Photoactivated nano-systems: self-assembled nano-scaled systems through cyclodextrin complexation, functionalized nanoparticles and hydrogen evolution
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In this chapter we describe the photophysical properties of a novel family of ruthenium and iridium complexes determined with steady-state and time-resolved spectrophotometric methods. The luminescence of the ruthenium complexes (at 610-615 nm) is not affected by oxygen, has a low quantum yield (~0.005) and short lifetime (20-30 ns). This is ascribed to the presence of a metal centered triplet state ($^3\text{MC}$) which for complexes with the new $\text{pytl}$ (pyridine-triazole) ligand is close in energy to the $^3\text{MLCT}$ state and allows decay of the excited state via a non-radiative pathway. The luminescence of $[\text{Ir(ppy)}_2(\text{pytl-ada})]\text{Cl}$ (at 475 nm) is oxygen sensitive and has a high quantum yield (0.23) and long lifetime (1000 ns); both are significantly enhanced (0.54, 2800 ns) when the $\text{pytl}$ is appended with a cyclodextrin in $[\text{Ir(ppy)}_2(\text{pytl-CD})]\text{Cl}$. There are significant differences between the quantum yields of the two separate diastereoisomers of this complex, attributed to a different interaction of the chiral cyclodextrin substituent with the $\Delta$ or $\Lambda$ isomer of the metal complex (“chiral hat” effect). The longer lifetime for the iridium complexes indicates that the excited state is a mixture of $^1\text{LC}$ and $^3\text{MLCT}$ states in this case. The (formally negatively charged) phenyl and neutral pyridine parts of the ppy ligand are expected to contribute most to the HOMO and LUMO of the complex respectively. Substitution of the phenyl with fluorine as in $[\text{Ir(Fppy)}_2(\text{pytl-ada})]\text{Cl}$ shifts the emission of the complex to the blue (450 nm).
4.1 Introduction

The Cu-catalyzed dipolar \([3+2]\) cycloaddition, known as ‘click’ chemistry,\(^1\) involves the efficient formation of 1,2,3-triazole rings by coupling terminal alkynes and azides, and can be used to synthesize a bidentate pyridine-triazole ligand, 1-substituted 4-(2-pyridyl)1,2,3-triazole (pytl, see scheme 1).\(^2\) This novel approach is extremely flexible; it allows in principle the functionalization of any azide-appended molecule with this ligand, as has been shown for 4-butoxyphenylazide\(^4\) as well as for relatively small\(^5\) and large carbohydrates, such as cyclodextrins.\(^6\)

Cyclodextrins (CDs) are well-known cyclic oligosaccharides that can form inclusion complexes with a variety of hydrophobic substrates in aqueous solution, such as...
Novel Ru(II) and Ir(III) complexes
adamantane-carboxylic acid, and have been widely applied as supramolecular building blocks in various areas\textsuperscript{7,8,9,10,11,12} including photoactivated energy and electron transfer.\textsuperscript{13,14} By applying click chemistry to 2-ethynylpyridine and monoazido-\textbeta-CD the cyclodextrin-appended triazole-pyridine (\texttt{pytl-\textbetaCD}, scheme 4.3) could be readily prepared\textsuperscript{15} and complexed with metal ions. Complexes of Ru\textsuperscript{16} and Ir\textsuperscript{17} have received increasing attention in recent years because of their promising photophysical properties; they have been described as efficient photo-sensitizers, applied in the manufacture of optical devices, and as components for OLEDs. Because of our interest in such properties\textsuperscript{15} we prepared and characterized a series of heteroleptic octahedral complexes containing one substituted pyridine-triazole ligand. In particular we report the properties of such complexes with Ru and Ir in which the coordination sphere is completed by bipyridine (bpy) for Ru(II) and phenylpyridine (ppy) for Ir(III), giving the complexes $[\text{Ru}(\text{bpy})_2(\text{pytl-\textbetaCD})]X_2$ (\texttt{Ru(bpy)$_2$(1)}$X_2$, $X = \text{Cl, TFA})$ and $[\text{Ir}(\text{ppy})_2(\text{pytl-\textbetaCD})]\text{Cl}$ (\texttt{Ir(ppy)$_2$(1)}$\text{Cl}$), respectively and the corresponding adamantyl and methyl functionalized equivalents.

There are only few examples in the literature of ruthenium complexes with 1,2,3-triazole ligands.\textsuperscript{18} As such, ruthenium complexes derived from ruthenium bis-terpyridine analogues in which one terpyridine ligand was substituted for a 2,6-(1,2,3-triazole)-pyridine ligand were reported, maintaining the linear symmetry but altering the photophysical properties of the complex. These complexes show similar properties to the parent compounds but present higher energy excited states than for terpyridine derivatives.\textsuperscript{19} This effect has been attributed to the LUMO orbital of the molecule localized on the ligand core, being located at higher energies in the triazole complexes compared to the pure terpyridine compounds.

