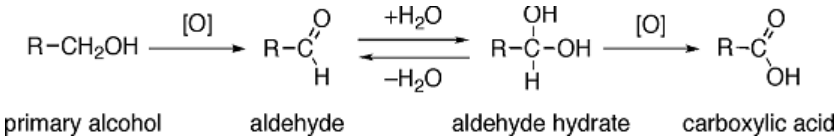
Scheme 1. PCET oxidation process characteristic of Ru-aqua complexes.

1.4 Ruthenium in oxidation catalysis

Ruthenium complexes can catalyze a variety of reactions. Our work will be focused on the process of alcohols oxidation.

1.4.1. Alcohol oxidation reactions.

The oxidation of primary and secondary alcohols to , aldehydes, ketones and carboxylic acids is a fundamental reaction in organic synthesis[24]. Primary alcohols (R-CH_2-OH) can be oxidized either to aldehydes (R-CHO) or to carboxylic acids (R-CO_2H). The direct oxidation of primary alcohols to carboxylic acids normally proceeds via the corresponding aldehyde, which is transformed via an aldehyde hydrate (R-$CH(OH)_2$) by reaction with water before it can be further oxidized to the carboxylic acid (see *Scheme 2).*



Scheme 2. Mechanism of oxidation of primary alcohols to carboxylic acids via aldehydes and aldehyde hydrates.[O]=oxidant reagent.

The use of hazardous chromium (VI) species in chemical processes supposes serious environmental risks associated with the use of large amounts of chlorinated or aromatic solvents, which have a considerable life-cycle impact, and the processing of waste mixtures of heavy metals and contaminated solvents, which is costly and must be done properly. These economic and environmental concerns have prompted intense research to develop greener and more atom-efficient methods that employ clean oxidants to perform this transformation[25]. Multivalent metal oxides and their mineral salts, in general, are widely used both in laboratory and in industry, but they are not free from disadvantages, rigorous control of the experimental conditions is required to obtain satisfactory and reproducible results, poor selectivity ,undesirable secondary reactions, low yields, and tedious isolation procedures[26].

1.4.2. Ruthenium in oxidation catalysis.

From an economical and environmental viewpoint, catalytic oxidation processes are thus extremely valuable and those employing molecular oxygen or air are particularly attractive[27]. However, few efficient, catalytic, aerobic oxidations are known that proceed under mild conditions and amenable to the preparation of fine chemicals[28].

The propensity of ruthenium complexes to transform alcohols into carbonyl derivatives has been well documented[29].

Few ruthenium-catalyzed oxidations of alcohols into carbonyl derivatives are known that employ molecular oxygen as the ultimate oxidant.

In 1978, Tang and co-workers reported that hydrated $RuCl_3$ catalyzed the aerobic oxidation of secondary alcohols into ketones, albeit in modest yields[30]. Subsequently, Matsumoto has

revealed that $RuO_2.H_2O$ is an effective catalyst for the transformation of allylic alcohols into enals and enones[31]. More efficient catalysis can be achieved by the use of trinuclear complexes[32].

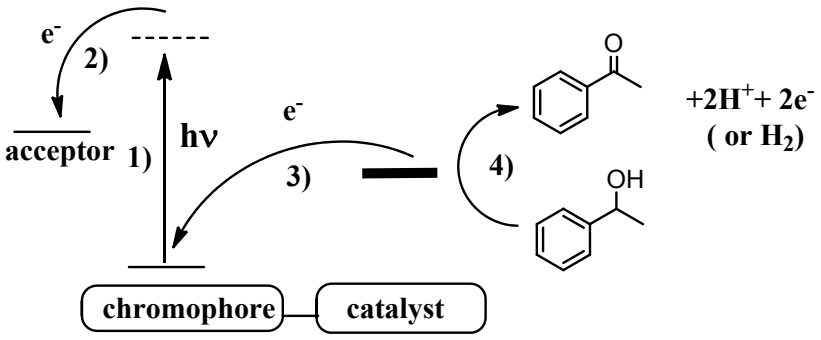
In oxidation processes catalyzed by transition metals, the reactivity of the complex is determined by the ability of the metal to achieve higher states of oxidation which, in turn, is governed by the thermodynamics of systems $M^{n+}/M^{(n-1)+}$ or $M^{n+}/M^{(n+2)+}$. In general, in the Ru^{II}-aqua ($Ru\text{-}OH_2$) complexes the active site of oxidation processes is the group Ru^{IV}=O, wherein the metal is in a high oxidation state (IV from).

Previous studies have shown that many oxidation processes are carried out generally by the use of chemical oxidants and organic media and it suppose a serious environmental problem.

The use of photocatalytic methods to carry out these processes is an excellent alternative from the point of view of sustainability, since the water would be the reaction medium and sunlight catalyst activator.

In this sense, families of pairs of ruthenium complexes Ru_p-Ru_c could be a good to perform the photo-oxidation of alcohols, using water as an oxygen source. One Ru center acts as the light-harvesting antenna, Ru_p, and the other center acts as a water oxidation catalyst, Ru_c, the two metals are connected by a bridging ligand. For these types of complexes, electron transfer (ET) between the catalyst (Ru_c) and the chromophore (Ru_p) can occur in an intramolecular manner through the bridging ligand. The latter dictates the degree of electronic coupling between Ru_p and Ru_c , and thus, is one of the crucial element in this type of materials. The bridging ligand also plays a crucial role, since, besides the influences exerted by the auxiliary ligands, it can also produce electronic coupling between the metal centers will cancel out or favor desired reactions[33].

The steps involving photooxidation process mediated by pairs of compounds are shown in *Scheme 3*, where the catalyst activation occurs upon sequential photoexcited electron transfers from the chromophore-centered MLCT state to the sacrificial acceptor[34].



Scheme 3. The main putative steps involved in the oxidation of alcohols (4) upon photoactivation of the resting Ru_p-Ru_c^{II}-OH_2 dyad to its catalytic state Ru_p-R_c^{IV}=O accompanying a sequential repetition of photoexcitation and electron transfer process (1)-(3).

A few examples have been reported in the literature of dyad molecules containing a light-harvesting site and an oxidation catalyst that can carry out redox transformations of organic substrates induced by light[35].

CHAPTER 2. OBJECTIVES

The aims of this work are the ones following:

1. To learn the techniques of synthesis and spectroscopic and electrochemical characterization, which are characteristic of a research laboratory.

2. The synthesis of a new chromophore-catalyst Dyad ruthenium (II) complex containing polypyridylic ligands and the corresponding intermediates compounds. The ligands used in this work are the ones following in the *Figure 1*.

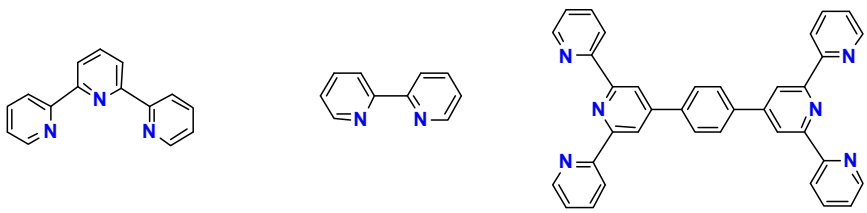


Figure 1. Plot for ligands used in this work: bpy, trpy and trpy-ph-trpy.

3. The spectroscopic and electrochemical characterization of the complexes synthesized.

4. The evaluation of the previously dyad ruthenium synthesized complex in the catalytic photooxidation of 1-phenylethanol in water.

CHAPTER 3. EXPERIMENTAL SECTION

3.1 Instrumentation and measurements

Elemental analyses

Elemental analyses were performed using a CHNS-O Elemental Analyser EA-1108 from Fisons. Monochromatic irradiations were carried out by using a 80 W lamp source from Phillips on complex solutions, typically 1mM.

UV-VIS

UV-VIS spectroscopy was performed on a Cary 50 Scan (Varian) UV-Vis spectrophotometer with 1 cm quartz cells.

Cyclic voltammetric

Cyclic voltammetric experiments were performed in an IJ-Cambria IH-660 potentiostat using a three electrode on one compartment cell. The working electrode potential is ramped linearly versus time; in this case glassy carbon electrode (3 mm diameter) from BAS was used as working electrode. Platinum wire was used as auxiliary electrode. Finally, Ag/AgCl , $Ag/AgNO_3$ and SCE were used as the reference electrodes. The voltammetry was recorded using acetonitrile and dichloromethane solutions using TBAH as supporting electrolyte to yield a 0.1M ionic strength solution.

