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Studies on RuPd, RuPt & RuRu, Complexes-radiated Aqueous Solutions of CH_3CN Using High Performance Liquid Chromatography, Resonance Raman & NMR spectroscopy

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ABSTRACT

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, which is very challenging due to their short lifetimes 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 on states localised on the peripheral ligands. UV/Vis, resonance-Raman, and transient-absorption spectroscopy have been employed to characterize the catalytically competent intermediate. [(tbbipy)2 Ru(tpphz) PdCl2] (PF6)2, (Ru/ Pd) 1, where tbbpy=4,4`-di-tert-butyl-2,2`-bipyridine, tpphz= tetrapyrido [3,2-a: 2`,3`c: 3``,2``, -h:2```, 3```-j] phenazine). [(tbbipy) 2Ru (tpphz) PtCl2] (PF6)2 2, (Ru/Pt), and [(tbbipy) 2Ru (tpphz) RuC l2] (PF6)2 3, photocatalyst for the hydrogenation of nicotinamide reduce the catalytic activity upon visible-light irradiation fowling by both chromatography and resonance-Raman spectroscopy.

الملخص

يتم اختيار مركبات Ru-polypyridyl بشكل واسع باعتبارها حساسة جدا للضوء ، و يعتمد Pt أو Pd للشقوق المرتبطة عبر رابط جسري لمراكز حفازة جذابة جدا للبروتونات ، وهذا أمر صعب للغاية نظرًا لفترة عمرها القصير ولقد لاحظنا في دراسة سابقة لسلاسل من المحفزات الضوئية Ru / Pd و Ru / Pt أن الاستثارة او الاهاجة الضوئية لا تؤدي فقط إلى الانتقالات الالكترونية وفق قانون فرانك كوندون الانتقالي على لجند التجسير ، و تعتمد أيضًا تلك الانتقالات الالكترونية على الروابط الطرفية لها. وفي هذه الدراسة تم استخدام التحليل الطيفي للأشعة المرئية وفوق البنفسجية وطيف رامان للرنين والامتصاص لوصف الوسائط المؤهلة وذات القدرة التحفيزية الضوئية للمركبات: [(tbbipy)2 Ru(tpphz) PdCl$_2$] (PF6)2, (Ru/ Pd) 1, حيث tbbpy=4,4`-di-tert-butyl-2,2`-bipyridine, tpphz= tetrapyrido [3,2-a:2`,3`c:3``,2``,-h:2```,3```-j]phenazine). [(tbbipy)$_2$ Ru(tpphz) PtCl$_2$] (PF$_6$)$_2$ 2, (Ru/Pt), [(tbbipy)$_2$Ru (tpphz) RuCl$_2$] (PF$_6$)$_2$ 3, ووجد ان المحفز الضوئي يقلل من هدرجة نيكوتيناميد من النشاط التحفيزي عند تسليط الاشعاع الضوئي المرئي المنظور بواسطة كل من التحليل اللوني للكروماتوجرافيا وطيف رامان الرنيني.

INTRODUCTION

Hydrogen is widely perceived to be one of the primary replacement fuels, in particular for transport, due to its exceptionally high energy density/mass ratio. The photocatalytic production of hydrogen is therefore a major challenge in converting solar energy directly to chemical energy (Gurmeet *et al* 2011). One of the most promising approaches towards this goal is the use of molecular photocatalysts that utilise visible light to drive proton reduction and it can be envisaged that such systems comprise of a light-harvesting antenna (photosensitiser) that can donate electrons to a catalytically active centre to which it is connected via a bridging ligand. while Pt- or Pd based moieties bound via a bridging ligand (Fig. 1) are attractive catalytic centers due to their low overpotential for proton reduction.

Due to their exceptional photophysical and redox properties Ru(II) polypyridyl complexes are an excellent choice as the light harvesting centre while Pd(II) or Pt(II) are the metal of choice for the catalytically active centres. Alternative combinations already reported are Re/Co, Ru/Pd, Ru/Pt, Os/Rh, Ru/Rh, Pt/Co & Ir/Rh, (Hironobu *et al* 2006).

The intramolecular approach inwhich a bridging ligand facilitates photoinduced electron transfer fromthe light harvesting centre to the hydrogen forming centre requires vectorial electron transfer to be mediated by the bridging ligand (Sven *et al* 2006). Here, the synthesis (Hironobu *et al* 2006), ^{1}H NMR, absorption, emission, and HPLC, characterization of the dinuclear complexes (1), (2) and (3), have been described together with their deuterated isotopologues. Both HPLC and ^{1}H NMR spectroscopy indicates that only one isomer is isolated for both complexes in which the chlorido ligand is trans to the triazolato ligand. (Fig. 1) Show the Structure of dinuclear complexes.