A number of approaches to increase the emission energy of cyclometalated Ir complexes have focused on the decrease of the HOMO energy while keeping the LUMO energy relatively unchanged. The addition of electron withdrawing groups to the phenyl ring has been used as one way to achieve this goal. The most common withdrawing group used for this purpose is fluoride.\textsuperscript{18} For this reason, we prepared complexes of \texttt{pytl-ada} in which the coordination sphere of Ir was completed either with ppy or its 3,5-bisfluorinated analogue F$_2$ppy.
4.2. Results and discussion

4.2.1. Synthesis of ligands and complexes – general scheme

Applying click chemistry to 2-ethynyl-pyridine and the azide-appended adamantane or -β-CD, we prepared the adamantane/β-CD-appended 1-substituted 4-(2-pyridyl)1,2,3-triazole (pytl-β-CD, 1 and pytl-ada, 2) and its Ru and Ir complexes. Starting from methyl azide, pytl-Me 3 was also prepared. The synthetic routes to the novel ligands and complexes are shown in scheme 4.3.

Scheme 4.3. Synthesis of the new ligands (pytl-R, with R=1,2 or 3) and subsequent synthesis of the novel ruthenium (II) and iridium (III) complexes.

The synthesis of the ruthenium complexes was completed by reaction of the corresponding ligand (pytl-R) with Ru(bpy)$_2$Cl$_2$. In order to prepare the iridium...
Novel Ru(II) and Ir(III) complexes

complexes the conveniently substituted ligand was reacted with the binuclear cyclometalated iridium precursor, scheme 4.3.
The compounds were synthesized mainly by M. Felici in Nijmegen in the framework of the Uni-Nanocups network.

4.2.2 Photophysical characterization in aqueous solution

The photophysical properties of the iridium and ruthenium triazole complexes were determined with steady state and time resolved spectroscopic methods. It has to be noted that a mixture of diastereoisomers was used as well as separated diastereoisomers in case of the iridium cyclodextrin complexes.

Steady state UV-VIS absorption spectra

The absorption spectra of all complexes show intense bands in the UV region (290 nm) and moderately intense bands in the visible region (350-500 nm) that are typical for ruthenium and iridium polypyridyl complexes.

By comparing the absorption spectra of the ruthenium complexes with that assigned to Ru(bpy)$_3^{2+}$ all bands for the ruthenium complexes can be interpreted. The bands at shorter wavelength than 300 nm belong to the allowed π−π* transitions of the coordinated ligands an in particular to the bipyridine units, and the shoulder that appears at 280 nm appears due to the substitution of one of the pyridine rings for the triazole ring.

All complexes present the typical 1MLCT band between 400 and 500 nm; however while Ru(bpy)$_3^{2+}$ shows a clear maximum at 460 nm in our complexes the coexistence of different ligands at similar energies leads to a set of MLCT bands due to the transition from the metal to the bipyridines or to the pyridine-triazole ligand. This can be interpreted as the result of some influence of the triazole substituted ligand in the 1MLCT transition in the studied molecules.

For the iridium complexes the absorption spectra are shown in the right part of figure 4.1 and resemble those of triazole iridium complexes. The bands in the 250-300 nm region belong again to the allowed intra-ligand π−π* transitions of the phenyl pyridine units and
of the pyridine triazole. The absorption spectra of these iridium complexes also show
$^1\text{MLCT}$ transitions at energies lower than the ligand $\pi-\pi^*$ transitions, in the 300-350 nm
region, partially overlapping with the spin forbidden $^3\text{MLCT}$ which extends above 400
nm.$^{21}$

![Figure 4.1. UV-VIS absorption spectra in water of (left) Ru complexes (solid, $[\text{Ru(bpy)}_2(1)\text{Cl}_2]$; dotted, $[\text{Ru(bpy)}_2(2)\text{Cl}_2]$; dashed, $[\text{Ru(bpy)}_2(3)\text{Cl}_2]$) and (right) Ir (solid, $[\text{Ir(ppy)}_2(2)\text{Cl}]$; dotted, $[\text{Ir(ppy)}_2(1)\text{Cl}]$; dashed, $[\text{Ir(F-ppy)}_2(2)\text{Cl}]$) complexes in water.](image)

Steady state luminescence spectra

The luminescence spectra of the ruthenium complexes show a broad band centered
around 610 nm typical for the radiative decay from a $^3\text{MLCT}$ state (Figure 4.2, left). In
the case of the iridium complexes with the phenyl-pyridine ligands and the substituted
pyridine triazole we can see the resolved vibronic structure typical for these type of
complexes. (Figure 4.2, right). The lowest excited state is also for iridium a $^3\text{MLCT}$ state,
however for such high energy emitting complexes a certain degree of mixing with the
$^3\text{LC}$ is present. Fluorination of the phenyl rings on the ppy ligands lowers the energy of
the HOMO orbital in the molecules. The lowering of the LUMO energy is significantly
less than for the HOMO, resulting in a widening of the HOMO-LUMO gap and leading
to an increase in the excited state energy. This is translated to a blue shift of the emission
when we go from the green emitters (non-fluorinated) to the blue emitters (fluorinated
complexes). In the homoleptic complexes Ir(ppy)$_3$ and the fluorinated homologue
Ir(F$_2$ppy)$_3$ a blue shift of 39 nm occurs.
The quantum yields of emission as well as the emission lifetimes for both Ru and Ir complexes were determined in aqueous solutions under air-equilibrated and deaerated conditions (Table 4.1). It appears that the ptt ligand influences in a different way the excited state of the ruthenium and the iridium complexes.

