

Photolysis of Novel Ir(II)-Ru(II)-Ir(III) Complexes as an Effective Photocatalyst for H₂ Production using HPLC.

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Abstract: Photoinduced electron-transfer processes within a precatalyst for intramolecular hydrogen evolution [Ir(LL)₂Cl₂](PF₆), [Ru(LL)₂Cl₂](PF₆) and [Ir(LL)₃Cl₃](PF₆), type [Ir(LL)₂(L-L')]X_n such as [Ir(dmbpy)₂(hppytr)](CF₃SO₃)₂, where LL is an N[^]N bound polypyridyl ligand [X₂bpy, X₂phen, where X = H-, CH₃-, (CH₃)₃C-, or phenyl-, and bpy = 2,2'-bipyridyl, phen = 1,10-phenanthroline], dmbpy is 4,4'-dimethyl-2,2'-bipyridyl and hppytr is (3-phenyl)-5-(pyridine-2-yl)-1,2,4-triazole) have been studied by High Performance Liquid Chromatography HPLC, absorption spectroscopy, and comparing the photophysics of the complexes subunit RuII, IrII with that of the supramolecular catalyst IrIII, the individual electron-transfer steps are assigned to kinetic components, and their dependence on solvent is discussed. HPLC data reveal that the initial excitation of the molecular ensemble is spread over the terminal (hppytr) and the (dmbpy) ligands. The subsequent excited-state relaxation of both IrIII and RuIrII on the picosecond timescale involves formation of the phenyl-centered intraligand charge-transfer state, which in RuII, IrII precedes formation of the IrIII-reduced state. The photoreaction in the heterodinuclear supramolecular complex is completed on a subnanosecond timescale. Taken together, the data indicate that mechanistic investigations must focus on potential rate-determining steps other than electron transfer between the photoactive center and the IrII unit. Furthermore, structural variations should be directed towards increasing the directionality of electron transfer and the stability of the chargeseparated states. Two distinct strategies can be adopted to realise homogeneous photocatalytic proton reduction into H₂. The inter-molecular approach is based on the use of a mixture containing both photosensitiser and catalyst components and a sacrificial agent to regenerate the photosensitiser after light-induced electron transfer to the catalyst has taken place.

Keywords: Iridium, Ruthenium, Photolysis, Complexes, Hydrogen Production, HPLC.

1. Introduction

Solar to chemical energy conversion is an important topic in the quest for clean and renewable energy.[1,2] Converting H₂O to H₂ fuel by harvesting solar energy is a complicated multi-electron process that involves bond breaking and formation.[3,4] Molecular photocatalysts provide a means for analysing and understanding the complicated processes involved in H₂O reduction.[5] Aiming to construct a durable supramolecular photocatalyst for H₂ generation, a new Ir-Ru-Ir complex was successfully developed,[6] where one Ru unit, acting as photosensitizer, was linked to two Ir units, acting as catalysts, through ethylene chains. Absorption spectra and mass spectroscopic data of the reaction solutions revealed a rapid consumption of the electrons on the one-electron reduced species of the Ir unit, which led to suppression of the Ru unit decomposition, thereby maintaining its photosensitizing ability and product selectivity.[7] Molecular photocatalysts provide a means for analysing and understanding the complicated processes involved in H₂O reduction,[8] redox

photosensitizers.[9] Cyclometalating ligands (i.e. C,N coordination), such as phenyl-pyridines (ppy) and phenyl-triazoles, are widely used in comparison to N-N coordinating ligands with pyridine and pyrazine-triazoles only introduced in heteroleptic ppy based complexes recently.[10] Indeed, Ir(III) complexes of the type [Ir(LL)₂Cl₂]⁺², [Ru(LL)₂Cl₂]⁺² and heteroleptic complexes [Ir(LL)₂(L-L')]ⁿ⁺ based on N-N coordinated ligands such as 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) derivatives have not been studied extensively since the 1990s,[11] principally due to the absence of efficient methods for their preparation. This contribution we further develop this approach to the synthesis of heteroleptic N-N coordinated complexes by introducing substituted polypyridyl ligands, thereby expanding the range of properties accessible (Figure 1).

