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# Comparing Activity and Effectiveness of (Ru/Pd), (Ru/Pt) Photocatalysts for Hydrogen Generation, Photochemical Reaction with HPLC

Hamid M. Younis [*1] and Johannes G. Vos [2]

[1]*Faculty of Sciences, Chemistry Department, Sirte University, Sirte-Libya,*
[2] *SRC for Solar Energy Conversion, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland* .

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**الملخص**

في هذه الدراسة تم مقارنة وتقييم التطورات الأخيرة في تصميم وتطبيق المحفزات الضوئية Ru / Pd و Ru / Pt لتوليد الهيدروجين عبر العمليات الجزيئية. ومعرفة المفاهيم الأساسية لمثل هذه التمركزات مع نظرة عامة على العوامل الجزيئية التي تؤثر على إمكاناتها كمحفزات ضوئية. وتم تحديد مدى تمركز حالة الإثارة الانبعاثية ومعرفة التفاعل بين المركزين المعدنيين بواسطة الكروماتوغرافيا HPLC و التحليل الضوئي والطيفي للمطيافية.

**الكلمات المفتاحية:**

الروثنيوم/البلاديوم والروثنيوم/البلاتين – المحفزات الضوئية –الكروماتوجرافيا- التحليل الطيفي.

**Abstract**

In this contribution recent developments in the design and application of Ru/Pd, Ru/Pt photocatalysts for the generation of hydrogen via intramolecular processes are assessed. The basic concepts of such assemblies are discussed together with an overview of the factors and molecular issues that affect their potential as photocatalysts. Issues that so far have limited progress are discussed and suggestions for future directions are made. The extent of localization of the emissive excited state was determined by HPLC chromatography and same wavelengths; however, whereas for Ru/Pd the emission is based on the Ru(tpy)Cl- center, for Ru/Pt the emissive state is localized on the $Ru(bpy)_2$ unit. This indicates that also in the excited state there is efficient interaction between the two metal centers was characterized by both HPLC, Spectroscopy.

**Keywords:** Ru/Pd, Ru/Pt, photocatalysts, HPLC, Photolysis, Spectroscopy.

## 1. INTRODUCTION

Ru-polypyridyl complexes are widely selected as the photosensitiser, while Pt- or Pd-based moieties bound via a bridging ligand are attractive catalytic centers due to their low overpotential for proton reduction [1]. As proton reduction into $H_2$ generation requires the accumulation of two electrons at the catalyst, the common design strategy is based on the bridging ligand functioning as an electron storage reservoir for the first photo-excited electron[2,3,4,5,6]. The reactivity of such assemblies depends on the structure of the individual components[7,8,9,10]. Ideally, light-induced electron transfer from the photosensitiser via the bridging ligand to the catalyst should occur with a high quantum yield for efficient $H_2$
generation. However, this is not always the case. We have

recently observed for a series of Ru/Pd and Ru/Pt photocatalysts that photoexcitation not only leads to population of Franck-Condon states localised on the bridging ligand, but also of states localised on the peripheral ligands[11,12,13]. A similar effect has been observed by others for a related Ru/Pd complex[14] the synthesis were reported[15].
The characterization of two binuclear complexes of ruthenium Pd, ruthenium and Pt containing both (bpy) (2,2'-bipyridine) and tpy (2,6-bis(pyridin-2'-yl)-pyridine) as peripheral ligands of the general formula The compound $[(tbbipy)_2 Ru(tpphz)PdCl_2](PF_6)_2$ **1**. where tbbipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine and tpphz = tetrapyrido [3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine **1**, and Ru/Pt complex with 4,7-diphenyl-1,10-phenanthroline peripheral ligands RuPt **2**. (Figure 1). In compounds **1** and **2** the bridging ligand 3,5-bis(pyridin-2'-yl)-1,2,4-triazolato (bpt) is egatively charged. [6,7] In contrast to related pseudo-symmetric systems[7,8], in complex **1** and complex **2** the non-bridging polypyridyl ligands at each center are geometrically and photophysically distinct, i.e. $(bpy)_2$ vs (tpy)Cl. The extent and directionality of the interaction between the triazolato bridged metal centers is found to be highly dependent on the nature of the metal center. The corresponding deuteriated isotopologues complex **1** and complex **2** were prepared to facilitate assignment of the chemical shifts of the protons in the bridging (bpt) ligand and (tpy) peripheral ligand as well as the vibrational and electronic spectroscopic features. The results obtained show that in these systems the location of the lowest emissive excited state and the first oxidation can be switched by judicious choice of the metal centers. Importantly this can be done with only minimal perturbation of the photophysical properties including electronic absorption and emission spectra[16].