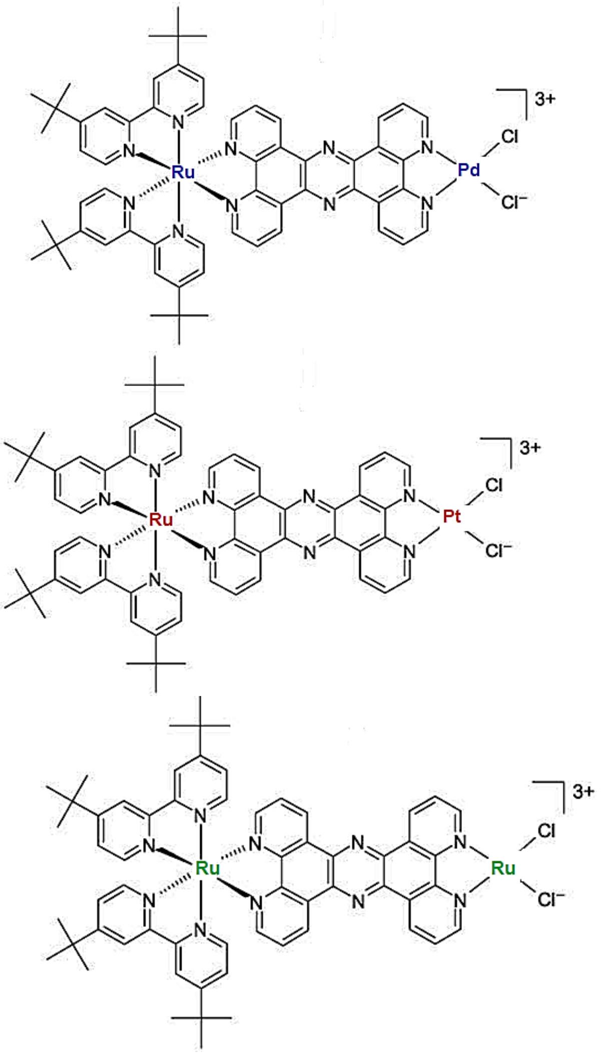

Fig. 1. Structure of dinuclear complexes [(tbbipy)$_2$Ru(tpphz)PdCl$_2$](PF$_6$)$_2$, (Ru/ Pd) left 1, [(tbbipy)$_2$Ru(tpphz)PtCl$_2$](PF$_6$)$_2$ 2, (Ru/ Pt) right, and [(tbbipy)$_2$Ru(tpphz)RuCl$_2$](PF$_6$)$_2$ 3 down (Michael et al 2015).

RESULTS AND DISCUSSION

2.1 Materials: All compounds were available from previous studies. With Prof. Sven Rau Research Group Friedrich-Alexander-University, Erlangen Nurnberg, Germany. The spectroscopic quality and intactness of the substances were verified by absorption and Raman spectroscopy prior to all experiments. Furthermore, absorption spectra recorded after the respective experiments revealed no photodegradation of the substances during the experiments.

2.2 ^{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 International Equipment Trading Ltd. Refurbished Lab Equipment USA. In deuterated solvents with either TMS or residual solvent peaks as ref (Benjamin *et al* 2009).

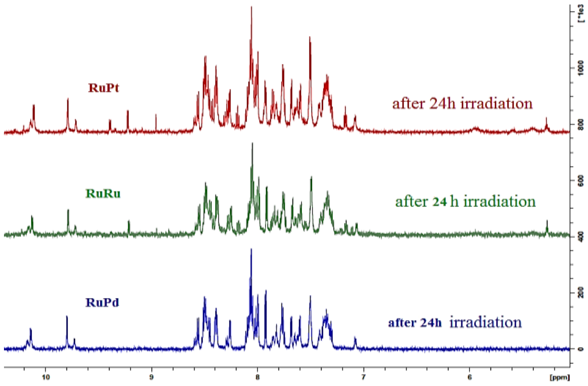

Fig. 2. ^{1}H-NMR spectroscopy of compounds during irradiation in d3-CH_3CN.