Ruthenium complexes exhibit rather short lifetimes and low quantum yields and their photophysical properties are therefore not affected by the presence of dioxygen (table 4.1). The lowest excited state most likely involves the bipyridine ligands due to the fact that the LUMO of the triazole is more electron rich and therefore higher in energy than the pyridines. In ruthenium complexes containing 1,2,4-triazole-pyridine ligands, the lowest energy excited electronic states are predominantly bipyridine based.\textsuperscript{22} We believe that also in our case we have the same trend which however is affected by the nitrogen substitution of the triazole, which renders the substituted triazole a worse sigma donor than the 1,2,4 unsubstituted triazole. As a consequence the a smaller ligand field for the pyridine triazole is expected which would cause a lowering of the metal centered triplet states ($^3$MC) which are known to be thermally populated and efficient non-radiative channels for the depopulation of the luminescent $^3$MLCT state.\textsuperscript{23} A similar behavior is also observed in ruthenium complexes with a 1,2,4-triazolopyridine ligand upon protonation of the nitrogen in position 4. Such electronic properties are reflected in the poor emitting properties of our complexes.
Table 4.1. Luminescence lifetimes and quantum yields of emission of the complexes. The solutions were measured in air equilibrated water (air) and argon saturated for degassing by bubbling argon for 20-30 minutes through the solutions (Ar). 1 = pytLβCD, 2 = pytL-ada, 3 = pytL-Me.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ (nm)</th>
<th>Φ (air)</th>
<th>Φ (Ar)</th>
<th>τ (ns, air)</th>
<th>τ (ns, Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)2(1)]Cl2</td>
<td>610</td>
<td>0.0056</td>
<td>0.0056</td>
<td>24.8</td>
<td>24.8</td>
</tr>
<tr>
<td>[Ru(bpy)2(2)]Cl2</td>
<td>615</td>
<td>0.0048</td>
<td>0.0048</td>
<td>19.6</td>
<td>19.6</td>
</tr>
<tr>
<td>[Ru(bpy)2(3)]Cl2</td>
<td>615</td>
<td>0.0062</td>
<td>0.0062</td>
<td>27.4</td>
<td>27.4</td>
</tr>
<tr>
<td>[Ir(ppy)2(1)]Cl</td>
<td>475</td>
<td>0.14</td>
<td>0.54</td>
<td>690</td>
<td>2800</td>
</tr>
<tr>
<td>[Ir(ppy)2(2)]Cl</td>
<td>475</td>
<td>0.076</td>
<td>0.23</td>
<td>435</td>
<td>1000</td>
</tr>
<tr>
<td>[Ir(F2ppy)2(2)]Cl</td>
<td>450</td>
<td>0.071</td>
<td>0.16</td>
<td>480</td>
<td>1100</td>
</tr>
</tbody>
</table>

*For quantum yield measurements ruthenium was excited at 448 nm and iridium at 402. For lifetimes measurements ruthenium was excited at 420 nm and iridium at 380 nm.*

Different situation is with the iridium complexes which display excited state lifetimes in the microsecond range typical for similar iridium complexes, all decaying with monoeponential kinetics. They also show high emission quantum yields. Due to their long lived excited states, related to the triplet character of the emission they are very sensitive to dioxygen that can therefore quench their luminescent excited states. In general the emission energies of luminescent cyclometalated iridium complexes are strongly influenced by the triplet energy of the ligand. The highest occupied molecular orbital (HOMO) is principally composed of p orbitals of the phenyl ring and metal d orbitals of the Ir. The pyridine instead is more electronegative and therefore responsible for the lowest unoccupied molecular orbital (LUMO). In many cases and in particular for blue emitters, the lowest excited state of the complex is best described as an admixture of 3LC and 3MLCT states.

Very interestingly the substitution with a β-cyclodextrin strongly alters the photophysical behavior compared with the adamantyl derivative. In particular it is interesting to notice that even though the emission maximum is unchanged, indicating the same nature and
involvement of coordinated ligand, the emission quantum yield dramatically increases ($\Phi=0.54$). Also the excited state lifetimes change, and in particular becomes longer for both air-equilibrated and deaerated solutions (see table 4.1). Such an elongation of the air-equilibrated lifetime point out to a shielding of the emitting core from dioxygen perhaps caused by the cyclodextrin, which could in some way interact with the phenyl-pyridine ligands, partially retaining the water and the oxygen away from the iridium core. Such effects on phosphorescent molecules inside cyclodextrin complexes have been observed before.\textsuperscript{13,26} The per-methylated cyclodextrin has a very flexible structure when compared to the native cyclodextrin due to the breaking of the internal H bonds of the structure. The primary side of the cavity is very close to the metal center and, due to its flexibility, it could adapt to the complex covering part of the ligands involved in the lowest excited states, with a consequent reduction of non-radiative decays \textit{vide infra}.

\textit{Quantum yields and lifetimes for the separate $\Lambda$ and $\Delta$ isomers of $\left[\text{Ir(ppy)}_2(\text{pyt-bCD})\right] \text{Cl}$}

The mixture of isomers and the individual diastereoisomers behave relatively similar in air-equilibrated solution with luminescence quantum yields close to 14%, table 4.1. In deaerated conditions however we observe clear differences among the mixture and the isomers. The mixture has an intermediate quantum yield relative to the separated diastereoisomers. Isomer B shows a much higher luminescence quantum yield, whereas isomer A shows ca. half of the emission intensity (table 4.2)

Organometallic complexes with metal centers coordinated in a tris-bidentate nature, may inherently possess right- or left-handed chirality (designated $\Delta$ or $\Lambda$ respectively). Although enantiomers should not have different photophysical properties, when chiral ligands/substituents are involved in the expansion of the molecular structure in three dimensional space, it is important to realize that the spatial relationship of the components can influence the nature of the intra- or intermolecular processes observed.