*Correspondence:

Dr. Hamid M. Younis
Faculty of Science, University of Sirte, Libya.
*hamid.younis@su.edu.ly*

# 2. Experimental Section

**Material and Methods**

All complexes investigated were synthesized by and received from Prof Sven Rau research group Erlangen, Germany. All samples were used as received, with no further purification. All solvents employed in spectroscopic measurements were of spectroscopic grade (Sigma-Aldrich). All other solvents were of HPLC grade or better. cis-$Ru(bpy)_2Cl_2.2H_2O$,[17] Ru $(d_8bpy)_2Cl_2.2H_2O$, $Pt(bpy)_2Cl_2$[18] and $Ru(tpy)Cl_3$, [19] $d_8$-bpy [20] and 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt)[21] were prepared by reported procedures. Gold colloid for SERS measurements were prepared by standard methods.[22]

Table 1 Spectroscopic and electrochemical data for complexes 1 and 2 and related analogs, solutions purged with Ar at 298 K.

**UV/V is absorption and emission spectroscopy:**

UV−Vis absorption spectra were recorded on a Shimadzu 3100 UV-Vis instrument with 1-cm quartz cells in spec grade DCM, ethanol or acetonitrile (Aldrich). Emission spectra were collected on a Perkin-Elmer LS50B luminescence spectrometer equipped with a red sensitive Hamamatsu R928 detector using 1-cm quartz 4 sided cell. Emission and excitation slit widths were typically 3, 5 or 10nm depending on individual circumstances.

Electronic absorption and emission data for the mononuclear and dinuclear complexes are listed in Table 1. All complexes exhibit absorption and emission properties that are characteristic of ruthenium(II) and Platinum (II) based polypyridyl complexes with triazolato containing bridging ligands [23].

The absorption spectra for complex **1** and complex **2** are shown in Figure 2. The shoulder at ca. 522 nm is typical for ruthenium (II) (N5) chlorido complexes [23,24]. The absorptions >570 nm are assigned to $^3$MLCT transitions in the case of complex **2**, however for complex **1** a significant absorption is observed in this region also which are reminscent of the absorption spectrum of $[Ru(tpy)_2]^{2+}$ [25].

| complexes | | Absorption $\lambda_{max}$ /nm ($\varepsilon$ / $10^4 M^{-1}cm^{-1}$) | Emission $\lambda_{max}$ /nm |
|---|---|---|---|
| RuPd | **1** | 470 (0.95), 465 (1.55) | 755 |
| RuPt | **2** | 481 (0.69), 606 (0.40) | 766 |

In the UV region (< 350 nm) the absorptions are assigned to π-π* intra-ligand electronic transitions associated with the (bpy), (tpy) and bridging triazolato ligands,[26,27]whereas those in the visble region (400-570 nm) are assigned to $^1$MLCT (metal ligand charge transfer) transitions [28].

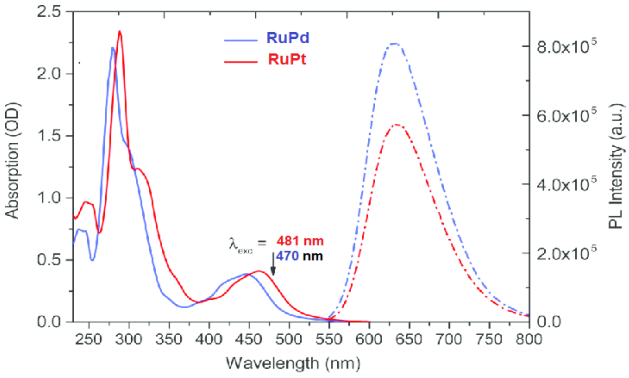



**Figure 1. Absorption, Emission spectra photolysis of complex 1 RuPd $\lambda_{max}$ 470 nm (blue line) and RuPt complex 2 $\lambda_{max}$ 481 nm (Red line) in $CH_3CN$.**

The emission spectra of both complex **1** and complex **2** show maxima at 755 nm and 766 nm, respectively (Figure 2). In both cases the emission energy and lifetime (Table 1) is typical of emission from a $^3$MLCT excited state, either localized on a (bpy) or on a (tpy) ligand. The near coincidence in energy of the emission of the two complexes could suggest that the emission is localized at the same metal center for both complexes, i.e. the $[Ru(tpy)Cl]^+$ center.

