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NANOCRYSTALLINE ELECTRODES FUNCTIONALIZED WITH LIGHT SENSITIZED [2FE-2S]-IRON-SULFUR CLUSTERS FOR HYDROGEN PRODUCTION (NEFIOS-HYDRO)

Jahresbericht 2007

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ZUSAMMENFASSUNG

Synthetic routes to biomimetic ruthenium(II)-iron sulfur cluster conjugates have been investigated. Components of biomimetic proton reduction systems have been combined with chromophores on surfaces. New conjugate systems are currently being investigated for hydrogen production.

Projektziele

Durchgeführte Arbeiten und erreichte Ergebnisse

The project is concerned with investigating the production of hydrogen using biomimetic catalysts. Nature utilises iron-sulfur cluster centers in hydrogenase enzymes for the production of hydrogen from water or protons. In biology, the energy input comes from ATP that is ultimately derived from trapping of photons. The target technology is presented in cartoon form in Figure 1. The modular approach has advantages that individual components can be tested and binary combinations optimised. Three targets have been prioritised: i) the synthesis of ruthenium(II) complexes functionalized with iron-based hydrogenase mimics, ii) the surface modification of photo- and semiconductors with the multi-component complex, iii) monitoring the reduction of protons to H_2 with respect to the negative bias applied (with and without illumination).

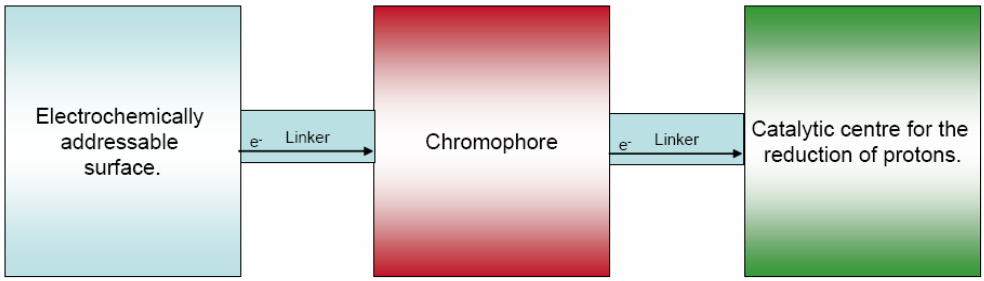


Figure 1. Schematic representation of photosynthetic hydrogen production.

A series of prototype compounds containing chromophores for the light absorption and iron-sulfur clusters for the eventual proton reduction have been prepared. The chemical structures and procedures are presented in detail in the appendix to this document. One issue became clear from the first attempts to prepare the chromophore-cluster conjugates – the fundamental chemistries of the ionic chropmophores and the neutral organometallic clusters were not readily compatible. In biology, this question is addressed by the use of proteins to provide isolated microreactor environments and the spatial separation of the various components. Much of the synthetic effort in this project addressed the challenges of preparing conjugate molecules. The appendix attached contains a research summary of the synthetic chemistry.

Even when these compounds were prepared we found them to be extremely short lived, and in the context of this project, they had the suicidal properties of light-sensitivity, water-sensitivity and sensitivity to metal oxide surfaces.Figure 2 presents a typical synthetic pathway to one of these conjugate species.

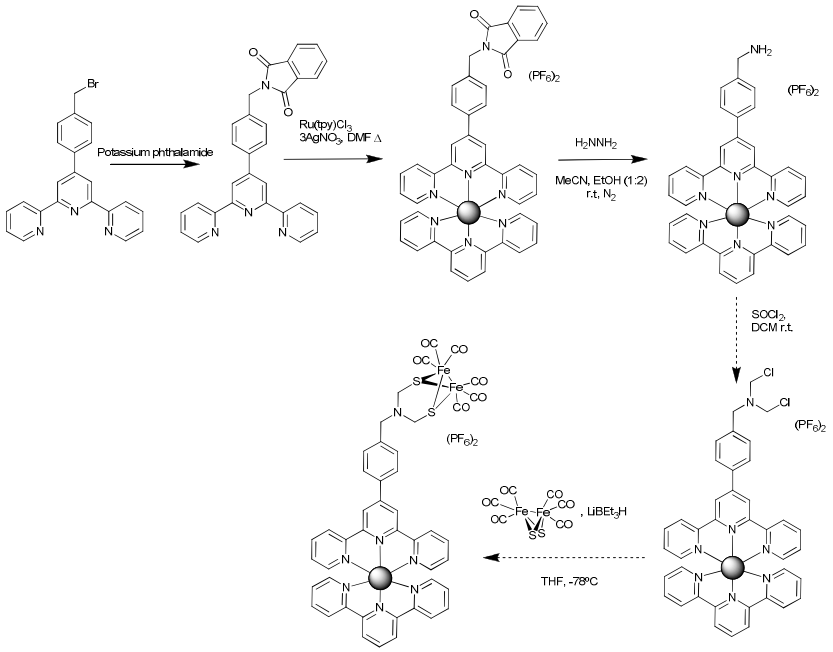


Figure 2 Typical synthetic route to chromophore-catalyst conjugates.

The emhasis of this project is the development of a functional system incorporating chromophores and catalytic hydrogen production centres rather than optimising of elegant synthetic routes to conjugates that would be unstable under proposed working conditions. The initial results with the conjugates were disappointing and we decided to take full advantage of the modular approach and evaluate systems in which the two components were not covalently linked but rather electronically coupled at the substrate surface.

Attempts to functionalise the iron-sulfur clusters with silyl substituents prior to subsequent attachment to substrate surface were also unsuccessful, again as a result of the fundamental incompatibility of the chemistries of the organometallic fragments and the required chemistry.

We therefore decided to develop a new method for surface functionalisation which did not involve covalent modification of the surface or the adsorbate. A standard glass-titania surface was functionalised with Nafion® perfluoronated ion-exchange resin and subsequently derivatised by treatment with a cationic ruthenium(II) complex (Figure 3a). The Ru III/II couple observed adsorbed on the glass substrate shows that the electronic transport through the Nafion® membrane is sluggish due to the large difference in the anodic and cathodic wave potentials (Figure 3b). We are currently investigating the ability of these conjugates to facilitate proton reduction

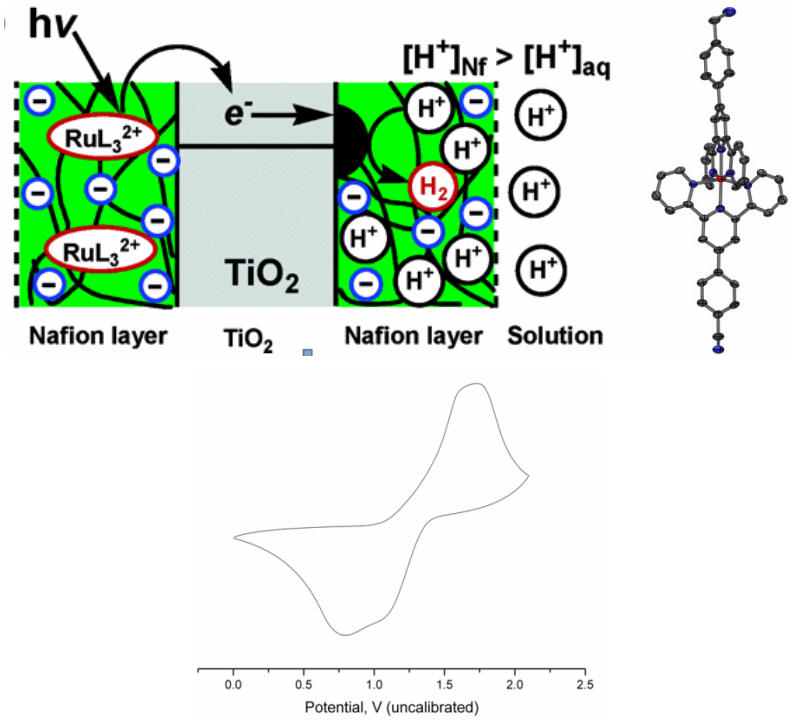


Figure 3 (a) The cation exchange-functionalised surface of the Nafion® membrane conjugate and (b) the electrochemical response of the Nafion®-ruthenium(II) surface

It was decided that the easiest method to monitor H_2 production would be using a two electrode system in which one working electrode is modified with Nafion® and ruthenium(II) complex**.** The electrochemical setup is shown in Figure 4. A small cylindrical trough was used with a hole large enough to close with the macro-electrode. A second, micro-working electrode was situated directly above the macro-electrode (400 µm). A platinum wire was employed as a counter-electrode and an Ag/AgCl reference electrode included in the system. An important parameter to consider and investigate for this experiment is the best potential to apply for both working electrodes. It is important that minimal H_2 production is observed during the experiment as H_2 bubbles can mechanically block the electrode surfaces. This experiment works under the principle of a change in current. The greater the current, the greater the H_2 turnover.

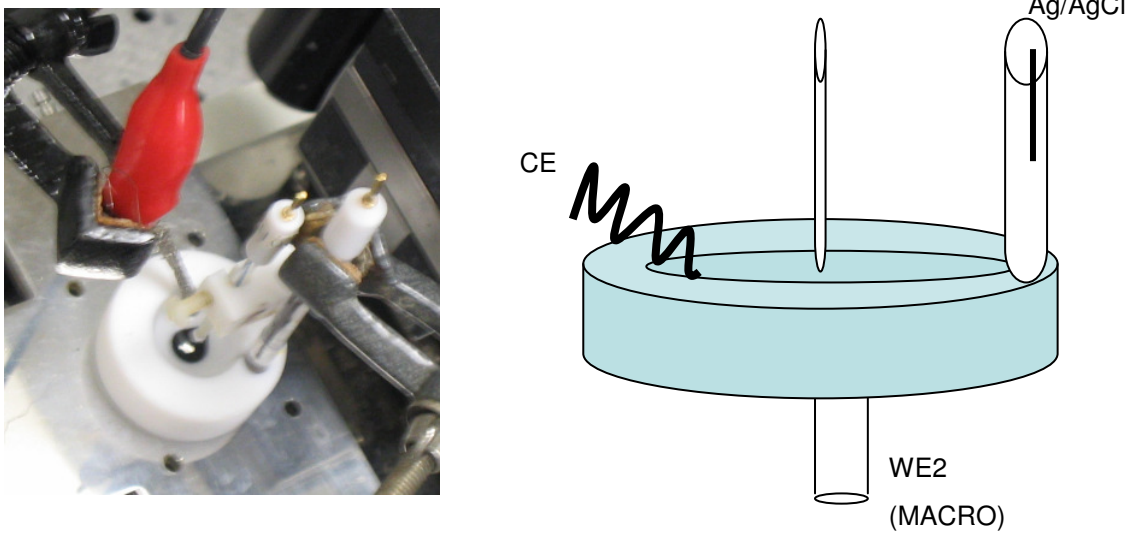


Figure 4: Electrochemical set-up for monitoring H_2 production.