We show that the yield and side product formation are critically dependent on both the temperature and the reaction duration, as determined by reaction progress monitoring with HPLC and absorption spectroscopy.

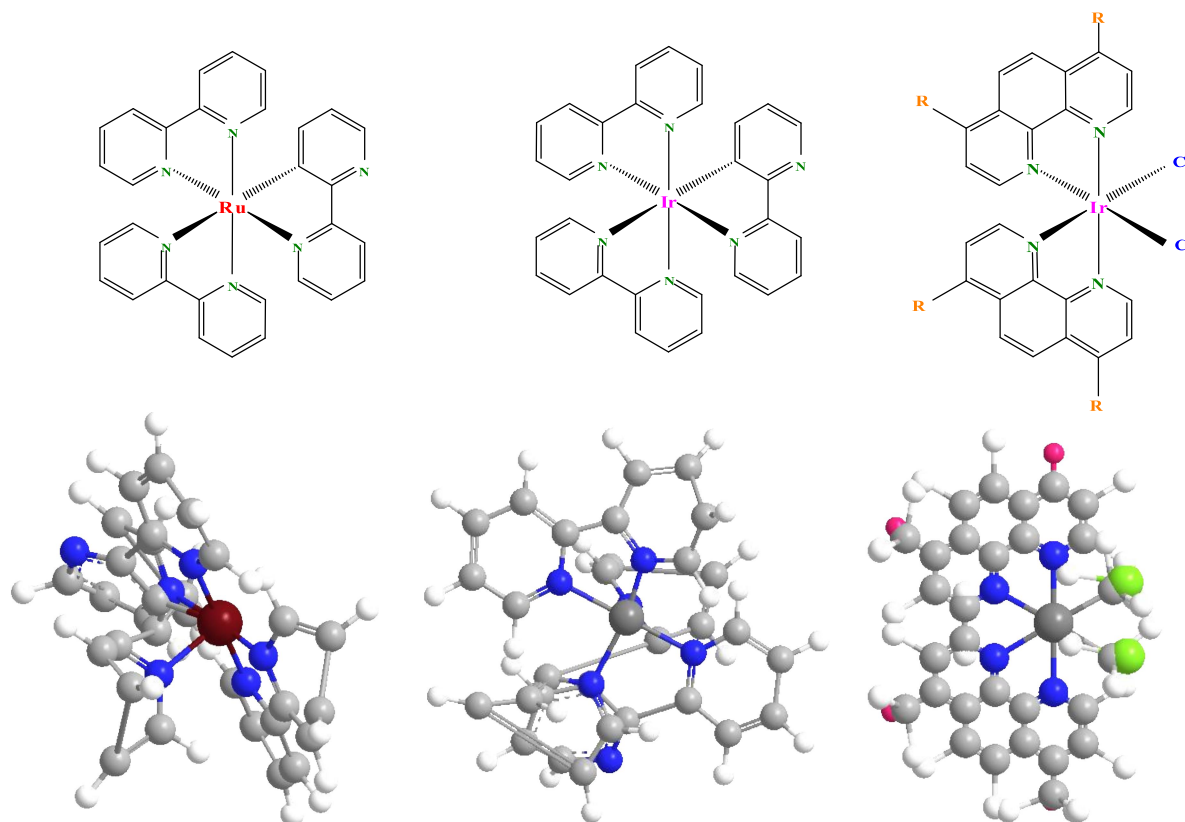


Figure. 1 3D optimized structures of all complexes RuII, IrII and IrIII.

2. Experimental Section

Experimental Details.

Material and Methods

All complexes investigated were synthesized by and received from the group of Prof. Johannes G. Vos, SRC for Solar Energy Conversion, School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland. All samples were used as received, with no further purification. All solvents employed were of HPLC grade or better and used as received unless otherwise stated.