All half-wave potential values reported in this work were estimated from cyclic voltammetric experiments as the average of the oxidative and reductive peak potentials:

$$E_{1/2} = \frac{(E_{pa} + E_{pc})}{2} \qquad (2)$$

IR

IR spectra were recorded using an Agilent Cary 630 FTIR Spectrometer.

^{1}H-NMR

The ^{1}H-NMR spectroscopies were performed on a Bruker DPX 400 and 300 MHz. Samples were run in different deuterated solvents indicated in each case. The chemical shifts (δ) are given in units (ppm) using as reference tetramethylsilane (TMS).

3.2 Preparations

$[Ru^{II}Cl_2(DMSO)_4]$ **[1]**, [36] cis(Cl),cis(S)-$[Ru^{II}Cl_2(bpy)(DMSO\text{-}S)_2$ **[2],** [37] $[Ru^{III}Cl_3(trpy)]$ **[4]**, [38] and $[Ru^{II}Cl_2(trpy)(DMSO)]$ **[6]** [39] complexes and ligand were prepared according to literature procedures. All synthetic experiments were performed in the absence of light. bpy, trpy and μ-trpy-ph-trpy ligands were supplied by Aldrich and $RuCl_3 \cdot 2.53H_2O$ by Johnson Matthey.

[$Ru^{II}Cl_2(DMSO)_4$] [1]. A 1 g (3.952 mmol) sample of $RuCl_3 \cdot 2.53H_2O$ were refluxed in 5 mL of DMSO for 10 min at 170°C. After cooling the mixture to room temperature, 10 mL of acetone were added. A yellow precipitate appeared, which was filtered and washed with acetone and ether and vacuum dried. Yield: 1.159 g (61%). Anal. Found (Calc.) for $C_8H_{24}Cl_2O_4RuS_4$: C, 19.79 (19.83); H, 4.81 (4.99). E_{pa} (CH_3CN + 0.1M TBAH): 1.15 V vs Ag/AgCl.

cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$ [2]. A solution of [$Ru^{II}Cl_2(DMSO)_4$] **[1]** 1 g (2.060 mmol) / bpy 0.322 g (2.060 mmol) in EtOH (18 ml) and DMSO (2 ml) was refluxed for 1.5 h. An orange precipitate, cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$ **[2]** , gradually appeared, then was collected by filtration, washed with cold EtOH, and dried in vacuo. Yield: 0.694 g (69%). Anal. Found (Calc.) for $C_{14}H_{20}N_2Cl_2O_2S_2Ru$: C, 34.72 (34.71); H, 4.12 (4.16); N, 5.88 (5.78) %. $E_{1/2}$ (CH_3CN + 0.1M TBAH): 1.06 V vs SCE. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.76 (d, *J= 5.3 Hz,* 1H, H6), 9.70 (d, *J*= 5.6 Hz, 1H, H6´), 8.18 (d, *J*= 8.3 Hz, 1H, H3), 8.13 (d, *J=8.0 Hz,* 1H, H3´), 8.03 (t, *J*= 7.8 Hz, *J*=7.8 Hz, 1H, H4), 7.91 (t, *J*=7.7 Hz, 1H, H4´), 7.60 (t, *J*= 6.6 Hz, 1H, H5), 7.45 (t, *J*=6.6, 1H, H5´), 3.44 (s, 3H, CH_3 DMSO), 3.47 (s, 3H, CH_3 DMSO) 3.07 (s, 3H, CH_3 DMSO), 2.46 (s, 3H, CH_3 DMSO) ppm. IR ($\nu_{max,}$ cm^{-1}): 3025, 1600, 1412, 1083, 957, 774, 718. UV-vis (DMSO, 0.5 mM) [λ_{max} nm (ε, cm^{-1} M^{-1})]:392 (1260).

[$Ru^{III}Cl_3$(trpy)] [4]. To 125 ml of absolute ethanol in a round-bottom flask was added 0.195 g (0.773 mmol) of $RuCl_3 \cdot 2.53H_2O$ and 0.184 g (0.789 mmol) of trpy. The mixture was heated at reflux for 3h while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder obtained was filtered from the reddish yellow solution. The product was washed with 3 x30 ml portions of absolute ethanol followed by 3 x 30 ml portions of Et_2O and air-dried. Yield: 0.232 g (66%) . Anal. Found (Calc.) for $C_{15}H_{11}N_3Cl_3Ru$: C, 40.42 (40.84); H, 2.56 (2.49); N, 9.29 (9.53) %. E_{pa} (CH_2Cl_2 + 0.1M TBAH): 1.22 V vs Ag/$AgNO_3$. IR ($\nu_{max,}$ cm^{-1}): 3100, 1592, 1413, 923, 776 . UV-vis (CH_3CN, 0.1 mM) [λ_{max} nm (ε, cm^{-1} M^{-1})]:230 (16456), 274 (6650), 282 (6336), 310 (7450), 318 (7269), 336 (3093), 408 (2169), 486 (1155).

[$Ru^{II}Cl_2$(trpy)(DMSO-S)] [6]. A mixture of [$Ru^{II}Cl_2(DMSO)_4$] **[1]** 0.200 g (0.410 mmol) and trpy 0.097 g (0.410 mmol) in absolute EtOH (20 ml) under atmosphere of N_2 was heated at 80°C for 6 h. During this time the solution turned deep-violet and a brown precipitate was deposited progressively. After cooling of the mixture to ambient temperature, the brown solid was recovered with a glass frit and washed twice with Et_2O affording the complex. Yield: 0.1759 g (86%). Anal. Found (Calc.) for $C_{17}H_{17}N_3OSCl_2$ Ru: C, 41.94 (42.24); H, 3.27 (3.55); N, 8.46 (8.69) %. ^{1}H NMR (400 MHz, CD_3CN): δ 8.74 (d, *J* = 8.2 Hz, 2H, H6, H6´´), 8.49 (d, *J*= 7.8 Hz, 2H, H3´, H5´), 8.40 (t, 1H, *J*= 8.0 Hz, H4´), 7.91 (td, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.6 Hz, 2H, H4, H4´´), 7.32 (d, *J* = 7.0 Hz, 2H, H3, H3´´), 7.15 (td , *J* = 6.5 Hz, *J* = 6.5 Hz, *J* = 1.3 Hz, 2H, H5, H5´´), 3.39 (s, 6H, 2 CH_3 DMSO) ppm. $E_{1/2}$(CH_2Cl_2 + 0.1M TBAH): 0.91 V vs Ag/AgCl. IR ($\nu_{max,}$ cm^{-1}): 3428, 2992, 1448, 1384, 1082, 1010, 776. UV-vis (CH_3CN, 0.1 mM). [λ_{max} nm (ε, cm^{-1} M^{-1})]:314 (35315), 324(41626), 322(33631), 478 (15102).

In order to obtain the complex **[5]**, we have followed two synthetic strategies.

Strategy I

[Ru^{II}Cl(bpy)(trpy-ph-trpy)](PF_6), Ru_c-Cl [3]. A solution of cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$ **[2]** 0.155 g (0.320 mmol) in 40 ml of DMF was slowly added dropwise (over 1.5 h) to a solution of trpy-ph-trpy ligand 0.261 g (0.480 mmol) in 100 ml of DMF at reflux. The reaction solution was refluxed for another 2.5 h and then cooled down to room temperature. After evaporation of the solvent, 40 ml of water was added to dissolve the solid and excess NH_4PF_6 was added to form the precipitate, which was filtered off and dried under vacuum. Further purification was performed by recrystallization in acetonitrile. The solvent was evaporated and the remaining dark red solid was collected and dried under vacuum. Yield 0.240 g (77 %). Anal. Found (Calc.) for $C_{46}H_{32}N_8F_6PClRu$ 2.5 H_2O . Et_2O : C, 54.33 (54.72); H, 4.50 (4.31); N, 9.99 (10.2) %. ^{1}H NMR (400 MHz, acetone-d_6) : δ 10.33 (d, *J* =5.2 Hz, 1H, H39), 8.76 (s, 2H, H23, H46), 8.71 (s, 2H, H7, H9), 8.48 (d, *J* = 8.1 Hz, 2H, H4, H12), 8.42 (d, *J* = 8.2 Hz, 1H, H43), 8.28 – 8.18 (m, 3H, H26, H33, H36), 8.01 – 7.94 (m, 4H, H1, H29, H30, H40), 7.90 – 7.82 (m, 2H, H15, H37), 7.74 – 7.58 (m, 6H, H3, H13, H27, H32, H42, H38), 7.55 – 7.49 (m, 1H, H41), 7.44 (d, *J* = 7.0 Hz, 2H, H18, H20), 7.34 (d, *J* = 7.0 Hz, 2H, H17, H21), 7.24 – 7.19 (m, 3H, H28, H31, H14), 6.94 – 6.88 (m, 1H, H2) ppm. IR ($\nu_{max,}$ cm^{-1}): 3058, 1599, 1462, 1389, 1039, 757. $E_{1/2}$(CH_3CN + 0.1M TBAH): 0.80 V vs SCE. UV/Vis (CH_3CN, 0.1 mM) [λ_{max} nm (ε, cm^{-1} M^1)]: 522 (15720).