One of the main problems with the electrode preparation was the uneven coverage of the Ru(II) complex due to an uneven Nafion® layer. Initial experiments using 0.5 M H_2SO_4 were promising and showed differences in the current depending on whether the macro-electrode was modified or left unmodified. We are currently extending these observations.

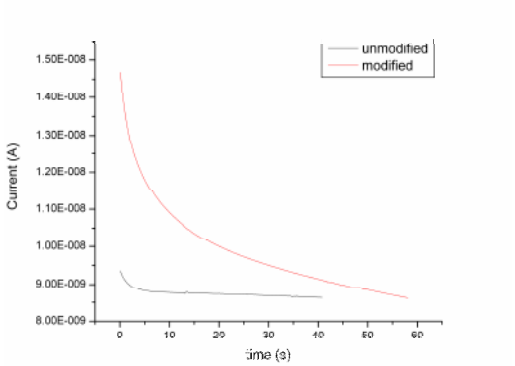


Figure 4 Current at the µ-electrode with a modified and unmodified macro-electrode.

Nationale Zusammenarbeit

This project is part of a wider interdisciplinary research palette from the group involving functionalised heterogeneous and interfacial materials. The projects are supported directly by the SNF and the NCCR "Nanoscale Science". The instrumental analysis is part of an ongoing collaboration with the group of Professor Uwe Pieles at the FHNW, Muttenz. Related chemistry is found in the KTI project ANWASP.

Internationale Zusammenarbeit

Some aspects of this project have some overlap with our currently running EU programme (HETEROMOLMAT) and will likely overlap with the planned daughter project HOPE.

Bewertung 2007 und Ausblick 2008

A library of components has been constructed for the assembly of conjugates or for the sequential derivatisation of substrate surfaces with chromophores and catalytic proton reduction sites. Prelimi-

nary studies of the electrochemical and photoelectrochemical behaviour of these systems have been completed and promising lead systems identified. The assay for hydrogen production selected involves monitoring the loss of protons rather than the direct identification of dihydrogen. Two manuscripts are currently in press resulting from the synthetic chemistry and the systematic investigation of the functionalisation of substrates with chromophores [1,2].

The outlook for the remaining part of the project involves optimising the assay methods and confirming the reproducibility of the proton reduction experiments with the hetero-functionalised surfaces.

Referenzen

[1] E.C. Constable, C.E. Housecroft, E.J. Medlycott, M. Neuburger, F. Reinders, S. Reymann and S. Schaffner, ***Bis(4'-phenyl-2,2':6',2''-terpyridine)ruthenium(II): holding the $\{Ru(tpy)_2\}^{2+}$ embraces at bay***, Inorg. Chem. Commun., In the press

[2] E.C. Constable, C.E. Housecroft, E.J. Medlycott, M. Neuburger, F. Reinders, S. Reymann and S. Schaffner, ***The first complex of 4'-(4-methylthiophenyl)-2,2':6',2''-terpyridine – a model for terpylated self-assembled monolayers***, Inorg. Chem. Commun., In the press

Anhang

Synthetic chemistry associated with this project.

Anhang
zu Jahresbericht 2007 - BFE-Projekt 152310-101877

NANOCRYSTALLINE ELECTRODES FUNCTIONALIZED WITH LIGHT SENSITIZED [2FE-2S]-IRON-SULFUR CLUSTERS FOR HYDROGEN PRODUCTION (NEFIOS-HYDRO)

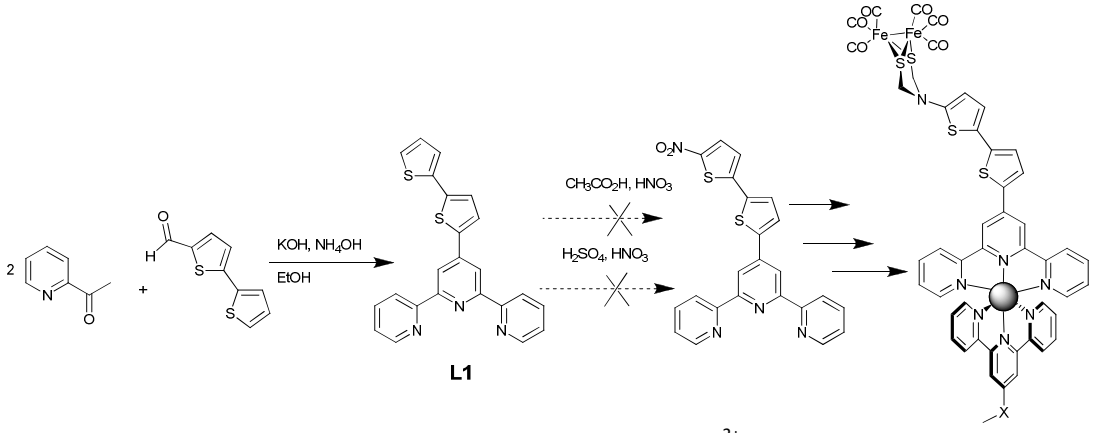
Associated synthetic chemistry

TiO_2 surfaces functionalised with light sensitized [2Fe-2S]-clusters for H_2 production

The project as detailed may be separated into three components: i) the synthesis of a Ru(II) complex functionalized with a Fe-based hydrogenase mimic, ii) the surface modification with the multi-component complex, iii) monitoring the conversion of protons to H_2 with respect to the negative bias applied (with and without illumination).

I Synthesis: Biomimetic approach

The initial approach required the synthesis of a Ru(II) complex functionalised with a terpyridine-tridentate ligand. A bithiophene unit was incorporated into the ligand to direct and facilitate electron transfer to the catalytic centre (scheme 1). The synthesis of the bithiophene-substituted terpyridine was trivial and could be carried out in one pot (scheme 1).[1] The characterisation of **L1** was consistent with previously published data.[2] I intended to initially carry out all of the chemistry on the ligand prior to complexation but this was not possible. Firstly, the nitro-functionalization of the bithiophenyl-tpy ligand proved difficult. The nitration reactions were carried out using nitric/acetic acid combinations which yielded only starting materials. Harsher nitration conditions using a combination of sulphuric and nitric acid resulted in the decomposition of the ligand through loss of bithiophene to yield [2,2':6',2''-Terpyridine]-4'-carboxylic acid.



Scheme 1: Initial proposed synthetic procedure for a $Ru(tpy)_2^{2+}$-based complex covalently linked to a diiron-disulfide cluster.

A second approach was attempted utilising the Buchwald-Hartwig cross-coupling reaction to introduce the cluster as a secondary amine to a bromo-functionalised tpy ligand (Scheme 2). **L1** could be brominated to give **L2** using a combination of NBS and acetic acid. It was found after further investigation (Dr. Sebastian Reymann) that this reaction is sensitive to the scale and best results were found with the reaction listed in this experimental section. Slow diffusion of hexane into a chloroform solution of **L2** yielded crystal blocks suitable for analysis by X-ray diffraction (Figure 1). One ligand molecule was found in the asymmetric unit with no solvent of recrystallisation. Ligand **L2** crystallised in the monoclinic space group P21/a.

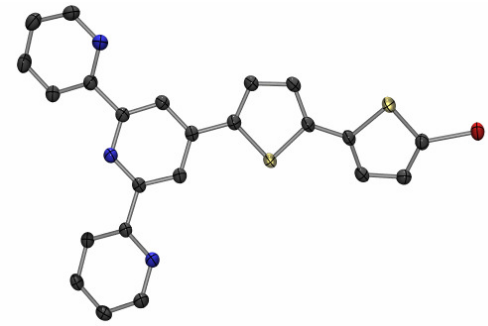


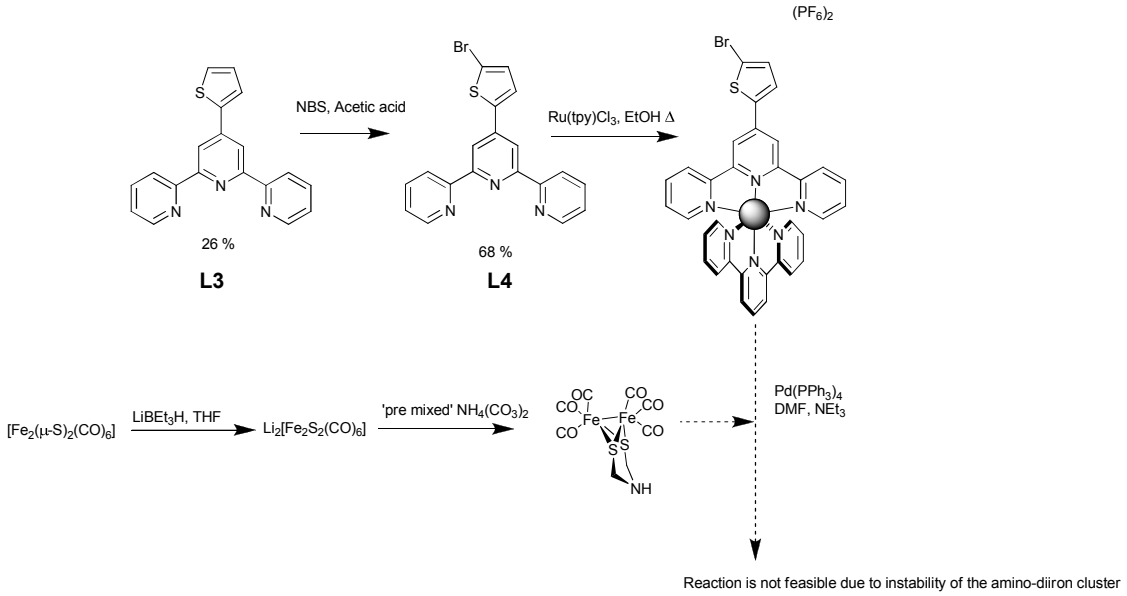
Figure 1: X-ray crystal structures of complex **L2** as an ORTEP representation. Thermal ellipsoids are set at 50%.

Both the pyridine rings in the tpy-moiety and the thiophene rings of bithiophene are in a transoid conformation. The ligand lies in a near coplanar arrangement with the outer-thiophene twisting by 14.14º with respect to the inner thiophene which in turn is twisted by 12.37º with respect to the central pyridine ring. The ligand stacks in the solid state with offset face-to-face π-stacking interactions between the outer thiophene of one molecule and the inner thiophene of a neighbouring molecule (centroid-to-centroid distance 3.84Å).

The same bromination reaction could be carried out on mono-thiophene tpy-ligand **L3** to give the brominated ligand **L4**. Primarily reactions were carried out on **L4** and **$[Ru(L4)_2](PF_6)_2$** as the synthesis of these starting materials were higher yielding. Additionally, reactivity should be enhanced in complex **$[Ru(L4)_2](PF_6)_2$** compared to **$[Ru(L2)_2](PF_6)_2$** as the reaction site is closer to the electron-withdrawing Ru(II) centre.