UV/Vis 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 10 nm depending on individual circumstances. Electronic absorption and emission data for the complexes in (Table 1). listed HPLC tracing and absorption and emission spectra with TEA, and without TEA for complexes exhibit absorption and emission properties that are characteristic of Iridium(II) ruthenium(II) and

Iridium(III) based polypyridyl complexes with triazolato containing bridging ligands.

Chromatographic Analysis

High performance liquid chromatography (HPLC) was carried out on using a Varian Pro Star. All Samples were dissolved in the eluent in CH₃CN and filtered through a 0.45 micron filter prior to injection. The samples-[Ir(LL)₂Cl₂]Cl, [Ru(LL)₂Cl₂]Cl and [Ir(LL)₃]Cl₃, in CH₃CN, without TEA/ or with TEA, were analysed using a mobile phase of CH₃CN/H₂O 75/25 containing 0.02 M LiCl and detection wavelengths of 280 - 430 nm and a flow rate 2.0 cm³ min⁻¹. The temperature control was set at 24° C.

3. Results and Discussion

The general synthetic procedure is as follows.[13] IrCl₂, RuCl₂, IrCl₃ was reacted with a two equivalents of the polypyridyl ligand (LL) in ethylene glycol, in ethanol, in methoxyethanol, and in ethanol:H₂O (1:1) and reaction times were varied systematically from 10 min to 120 min, with their progress monitored by HPLC and absorption spectroscopy. The highest yields of the desired products, [Ir(LL)₂Cl₂]⁺², [Ru(LL)₂Cl₂]⁺² and [Ir(LL)₃Cl₃]⁺³ were obtained in glycerol under vigorous reflux, consistent with the need to

displace the kinetically inert chlorido ligands. HPLC chromatograms (Figures 2 a,b,c). Absorption and emission spectra (Figure 3) were

recorded at (0,60 and 120 min) intervals during the photolysis of complexes I,II and III,

Table 1. HPLC tracing, absorption and emission spectra of complexes.

Complexes	Retention time (min)		UV/vis spectrum/ λ_{\max} (nm)	Emission (t/ns)
	with TEA	without TEA		
[Ir(LL) ₂ Cl ₂]Cl	1.88,	2.11	442	555
[Ru(LL) ₂ Cl ₂]Cl	1.66,	2.14	454, 508	560
[Ir(LL) ₃]Cl ₃	1.98,	2.32	418, 514	578

The concentration of bpy decreases over 120 min, as expected, concomitant with the increase in peaks at 1.66 and 2.11 min. The HPLC feature at 2.10 min is assigned to the target compound [Ir(bpy)₂Cl₂]⁺² (I), while the peak at 1.88 min is ascribed to [Ir(bpy)₂(bpy-C,N)]⁺² (II) as confirmed by absorption spectra of these two samples. The doublet at λ_{\max} 497nm and a multiplet at λ_{\max} 500 nm are characteristic of ring A in a cyclometallated bpy ligand (Figure 3).[14] Complexes I, II and III were isolated following repeated washing and re-precipitation steps and notably other side products Table 2. Photophysical properties of complexes.

were not observed with a reaction time of 120 min. An important aspect of the synthetic procedure developed is that attempts to directly precipitate [Ir(bpy)₂Cl₂]⁺² in the original reaction mixture by adding PF₆ leads to the precipitation of a mixture of products I and II that are tedious to separate chromatographically. The UV-vis absorption spectra of the [Ir(LL)₂Cl₂]⁺² complexes are dominated by Ir(III) to LL charge transfer bands (d- π^*) in the visible region and ligand based bands (π - π^*) in the UV.[14,15,16]

Complexes	λ_{ex} (nm) ^a [ϵ (LM ⁻¹ cm ⁻¹) $\times 10^3$]	λ_{ex} ^b (nm) (298 K)	λ_{ex} ^c (nm) (298 K)	λ_{ex} ^d (nm) (77 K)
I	276, 362, 383	533	497, 535	450, 498
II	239, 380	456	454	450, 428
III	274, 358, 376	523	532	453, 429

^a at 298 K in CH₃CN, ^b in CH₃CN, ^c in Ethanol/methanol (4:1), λ_{ex} 380 nm, ^e at 298 K in CH₃CN, ^d at 77 K in CH₃CN, λ_{ex} 355 nm.