[Ru^{II}Cl(bpy)(trpy-ph-trpy)Ru^{II}(trpy)](PF_6)$_3$, Ru_pRu_c-Cl [5]. A mixture of compound Ru_c-Cl **[3]** 0.2150 g (0.220 mmol) and [$Ru^{III}Cl_3$(trpy)] **[4]** 0.096 g (0.22 mmol) was dissolved in 100 ml of EtOH in presence of 0.95 ml of triethylamine under N_2. The reaction mixture was refluxed under N_2 overnight. Then the reaction solution was cooled down to room temperature and excess NH_4PF_6 was added to the solution to form a reddish precipitate, which was collected by filtration. The crude product was purified by column chromatography using silica gel and a mixture of 7:1 (v/v) acetonitrile/saturate KNO_3 aqueous solution as the eluent . Yield: 0.125 g (%35). ^{1}H NMR (400 MHz, CD_3CN): δ 10.24 (d, *J* = 5.0 Hz, 1H, H54), 9.20 (s, 2H, H38, H61), 8.95 (s, 2H, H7, H9), 8.78 (d, *J* = 8.2 Hz, 3H, H58, H4, H41), 8.64 (d, *J* = 7.8 Hz, 3H, H48, H51, H12), 8.59 – 8.47 (m, 6H, H27, H19, H30, H1, H16, H15), 8.42 (t, *J* = 8.0 Hz, 1H, H23), 8.36-824 (m, 3H, H44,H45, H55), 7.94 (dt, *J* = 15.4 Hz, *J* = 7.8 Hz, 7H, H42, H47,H52,H57,H3,H13,H28), 7.70 (dd, *J* = 12.1, 7.0 Hz, 3H, H18, H24, H22), 7.47 (d, *J* = 7.7 Hz, 2H, H33, H35), 7.42 (d, *J* = 5.4 Hz, 1H, H53), 7.37 (d, *J* = 7.7 Hz, 2H, H32, H36), 7.31 (dd, *J* = 7.9, 6.4 Hz, 2H, H43, H56), 7.22 – 7.15 (m, 4H, H29, H17, H14, H2), 6.98 (d, *J* = 6.5 Hz, 1H, H46) ppm. ^{13}C NMR (400MHz, CD_3CN) δ 160.68 (s), 158.80 (s,C10), 158.44 (s,C60), 158.28 (s,C39), 158.18 (s,C6), 158.08 (s,C21), 157.88 (C20), 157.42 (C26), 157.13 (C5), 156.90 (C11), 156.14 (C40), 156.05 (C59), 155.63 (C30), 155.55 (C40), 155.35 (C50), 153.69 (C45), 153.52 (C44), 153.11 (C37), 152.98 (C8), 152.83 (C55), 152.73 (C15), 152.57 (C16), 152.42 (C1), 152.32 (C54), 151.98 (C31), 147.10 (C34), 144.58 (C23), 138.36 (C52), 138.22 (C3), 138.12 (C13), 137.99 (C28), 137.06 (C18), 136.20 (C47), 135.87 (C42), 135.64 (C57), 132.11 (C19), 131.78 (C27), 129.49 (C12), 128.79 (C33), 128.62 (C35), 127.49 (C32), 127.34 (C36), 126.94 (C48), 126.07 (C51), 124.71 (C4), 124.67 (C41), 124.49 (C58), 123.78 (C22), 123.62 (C24), 123.51 (C46), 123.28 (C43), 123.12 (C56), 122.94 (C38), 122.66 (C61), 122.06 (C17), 121.81 (C14), 121.72 (C29), 121.70 (C2), 120.97

(C53), 120.64 (C7), 120.52 (C9). ppm. IR ($\nu_{max,}$ cm^{-1}): 3063, 1600, 1337, 824, 766 . $E_{1/2}(CH_3CN$ + 0.1M TBAH): 0.81 V, 1.28 V vs SCE . UV/Vis (CH_3CN, 0.1 mM) [λ_{max} nm (ε, cm^{-1} M^{-1})]: 494 (18185), 540 (12088) . ESI-MS (m/z): 389.3 $[M-(PF_6)_3]^{3+}$.

Strategy II

$[Ru^{II}(trpy)(trpy\text{-}ph\text{-}trpy)](PF_6)_2$, Ru_p [7]. A solution of $[Ru^{II}Cl_2(trpy)(DMSO\text{-}S)]$ **[6]** 0.06 g (0.120 mmol) in 16 ml of DMF was slowly added dropwise (over 1.5 h) to a solution of trpy-ph-trpy ligand 0.08 g (0.144 mmol) in 35 ml of DMF at reflux. The reaction mixture was refluxed under N_2 for additional 2.5 h and then cooled down to room temperature. After evaporation of solvent on a rotavap, 15 ml of water was added to dissolve the solid and excess NH_4PF_6 was added to the solution to form an orange precipitate, which was filtered off and dried under vacuum. Yield 0.06 g (43 %). ^{1}H NMR (400 MHz, CD_3CN): δ 8.75 (s, 2H, H23, H26), 8.73 (s, 2H, H7, H9), 8.48 (ddd, *J* = 8.2 Hz, *J* = 1.4 Hz , *J*=0.8 Hz, 4H, H26, H33, H14, H12), 8.40 (t, *J* = 8.0 Hz , 1H, H44), 7.91 (ddd, *J* = 8.1 Hz, *J* = 7.7 Hz , *J* = 1.5 Hz, 4H, H40, H48, H37, H51), 7.50-7.44 (m, 6H , H1, H15, H29, H30, H43, H45), 7.33 (ddd, *J* = 5.6 Hz , *J*= 1.5 Hz, *J* = 0.8 Hz, 6H, H39, H3, H49, H13, H27, H32), 7.22 (d, *J* = 8.6 Hz, 2H, H17, H21), 7.24(d, *J* = 8.6 Hz, 2H, H18, H20), 7.15 (ddd, *J* = 7.6 Hz, *J*= 5.6 Hz , *J*= 1.3 Hz, 6H, H2, H14, H28, H31, H38, H50) ppm. $E_{1/2}(CH_3CN$ + 0.1M TBAH): 1.27 V vs SCE. [λ_{max} nm (ε, cm^{-1} M^{-1})]: 488 (18137) . ESI-MS (m/z): 1020 $[M-(PF_6)]^+$.

$[Ru^{II}Cl(bpy)(trpy\text{-}ph\text{-}trpy)Ru^{II}(trpy)](PF_6)_3$, Ru_pRu_c-Cl [5]. Compound Ru_p **[7]** 0.030 g (0.020 mmol) and cis(Cl),cis(S)-$[Ru^{II}Cl_2(bpy)(DMSO\text{-}S)_2$ [2] 0.009 g (0.020 mmol) were mixed into 20 ml of methanol in a 50 ml round-bottom flask. The reaction mixture was refluxed under nitrogen atmosphere overnight. Then the reaction solution was cooled down to room temperature and excess NH_4PF_6 was added to the solution to form a reddish precipitate, which was collected by filtration. The crude product was purified by column chromatography using silica gel and a mixture of acetonitrile/saturate KNO_3 aqueous solution (7:1) as the eluant. A reddish band was collected and the solvent was condensed down to 5 ml ca. The dark colored precipitate was collected by filtration and washed thoroughly with water, rinsed with ether, and the product was dried under vacuum. The product was verified by NMR and cyclic voltammetry and ESI-MS to be the same as that from method in strategy I . Yield 0.003 g (7 %)

For the NMR assignment we have used the following numeration, displayed in Chart 1