\textit{Table 4.2. Photophysical data for the mixture of isomers and the components from the chromatographic separation. The solutions were measured in air equilibrated solvent (air) and argon saturated for degassing by bubbling argon for 20-30 minutes through the}
solutions (Ar). Alternatively degassing was also achieved with 3 freeze-pump-thaw cycles. The optical density at the excitation wavelength was kept below 0.1

<table>
<thead>
<tr>
<th>complex</th>
<th>$\lambda_{\text{exc}}$ (nm)</th>
<th>$\Phi_{\text{air}}$</th>
<th>$\Phi_{\text{Ar}}$</th>
<th>$\tau$ (ns, Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(ppy)$_2$(pyt-βCD)]Cl mixture</td>
<td>380</td>
<td>0.14</td>
<td>0.54</td>
<td>2800</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(pyt-βCD)]Cl isomer (A)</td>
<td>380</td>
<td>0.13</td>
<td>0.49</td>
<td>2700</td>
</tr>
<tr>
<td>[Ir(ppy)$_2$(pyt-βCD)]Cl isomer (B)</td>
<td>380</td>
<td>0.14</td>
<td>0.70</td>
<td>2900</td>
</tr>
</tbody>
</table>

As we discussed in the previous section, the substitution of an aliphatic system with the β-cyclodextrin results in a strong elongation of the lifetime and a large increase of emission quantum yields. We have speculated that such effect could be due to a non-covalent interaction of the ppy ligands coordinated to the iridium with the hydrophobic cavity of the covalently attached cyclodextrin.

Scheme 4.4. Model structures of [Ir(ppy)$_2$(1)]Cl. The optimized molecular geometries of complexes show the interaction of the emissive center with the cyclodextrin primary side (top: left, lateral: right). The structures correspond to the Δ iridium complex isomer, modeling has shown an even more obvious interaction between the Λ complex and the cyclodextrin.27

Indeed it is known that cyclodextrins can act simultaneously as first- and second-sphere ligands when covalently attached to a potential guest.28 This can enhance the
photophysical properties of the guest mainly in three ways: i) limiting the molecular
degrees of freedom of the chemical bonds, thus reducing the non-radiative deactivation of
the triplet excited state, ii) changing the micro-environmental polarity, and iii) preventing
the excited state quenching from dynamic collision or oxygen energy transfer.

The observed changes in guest phosphorescence in the presence of cyclodextrin provide
clear evidence that the inclusion complex has formed but it gives limited structural
information on the geometry and mode of inclusion. More data can be obtained from
molecular modeling NMR studies, which can show specific interactions between specific
part of the guest and host. Inspection of a molecular model (scheme 4.4) of our system
reveals that a hydrophobic pocket is formed on the primary side of the cavity due to the
methylation of the hydroxyl groups. Moreover the metal complex with the cyclodextrin
appended is forced to be close to this substituted rim because the covalent link is
relatively short. Preliminary HR-NMR investigations (not shown) on the A (Δ)
diastereoisomer show that there is interaction between the iridium complex and the
primary side of the attached cyclodextrin. The rather large size of the Ir complex
compared to the diameter of β-cyclodextrin cavity, however, would not allow the
formation of a real inclusion complex but instead a ‘semi-inclusion’, for example of the
aromatic ligands. A full account giving the assignments and analyzing the ROESY
contacts in terms of a 3-dimensional structure will be given elsewhere.

An additional effect of the β-cyclodextrin is the large and unexpected difference in the
quantum yields of the two diastereoisomeric forms of the complex [Ir(ppy)2(1)]Cl (Table
4.2). This can be explained by a preferential interaction of the chiral cavity with one of
the enantiomers of the attached metal complex. The inherent chirality of the octahedral
tris-bidentate complex (scheme 4.4) is recognized by the cyclodextrin and probably leads
to a stronger or deeper interaction in the case of one diastereoisomer compared to the
other. One of the chiral complexes fits better into the chiral “hat”. This idea is
corroborated by the example of chiral recognition of helical metal complexes by CD’s
reported by Kano29 who has investigated the interaction of the Ru(phen)3 in water with
cyclodextrins fully carboxylated on their primary side.
Figure 4.3 shows the low temperature luminescence measurements for the ruthenium and iridium complexes at 77K in EtOH:MeOH glassy matrix.

![Graphs showing luminescence spectra](image)

**Figure 4.3.** 77 K luminescence spectra in glassy EtOH:MeOH (1:1) matrix of (left, $\lambda_{\text{exc}}$ 445 nm) ruthenium compounds (solid, $[\text{Ru}(bpy)_2]^2\text{Cl}_2$; dotted, $[\text{Ru}(bpy)_2]^2\text{Cl}_2$; dashed, $[\text{Ru}(bpy)_2]^2\text{Cl}_2$; and (right, $\lambda_{\text{exc}}$ 380 nm) iridium compounds (solid, $[\text{Ir}(ppy)_2]^2\text{Cl}$; dotted, $[\text{Ir}(ppy)_2]^2\text{Cl}$; dashed, $[\text{Ir}(Fppy)_2]^2\text{Cl}$).