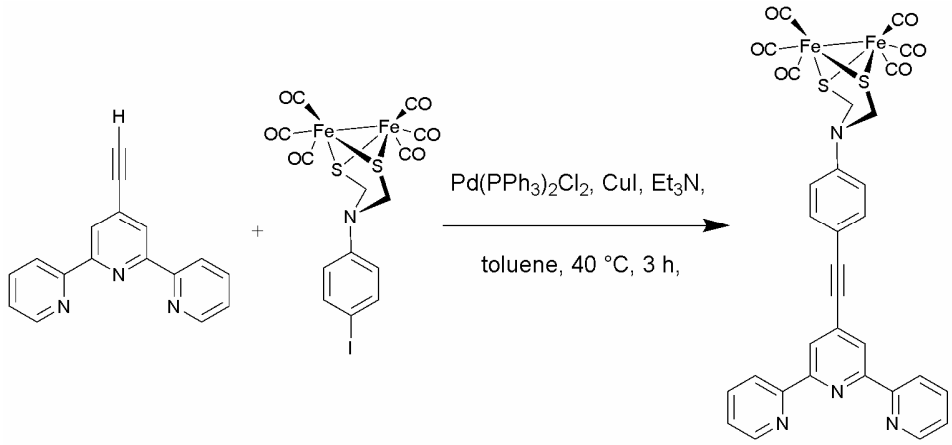
The Buchwald-Hartwig reaction was carried out on both the ligand and the complex to couple an amino-substituted 2Fe-cluster with a brominated ligand or complex.

In both cases only starting materials and mixtures and decomposition products were observed. For the ligand, the major decomposition product was the formation of the Fe(II) complex of the tpy-ligand. This process is a result of the high affinity of the tpy-based ligand for Fe extraction from the 2Fe-2S cluster followed by the oxidation to Fe(II).[2] The reaction on the complex resulted in the formation of brown decomposition products which stuck to the base line.



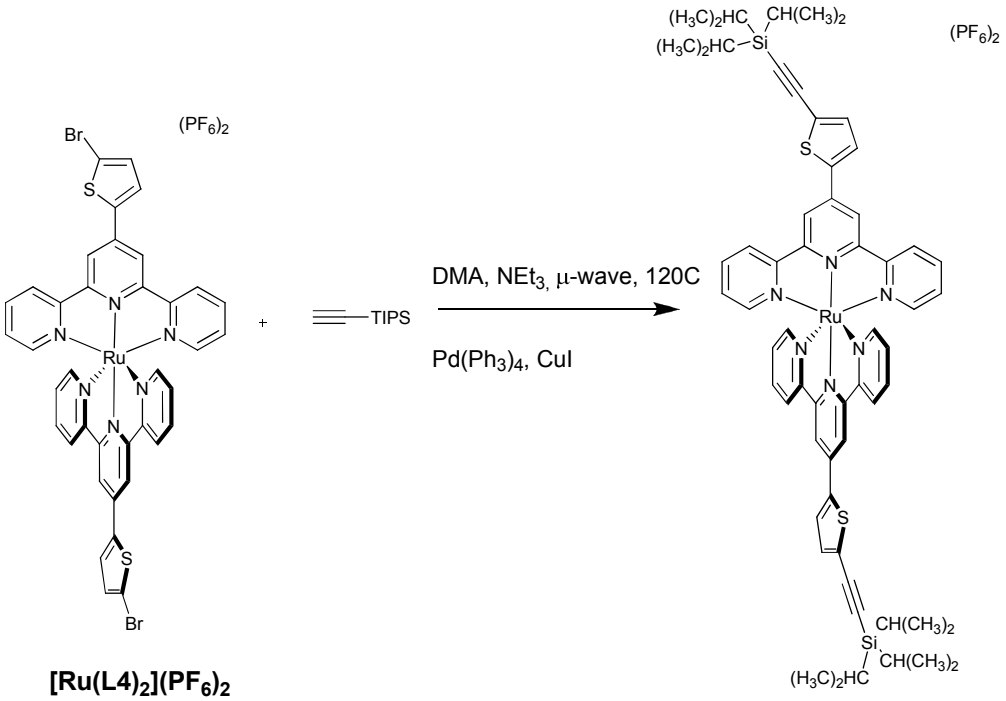
Scheme 2: Second approach employing a Buchwald-Hartwig cross-coupling reaction.

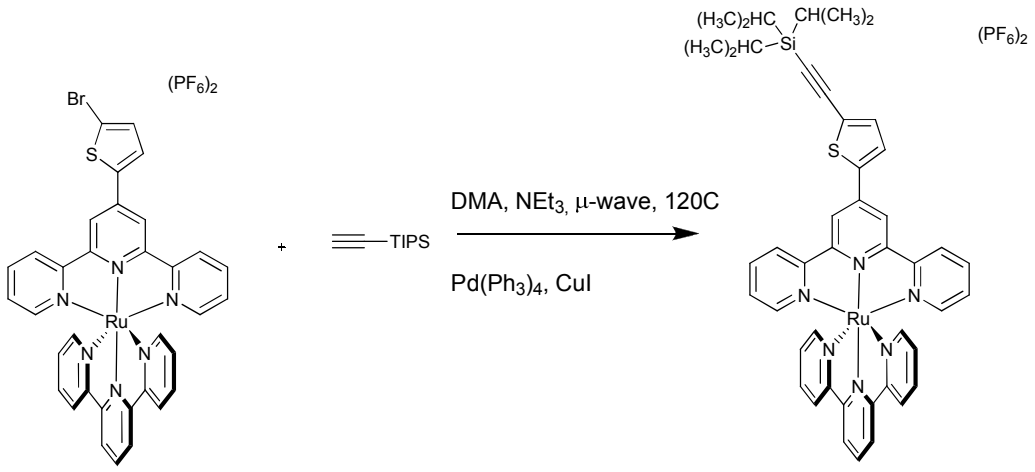
It was previously shown that the diiron-disulfide cluster is compatible and could be introduced into the ligand through a Sonogashira cross coupling reaction (scheme 3).[3, 4]



Scheme 3: Previously reported synthesis of a Ru(II) bis-tpy complex functionalised with a hydrogenase mimic.[4]

In this regard, I functionalised complexes of bromo-thiophene-tpy ligands with alkyne substituents thereby intending to couple the iodo-aniline- hydrogenase derivatives as in scheme 3. The funtionalisation could also be carried out on the free ligand **L4** or on the complexes. The Sonogashira reactions were carried out in the microwave in a 2:1 DMA:NEt_3 mixture. The catalyst employed was Pd(PPh3)4/CuI and the deaerated mixture was heated at 120ºC for one hour.





Scheme 4: The synthesis of the TIP protected complex **[Ru(L5)$_2$](PF$_6$)$_2$** and **[Ru(tpy)L5](PF$_6$)$_2$**.

The TIPS protected complexes were isolated and characterised. I was able to isolate both the TIPS protected complexes of **[Ru(L5)$_2$](PF$_6$)$_2$** and **[Ru(tpy)L5](PF$_6$)$_2$**. When TMS was employed as a protecting group the reaction yielded mixtures of products which couldn't be purified. Crystals of the TIPS protected complex **[Ru(L5)$_2$](PF$_6$)$_2$** were obtained by slow evaporation of a CD_3CN NMR solution (EM97).

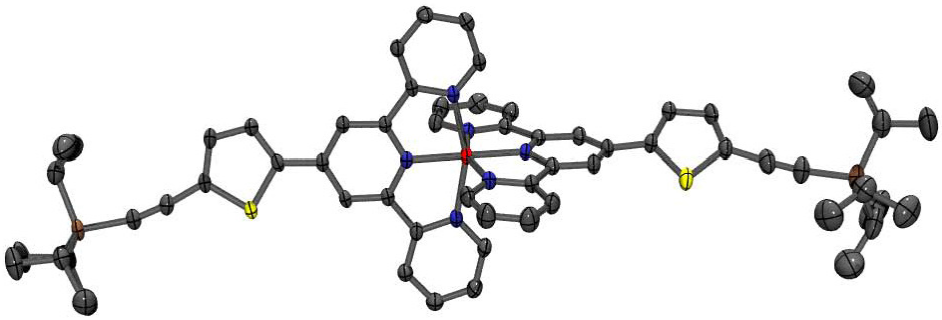


Figure 2: X-ray crystal structures of complex **C5** as an ORTEP representation. Thermal ellipsoids are set at 50%. The PF_6^- anions have been omitted for clarity.

Complex **$[Ru(L5)_2](PF_6)_2$** crystallises in the triclinic space group $P\bar{1}$ with one cation and two PF_6^- anions in the asymmetric unit. Unlike many thiophene-containing complexes no disorders of the thiophene rings are observed in **$[Ru(L5)_2](PF_6)_2$** presumably due to the adjacent bulky triisopropyl-acetylene groups. One of the thiophene rings is almost co-planar with the central pyridine ring of the ligand with a twist of 10.56º. However, the second thiophene ring on the orthogonal ligand is twisted more significantly (34.76 º).

In the literature, deprotection of TIPSA requires TBAF. This is in comparison to milder conditions in the deprotection of TMSA such as K_2CO_3. In this example as expected, K_2CO_3 is not strong enough and TBAF was employed. However, the work up was quite challenging. The excess fluoride in solution resulted in significant salt exchange and metathesis back to the PF_6^- salt was required. Initially, I tried the conversion with an excess of NH_4PF_6 (aq) but on collection of the material the majority of the product remained insoluble on the celite due to insufficient salt exchange and was irretrievable. The material that was isolated was characterised by NMR Medlycott_.085 and was not sufficiently pure. However, slow diffusion of diethyl ether into the NMR solution yielded crystals of the deprotected complex suitable for analysis by X-ray diffraction (EM100).