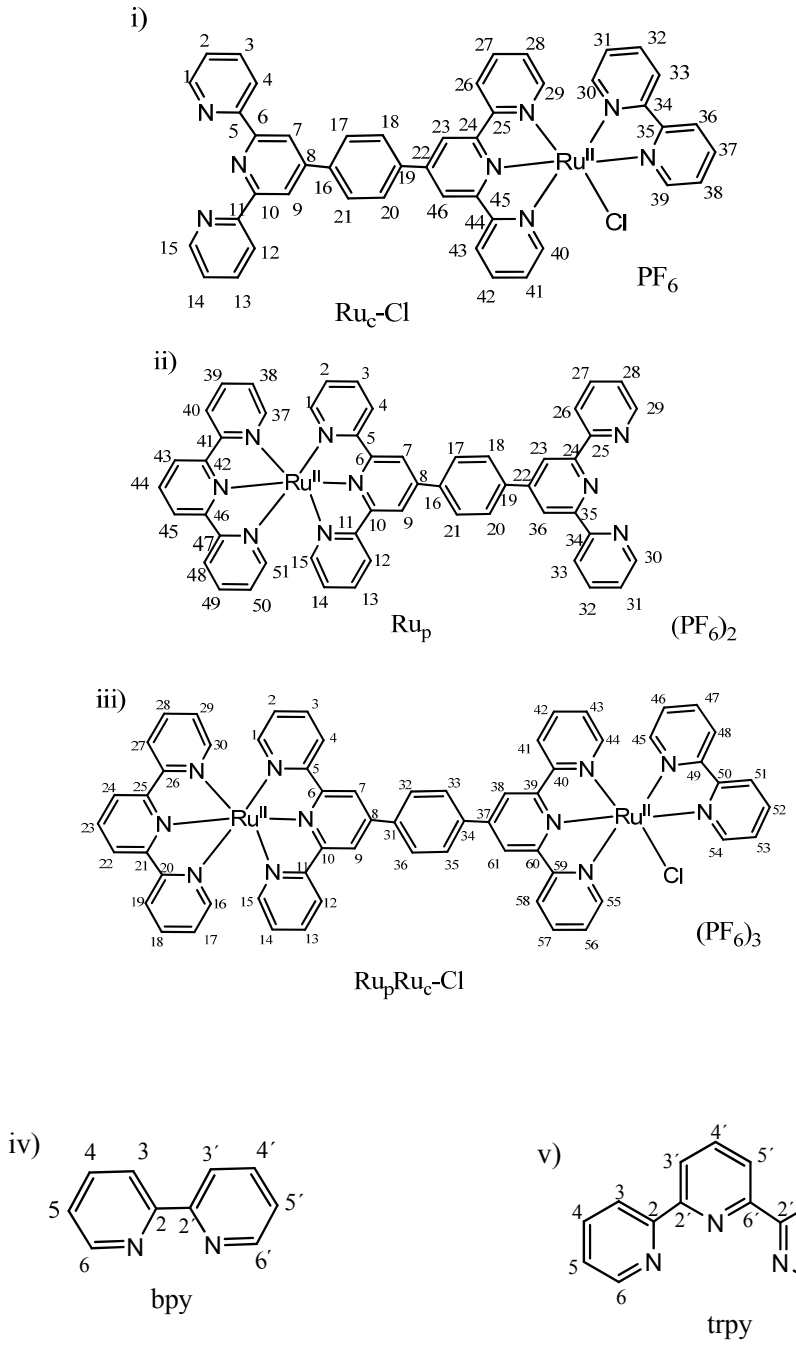


Chart 1.

Conditions of photocatalytic oxidation :

A quartz tube (15 ml) containing an aqueous solution (5ml, pH 7.0) of Ru_pRu_c-Cl **[5]** 0.4 mM 0.003 g (0.002 mmol) , 200 mM 1-phenilethanol 4.920 ml (1 mmol), 400 mM $[Co(NH_3)_5Cl]Cl_2$ 0.501 g (2 mmol), 0.1 M phosphate buffer was irradiated (λ ~ 589 nm) for 17 h at room temperature under air atmosphere and stirring. Light illumination was supplied by sodium lamp that produce monochromatic light (400 W). The resulting solution was extracted with CH_2Cl_2 (30 ml) for three times. The solvent was evaporated in vacuo. The reaction product was characterized by ^{1}H NMR spectroscopy through quantitative analyse the ratio of integrated

peak intensities of the product and the corresponding substrate.

We calculated the efficiency of catalyst based on the number of catalytic cycles or TON, as, is followed at the *equation 1*:

$$TON = \frac{mmols\ product}{mmols\ catalyst} \qquad (1)$$

3.2.1 Ethical and sustainability criteria.

Due to the experimental processes carried out in a synthetic laboratory, sometimes large quantities of solvent was need, especially in processes of purification of products. However, the waste generated residues were stored properly, in containers intended for properly labeled purpose. It has tried to work maximizing the atomic economy, but sometimes it has not been possible because the reactions gave some byproducts.

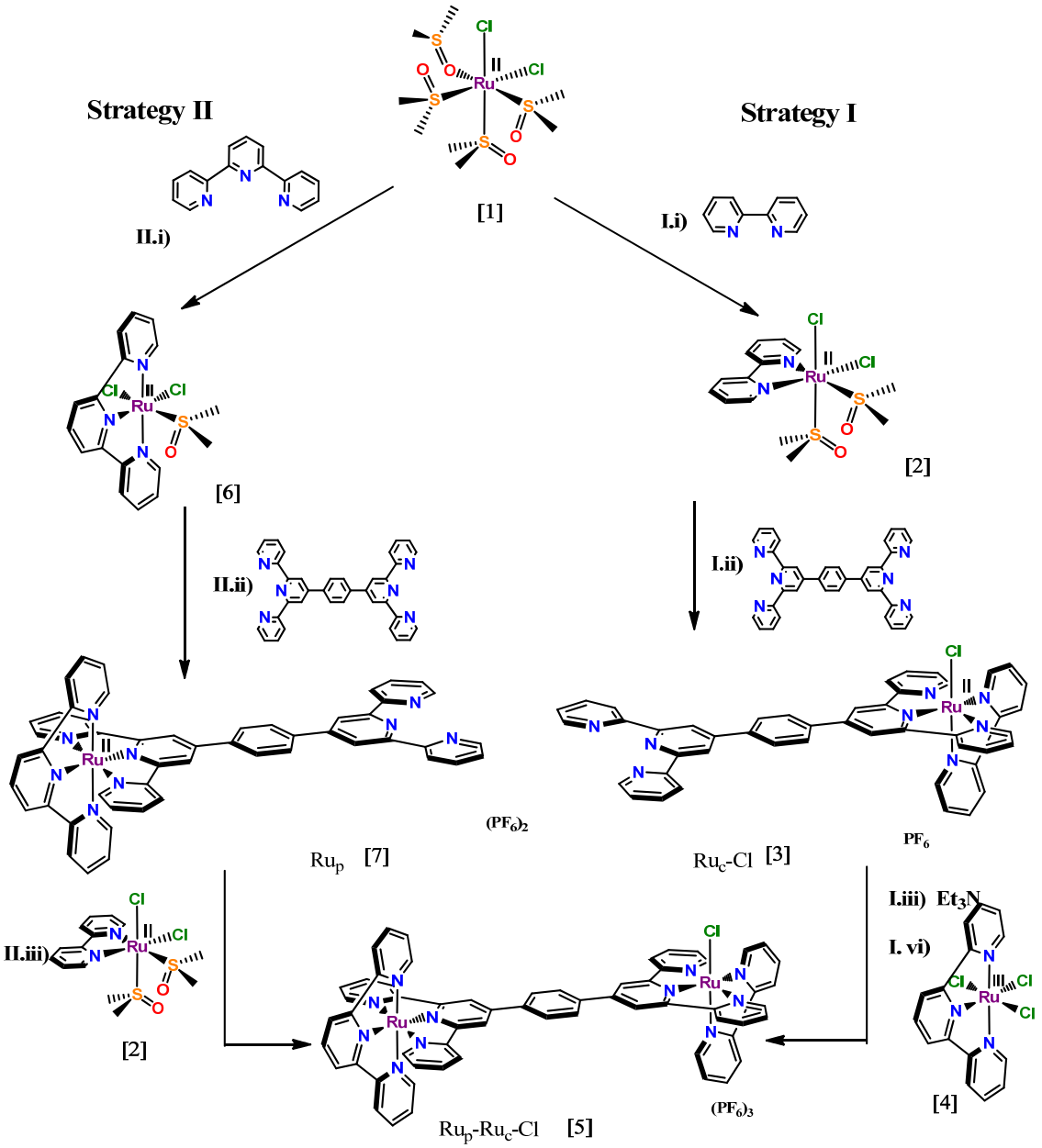
It is worth mentioning that our catalytic research leads i) to the use of solar energy as a clean and economical energy source to convert solar to chemical energy and ii) to the use of water as reaction medium avoiding organic solvents.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Synthesis