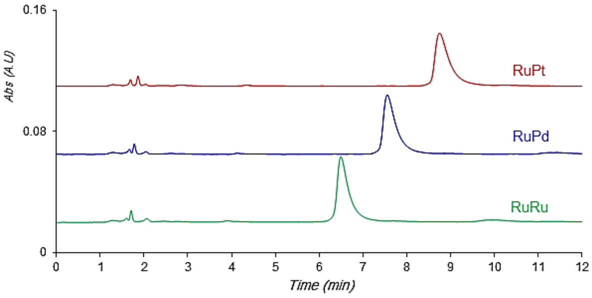

Fig. 3. HPLC trace for complex 1 Ru/Pt complex, Ru/Pd complex 2, and complex 3 Ru/Ru in CH_3CN (mobile phase CH_3CN: H_2O with volume ratio 85:25 containing 0.6 M LiCl). Flow rate: 1.0 cm^3 min^{-1}; detection wavelength at 280 nm.

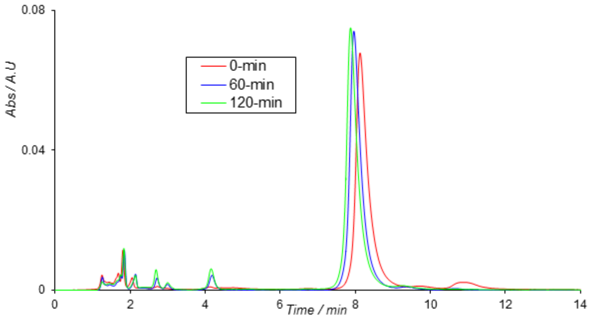

Fig. 4. HPLC trace of irradiation of compound RuPd in in CH_3CN (mobile phase CH_3CN: H_2O with volume ratio 85:25 containing 0.6 M LiCl). Flow rate: 1.0 cm^3 min^{-1}; detection wavelength at 280 nm.

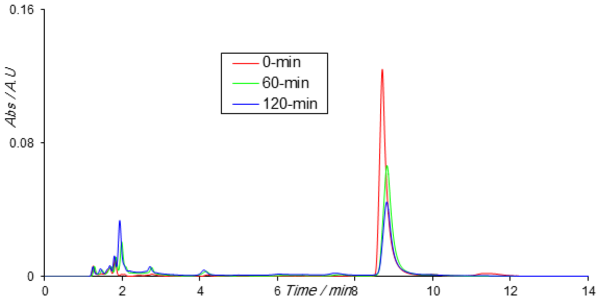

Fig. 5. HPLC trace of irradiation of compound **RuPt** in in CH_3CN (mobile phase CH_3CN: H_2O with volume ratio 85:25 containing 0.6 M LiCl). Flow rate: 1.0 cm^3 min^{-1}; detection wavelength at 280 nm.

Table 1: Retention times, absorption maximum and emission data of compounds in Acetonitrile solution.

Compound	Retention time (min)	UV/vis (nm) (t/ns)	Emission
RuPt	**8.80**	**442**	**645**
RuPd	**8.22**	**415, 508**	**773**
RuRu	**6.18**	**415, 514**	**778**

2.3 Resonance Raman spectroscopy: The resonance Raman spectra were recorded in a conventional 90º scattering arrangement. Excitation light at 488 and 458 nm was delivered by an argon ion laser (Coherent Innova 300C MotoFreD Ion Laser) and used for resonant excitation of both Ru and RuPd in the range of the Ru MLCT absorption band. A rotating cell was utilized to prevent heating of the samples. No changes in the absorption spectra of the complexes could be observed after exposure to the resonant laser light. The scattered light was collected with a lens (f1= 35 mm) and subsequently focussed (f2=50 mm) onto the entrance slit of an Acton SpectraPro 2758i spectrometer (Michael *et al* 2015). The dispersed light was detected with a CCD camera (Princeton Instruments). The concentration of the sample in the millimolar range was optimized to obtain the maximum signal-to-noise ratio.

2.4 UV-vis absorbance spectra: Were recorded using a Shimadzu UV-1800 spectrophotometer. Shimadzu Schweiz, Switzerland Steady state. Photoluminescence spectra were measured by excitation at 480 nm using a Horiba JobinYvon FluoroMax-4 spectrofluorometer. Both UV-vis absorbance and photoluminescence spectra were recorded at room temperature.

2.5 Chromatographic Analysis: High performance liquid chromatography (HPLC) was carried out on using a Varian Pro Star USA, photodiode array, international Equipment Trading Ltd. Refurbished Lab Equipment USA. The mobile phase used for routine work was $CH_3CN:H_2O$, volume ratio , 85:25, containing 0.06 M LiCl, the flow rate for routine work was in between 1.0-2.0 cm^3min^{-1} in case of photochemical experiments.