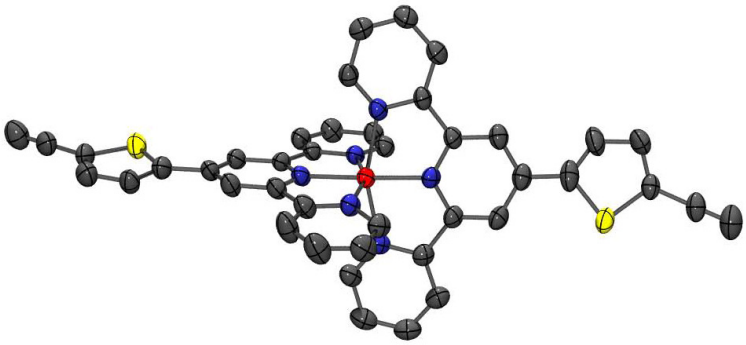
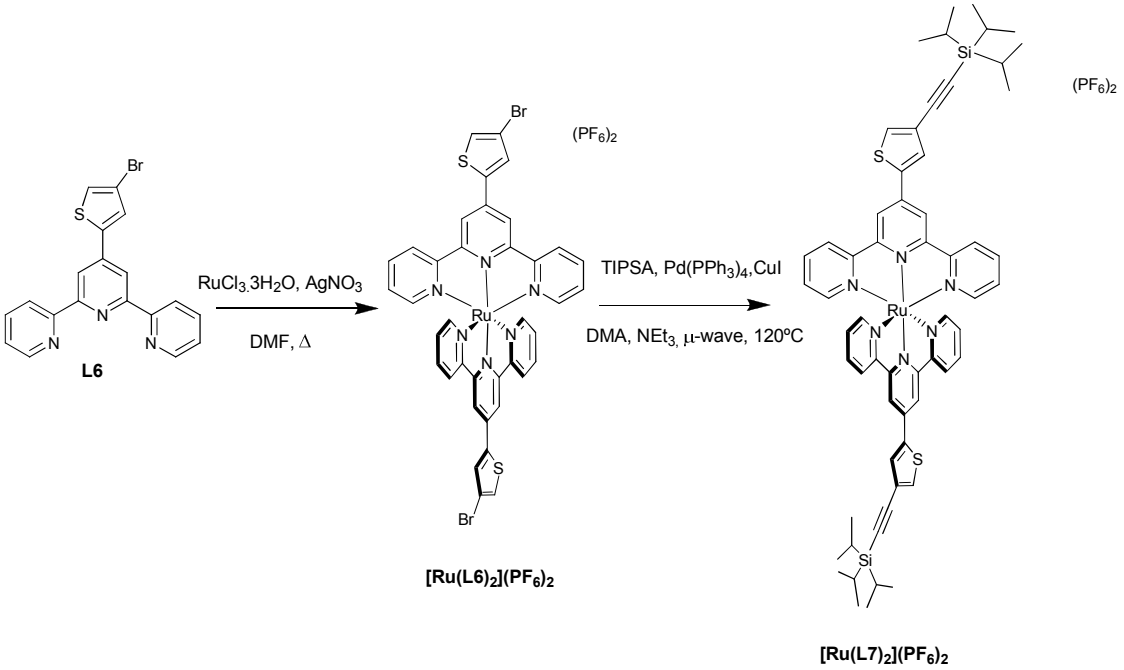


Figure 3: X-ray crystal structures of **$[Ru(L5)_2](PF_6)_2$** deprotected as an ORTEP representation. Thermal ellipsoids are set at 50%. The PF_6^- anions have been omitted for clarity and only one orientation of a disordered acetylene-thiophene has been displayed.

The complex crystallised in the triclinic space group Pī with one cation, two full PF_6^- counter anions and an acetonitrile solvent molecule in the asymmetric unit. An acetylene-thiophene on one of the ligands is disordered over two positions with occupancies of 80:20. In addition the PF_6^- counter anions are disordered over three positions with half occupancies on two sites.

To try and improve the purification of the deprotection step of complex **$[Ru(L5)_2](PF_6)_2$** the same reaction was carried out and purification by column chromatography was attempted. The column was run under standard conditions employing an eluent of 9:0.9:0.1, $MeCN:H_2O:KNO_{3\,(sat)}$ in order to convert all the material to the NO_3^- salt and then return to the PF_6^- salt in the final step. However, the deprotected product decomposes on the column and the only product obtained from this column was complex **$[Ru(L4)_2](PF_6)_2$** through loss of the acetylene units.

The same chemistry is observed in the deactivated ligand brominated in the 4-position, 4'-(4-Bromothiophene-2-yl)-2,2':6',2''-terpyridine, **L6** (Scheme 5).



Scheme 5: Functionalisation of 4'-(4-Bromothiophene-2-yl)-2,2':6',2''-terpyridine, **L6**.

Crystals suitable for analysis by X-ray diffraction of **L6** and **$[Ru(L6)]_2(PF_6)_2$** were obtained by slow diffusion of hexane into a chloroform solution of L6 and slow diffusion of diethyl ether into an acetonitrile solution of **$[Ru(L6)_2](PF_6)_2$** (Figure 4).

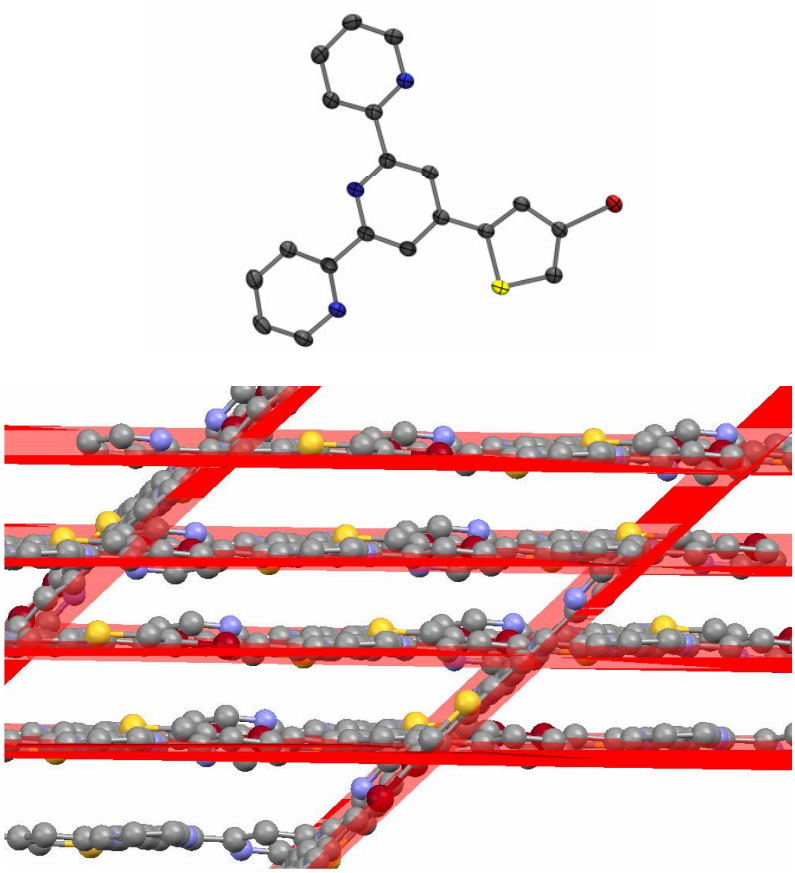


Figure 4: a) X-ray crystal structures of **L6** (above) and as an ORTEP representation. Thermal ellipsoids are set at 50%. b) Bisecting sheets in the extended lattice as a ball and stick representation (below).

L6 crystallised in the monoclinic space group P21/n with one ligand molecule in the asymmetric unit. The thiophene ring is coplanar to the terpyridine unit with a twist of only 7.0º with respect to the central pyridine ring. The molecules are linked to neighbouring ligand molecules by short S-S interactions (3.57Å) and Br-N interactions (3.12 Å) all shorter than the sum of the Van der Waals radii. This results in the formation of sheets lying horizontally parallel which bisect a second sheet layer by approximately 44 º (figure 4b).

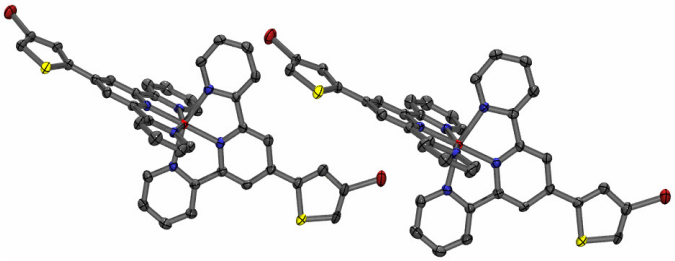
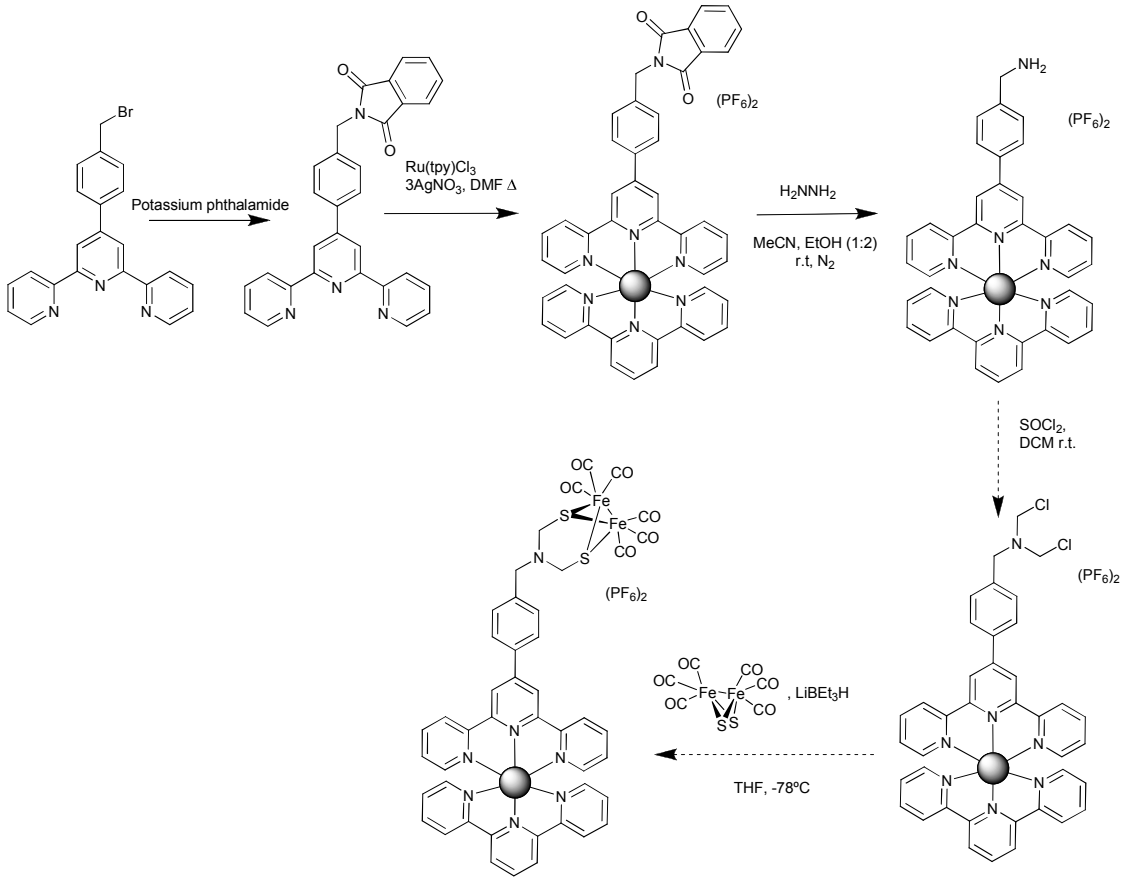


Figure 5: X-ray crystal structures of **$[Ru(L6)_2](PF_6)_2$** as an ORTEP representation. Thermal ellipsoids are set at 50%. The PF_6^- anions and solvent of crystallisation have been omitted for clarity.

[Ru(L6)$_2$](PF$_6$)$_2$ crystallised in the monoclinic space group P21/c with two cations, four PF_6^- counter anions, and five acetonitrile solvent molecules in the asymmetric unit (figure 5).