The synthetic strategies followed for the preparation of the Ru(II) complex Ru_pRu_c-Cl **[5]** is outlined in *Scheme 4* .We followed two synthetic strategies to prepare this compound. At the strategy I , the catalytic fragment (Ru_c) is used as an intermediate to the dyad. The reaction of $[Ru^{II}Cl_2(DMSO)_4]$ **[1]** with bpy ligand generates the mononuclear complex cis(Cl),cis(S)-$[Ru^{II}Cl_2(bpy)(DMSO\text{-}S)_2]$ **[2].** This mononuclear complex reacts further with the bridging ligand trpy-ph-trpy to generate the mononuclear complex $[Ru^{II}Cl(bpy)(trpy\text{-}ph\text{-}trpy)](PF_6)$ **[3]** (Ru_c-Cl) that after reaction with $[Ru^{III}Cl_3(trpy)]$ **[4]** generates the complex $[Ru^{II}Cl(bpy)(trpy\text{-}ph\text{-}trpy)Ru^{II}(trpy)](PF_6)_3$ **[5]** (Ru_pRu_c-Cl) . At the strategy II, the chromophore fragment is used as an intermediate. The reaction of $[Ru^{II}Cl_2(DMSO)_4]$ **[1]** with trpy ligand generates the mononuclear complex $[Ru^{II}Cl_2(trpy)(DMSO\text{-}S)]$ **[6]** that reacts with the bridging ligand trpy-ph-trpy to generate the mononuclear complex $[Ru^{II}(trpy)(trpy\text{-}ph\text{-}trpy)](PF_6)_2$ **[7]** (Ru_p). This mononuclear intermediate reacts further with **[2]** to generate complex $[Ru^{II}Cl(bpy)(trpy\text{-}ph\text{-}trpy)Ru^{II}(trpy)](PF_6)_3$ **[5]** (Ru_pRu_c-Cl), as well. To obtain the intermediate complexes **[3]** and **[7]** it was necessary to carry out different purification processes to obtain the desired intermediate complex. In the case of complex **[3]** purification it was carried out by simple recrystallization. By contrast, to purify the complex **[7]** it was necessary to perform a complex purification by column chromatography, although the yield in this case was less than to obtain

the complex **[3].** Finally, complex **[5]** was obtained with diferent yields in the two synthetic strategies.



Scheme 4. *Synthetic strategies and ligands used in this work.*

4.2 Spectroscopic properties

4.2.1 IR spectroscopy

Figures 4, 5, 6 show the IR spectra corresponding to the complexes Ru_c-Cl **[3]** ,Ru_p-Ru_c-Cl **[5]** and **[2]**, respectively. All three, show, peaks around 3090 cm^{-1}, that can be assigned to the the ν(C-H) stretching corresponding to the polypyridylic ligands, also the IR spectra of compounds shows peaks between 1389-1412 cm^{-1} that can be assigned to the ν(C=N) stretching of the pyridyl compounds. The spectra of isomer cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$ **[2]** , see *Figure 6*, shows a band around 1100 cm^{-1} that can be assigned to the sulphur-coordinated dmso ligands as S-coordination increases the S-O bond order in the dmso molecule, thus shifting the corresponding ν(S-O) stretch frequency to values above that of free dmso (1050 cm^{-1}). This is also corroborated by the absence of any S-O stretching vibration in the 920-930 cm^{-1} range, which would conversely indicate O-coordinated dmso ligands.

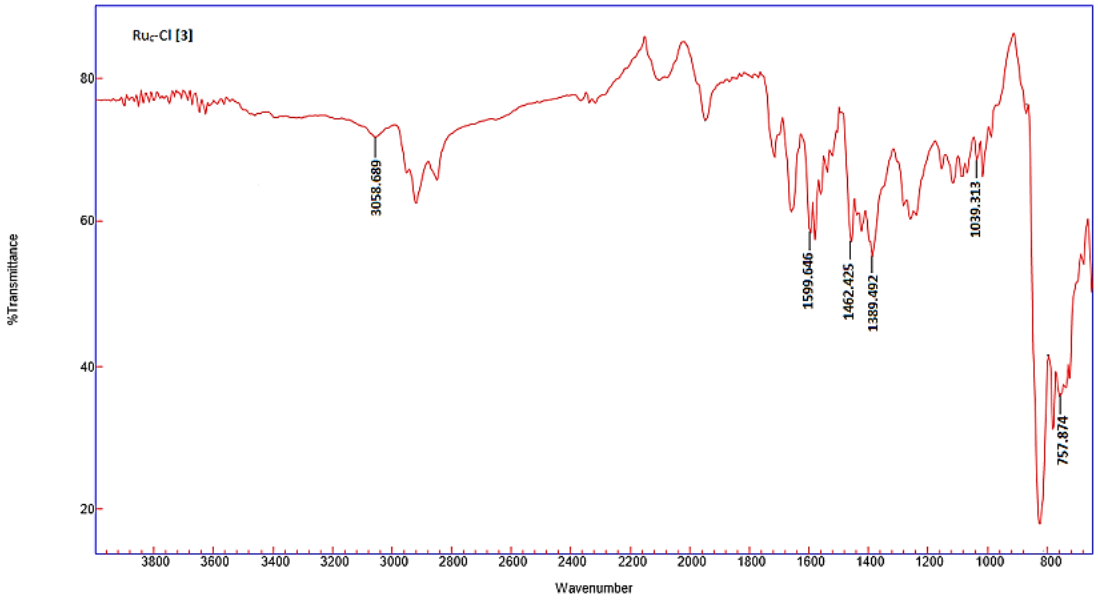


Figure 4. FTIR spectrum of complex **[3]**.

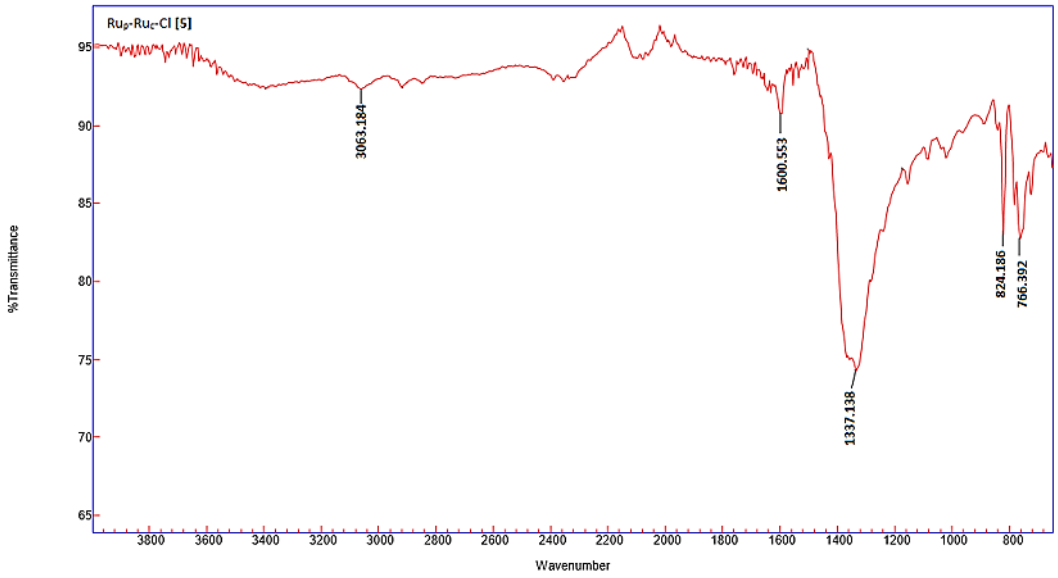


Figure 5. FTIR spectrum of complex **[5]**.