2.6 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 $\lambda = 470$ 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).

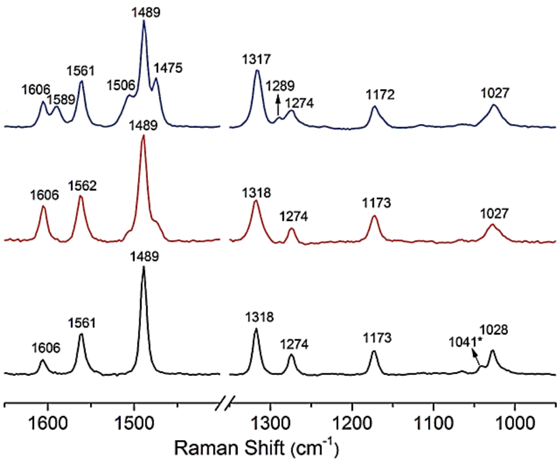

Fig. 6. Resonance Raman spectra of the precursor of compounds (RuPt) (red), (RuPd) (blue) and (RuRu) (black) in acetonitrile (ca. 0.1 mM, solvent contributions have been removed by scaled subtraction) recorded at l_{max} 470 nm. Reproduced from ref (Kowacs el al 2015).

Table 2. Photophysical and electrochemical properties of the dinuclear complexes RuPd, RuPt and their mononuclear precursors RuRu, in Acetonitrile solution.

Compounds	Abs. (log *e*)/nm	Em./nm
RuPd	**539 (4.00)**	**807**
RuPt	**526 (4.20)**	**778**
RuPt	**483 (3.98)**	**685**

RESLURS AND DISCUSSION

Resonance Raman spectroscopy has been shown to be a powerful tool to study the wave packet motion in the Franck–Condon region. Hence, identification of vibrational modes with strong resonance enhancement provides information about the orbital parentage (i.e. localisation) of the Franck–Condon states. This information is complementary to the photophysical studies such as transient absorption (TA) spectroscopy, which has a time resolution of 100–150 fs. Resonance Raman spectra of RuPt, its precursor $Ru(tbbipy)_2$ and Ru(tpphz) recorded in acetonitrile are shown in (Fig. 6). Band assignments were reported earlier (Qing *et al* 2014). At λ_{max} 470 nm, which is close to the pump wavelength (480 nm) used in the TA experiments, the Raman scattering from the ligands associated with the ^{1}MLCT) GS (GS: ground state) transitions is resonantly enhanced. In all three spectra, the characteristic modes of $[Ru(tbbipy)_2]^{2+}$ are observed and indicate resonance with ^{1}MLCT(t2-Ru(II) to π *-bipy) transitions at 470 nm.

Resonance with ^{1}MLCT(t2-Ru(II) to π*-2,5-tbbipy) transition is observed for the precursor also, in particular the bands at 1606,~ 1507,~ 1473 and 1318 cm-^{1}. In the case of RuPt, additional bands associated with the 2,5-bpp ligand are observed, (Fig. 6) Resonance Raman spectra of the precursor of RuPt (red), RuPd (blue) and RuRu (black) in acetonitrile (ca. 0.1 mM, solvent contributions have been removed by scaled subtraction) recorded at λ_{max} 470 nm. Reproduced with in ref (Sven *et al* 2006), (Benjamin *et al* 2009). The band at 1041 cm^{-1} is due to imperfect subtraction of the solvent signal (Akinari *et al* 2020). Both complexes RuPt and RuPd are relatively photostable in contrast to related mononuclear chlorido containing systems. Emission on (Fig. 4) and

HPLC in (Fig. 3) befer irradiation time, (Fig.s 4,5) after 24 hour of irradiation indicate that for compounds RuPd the emissive excited state is localized on the [Ru(tpy)Cl] center, whereas for RuPt the emissive state is localized on the $Ru(bpy)_2$ unit. HPLC and UV/vis, and NMR spectra of compounds are illustrates in (Fig.1). Both Emission and Absorption spectra during irradiation of compounds are illustrates in (Fig.s 7,8).

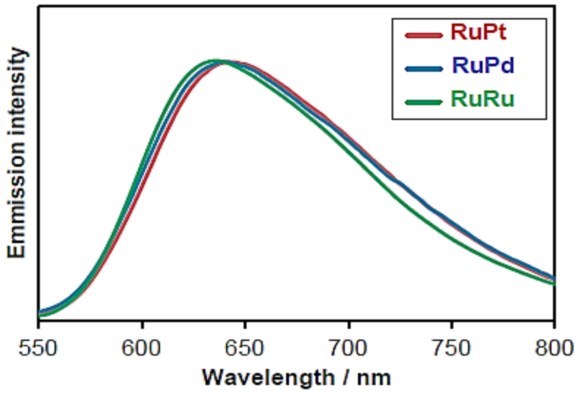

Fig. 7. . Emission spectra of RuPt (red), RuPd (blue), and RuRu (green) under irradiation at λ_{max} = 500 nm in Acetonitrile solution.