In order to try and simplify the synthetic route we decided to try and carry out all of the chemistry on the complex employing a tpy-phenyl-methylamine ligand (scheme 6).



Scheme 6: Proposed synthetic route to Ru(II) bis-terpyridine complex functionalised directly with a 2Fe-2S cluster.

Tolyl-terpyridine was synthesised in one step which could then be subsequently brominated.[1, 5] The 4'-(4-bromomethylphenyl)-2,2':6',2''-terpyridine could be converted to the 4'-(4-Phthalimidomethylphenyl)-2,2':6',2''-terpyridine according to the previously published procedure.[5] The homo- **[Ru(L8)$_2$](PF$_6$)$_2$** and heteroleptic **[Ru(tpy)L8](PF$_6$)$_2$** complexes of this ligand were synthesized by refluxing in DMF with either 0.5 equivalents of $RuCl_3$.3H2O (**[Ru(L8)$_2$](PF$_6$)$_2$**) or one equivalent of RutpyCl$_3$ (**[Ru(tpy)L8](PF$_6$)$_2$**) in the presence of 3 equivalents of $AgNO_3$ as a dechlorinating agent. These complexes could be readily purified by column chromatography. Subsequent deprotection of complexes **[Ru(L8)$_2$](PF$_6$)$_2$** and **[Ru(tpy)L8](PF$_6$)$_2$** by hydrazine in an ethanol:acetonitrile mixture resulted in the formation of the complexes **[Ru(L9)$_2$](PF$_6$)$_4$** and **[Ru(tpy)L9](PF$_6$)$_3$** of 4'-(4-aminomethylphenyl)-2,2':6',2''-terpyridine. Initially, it was attempted to carry out the deprotection on the ligand and synthesise the deprotected complexes directly. However, purification was complicated by the

fact that the amino-substituted complexes stuck to the silica. On characterisation of complexes **[Ru(L9)$_2$](PF$_6$)$_4$** and **[Ru(tpy)L9](PF$_6$)$_3$** by NMR, elemental analysis and in the case of **[Ru(L9)$_2$](PF$_6$)$_4$**, X-ray crystallography, it was evident that the complexes were in fact protonated. Such complexes easily pick up a proton in the presence of even weak protic sources. Despite the fact that the deprotection reactions were carried out under basic conditions, the subsequent precipitation in NH_4PF_6(aq) provided the protons for the protonation. Both **[Ru(tpy)L8](PF$_6$)$_2$** and **[Ru(L9)$_2$](PF$_6$)$_4$** could be crystallised by slow diffusion of diethylether into a concentrated acetonitrile solution of the complexes.

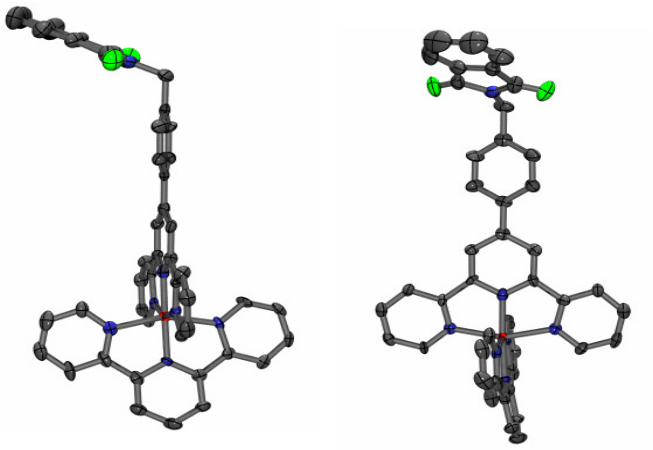


Figure 6: X-ray crystal structure of **[Ru(tpy)L8](PF$_6$)$_2$** as an ORTEP representation.

Thermal ellipsoids are set at 50%. The PF_6^- anions have been omitted for clarity.
Due to twinning in the crystals of complex **[Ru(tpy)L8](PF$_6$)$_2$** the resolution of the structure was unsatisfactory (EM119). However, the structure does clearly show the near-perpendicular angle (112.8º) of the phthalamide group with respect to the benzene ring. Consequently, the phthalamide group may be considered as electronically independent of the terpyridine ligand in the solid state.

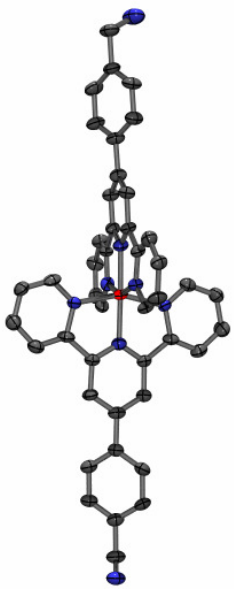


Figure 7: X-ray crystal structure of **[Ru(L9)$_2$](PF$_6$)$_4$** as an ORTEP representation. Thermal ellipsoids are set at 50%. The PF_6^- anions have been omitted for clarity.

The asymmetric unit in the crystal of complex **[Ru(L9)$_2$](PF$_6$)$_4$** consists of one cation, four PF_6^- counter anions (providing evidence for protonation), two molecules of acetonitrile and one molecule of water. One of the protonated amines is involved in hydrogen bonding to the oxygen atom of the water molecule (N-H---O bond distance of 2.826 (2) Å). The second protonated amine has short contacts between two N atoms of acetonitrile solvent molecules (N-H---N bond distances of 2.795 (14) Å and 2.912 (2) Å).

The attachment of the diiron-disulfide cluster to the complex **[Ru(tpy)L9](PF$_6$)$_3$** was attempted using a strategy previously employed for simpler ligand systems.[3, 4] The complex was dissolved in the minimal acetonitrile and the mixture was added to DCM and paraformaldehyde. Thionyl chloride was added drop wise and the mixture stirred for 30 minutes at room temperature. The solvent was then removed on the vacuum pump whilst maintaining the residue at 0ºC. The dimethyl-chloride amine was not characterised and used directly in the next step but was kept cold and under and inert atmosphere until used. The diiron disulphide cluster was synthesised as previously described (***Care should be taken during this reaction as $Fe(CO)_5$ is toxic and large quantities of H_2S are evolved***).[6] The reaction was carried out under Schlenk conditions but the optimised reported yield of 30-35% was never obtained. The best yield obtained was 5-12 % with significant amounts of the $Fe_3S_2(CO)_9$ as a side product. An acetone solution of the unpurified mixture was evaporated to dryness to yield crystals suitable for analysis by X-ray diffraction. The crystals were shown to be a co-crystallisation of $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ (Figure 8). Unfortunately, this was isostructural with the co-crystal structure previously reported in 1965.[7]

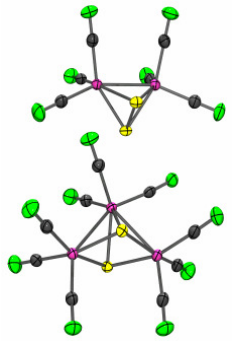


Figure 8: An ORTEP representation of the co-crystal of $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$. Thermal ellipsoids are set at 50%.

Once purified, the $Fe_2S_2(CO)_6$ cluster could be lithiated using lithium super hydride to break the S-S bond and this is observed with a colour change from red to green. The dimethyl-chloride amine complex was added in a minimal amount of dry, dearated acetonitrile to the lithiated cluster at -78C and the mixture was warmed to room temperature which was followed by a change of colour from green back to red. However, only starting complex **[Ru(tpy)L9](PF$_6$)$_3$** and brown decomposition product on the baseline were observed by tlc.

Complexes **[Ru(L8)$_2$](PF$_6$)$_2$**, **[Ru(tpy)L8](PF$_6$)$_2$**, **[Ru(L9)$_2$](PF$_6$)$_4$** and **[Ru(tpy)L9](PF$_6$)$_3$** were characterised by UV-visible spectroscopy and electrochemistry (Table 1).

	Absorption λ_{max}, nm (ε, $M^{-1}cm^{-1}$ x 10^{-3})	**Electrochemistry** $E_{1/2}$(oxidn)	$E_{1/2}$(redn)		
[Ru(L8)$_2$](PF$_6$)$_2$	285 (78.6), 309 (73.2), 490 (29.1)	0.85 (73)	-1.64 (74)	-1.86 (85)	
[Ru(tpy)L8](PF$_6$)$_2$	274 (52.9), 283 (54.4), 308 (74.1), 483 (23.5)	0.87 (80)	-1.65 (70)	-1.88 (100*)	
[Ru(L9)$_2$](PF$_6$)$_4$	284 (62.2), 310 (71.0), 490 (27.5)	0.86 (71)	-1.64 (60)	-1.87 (97)	
[Ru(tpy)L9](PF$_6$)$_3$	273 (48.0), 282 (46.9), 308 (73.8), 483 (22.9)	0.88 (70)	-1.65 (71)	-1.89 (108)	
[Fe(L8)$_2$](PF$_6$)$_2$	286 (111.1), 300 (81.8), 320 (72.7), 358 (sh), 568 (36.8)	0.69 (70)	-1.63 (79)	-1.73 (67)	-1.87 (75)
[Fe(L9)$_2$](PF$_6$)$_4$	285 (65.1), 320 (60.8), 358 (sh, 12.7), 568 (25.5)				

Table 1: Spectroscopic data and half wave potentials for Ru(II) and Fe(II) complexes of **L8** and **L9** in deaerated acetonitrile solution (298 K).

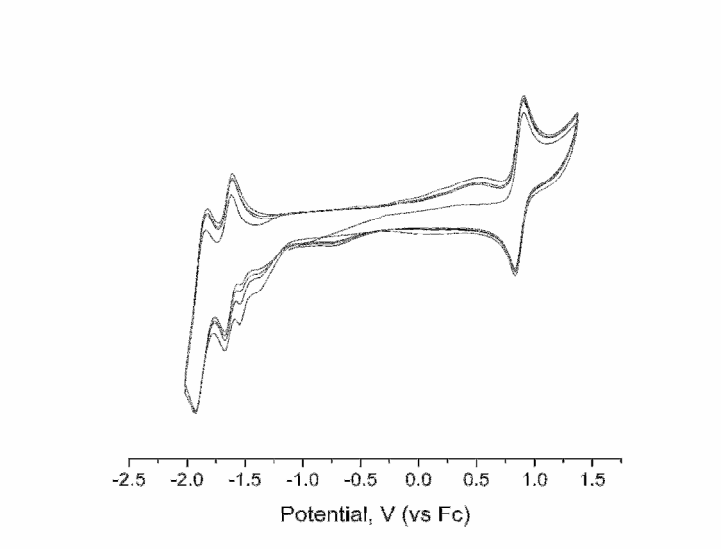


Figure 9:

Both complexes **[Ru(L8)$_2$](PF$_6$)$_2$** and **[Ru(tpy)L8](PF$_6$)$_2$** initially appear to have relatively reversible behaviour. However, after cycling out to -2.0 V, an additional, irreversible anodic peak grows at approximately 0.33 V and 0.51 V in **[Ru(L8)$_2$](PF$_6$)$_2$** and **[Ru(tpy)L8](PF$_6$)$_2$** respectively. This is followed by an additional cathodic peak at -1.54 V in complex **[Ru(tpy)L8](PF$_6$)$_2$** (Figure 9). This irreversible behaviour is a consequence of the phthalamide-based reduction at 1.86 V and -1.88 V in **[Ru(L8)$_2$](PF$_6$)$_2$** and **[Ru(tpy)L8](PF$_6$)$_2$** respectively. In complex **[Ru(L8)$_2$](PF$_6$)$_2$** there is an initial tpy-based reduction -1.65 V which is followed by the phthalamide-based reduction at -1.88 V. This is in fact three, coincidental one-electron process corresponding to the reduction of the second tpy-ligand and one-electron reductions on each of the phthalamide functions. The fact that these process overlaps is further evidence for the electronic separation of the tpy-unit from the phthalamide group. The integration in the square wave scan (Figure 10) confirms that this is in fact a 3-electron process. In complex **[Ru(tpy)L8](PF$_6$)$_2$** this second reduction is a 2-electron process because only phthalamide unit is present in the complex.