A comparison of Figure 4.2 and Figure 4.3 clearly shows that the emission spectra become nicely structured for the iridium and the ruthenium compounds in the low temperature experiments. $[\text{Ir}(ppy)_2]^2\text{Cl}$ and $[\text{Ir}(ppy)_2]^2\text{Cl}$ have spectra that nearly overlap in peak position and relative peak intensities. As expected a difference arises with the fluorinated complex $[\text{Ir}(Fppy)_2]^2\text{Cl}$ which shows a blue shift in the emission. In the case of the ruthenium compounds all three emission spectra are clearly very similar.

In the case of the iridium complexes the vibronic structure corresponds to 1200 cm$^{-1}$ the ring vibrations of the phenylpyridine ligand, confirming the participation of the ligand in the emission.$^{30}$ For the ruthenium complexes the vibronic structure corresponds to 1400 and 1500 cm$^{-1}$ the ring breathing of the bipyridine ligand confirming as well the participation of this ligand in the excited state luminescence emission of the complex.$^{31}$ This confirms the above assumption that the lowest emitting state involves the bipyridine ligands and that the triazole has little or no influence in the energy of the emissive state. The emission
maximum is blue shifted (relative to RT), as expected for charge transfer states and already observed for bipyridine complexes.

From previous work in our group in model complexes [Ir(ppyFF)$_2$(bpy)] the lowest excited state has mostly a metal to bipyridine charge transfer character. The [Ir(ppy)$_2$(bpy)] has a behavior explained by two excited states lying close to each another, one $3^\text{LC}$ and one $3^\text{MLCT}$ in nature. The energy of the latter is much more dependent on the polarity of the surrounding medium than the former. By lowering the temperature the rigidity of the medium increases and the $3^\text{MLCT}$, being less stabilized by the lack of solvent mobility, moves up in energy. If the $3^\text{MLCT}$ state is close enough to the $3^\text{LC}$ state a possible inversion of the lowest excited state is observed. For completely cyclometalated and the [Ir(ppyFF)$_2$(bpy)] complexes, we can certainly assign the low temperature emission to a predominant MLCT state.

Comparison of the homoleptic tris-ppy and heteroleptic complexes where one of the ppy has been substituted by a phenyl pyrazole has been made before. The authors observed a significant decrease in the phosphorescence quantum yield by introduction of the pyrazole ring. In our case we observe a similar decrease of the luminescence efficiency when compared to the tris-ppy complexes. However within our new family of complexes the quantum yield vary as the substituents on the third nitrogen of the triazol change giving to the Ir(ppy)$_2$(I) the highest quantum yield (about 3 times higher) and longest lifetime.
Nanosecond transient absorption measurements

Transient absorption of the iridium the complexes

As discussed before, the excited state properties of the iridium complexes can be described by an admixture of $^3$LC and $^3$MLCT states. Transient absorption spectra of the complexes $[\text{Ir(ppy)}_2(\text{I})]\text{Cl}$, $[\text{Ir(ppy)}_2(\text{II})]\text{Cl}$, and $[\text{Ir(Fppy)}_2(\text{II})]\text{Cl}$ were recorded to further investigate the exact nature of the excited state in air equilibrated water at room temperature. Complexes $[\text{Ir(ppy)}_2(\text{I})]\text{Cl}$ and $[\text{Ir(ppy)}_2(\text{II})]\text{Cl}$ present two absorption bands each at 360 and 450 nm. Both bands decay mono-exponentially with similar lifetimes as observed with time resolved emission suggesting that the emissive and absorbing states are identical. In the case of $[\text{Ir(Fppy)}_2(\text{II})]\text{Cl}$ a similar behaviour is observed; however in this case the transient is formed by only one less defined band between 300 and 500 nm with a maximum at 380 nm. All transient spectra for these complexes show an absorption band tailing into the infrared.

Figure 4.4. Transient absorption spectrum (left) of $[\text{Ir(ppy)}_2(\text{I})]\text{Cl}$ after laser light excitation at 380 nm, with decay kinetics at 360 nm (upper trace right) and 449 nm (bottom trace right). 250 accumulations per frame, 25 frames (only first and uneven numbered frames are shown in the transient spectrum for clarity). 100 ns increment in between frames. Decay at $\lambda = 360 \text{ nm}$, $\tau = 754 \text{ ns}$. Decay at $\lambda = 449 \text{ nm}$, $\tau = 723 \text{ ns}$. 
Ichimura et al. reported for the ortho-metalated complex \( \text{Ir}(\text{ppy})_3 \) the transient spectrum characterized by a band centered at 370 nm with a shoulder around 480 nm and a featureless tail extending to the near infrared region. In our case similar bands appear, which could thus be ascribed to an excited state localized on the ppy ligands.