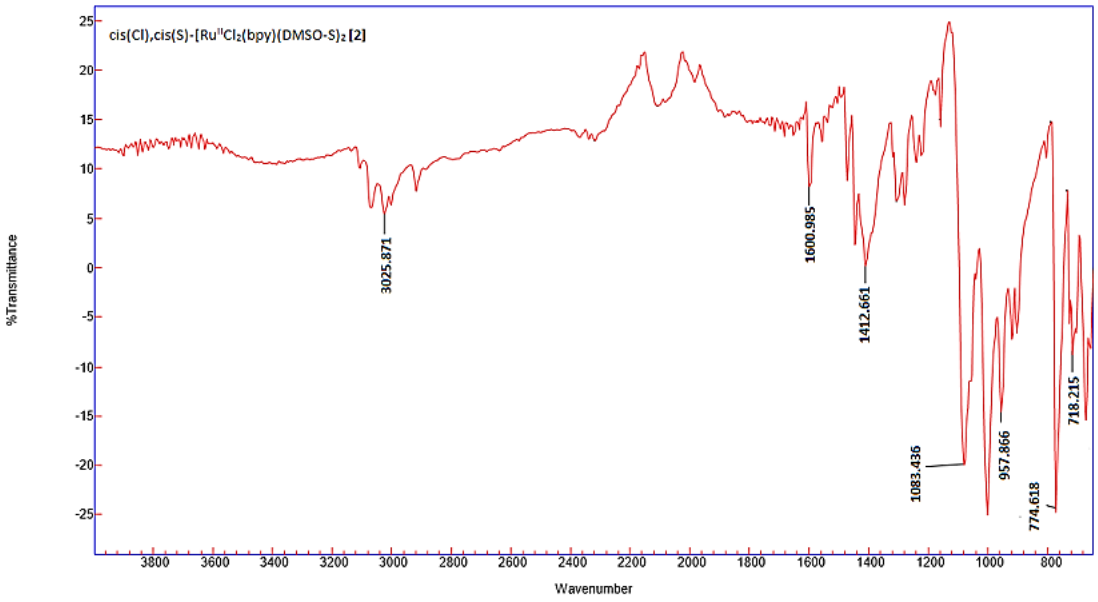


Figure 6. FTIR spectrum of complex **[2]**.

4.2.2 NMR spectroscopy

The one-dimensional (1D) NMR and two-dimensional (2D) spectra of complex **[3-5]** and **[7]** were recorded in acetonitrile-d_3 and acetone-d_6.. *Figure 7- 9 s*how the ^{1}H-NMR spectra of complexes intermediates **[3]** Ru_c-Cl and **[7]** Ru_p and the final complex **[5]**. All the spectra exhibit one set of signals in the aromatic region associated with the presence of polypyridyl ligands; in the case of complex **[5]** corresponding to the forty-three protons of the complex. The most interesting feature of the spectra of complexes **[3]** and **[5]** (chloro-complexes) (*figures 7, 9*), respectively, is the deshielding effects exerted by the chlorido ligand over the H54 in **[5]** and over the H39 in **[3]** . It is worth mentioning that spectra of **[3]**, **[5]** and **[7]** show two distinct doublets-corresponding to the phenyl group of the trpy-ph-trpy bridging ligand as consequence of the coordination of this ligand to the ruthenium atom ; in the "free ligand" the four protons appear as a singlet. In the case of Ru_pRu_c-Cl **[5]**, the doublets appear at δ= 7.47 and 7.37 ppm, that are assigned to protons (H33, H35) and (H32, H36), respectively; for compound **[3],** at δ= 7.44 and 7.34 ppm, assigned to (H18, H20) and (H17, H21), respectively; and finally, in the case of **[7]** two doublets at δ= 7.22 and 7.24 ppm assigned to protons (H17,H21) and (H18,H20) respectively.

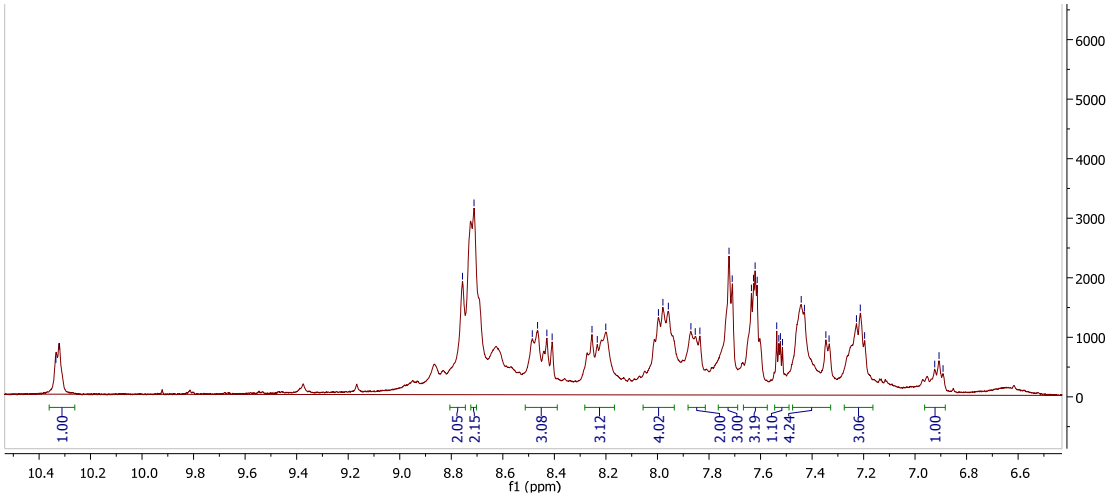


Figure 7. ^{1}H-RMN spectrum of complex **[3]**.

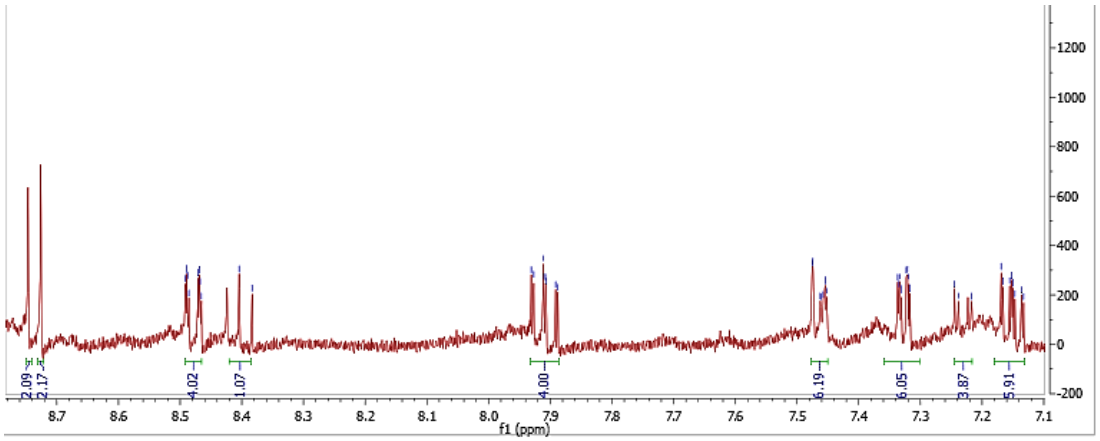


Figure 8. ^{1}H-RMN spectrum of complex **[7]**.

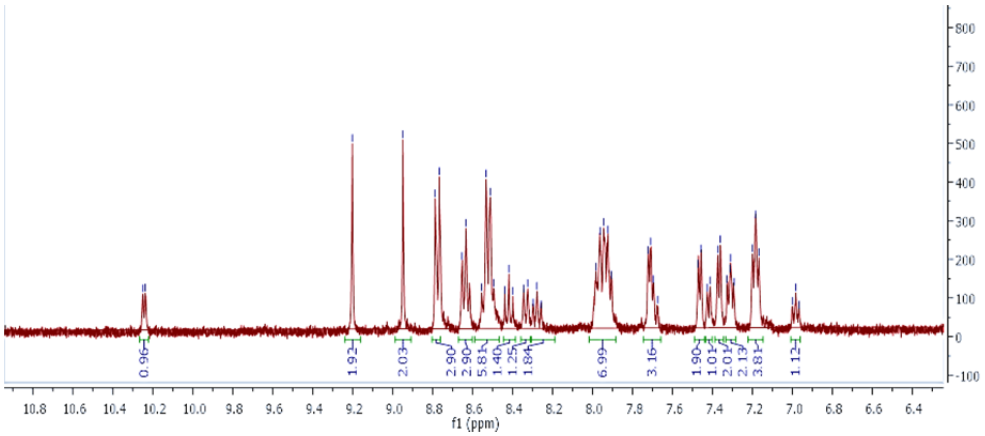


Figure 9. ^{1}H-RMN spectra of complex **[5]**.

4.2.3 UV-Vis spectroscopy

UV-Vis spectra of complex **[3]** (dashed line) , **[5]** (black line) and **[7]**(dotted line) in 0.1 mM solution of CH_3CN are displayed in Figure 10 . All the spectra displayed strong and broad absorption bands in the visible light region above 400 nm corresponding to dπ (Ru)→π* (trpy/trpy-ph-trpy) , metal-to-ligand charge transfer (MLCT) transitions on each moiety, and below 300 nm exhibit intense ligand based π→π* (not shown).