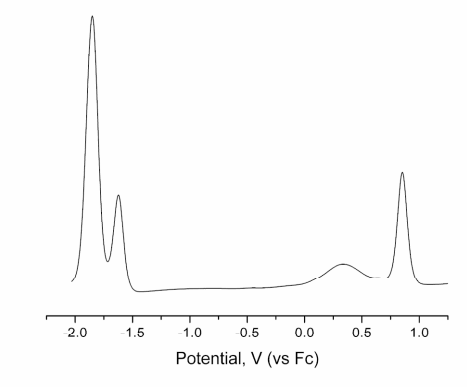


Figure 10: The Square wave of complex **[Ru(L8)$_2$](PF$_6$)$_2$**.

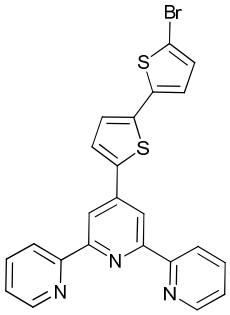
In order to verify the assignments to the electrochemical data the Fe(II) complexes of **L8** and **L9** were synthesised as the tpy-based reductions should occur at a less negative potential and therefore should move out of the region of the phthalamide-based reductions. **$[Fe(L8)_2](BF_4)_2$** could be synthesised by the reaction of one equivalent of $Fe(BF_4)_2.6H_2O$ with two equivalents of **L8** in refluxing acetonitrile for 20 minutes. Filtration followed by precipitation in diethyl-ether resulted in the formation of the complex as a purple solid. **$[Fe(L9)_2](PF_6)_4$** was synthesised by the hydrazine-based deprotection used in the above Ru(II) complexes. Precipitation in NH_4PF_6(aq) resulted in the formation of the complex as the PF_6^- salt. The electrochemistry as expected showed the ligand-based reductions shifting to a less-negative potential (particularly the second tpy reduction). This enabled us to see both reversible tpy-based reductions followed by a 2-electron coincidental reduction on each of the phthalamide units.

The UV-visible spectrum of all of the complexes of **L8** and **L9** consisted of ligand-based transitions in the UV region. The ^{1}MLCT absorption bands occurred at a longer wavelength in the Fe(II) complexes compared to the Ru(II) complexes as expected for Fe(II) complexes. The λ max of the ^{1}MLCT absorption bands of the Ru(II) complexes of **L8** and **L9** were the same despite the difference in the charge. This also indicates the methyl-bridge is acting as an insulating unit.

Experimental

L2

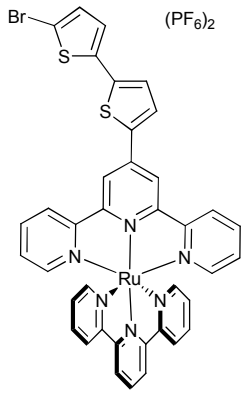
4'-(5-bromo-2,2'-bithiophene)-2,2':6',2''-Terpyridine



4'-(2,2'-bithiophene)-2,2':6',2''-Terpyridine (0.31 g, 0.81 mmol) was dissolved in a mixture of glacial acetic acid (5 ml) and N-bromosuccinimide (0.17 g, 0.97 mmol) and stirred at room temperature overnight in the absence of light. The mixture was neutralized with $NaHCO_3$ (aq) and the solution extracted with DCM. The DCM extracts were dried over Na_2SO_4 and the solvent was removed to afford **L2** as a yellow solid (0.26 g, 68 %).

EM65 medlycot.013

[Ru(tpy)L2](PF$_6$)$_2$



RutpyCl$_3$ (0.12 g, 0.27 mmol) was added on stirring to a solution of **L2** (0.24 mmol) in EtOH (20 mL) with a few drops of *N*-ethymorpholine. The mixture was stirred at room temperature for 15 minutes and then heated to reflux for five hours in the absence of light. The mixture was cooled and added to NH_4PF_6 (aq) and the solution was diluted with water (100 mL). The resulting solid was collected and dissolved in acetonitrile and purified by column chromatography (SiO2, MeCN: water: KNO_3(aq); 9:0.9:0.1). The nitrate salt was metathesized to the PF_6 salt, and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **[Ru(tpy)L2](PF$_6$)$_2$** as a red solid in 13% yield.

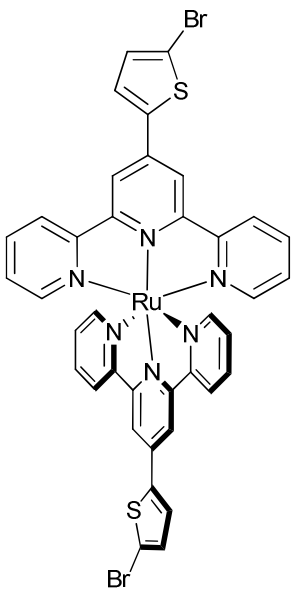
Anal. Calcd. for $C_{38}H_{25}Br_1F_{12}N_6P_2Ru_1S_2$. H_2O: C, 40.80; H, 2.43; N, 7.51. Found C 41.10, H 2.77, N 7.18.

^{1}H NMR (400 MHz, CD3CN): 8.88 (s, 2H) $H_{3',5'}$; 8.76 (d, 2H, J= 8.2 Hz); $HTpy_{3',5'}$; 8.4 (d, 2H, J= 8.0 Hz) $H_{3,3''}$; 8.50 (d, 2H, J= 8.0 Hz) $HTpy_{3,3''}$; 8.42 (t, 1H, J= 8.2 Hz) HTpy4'; 8.10 (d, 1H, J= 3.9 Hz) Hthiop; 7.94 (m, 4H) $H_{4,4''}$, $HTpy_{4,4''}$; 7.49 (d, 1H, J= 3.9 Hz) Hthiop; 7.44 (d, 2H, J= 5.0 Hz) $H_{6,6''}$; 7.35 (d, 2H, J= 5.5 Hz) $HTpy_{6,6''}$; 7.28 (d, 1H, J= 3.9 Hz)H_{thiop}; 7.19 (m, 5H) $H_{5,5''}$, $HTpy_{5,5''}$, H_{thiop}.

^{13}C NMR (100 MHz, CD_3CN): 112.56, 119.61, 124.13, 124.83, 125.02, 126.14, 126.55, 127.87, 127.97, 129.74, 132.24, 136.25, 138.21, 138.44, 138.51, 139.18, 139.87, 141.09, 152.83, 152.95, 155.74, 155.87, 158.29, 158.43.

EM70 medlycot.018

$[Ru(L4)_2](PF_6)_2$



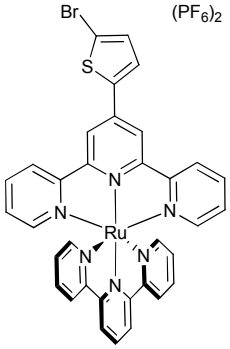
$RuCl_3.3H_2O$ (0.10 g, 0.38 mmol) and $AgNO_3$(0.39 g, 2.3 mmol) were added to EtOH (15 mL) and refluxed for 30 minutes. L4 (0.30 g, 0.77 mmol) in 'wet' DMF (20 mL) was added and the mixture refluxed for a further 4 hours. The mixture was filtered to remove AgCl and the filtrate precipitated in NH_4PF_6 (aq). The red precipitate was collected and dissolved in the minimum acetonitrile. The mixture was purified by column chromotography (SiO2, Acetone: water: KNO_3(aq); 9:0.9:0.1. The nitrate salt was metathesized to the PF_6 salt, and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **$[Ru(L4)_2](PF_6)_2$** in 62 % yield.

^{1}H NMR (400 MHz, CD3CN): 8.84 (s, 4H) $H_{3',5'}$; 8.63 (d, 4H, J= 7.9 Hz)$H_{3,3''}$; 7.96 (d, 2H, J= 4.0 Hz) H_{thiop}; 7.95 (td, 4H, J= 1.3, 7.9 Hz) $H_{4,4''}$;7.46 (d, 2H, 4.0 Hz) H_{thiop}; 7.42 (d, 4H, J= 5.6 Hz) $H_{6,6''}$; 7.18 (m, 4H) $H_{5,5''}$.

^{13}C NMR (100 MHz, CD_3CN): 119.76, 125.08, 128.00, 129.21, 133.09, 138.50, 140.73, 141.88, 152.91, 155.95, 158.23, 162.83.

NMR medlycot_.045

[Ru(tpy)L4](PF$_6$)$_2$

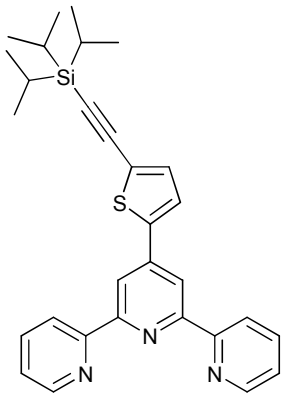


RutpyCl$_3$ (0.50 g, 1.13 mmol) was added on stirring to a solution of AgNO3 (0.58 g, 3.40 mmol) in EtOH (50 mL). The mixture was heated for 30 minutes at reflux at which point **L4** (0.45 mg, 1.13 mmol) was added as a solid. The mixture was refluxed for a further six hours in the absence of light and then cooled and added to NH_4PF_6 (aq). The solution was diluted with water (100 mL) and the resulting solid was collected. The crude mixture was dissolved in the minimum acetonitrile and purified by column chromatography (SiO2, MeCN: water: KNO_3(aq); 9:0.9:0.1. The second red band was collected and the NO_3^- salt was metathesized to the PF_6^- salt and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **[Ru(tpy)L4](PF$_6$)$_2$** as a red solid in 48 % yield.