![Figure 4.5](image)

**Figure 4.5.** Transient absorption spectrum (top) of \([\text{Ir}(\text{ppy})_2(2)]\text{Cl}\) after laser light excitation at 380 nm, with decay kinetics at 357 nm (bottom left) and 449 nm (bottom right). 400 accumulations per frame, 20 frames (only first and uneven numbered frames are shown in the transient spectrum for clarity), 100 ns increment in between frames. Decay at \(\lambda = 357 \text{ nm}, \tau = 428 \text{ ns}\). Decay at \(\lambda = 449 \text{ nm}, \tau = 404 \text{ ns}\). For the ortho-metalated complex \(\text{Ir}(\text{ppy})_3\), the transient spectrum characterized by a band centered at 370 nm with a shoulder at 480 nm and a featureless tail extending to the near infrared region has been reported. In our case similar bands appear, which could thus be ascribed to an excited state localized on the ppy ligands with a MLCT character and the lower energy tentatively assigned to \(T_1-T_n\) transitions. In the case of \([\text{Ir}(\text{Fppy})_2(2)]\text{Cl}\) the presence of the fluorine atoms, which lower the HOMO level, the higher degree of mixing between the MLCT and LC states results in a featureless broad band, figure 4.6.
Chapter 4

Figure 4.6. Transient absorption spectrum (left) of [Ir(F2ppy)2(2)]Cl after laser light excitation at 380 nm, with decay kinetics (inset) at 380 nm. 400 accumulations per frame, 26 frames (only first and odd numbered frames are shown in the transient spectrum for clarity), 100 ns increment in between frames. Decay time at 427 nm, τ = 580 ns.

Transient absorption of the ruthenium complexes

The transient absorption spectra of the ruthenium complexes were recorded in argon saturated water (degassed conditions), again to get more insight in the nature of the excited states. In all three cases the spectra are very similar indicating that the substituents attached to the triazole do not induce significant changes in the excited state absorption properties.

The transient absorption spectrum of Ru(bpy)32+ is very well known and the comparison with our systems can be very useful in assigning the observed bands. Transient absorption spectra show a strong bleaching of ground state absorption upon excitation with a recovery comparable to that obtained from emission lifetime measurements (between 25-30 ns). All of the studied complexes show a strong excited state absorption at about 380 nm that has been identified as the radical anion bpy− absorption, which confirms the assignment of a MLCT involving the bpy as the lowest excited state. We also observed a weak and broad absorption into the near IR region in the new type of complex indicating that the triazole ligand has little but no major contribution to the
excited state, a similar behavior was observed for the 1,2,4-triazolepyridine complexes before.\textsuperscript{24}

**Figure 4.6.** Transient absorption spectrum (top) of $[^{1}\text{Ru(bpy)}_2]^{2+}\text{Cl}_2$ upon 445 nm laser light excitation, with decay at 357 nm (bottom left) and rise at 412 nm (bottom right). 20 frames, 50 accumulations per frame, 10 ns increment per frame. Decay time at 357 nm, $\tau = 29 \pm 2.3$ ns; rise time at 412 nm, $\tau = 25 \pm 1.9$ ns.

The lifetime of this band corresponds well to the excited state lifetimes measured with time resolved luminescence indicating that the absorbing state in the transient spectrum is also responsible for the emission of the excited complex ($^1\text{MLCT}$ state).

### 4.2.3. Inter-component interactions

**Self assembled dyads for energy transfer**

The individual compounds presented in the first part of this chapter can in principle be used for various purposes, like dye sensitized solar cells, LEDs or FETs. Another option is to use them as components in supramolecular systems for directional energy transfer. The formation of self-assembled dyads for photoinduced inter-component processes can be pursued with the systems presented here. Such assemblies formed in aqueous solution
are equivalent to those described in chapter 3 of this thesis and others known from the literature. Interestingly, we have only been able to detect intercomponent interaction in assembly 4, containing the ruthenium as donor and osmium as acceptor. The other three systems in which iridium is envisaged to be the energy donor, no clear signs for photoinduced interactions have been observed.

Scheme 4.5. Studied self-assembled dyads in aqueous solution. The properties of separate compounds are described in the first part of this chapter.

Shown in scheme 4.5 are the dyads studied. The energy transfer from iridium to ruthenium polypyridine complexes has been studied in several examples. The iridium has a triplet state that lies approximately 150 nm (0.75 eV) higher in energy than the ruthenium, making the former the candidate for triplet energy transfer to the latter.

It has to be said here that despite all our efforts we were not able to measure clearly such an energy transfer process from an iridium (III) center to a ruthenium (II) acceptor. In the case of assemblies 4.1 and 4.3 it can be deduced after reading previous sections of this chapter that there is a strong interaction between the iridium chromophoric center and the attached cycloextrin cavity on the primary side. It is possible thus that the cycloextrin is partially occupied by the attached iridium center and does not allow further guest complexation. The cavity has to consequently lose some of its hydrophobicity because of
the presence of the strong electrostatic charge on the complex. This in turn makes the driving force for binding of guest much lower. This effect is not unknown to chemists that work in the field of cyclodextrins, however it is rather difficult to find examples of such behavior in the literature for obvious reasons.36

All iridium complexes studied here present very high luminescence quantum yield and very long lifetimes when compared to the ruthenium energy accepting counterparts present in the dyads. This characteristic property of the iridium complexes is very interesting for several applications but it introduces inherent experimental difficulties in the characterization of the energy transfer processes.

Overlap of luminescence, even if only partial, of the emissive centers is clearly a disadvantage if the properties of the components differ greatly. In the present cases the iridium luminescence overpowers the ruthenium greatly. This makes that even at low concentrations overlap of signal coming from the iridium covers completely the emission from the ruthenium. The recording of signals from the ruthenium in the assembly is thus technically impossible or very difficult. Use of minimal concentrations of iridium and high concentration of ruthenium to favor complexation of the iridium and reduce the interference with the ruthenium luminescence has been studied, but at these concentrations the ruthenium concentration becomes too high for the excitation light to reach the iridium with enough intensity. When the ruthenium concentration is reduced to compensate for this effect, the dyad concentration is also reduced because we depend on the concentration of both components for complexation (see chapter 1).