Ru_p-Ru_c-Cl **[5]** shows two (MLCT) transitions separated in energy at λ_{max} =494 and 540 nm, that correspond to the Ru_p and Ru_c-Cl moieties, respectively. This suggest that the extinction coefficient of the MLCT for the assembly (λ_{max} =494, Ɛ~18185$M^{-1}cm^{-1}$; λ_{max} = 540 nm Ɛ~12088 $M^{-1}cm^{-1}$) is almost the sum of the MLCT molar absorptions for Ru_p (λ_{max} = 488 nm, Ɛ~18137 $M^{-1}cm^{-1}$) and Ru_c-Cl (λ_{max} = 522 nm, Ɛ~15720 $M^{-1}cm^{-1}$) species and indicates weak electronic coupling between the two metal sites in complex **[5]**. Therefore, high electron efficiencies from the catalytic center to the chromophore fragment may be expected, as well as diminished excited-state electron recombination. However, it should be noted that the weak electronic coupling between the Ru_p and Ru_c shifts the position of the MLCT transition absorption for two moieties compared with their corresponding mononuclear complexes .

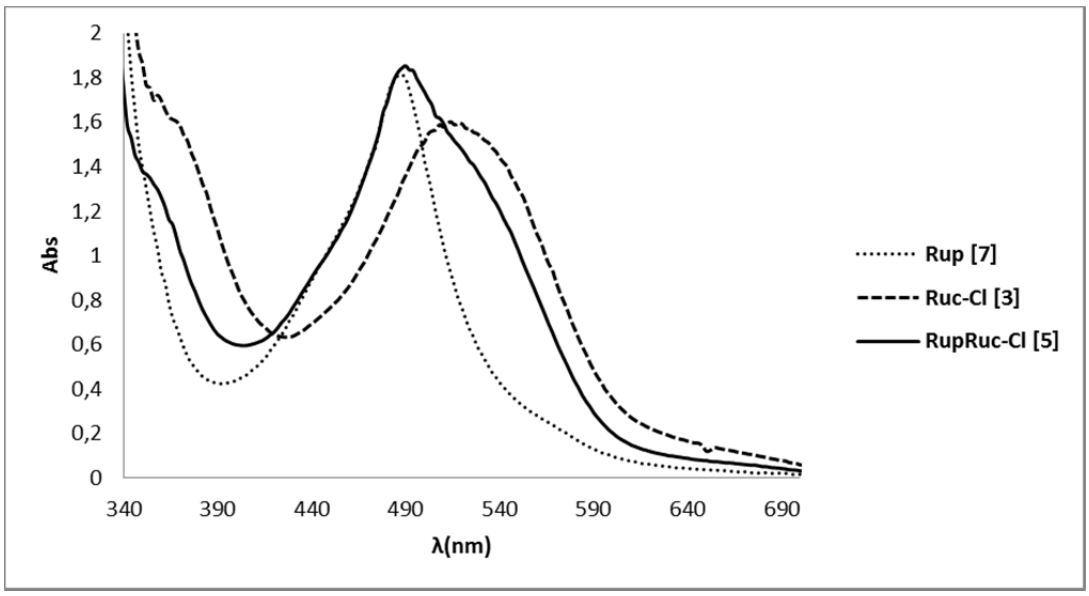


Figure 10. UV/Vis spectra of complex **[5]** (black line) and **[3]** (dashed line) and **[7]** (dotted line) in CH_3CN.

4.3 Electrochemical properties

The redox properties of the complexes **[2], [6], [3]**, **[7], [5]** were investigated by means of cyclic voltammetric technique (CV). The electrochemical data of complexes are presented in *Table 1* and the CV of [3], [5] and [7] are shown in the *Figure 11*. The cyclic voltammogram of the compounds were made in CH_3CN or CH_2Cl_2 with 0.1 M TBAH as supporting electrolyte using SCE as reference electrode , in the case of compound **[6],** Ag/AgCl was used as reference electrode.

Table 1. Electrochemical data for complexes **[2], [3], [5] and [7]** in CH_3CN with 0.1 M TBAH as supporting electrolyte using SCE as reference electrode.

Compound	$E_{1/2}$ (II/III) (V)	E_{pa} (V)	E_{pc} (V)
cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$ [2]	1.06	1.13	I. 0.99 II. 0.29
[Ru^{II}Cl(bpy)(trpy-ph-trpy)](PF_6), Ru_c-Cl [3]	0.80	0.81	0.78
[Ru^{II}Cl(bpy)(trpy-ph-trpy)Ru^{II}(trpy)](PF_6)$_3$, Ru_pRu_c-Cl [5]	I. 0.81 II. 1.28	I. 0.82 II. 1.29	I. 0.79 II. 1.26
[$Ru^{II}Cl_2$(trpy)(DMSO-S)] [6]	0.91[a]	0.92	0.88
[Ru^{II}(trpy)(trpy-ph-trpy)](PF_6)$_2$, Ru_p [7]	1.27	1.28	1.26

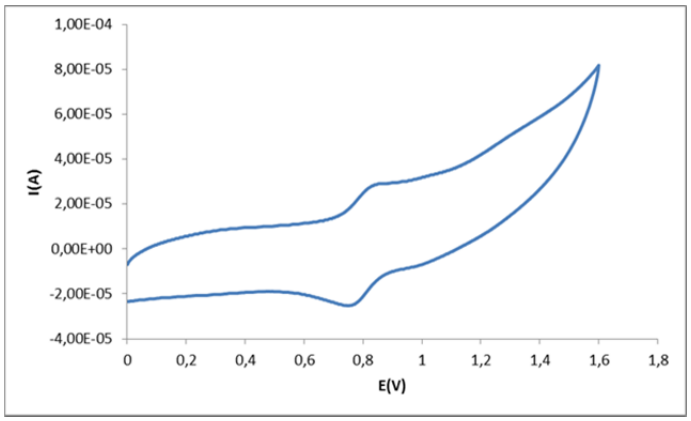
[a] cyclic volmmogram in CH_2Cl_2 with 0.1 M TBAH as supporting electrolyte using Ag/AgCl as reference electrode.

Complexes **[2]** and **[6]** containing dmso ligands exhibit one-electron reversible redox vawes at $\mathbf{E}_{1/2}$=1.06 and 0.91 V respectively, corresponding to the redox process Ru(II/III). The redox potential values are consistent with the electronic characteristics of the ligands present in both compounds; in the case of **[2]** , containing two π-acceptor dmso ligands, the compound shows higher $\mathbf{E}_{1/2}$ value than complex **[6]** containing one dmso ligand. Moreover, **[2]** presents some degree of linkage isomerization Ru^{III}(dmso-S)→Ru^{III}(dmso-O) due to the presence of DMSO ligand, not observed in the case of complex **[6]**. This evidence is confirmed by the cathodic peak at E_{pc}=0.29 V, which is consistent with the reduction of the isomerized species to form Ru^{II}(dmso-O) that after reduction rearranges to restore the initial complex.

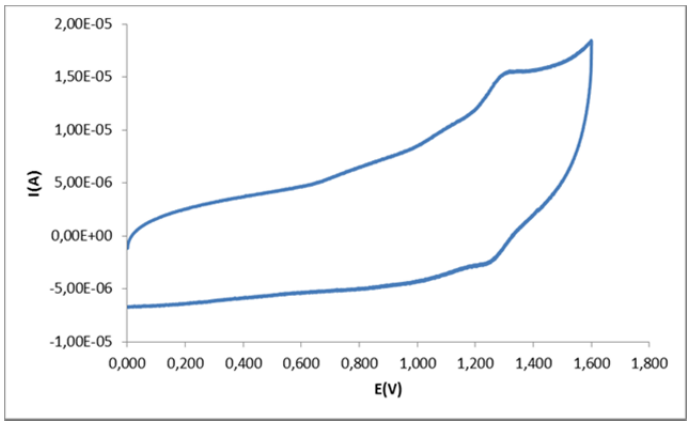
Complexes **[3]** and **[7]** exhibit one-electron reversible redox waves at $\mathbf{E}_{1/2}$=0.80 and 1.27 V respectively, corresponding to the redox process Ru(II/III). Comparing the redox values of these intermediate complexes, the existence of one chlorido ligand with π-donor character in **[3]** gives a lower potential values than the complex **[7]** where all the pyridylic ligands present π-acceptor character.

Finally, complex **[5]** show two reversible waves, according to the existence of two ruthenium atoms in the complex, at $E_{1/2}$= 0.81 and 1.28 V, corresponding to the redox process Ru_c(II/III) and Ru_p(II/III), respectively. These $E_{1/2}$ values observed in complex **[5]**, for comparison of the intermediate complexes **[3]**, **[7]**, confirmed that the electronic properties of the metal centers are weakly perturbed in the bimetallic complex by comparison with their monometallic components.