However, the differences in emission lifetimes and intensities indicate otherwise. For complex **1**, the emissive $^3$MLCT state is assigned to be localized on the $[Ru(tpy)Cl]^+$ moiety on the basis that the related complex [29,30], $[(tbbipy)_2 Ru(tpphz)PdCl_2](PF_6)_2$ **1** has an emission maximum at 755 nm (Table 1), the substitution of the (bpy) ligand of $[Ru(tpy)(bpy)Cl]^+$ with the strongly σ-donating triazolato ligand will raise the energy of the $^3$MC excited state which is typically the major excited state deactivation channel for ruthenium(II) polypyridyl complexes.

Furthermore the relatively higher intensity of emission for complex **2** over complex **1** despite the shorter excited state lifetime (Figure 2) indicates that complex **2** has a shorter radiative lifetime in accordance with a switch from a ruthenium(tpy) to an Platinum(bpy) centered emission between complex **1** and complex **2**.

The concentrations were approximately 1-2 $\times 10^{-5}$ M. A direction of energy and optical electron transfer in a heterobimetallic polypyridyl complex is switched without significant changes in electronic absorption or emission properties [31].

## 3. High Performance Liquid Chromatography

(HPLC) experiments were carried out using an analytical HPLC system consisting of a Varian Prostar HPLC pump fitted with a 10 µL injection loop, a Varian Prostar PDA detector connected to a dedicated PC, and a HiChrom Partisil P10SCX-3095 cation exchange column. The mobile phase used was acetonitrile : water 80:20 (v:v) containing 0.01-0.04 M $LiClO_4$; the flow rate was 1.0 $cm^3$/min. The monitoring wavelength used was 280 nm. Photostability of complexes **1**and **2** was monitored by HPLC. Samples were irradiated at 470 nm with a 9 W LED-array.

## Photochemical Studies

The photochemical experiments were carried out at room temperature in air-equilibrated solution in a 1 cm quartz, Light sources For illumination, we used LED light emitting diodes λ =

470 nm LAMP type L-7113PBC-BLUE. (sacrificial agent) and took 5 ml sample of above concentration solution for irradiation at 470nm (blue light) (irradiation time).

## $^1$H-NMR Spectroscopy.

*$^1$H NMR* (400 MHz) and $^{13}$C NMR (100 MHz) spectra were obtained on a Bruker Avance 400 NMR Spectrometer in deuterated solvents with either TMS or residual solvent peaks as reference [32] .

The $^1$H NMR spectroscopic and mass spectral data for the mononuclear complexes are in agreement with previous reports (28). For the dinuclear complexes the availability of complex **1** and **2** allow for analysis of the proton chemical shifts in (bpt) and (tpy) ligands. The coordination mode of the Ru(tpy)Cl- unit in complex **1** and **2** can, potentially, be such that the chlorido ligand is trans to either the triazolato or the pyridyl ring of the (bpt) bridging ligand (Figure 3).

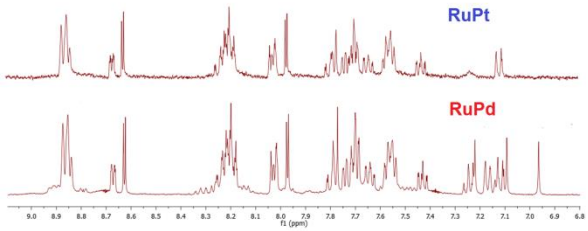



**Figure 3. $^1$H-NMR of complex 1 RuPd. (bottom) and complex 2 RuPt (top) in dmso-d$_6$. The signals arising from the complexes are identical. The additional signals in the spectra of the monomer are due to toluene and ammonium salt impurities.**