The experiments on assemblies 4.1-4.4 allow us to condense a summary of properties the individual components have to present as to make not only the energy transfer process but also the monitoring of such a process feasible; an example of this is given in the following section where energy transfer from ruthenium to an osmium complex (assembly 4.4) could be successfully measured.

a) Chromophores emissive states should overlap only partially to allow interference free measurement.
b) The chromophores need to have similar lifetimes/quantum yields to minimize the interferences that arise from the overlap of the luminescent tails and free species in solution.

c) The distance between cyclodextrin and chromophore attached to it has to have an equilibrium value between two factors: too close may change the binding strength to the cavity by exclusion of the hydrophobic effect and too far may prevent any interaction because of the distance.

It is interesting in any case to note here that changes in the molecular structure, e.g. for the $[\text{Ir}({\text{ppy}})_2(1)]\text{Cl}$, can induce very interesting properties as well. As consequence of making the compound less suitable for inclusion experiments because of the proximity of the cyclodextrin, we increase the chromophores quantum yield by a factor of 3, which is in turn interesting for other applications.

Osmium metalloguest communication, triplet energy transfer from a ruthenium $^3\text{MLCT}$ to an osmium $^1\text{MLCT}$ state

**Properties of the osmium guest**

The absorption spectrum of osmium bis-terpyridine complexes is characterized by strong bands in the UV that correspond to $\pi-\pi^*$ transitions within the aromatic ligands. Around 480 nm the $^1\text{MLCT}$ band is located. In this case the $^1\text{MLCT}$ absorption band for Os-adatpy-pytpy (see scheme 4.5 assembly 4.4) appeared at 486 nm with $\varepsilon = 5300 \text{ M}^{-1}\text{cm}^{-1}$ a value relatively low for these kind of compounds. Another characteristic band is centered around 670 nm and has a weak character. This band corresponds to the absorption of the $^3\text{MLCT}$ state of the osmium complex.
Figure 4.7. Absorption spectrum for the Os-adatpy-pytpy complex in air equilibrated aqueous solution.

The lifetime of this compound was measured in deaerated acetonitrile with a streak camera. The result obtained was $\tau = 120$ ns as shown in figure 3B.9. From the streak camera image also the emission maximum can be seen to be centered close to 775 nm.

The properties of the ruthenium polypyridyl complex with the triazole ligand functionalized with cyclodextrin are described in this chapter (vide supra).

Figure 4.8. Luminescence decay profile for Os-tpyada-tpypy in deaerated acetonitrile (left), and luminescence spectrum from streak camera measurement and Infinity laser excitation at 485 nm.

Steady state measurements in the assembly of Ru-(bpy)$_2$-(1) with Os-tpyada-tpypy

Figure 4.9 shows the UV-Vis absorption spectra of the individual components and the supramolecular assembly. It is clear that the spectrum corresponding to the assembly is the sum of the spectra of the individual components indicating no electronic interaction in the ground state. The absorption spectrum of the control experiment were Ru-(bpy)$_2$-(1) was employed did not show a significant difference. The individual luminescence spectra
of the ruthenium and the osmium complexes are also shown. We can see that the position of the $^3$MLCT states give a proper pathway for energy transfer from the higher ruthenium triplet state to the lower lying osmium triplet state.

![Graph](image1)

**Figure 4.9.** UV-VIS absorption (left) and steady state emission (right) spectra of the components of the assembly Ru-(bpy)$_2$-(1) and Os-tpyada-tpypy. Excitation of the complexes at 464 nm.

Figure 4.10 shows the luminescence spectra of the ruthenium and the osmium mixture together with the individual luminescence spectra. The concentration of the individual components is the same as in the mixture. Excitation was at 464 nm, an iso-absorptive point in the overlay of the absorption spectra of the individual ruthenium and osmium complexes.

![Graph](image2)

**Figure 4.10.** Steady state luminescence spectrum of the mixture of Ru-(bpy)$_2$-(1) and Os-tpyada-tpypy in aqueous medium. Excitation at 464 nm. The reduction of the ruthenium emission is significantly stronger than the reduction in the osmium emission in the mixture.
Novel Ru(II) and Ir(III) complexes

The steady state luminescence spectra of separate components and mixture can give us information on the energy transfer process. First the spectra for the Ru-(bpy)$_2$-(I) and Os-tpyada-tpypy were measured. Then a mixture containing the supramolecular assembly (50% of the ruthenium should be bound and 27% of the osmium) in the exact same concentrations as the previous measurement for the separated components was measured. We expect a difference between free components and the assembly shown as a reduction of the emission intensity for both complexes as due to an internal filtering effect of the solution as a consequence of the high concentration of chromophores present. The luminescence of the ruthenium can be used as an internal standard in the mixture because it has regions where no overlap with the osmium luminescence occurs. From the decrease in the ruthenium luminescence due to the filter effect at 615 nm, we calculate that approximately 30% of the luminescence disappears due to the mixture of chromophores (both chromophores absorb in the same regions of the visible spectrum so that no selective excitation is possible, at the employed concentration the optical density of the solution is too high to consider all molecules being excited by the light source for which we need optically diluted conditions). Thus, in the case of the osmium this 30% reduction in the luminescence should be observed as well. We have to account for the overlap of the ruthenium luminescence tail in the infrared. The difference between the calculated number (30% reduction in the luminescence plus the ruthenium tail overlap) and the real luminescence measured is the increase in luminescence due to a triplet energy transfer from the ruthenium to the osmium. From our data we estimate an increase in the osmium luminescence of 15% and that the emission of the ruthenium is quenched accordingly. It must be taken into account that these measurements include an interference coming from free ruthenium emitting in solution and free osmium emitting in solution that have not complexed through the cyclodextrin cavity.