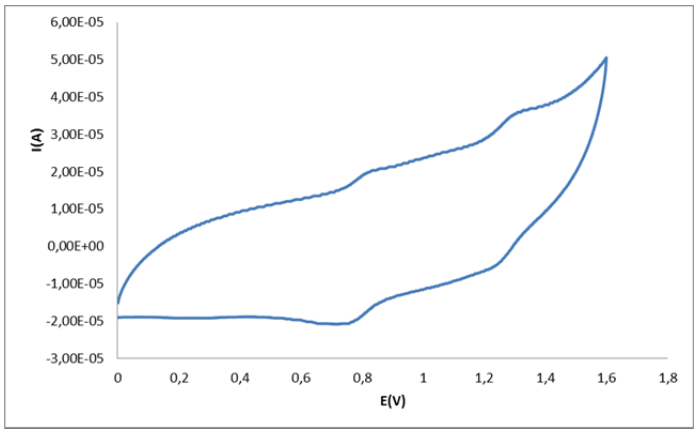
a)



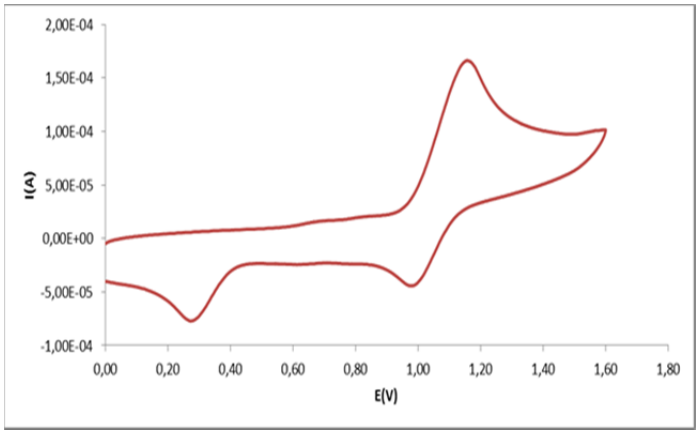
b)



c)



d)



e)

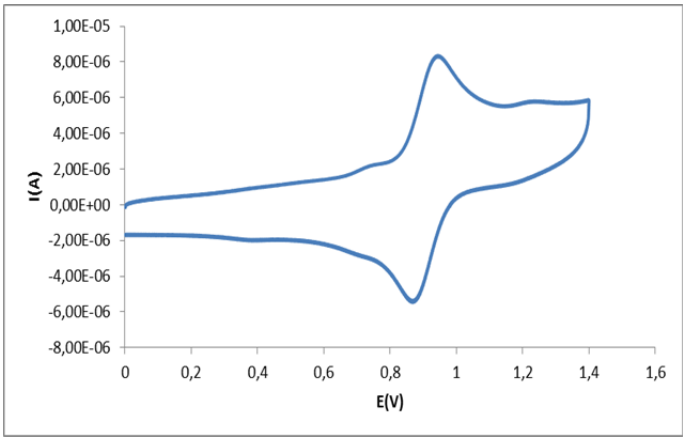


Figure 11. Voltammogram in CH_3CN solution: **a)** for complex **[3]** , **b)** for complex **[7]** , **c)** for complex **[5]** , **d)** for complex **[2] . e)** for complex **[6]**, in CH_2Cl_2 with 0.1 M TBAH as supporting electrolyte using Ag/AgCl as reference electrode.

4.4 Catalytic oxidation of alcohols.

A preliminary assay of photocatalytic oxidation of 1-phenylethanol were evaluated in deoxygenated phosphate buffer (0.1 M, pH7.0) containing $[Co(NH_3)_5Cl]Cl_2$ as sacrificial electron acceptor irradiated with monochromatic light irradiation (λ ~ 589 nm) at room temperature under an air atmosphere , for17 h. The ratio complex **[5]** : substrate : Co(III) was 1:500: 1000. The corresponding product was extracted with dichloromethane three times, dried with anhydrous Na_2SO_4 and quantified using ^{1}H NMR spectroscopy. In absence of catalyst no product were found.

In presence of Ru_pRu_c-Cl as precatalyst, 1-phenylethanol substrate, was oxidized into the corresponding ketone with a TON of 20.

The results were analyzed through ^{1}H NMR spectroscopy by the ratio of integrated peak intensities of products to that of corresponding substrates (*see figure 12*).

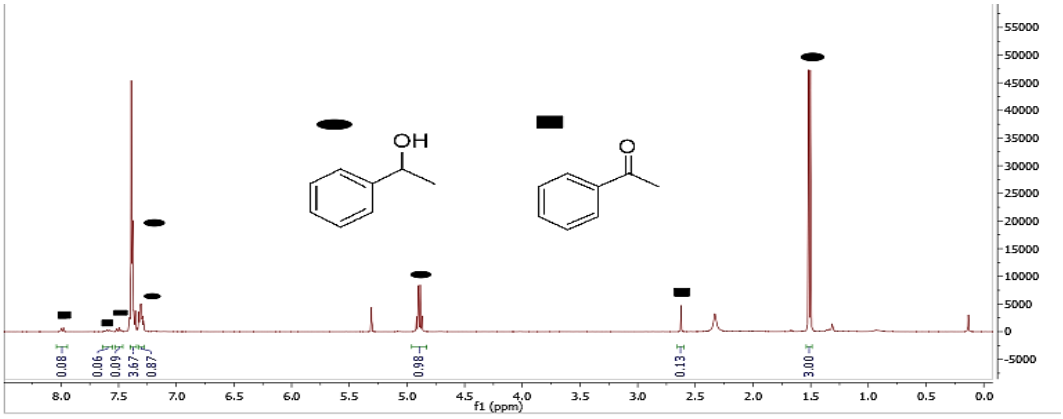


Figure 12 . ^{1}H NMR spectra ($CDCl_3$) of the product (acetophenone) and substrate (1-phenylethanol) using **[5]** as catalyst.

The catalytic experiment exhibited a low conversion value. Different reasons can explain these results :

1) The chlorido complex is a precatalyst that should be converted to its aqua form by a fast Cl^-/H_2O ligand exchange to achieve a high efficiency , probably the generation “in situ” of the corresponding aqua-complex responsible of the oxidation of substrate is slow.

2) The irradiation of the experiment should be more energetic and in a broader range of emission in the visible.

3) The ratio of the components in the catalysis is not the correct.

5. CONCLUSIONS

The main conclusions drawn from this research work are listed below:

- I have learnt the techniques of synthesis and spectroscopic and electrochemical characterization characteristic of a research laboratory.

- We have prepared a new dyad molecule based on dinuclear Ru complex, in which one metal acts as the light harvester, Ru_p and the other acts as the oxidation catalyst, Ru_c-Cl, through two different synthetic strategies; the corresponding intermediates complexes have been also synthetized.

- According to the two procedures followed in the synthesis of the dyad molecule, the yields obtained through the Ru_c compound (strategy I) is higher than the yield obtained through the Ru_p compound (strategy II).

- All the complexes have been thoroughly characterized spectroscopically and electrochemically. The spectroscopic ^{1}H-NMR analysis are consistent with the presence of the corresponding compounds and in the case of complexes **[3]** and **[5]** exhibit a strong downfield shift for the pyridylic proton next to the chlorido ligands, in both complexes.

- The spectroscopic analysis UV-Vis revealed the presence of bands in the visible region attributed to metal-to-ligand charge transfer (MLCT) transitions dπ(Ru)→π*(trpy/trpy-ph-trpy). For compound [5] the MLCT absorptions of each moiety are separated in energy which indicate, weak electronic coupling between the two metal sites in the complex. These MLCT bands are weakly shifted compared with their corresponding mononuclear complexes.

- Electrochemical analysis revealed that complex **[5]** shows two reversible waves, according with the existence of two reversible waves, according with the existence of two ruthenium centers. The coupling of the catalyst to the chromophore through the bridging ligand, weakly modifies the redox potential values with respect to the monomeric compounds.

- In the case of compounds that containing dmso ligands, some degree of linkage isomerization Ru^{III}(dmso-S)→Ru^{III}(dmso-O) has been observed in the case of the complex that presents two DMSO ligands, cis(Cl),cis(S)-[$Ru^{II}Cl_2$(bpy)(DMSO-S)$_2$ **[2]**; this behaviour has not been observed in the case of complex [$Ru^{II}Cl_2$(trpy)(DMSO-S)] **[6]**, with only one dmso ligand.

- A preliminary catalytic experiment with Ru_pRu_c-Cl as precatalyst, exhibited low conversion value in the oxidation of 1-phenylethanol to the corresponding ketone with a TON of 20.

CHAPTER 6. BIBLIOGRAPHY

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