EM99

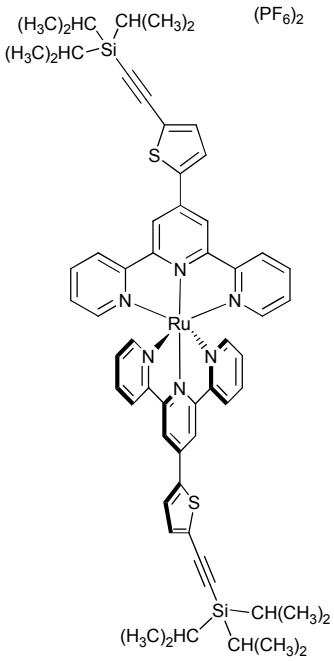
^{1}H NMR (400 MHz, CD_3CN): 8.83 (s, 2H) $H_{3',5'}$; 8.74 (d, 2H, J= 8.2 Hz) $HTpy_{3',5'}$; 8.63 (d, 2H, J= 8.0 Hz) H3,3''; 8.49 (d, 2H, J= 8.0 Hz)$HTpy_{3,3''}$;8.42 (t, 1H, J= 8.2 Hz) $HTpy_{4'}$; 7.90- 7.97 (m, 5H) $H_{4,4''}$, $HTpy_{4,4''}$, H_{thiop}; 7.46 (d, 1H, J= 4.0 Hz) H_{thiop}; 7.41 (d, 2H, J= 5.0 Hz) $H_{6,6''}$; 7.35 (d, 2H, J= 4.9 H) $H_{6,6''}$; 7.14-7.19 (m, 4H) $H_{5,5''}$, $HTpy_{5,5''}$.
EM75 and EM99 medlycot.021

L5



L4 (0.50 g, 1.27 mmol), TIPSA (0.36 mL, 1.65 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (5 mol %) and NEt3 (2 mL) were added to DMA (10 mL) in a microwave vial and the mixture was degassed for 10 minutes. The vial was capped and the mixture heated to 120ºC for 90 minutes. The crude mixture was evaporated to dryness and the residue dissolved in MeOH (20 mL). The solution was filtered and water added to the methanolic solution until a white precipitate formed. The precipitate was collected by filtration and dried to give 0.43 g of **L5** as a white solid in 68 % yield.
^{1}H NMR ($CDCl_3$, 250 MHz): 8.73 (2H, d, J= 4.7 Hz) $H_{6,6''}$; 8.65 (2H, s) $H_{3',5'}$; 8.64 (2H, d, J= 9.0 Hz) H3,3''; 7.87 (2H, td, 1.8Hz, 7.7 Hz) H4,4''; 7.63 (1H, d, J= 3.6 Hz) H_{thiop}; 7.36 (2H, m) $H_{5,5''}$; 7.25 (1H, d, solvent overlap) H_{thiop}; 1.13 (21H, overlap of TIPS signals).
EM80 (improved work-up EM98) medlycot_.076

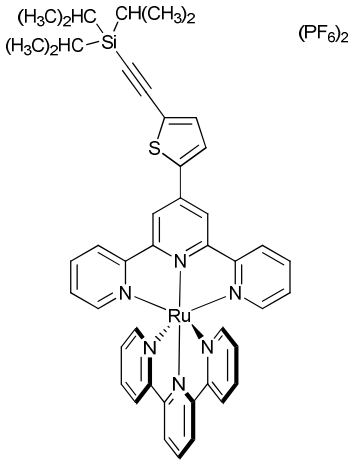
$[Ru(L5)_2](PF_6)_2$



$[Ru(L4)_2](PF_6)_2$ (0.25 g, 0.21 mmol), TIPSA (0.04 mL, 0.16 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (10 mol %) and NEt_3 (5 mL) were added to DMA (10 mL) in a microwave vial and the mixture was degassed for 10 minutes. The vial was capped and the mixture heated to 120ºC for 90 minutes and on cooling precipitated in NH_4PF_6(aq). The precipitate was collected and the crude mixture was dissolved in the minimum acetonitrile and purified by column chromatography (SiO2, MeCN: KNO_3(aq); 10:1. (The separation of the first and second band is difficult and so a long column is required). The 1st red band was collected and the NO_3^- salt was metathesized to the PF_6^- salt and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **$[Ru(L5)_2](PF_6)_2$** as a red solid in 41 % yield.

^{1}H NMR (250 MHz, CD_3CN): 8.88 (s, 4H) $H_{3',5'}$; 8.64 (d, 4H, J= 8.0 Hz) $H_{3,3''}$; 8.07 (d, 2H, J= 3.9 Hz) H_{thiop}; 7.95 (t, 4H, J= 7.3 Hz)) $H_{4,4''}$; 7.54 (d, 2H, J= 3.9)Hthiop; 7.42 (d, 4H, J= 5.5 Hz) $H_{6,6''}$; 7.18 (m, 4H) $H_{5,5''}$; 1.20 (42H, overlap of TIPS signals).
ESMS: $[M-2PF_6]^{2+}$ 546.2.
EM97 medlycot_.084

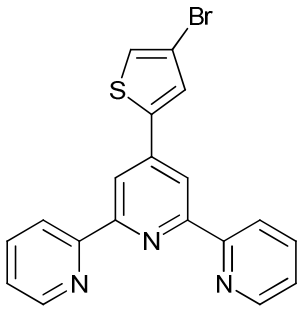
[Ru(tpy)L5](PF$_6$)$_2$



[Ru(tpy)L4](PF$_6$)$_2$ (0.11 g, 0.11 mmol), TIPSA (0.04 mL, 0.16 mmol), Pd(PPh$_3$)$_4$ (5 mol%) and NEt3 (1 mL) were added to DMA (5 mL) in a microwave vial and the mixture was degassed for 10 minutes. The vial was capped and the mixture heated to 120ºC for one hour and on cooling precipitated in NH_4PF_6(aq). The precipitate was collected and the crude mixture was dissolved in the minimum acetonitrile and purified by column chromatography (SiO2, MeCN: KNO_3(aq); 7:1 then increased to 7:1.5. (The separation of the first and second band is difficult and so a long column is required). The 1st red band was collected and the NO_3^- salt was metathesized to the PF_6^- salt and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **[Ru(tpy)L5](PF$_6$)$_2$** as a red solid in 25 % yield.

^{1}H NMR (500 MHz, CD_3CN): 8.88 (s, 2H) $H_{3',5'}$; 8.75 (d, 2H, J= 8.2 Hz) $HTpy_{3',5'}$; 8.63 (d, 2H, J= 8.1 Hz) $H_{3,3''}$; 8.49 (d, 2H, J= 8.1 Hz) $H_{3,3''}$; 8.42 (t, 1H, J= 8.2 Hz) $HTpy_{4'}$; 8.07 (d, 1H, 3.9 Hz) H_{thiop}; 7.93 (m, 4H) $H_{4,4''}$, $HTpy_{4,4''}$; 7.54 (d, 1H, J= 3.8 Hz) H_{thiop}; 7.41 (d, 2H, J= 5.4 Hz) $H_{6,6''}$; 7.34 (d, 2H, J= 5.3 Hz) $HTpy_{6,6''}$; 7.17 (m, 4H) $H_{5,5''}$, $HTpy_{5,5''}$, 1.20 (21H, overlap of TIPS signals).
ESMS: $[M-2PF_6]^{2+}$ 415.2, $[M-PF_6]^+$ 975.1.
EM95A (500 NMR list)

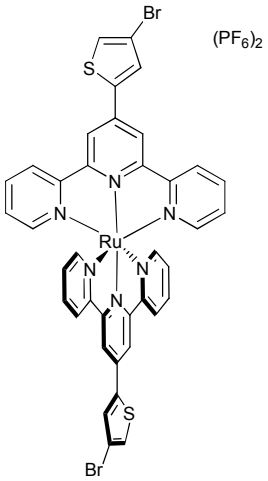
L6



3-Bromo-5-thiophenecarboxaldehyde (4.01 g, 0.021 mol) was added on stirring to a mixture of 2-acetylpyridine (5.0g, 0.041 mol), KOH (2.9 g, 0.052 mol), ammonium hydroxide (25 %, 25 equivalents) in ethanol (200 mL). The solution was stirred at room temperature overnight and then heated to reflux for 5 hours. The mixture was cooled and the precipitate was collected and crystallized from $CHCl_3$/MeOH 1:4 to give a white powder in 45 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): 8.72 (dd, J= 4.8 Hz, 0.8 Hz, 2H) $H_{6,6''}$; 8.63 (d, J= 8.0 Hz, 2H) H3,3''; 8.8.63 (s, 2H) $H_{3',5'}$; 7.87 (td, J= 1.6 Hz, 7.6 Hz, 2H) $H_{4,4''}$; 7.67 (d, J = 1.2 Hz, 1H) H_{th}; 7.36 (ddd, J= 1.2 Hz, 4.8Hz, 3.6 Hz, 2H) $H_{5,5''}$; 7.33 (d, J= 1.2 Hz, 1H) H_{th}.
^{13}C NMR (100 MHz, $CDCl_3$): 111.47, 117.18, 121,72, 124.46, 124.53, 128.66, 137.30, 142.53, 143.22, 149.58, 156.14, 156.68.
EM2 Medlycot.001

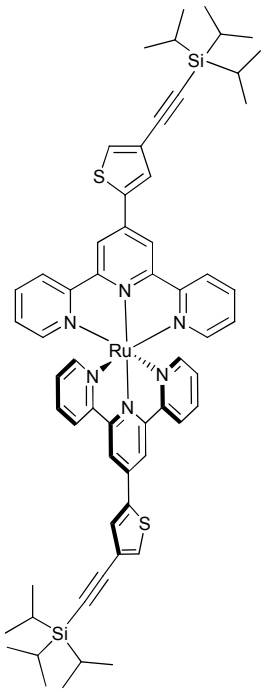
C6



$RuCl_3.3H_2O$ (0.08 g, 0.32 mmol) and $AgNO_3$ (0.16 g, 0.95 mmol) were added to EtOH (15 mL) and refluxed for 30 minutes. **L6** (0.25 g, 0.63 mmol) in 'wet' DMF (20 mL) was added and the mixture refluxed for a further 4 hours. The mixture was purified in the same manner as **$[Ru(L4)_2](PF_6)_2$** to afford **$[Ru(L6)_2](PF_6)_2$** as a red solid in 75 % yield.