(Fig. 8) illustrates the absorption spectra of RuPt,RuPd, and RuRu in Acetonitrile solution. The spectrum is very similar to a 1:2 sum spectrum of the corresponding model complexes, RuPt and RuPd. This result clearly indicates that there is no strong electronic interaction between the RuRu and RuPt units in the ground state. It also indicates that irradiated light at λ_{max} > 450 nm selectively excited the RuPd unit. The absorption spectrum of RuPt was also in good agreement with a 1:1 sum spectrum of RuPd and RuRu . (Fig. 7) shows depicts the emission spectra of RuPt, RuPd, and RuRu measured by excitation at λ_{max} = 500 nm. A broad emission from the triplet metal-to-ligand-charge-transfer (^{3}MLCT) excited state of the RuPt complex, or the RuPd unit was observed in all spectra, and their shape was very similar (Stefanie *et al* 2009). However, the emission maxima of RuPt, RuPd and RuRu were 45nm red shifted compared with that of RuRu, while they were slightly more red-shifted by increasing the number of the Ru units. It is thus demonstrated that there was a weak electronic interaction between the Ru and Pt units in the excited RuPd and RuPt. The emission lifetime (τ_{em}) and emission quantum yield of RuPd, RuRt were also similar to those of RuPt and RuRu (Pascal *et al* 2020). In (Table 2).

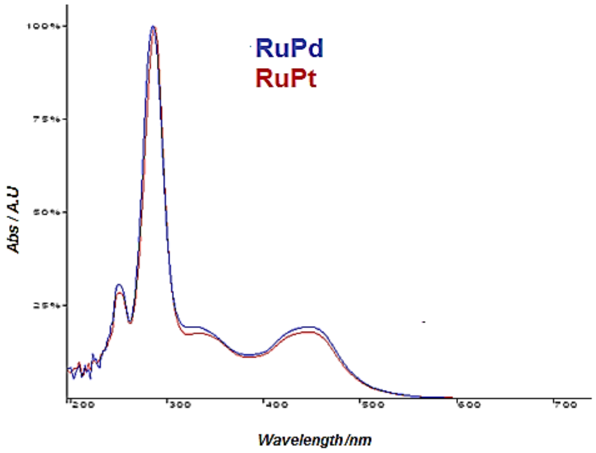

Fig. 8. Absorption spectra (normalized) spectra of (RuPt) (red), (RuPd) (blue) during irradiation.

(Fig. 8) shows the absorption spectra of RuPt and RuPd dissolved in acetonitrile and dichloromethane. In acetonitrile both compounds show absorption properties which are common for the class of ruthenium polypyridine compounds. Table 2 show 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 a qualitatively similar absorption spectrum with only minor differences is recorded (Sebastian *et al* 2008).

CONCLUSION

A similar result was obtained by RuPt NMR spectroscopy investigations on related $[(bpy)PtX_2]$ (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 (Jessica *et al* 2011). In addition, electrochemical investigations were carried out to test whether the increased electron density at the Pt center, induced by the chloride ligands, is also expressed by a corresponding change of the reduction potential of the Pd center. However, no significant difference in the reduction potentials was observed comparing photocatalyst RuPd and RuPt (Sven *et al* 2004). The photochemical processes observed are in a general sense in agreement with these obtained before (Michael.*et al* 2011). For the first time however have the products obtained been identified by NMR spectroscopy, since in this study semi-preparative HPLC was used. The instability of compound RuRd is surprising since in earlier studies its decomposition was not observed. Also for the analogous bpt mononuclear compound temperature dependent measurements have predicted its photochemical stability (Hironobu.*et al* 2007), (Linda.*et al* 2019) Its decomposition is this study is most likely due to the much longer irradiation times and the use of a stronger more focused light source with λ_{max} 430 nm. The inability to separate the two enantiomers of compound RuPt was disappointing. This prevents a direct comparison of the photochemical behaviour of the RuPd and RuPt dinuclear complexes. Nevertheless the observation that for both compounds the mononuclear compounds will decompose when more intense light and longer irradiation times are used is an important observation clearly with chromatography.

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