Time resolved SPC measurements

We have observed that the excited state of the Ru-(bpy)$_2$-(I) complex is quenched in the presence of Os-tpyada-tpypy when the latter is used as guest for binding into the cyclodextrin cavity. The graph shown in figure 3B.12 clearly shows that the decay
corresponding to the Ru-(bpy)$_2$-(1) excited state becomes bi-exponential in the presence of the Os-tpyada-tpppy compound. A fast component can be observed of 1.22 ns (36%) for the process of $^3$E$_2$ Ru$\Rightarrow$Os: it indicates triplet energy transfer from Ru-(bpy)$_2$-(1) to Os-tpyada-tpppy with a rate of ca $7.8 \times 10^8$ s$^{-1}$. From the amplitude of the fast component and the initial concentration of the components a binding constant can be deduced of 7000 M$^{-1}$.

Figure 4.11. Comparison of the decay of the Ru-(bpy)$_2$-(1) alone (left trace) and the ruthenium in the assembly (right trace). Concentration of components Ru-(bpy)$_2$-(1) = $7.1 \times 10^{-5}$ M; Os-tpyada-tpppy $\sim 10^{-4}$ M; self assembled complex (K=7000 M$^{-1}$) = $3.5 \times 10^{-5}$ M. As an estimation approximately 50% of Ru should be bound and 27% of Os. The decay profile becomes clearly biexponential indicating an energy transfer process. A fast component for the ruthenium decay can be observed with an amplitude of 36% (right). Excitation at 324 nm.

The assembly of the Ru-(bpy)$_2$-(1) compound with the osmium complex clearly shows a shortening of the ruthenium lifetime indicating an energy transfer process from Ru-(bpy)$_2$-(1) to Os-tpyada-tpppy. This shortening of the lifetime is not observed in the control experiment where Ru-(bpy)$_2$-(3) was used in the mixture with Os-tpyada-tpppy, indicating that this effect is induced by supramolecular interaction due to inclusion of the adamantane tail of the osmium complex in the cyclodextrin cavity of the ruthenium complex. The fast component of 1.22 ns indicates an energy transfer rate of $k=7.8 \times 10^8$ s$^{-1}$ (for a free ruthenium lifetime of 25 ns in deaerated aqueous medium) similar to transfer rates described in the literature for similar systems.$^{38}$
Our measurements did not show a clear rise time for the osmium excited state, due to overlapping of the emissions. The lower response of the detector in the near infrared when compared to the rest of the visible spectrum is also an important factor that complicates the recording of these processes at the ideal wavelengths.

4.3 Conclusions

We have fully characterized a new family of luminescent organometallic complexes with remarkable properties. The novelty lies in the introduction of pytl (pyridine triazole) as third coordinating bidentate ligand. This new ligand reduces significantly the lifetime and luminescence quantum yield in the ruthenium complexes. In the case of iridium cyclometalated complexes the luminescence quantum yield and lifetimes are greatly enhanced. When a β-cyclodextrin is directly attached to the pytl ligand this enhancement is even greater. Moreover, the separation of the diastereoisomers of the Ir(ppy)$_2$(pytl-βCD) complex leads to the observation of marked different photophysical characteristics. This is due to an effect introduced by the cyclodextrin. A more favorable interaction between the primary side of the chiral cyclodextrin and one of the enantiomers of the iridium chromophoric unit (Λ or Δ) is responsible for this observed rim effect. The observed enhanced luminescent properties through the shown structural modifications opens the possibility for further studies in this direction.

The short lifetime of the ruthenium complexes allows a good monitoring of energy transfer processes with other lowly emitting complexes such as Os(tpy)$_2$ analogue. We have been able to observe the triplet energy transfer from Ru(bpy)$_3$(pytl-βCD) to an osmium guest complex that is conveniently functionalized to attach to metal surfaces via chemisorption thanks to a pyridine anchoring group.
The energy transfer rate is in agreement with other systems that show photoinduced processes between ruthenium and osmium. The linearity of this assembly makes it clearly interesting for the formation of linear wires in solution. Furthermore, the possibility of chemisorption on a metal surface through the pyridine unit, opens the possibility of further investigations in the direction of surface/particle functionalization.
4.4 References


[3] We prefer the designation pyt1 for the 1-substituted 4-(2-pyridyl)1,2,3-triazole ligand to the pyt1 coined by Obata et al. (ref. 5), because the latter is already in use for 4-pyridylthioacetate: M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno, F. Uchida, Chem. Commun. 2002, 2156-2157.


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[27] We gratefully acknowledge Marco Felici for providing the images shown in this scheme.