^{1}H NMR (400 MHz, CD_3CN): 8.89 (s, 2H) $H_{3'5'}$; 8.63 (d, 2H, J= 7.9 Hz) $H_{3,3''}$; 8.14 (d, 1H, J= 1.4 Hz) H_{thiop}; 7.95 (td, 2H, J= 1.5, 7.7 Hz) $H_{4,4''}$; 7.80 (d, 1H, J= 1.4 Hz) H_{thiop}; 7.42 (d, 2H J= 5.5 Hz) $H_{6,6''}$; 7.19 (m, 2H) $H_{5,5''}$.
^{13}C NMR (100 MHz, CD_3CN): 112.24, 120.46, 125.61, 127.94, 128.55, 131.33, 139.05, 141.01, 142.00, 153.43, 156.50, 158.71.
EM148 medlycot.037

C7



$(PF_6)_2$

^{1}H NMR (400 MHz, CD_3CN): 8.91 (s, 4H) $H_{3',5'}$; 8.65 (d, 4H, J= 8.1 Hz) $H_{3,3''}$; 8.18 (d, 2H, J= 1.3 Hz) H_{thiop}; 7.95 (m, 6H) $H_{4,4''}$, H_{thiop}; 7.41 (d, 4H, J= 5.5 Hz) $H_{6,6''}$; 7.18 (m, 4H) $H_{5,5''}$; 2.09 (s, 6H)H_{TIPSA}; 1.21 (42H, overlap of TIPS signals).

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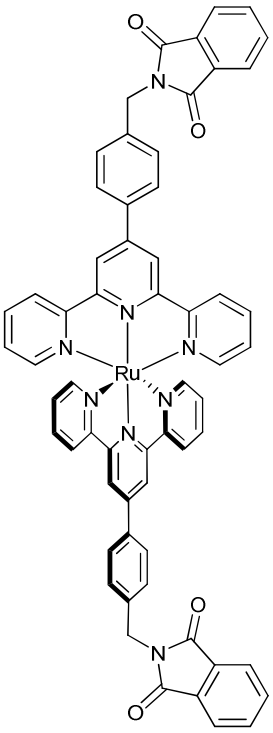
ESMS: $[M\text{-}2PF_6]^{2+}$

EM150 medlycot.043

$[Ru(L8)_2](PF_6)_2$

$(PF_6)_2$

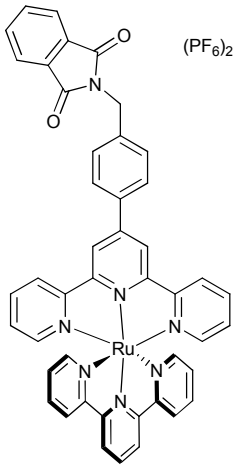


L8 (0.25 g, 0.53 mmol), $RuCl_3.3H_2O$ (0.07g, 0.27 mmol) and $AgNO_3$ (0.14 g, 0.80 mmol) were added to DMF 'wet' (20 mL) and stirred at room temperature. The mixture was heated to reflux for 4 hours, cooled and filtered to remove AgCl. The filtrate was precipitated in NH_4PF_6 (aq) and the precipitate collected. The crude mixture was dissolved in the minimum acetonitrile and injected onto a silica column and eluted with MeCN:KNO_3 (sat) 10:1. The polarity of the eluent was increased to 8:1 and the first red band collected. The NO_3^- salt was metathesized to the PF_6^- salt and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **$[Ru(L8)_2](PF_6)_2$** as a red solid in 13 % yield (reaction looked complete by tlc but poor yield probably as reaction required longer-poor solubility of ligand!).

^{1}H NMR (CD_3CN, 500 MHz): 8.98 (s, 2H) $H_{3',5'}$; 8.61 (d, 2H, J= 8.1 Hz) $H_{3,3''}$; 8.15 (d, 2H, 8.2 Hz) $H_{2''',6'''}$; 7.91-7.92 (m, 4H) $H_{4,4''}$, $2H_{phth}$; 7.84-7.86 (m, 2H) $2H_{phth}$; 7.73, (d, 2H, J= 8.2 Hz) $H_{3''',5'''}$; 7.40 (d, 2H, J = 5.2 Hz) $H_{6,6''}$; 7.16 (m, 2H) $H_{5,5''}$; 5.04 (s, 2H) H_{meth}. ESMS: $[M\text{-}2PF_6]^{2+}$ 519.0. Anal. Calcd. for $C_{60}H_{40}F_{12}N_8O_4P_2Ru_1$. $3H_2O$: C, 52.14; H, 3.35; N, 8.11. Found C 51.94, H 3.26, N 8.46.

EM141 (500 NMR)

[Ru(tpy)L8](PF$_6$)$_2$



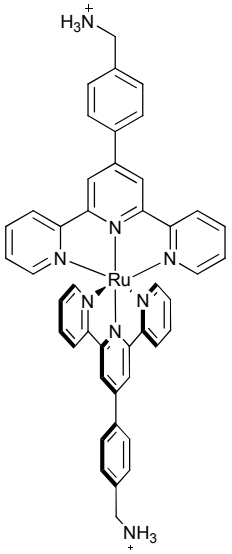
L8 (0.20 g, 0.43 mmol) was added on stirring to a solution of RutpyCl$_3$ (0.19 g, 0.43 mmol) and AgNO$_3$ (0.22 g, 1.28 mmol) in DMF (20 mL). The mixture was heated to reflux in the absence of light for 7 hours, cooled and then filtered to remove AgCl. The filtrate was precipitate in NH4PF6(aq) and the precipitate collected. The crude mixture was dissolved in the minimum acetonitrile and purified by column chromatography (SiO$_2$, MeCN: KNO$_3$(aq); 7:1. The second red band was collected and the NO_3^- salt was metathesized to the PF_6^- salt and the solvent removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallisation from acetonitrile/diethyl ether afforded **[Ru(tpy)L8](PF$_6$)$_2$** as a red solid in 51 % yield.

^{1}H NMR (500 MHz, CD$_3$CN): 8.97 (s, 2H, H$_{3',5'}$), 8.75 (d, 2H, J= 8.1 Hz, Tpy$_{3',5'}$), 8.61 (d, 2H, J= 8.1 Hz, H$_{3,3''}$), 8.49 (d, 2H, J= 8.1 Hz, Tpy$_{3,3''}$), 8.41 (t, 1H, J= 8.1 Hz, T$_{4'}$), 8.16 (d, 2H, J= 7.9 Hz, H$_{2''',6'''}$), 7.92 (m, 6H, H$_{4,4''}$, Tpy$_{4,4''}$, Phth$_{2,5}$) 7.85 (m, 2H, Phth$_{3,4}$), 7.73 (d, 2H, J= 8.1 Hz, H$_{3''',5'''}$), 7.41 (d, 2H, J= 5.4 Hz, H$_{6,6''}$), 7.34 (d, 2H, J= 5.3 Hz, Tpy$_{6,6''}$), 7.16 (m, 4H, H$_{5,5''}$, Tpy$_{5,5''}$), 5.00 (s, 2H, H$_{meth}$).

Anal. Calcd. for C$_{45}$H$_{31}$F$_{12}$N$_7$O$_2$P$_2$Ru. 2H$_2$O: C, 47.88; H, 3.13; N, 8.69. Found C 47.90, H 2.93, N 8.65.

EM127 EM144A (500 NMR)

$[Ru(L9)_2](PF_6)_4$

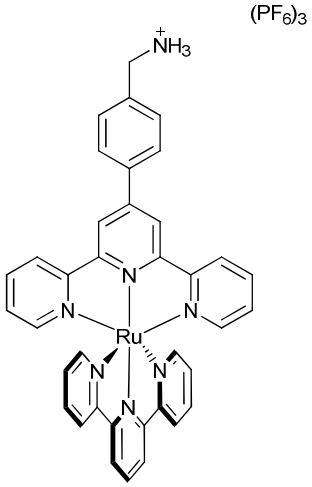


$[Ru(L8)_2](PF_6)_2$ (.05 g, 0.038 mmol) in MeCN (5 mL) was added to hydrazine (0.4 mmol) in ethanol (20 mL) and the mixture was argon bubbled through for ten minutes. The solution was stirred at room temperature for 3 days and then precipitated in NH_4PF_6(aq). The precipitate was collected and dissolved in the minimum acetonitrile and again precipitated in diethyl ether, collected and dried to yield **$[Ru(L9)_2](PF_6)_4$** as a red solid in 78 % yield.

^{1}H NMR (CD_3CN, 400 MHz): 9.02 (s, 2H) $H_{3',5'}$; 8.66 (d, 2H, J= 8.1 Hz) $H_{3,3''}$; 8.28 (d, 2H, J= 8.2 Hz) $H_{2''',6'''}$; 7.96 (td, 2H, J= 8.0, 1.3 Hz) $H_{4,4''}$; 7.80 (d, 2H, J= 8.2 Hz) $H_{3''',5'''}$; 7.44, (d, 2H, J= 5.0 Hz) $H_{6,6''}$; 7.19 (m, 2H) $H_{5,5''}$; 4.34 (s, 2H) H_{meth}. ^{13}C NMR (CD_3CN, 100 MHz): 44.27, 122.60, 125.51, 128.47, 129.28, 131.39, 135.17, 138.64, 139.02, 148.20, 153.38, 156.45, 159.02. ESMS: [M^+-PF_6] 923.3, [M^+-2PF_6] 389.5 (only see unprotonated in solution MS). Anal. Calcd. for $C_{44}H_{38}F_{24}N_8P_4Ru_1.3H_2O$: C, 37.38; H, 3.14; N, 7.93. Found C 37.47, H 3.41, N 7.95.

EM141B Medlycot_.118

[Ru(tpy)L9](PF$_6$)$_3$



[Ru(L8)$_2$](PF$_6$)$_2$ (.15 g, 0.14 mmol) in MeCN (5 mL) was added to hydrazine (1.4 mmol) in ethanol (20 mL) and the mixture was argon bubbled through for ten minutes. The solution was stirred at room temperature for 3 days and then precipitated in NH_4PF_6(aq). The precipitate was collected and dissolved in the minimum acetonitrile and again precipitated in diethyl ether, collected and dried to yield **[Ru(tpy)L9$_2$](PF$_6$)$_3$** as a red solid in 79 % yield.

^{1}H NMR (250 MHz, CD_3CN): 9.01 (s, 2H, $H_{3',5'}$), 8.76 (d, 2H, J= 8.1 Hz, $Tpy_{3',5'}$), 8.64 (d, 2H, J= 7.8 Hz, $H_{3,3''}$), 8.50 (d, 2H, J= 8.1 Hz, $Tpy_{3,3''}$), 8.41 (t, 1H, J= 8.1 Hz, $T_{4'}$), 8.17 (d, 2H, J= 8.3 Hz, $H_{2''',6'''}$), 7.93 (m, 4H, $H_{4,4''}$, $Tpy_{4,4''}$) 7.85 (m, 2H, $Phth_{3,4}$), 7.73 (d, 2H, J= 8.3 Hz, $H_{3''',5'''}$), 7.43 (d, 2H, J= 4.8 Hz, $H_{6,6''}$), 7.35 (d, 2H, J= 4.8 Hz, $Tpy_{6,6''}$), 7.17 (m, 4H, $H_{5,5''}$, $Tpy_{5,5''}$), 4.02 (s, 2H, H_{meth}) (NH_3 was not observed).

Anal. Calcd. for $C_{37}H_{26}F_{18}N_7P_3Ru$. $2H_2O$: C, 38.82; H, 2.99; N, 8.57. Found C 38.69, H 3.00, N 8.62.

EM144B

Medlycot_.103

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