The excited state properties of compounds I,II and III compare well with literature data, where available (Table 1).[17,18] The influence of phenyl moieties in the UV-vis absorption spectra on the phenanthroline based complexes is apparent in Figure 5. The spectra of (Hphpytr) based complexes I,II and III, (Figure 3) indicate that the absorption and emission features for (dmbpy) complexes are less affected by the nature of substituents.

All complexes examined are emissive in acetonitrile at room temperature at ca. 500-550 nm (Table 1). The spectra at 77 K are blue shifted as expected due to rigidochromic effects. In contrast to ruthenium(II) polypyridyl complexes where the electronic properties are mainly related to metal to ligand charge transfer transitions (MLCT), for [Ir(LL)₂Cl₂]⁺² complexes, the energy gap between π - π^* and d- π^* states is generally small resulting in mixing of states. Previous results suggested that at

298 K emission may take place from an equilibrated (π - π^*)-(d- π^*) excited state.[17,18,19] Accordingly the luminescence spectra of [Ir(phen)₂Cl₂]⁺² and [Ir(bpy)₂Cl₂]⁺² [20] recorded at 77 K were assigned by Crosby to a mixture of charge-transfer (d- π^*) and ligand centered (π - π^*) transitions.[,21,22]. This indicates a more important role for the peripheral ligands in realising efficient photocatalytic H₂ generation in the Ir-Ru/Ir systems than generally thought. Studies from Brewer and colleagues have shown that altering the bpy ligand (LL) in [Ir(LL)₂Cl₂]Cl, [Ru(LL)₂Cl₂]Cl and [Ir(LL)₃]Cl₃ type [Ir(LL)₂(L-L')]X_n The increased levels of H₂ generation with the introduction of dppe have been attributed to the steric demands of this peripheral ligand, thereby protecting the reduced catalytic species from other side reactions. The choice of peripheral ligands may also affect the photocatalytic H₂ production by influencing the visible light absorption. [23,24]