## 4. RESULTS AND DISCUSSION

***Synthesis***. The dinuclear complexes **1** and **2** were prepared by addition of the soluble mononuclear complexes [(tbbipy)$_2$Ru(tpphz)PdCl$_2$](PF$_6$)$_2$ **1**, and RuPt, respectively to a solution containing the mononuclear complex Ru(tpy)Cl$_3$ in EtOH/H$_2$O followed by heating at reflux and isolation by chromatography.(13) the first peak in HPLC at 6.18min splits up into two, corresponding to the unreacted bpy and the intermediate species. In (Figure 4) the peak at retention time 6.77min corresponds to[(tbbipy)$_2$Ru(tpphz)PtCl$_2$](PF$_6$)$_2$ (**2**).

At up to 120min most of the intermediates get converted into complex **1**, which is evident from HPLC (Figure 4) and the peaks have disappeared on going from 6.18min to 6.77min. up 6 hours almost all of the bipyridine has reacted and we are left with the final two products [Pt(bpy)$_2$ (bpt) Ru(tpy) PdCl$_2$]$^{2+}$ complex 1. (Figure 5).

Figure shows the absorption spectra of Ru and RuPd complex 1 dissolved in acetonitrile and dichloromethane. In acetonitrile both compounds show absorption properties which are common for the class of ruthenium polypyridine compounds. The absorption spectrum of Ru reveals four absorption maxima in the spectral range between 250 and 700 nm: The maximum at 283 nm can be assigned to a ligand-centered π– π* transition of tbbpy. The following maxima at 359 and 382 nm reflect ligand-centered π – π* transitions of tpphz. The energetically lowest lying broad transition which is pumped in our pump–probe experiments at 507 nm is assigned to MLCT transitions between the ruthenium ion and the coordinated ligands. For RuPd complex 1 a qualitatively similar absorption spectrum with only minor differences is recorded [33].

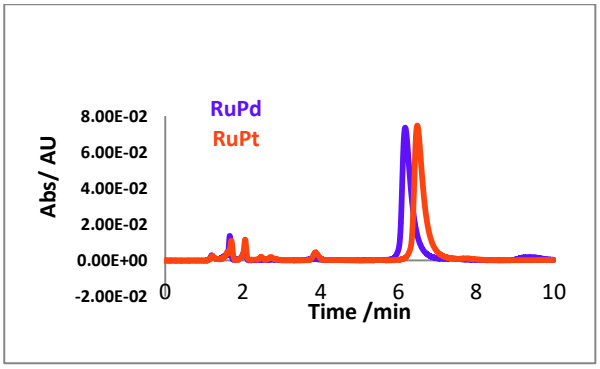



**Figure 4.** HPLC trace for Ru/Pd complex 1 and Ru/Pt complex 2, in CH$_3$CN (mobile phase CH$_3$CN: H$_2$O with volume ratio 80:20 containing 0.1 M KNO$_3$). Flow rate: 1.0 cm$^3$ min$^{-1}$; detection wavelength at 280 nm.

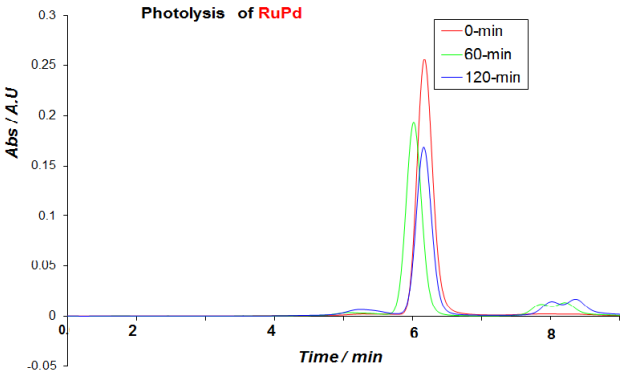



**Figure 5.** HPLC trace during photolysis of RuPd complex 1 in CH$_3$CN (mobile phase CH$_3$CN: H$_2$O with volume ratio 80:20 containing 0.1 M KNO$_3$). Flow rate: 1.0 cm$^3$ min$^{-1}$; detection wavelength at 280 nm

We continued the study up to 120min which showed that most of the metal got charred at this higher temperature resulting in a decrease of yield to 40% at 120min in RuPt complex 2. In (Figure 6).