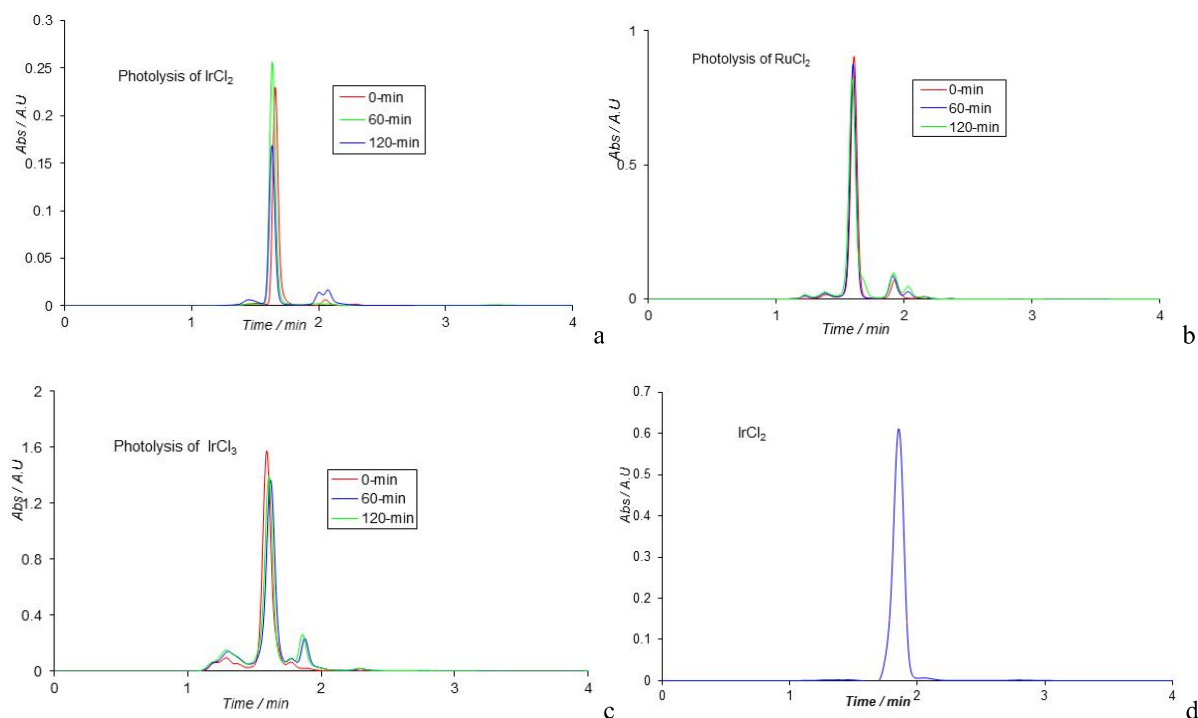


Figure 2. HPLC chromatograms during Photolysis reaction of a) IrCl_2 , b) RuCl_2 , c) IrCl_3 and d) IrCl_2 at 0, 60, and 120 min. in CH_3CN 1×10^{-4} M Mobile phase $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 75/25 containing 0.02 M LiCl at 430 nm and 24°C flow rate $2.0 \text{ cm}^3 \text{ min}^{-1}$.

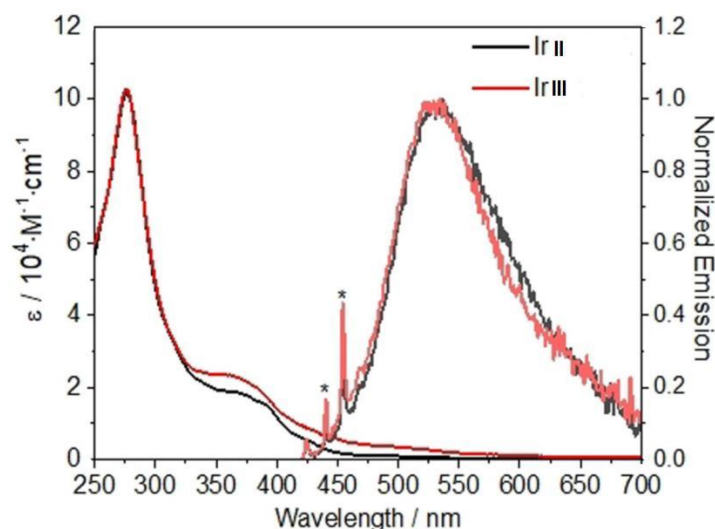


Figure 3. UV-vis absorption and emission spectra of complexes IrCl_2 (Black), and IrCl_3 (Red) in acetonitrile (0.1 mM), with TEA.

4. Conclusion

In conclusion, the photostability of the photocatalyst compounds I,II and the model compound III have been investigated both in acetonitrile and in acetonitrile containing triethylamine. In acetonitrile all compounds are photostable for up to 120 min. However, upon irradiation under “catalytic conditions”, that was in the presence of TEA, compounds I,II and III showed photo induced rearrangements. The photolysis of the photocatalyst, compound II, showed that after 120 min of irradiation, the compound was transformed in a range of

compounds I,II. The nature of these photolysis cannot be established, apart from the fact that like for compound I the bis(acetonitrile) compound is observed as a product. The most interesting observation was other bpy complexes were formed. However, the formation of bpy complexes were not observed in compounds I and III, since these compounds decompose to the acetonitrile complexes and free bridging ligands A novel Ru/Ir photocatalyst based on (Hphpytr) peripheral ligands has been designed and the photodynamical and H_2 generating ability was studied. After photoexcitation and ultrafast intersystem crossing,

both triplet excited states localised on the peripheral (dmbpy) ligands and states on the bridging ligand/Ir moiety became populated in a non-equilibrated way. The absence of an excited state equilibrium might explain the modest

photocatalytic H₂ activity observed. The combination of long-lived excited states with an excited state equilibrium holds promise to further increase the H₂ generation ability of this class of complexes.

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