Photostability, previously it was shown for complexes of the type [Ru(bpy)$_2$(L)Cl]+ where L = pyridine, (15) 4-vinyl-imidazole (16) and poly-4-vinyl-pyridine,(15) that rapid loss of a chlorido ligand can be observed by photochemical or thermal activation and photoinduced ligand loss has been observed for [Ru(tpy)(bpy)Cl]$^+$ also (17,18). The photostability under visible excitation of [(tbbipy)$_2$Ru(tpphz)PdCl$_2$](PF$_6$)$_2$ complex **1** and RuPt complex **2**, in acetonitrile was determined by HPLC. Formation of a main photolysis product is detected only on extended photolysis after 90min and 120min irradiation for complex **1** (Figure 5), and complex **2**,
(Figure 6). respectively.

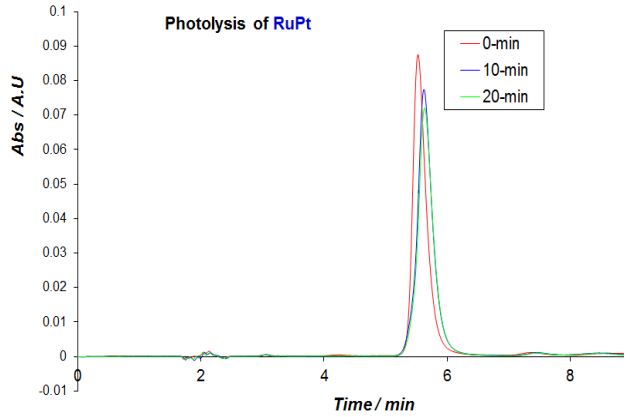



**Figure 6.** HPLC trace during photolysis of RuPt complex 2 in $CH_3CN$ (mobile phase $CH_3CN$: $H_2O$ with volume ratio 80:20 containing 0.1 M $KNO_3$. Flow rate: 1.0 $cm^3$ $min^{-1}$; detection wavelength at 280 nm.

A similar result was obtained by Pt NMR spectroscopy investigations on related [(bpy)PtX2] (X=Cl or I) complexes showing an increase in electron density (more negative chemical shift values) at the Pt nucleus induced by the softer iodide ligand compared to chloride (28). In addition, electrochemical investigations were carried out to test whether the increased electron density at the Pt center, induced by the iodide ligands, is also expressed by a corresponding change of the reduction potential of the Pt center. However, no significant difference in the reduction potentials was observed comparing photocatalyst complex **2** and complex **1**.

## 5. CONCLUSIONS

Here, the synthesis, $^1$H NMR, absorption, emission, and HPLC, characterization of the dinuclear complexes **1**, and 2. Have been described together with their deuterated isotopologues. 1H NMR spectroscopy indicates that only one isomer is isolated for both complexes in which the chlorido ligand is trans to the triazolato ligand. Both complexes 1 and 2 are relatively photostable in contrast to related mononuclear chlorido containing systems.Emission and HPLC indicate that for compounds **1** the emissive excited state is localized on the [Ru(tpy)Cl] center, whereas for **2** the emissive state is localized on the $Ru(bpy)_2$ unit. HPLC and UV/vis/NMR spectroelectrochemistry

This product manifests itself in the appearance of a peak in the HPLC chromatogram at a retention time longer than observed for complex **1** and complex **2** in (Figures 5 and 6), which indicates that the photoproduct is more positively charged. Comparison of the absorption spectra of complex **1** and complex **2** and the primary photolysis product indicates the loss of the chloride ligand. This indicates that cleavage of the Ru-Cl bond reaction of Ru and Pt metal is unlikely to be significant on the time scale of the absorption, Emission and Raman spectroscopic studies [34,35].

We completely succeeded in eliminating quite a numerous side products in the conventional reaction of Ru and Pt metal with (bpy) by employing a higher temperature resulting in separation of only two products at the end of the reaction clearly proved using the HPLC. Note that in these experiments a proton donor was not present and hence stabilisation of such a negative charge by hydrogen bonding would be expected under catalytic conditions. The results presented here demonstrate that the light-induced processes lead to a reduction of the poth PdII, PtII, center already within the first few nanoseconds of the excited-state lifetime and thus much faster than has been previously suggested in the framework of a catalytic mechanism [36].

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