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From solution to solid state: energy- and electron-transfer in complex materials

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Chapter 3

Electronic energy transfer and electron transfer in dinuclear metal complexes containing meta-substituted phenylene unit

Abstract

The synthesis and photophysical properties of heterometallic dinuclear complexes based on ruthenium and osmium trisbipyridine units, Ru-mPh\(_3\)-Os and Ru-mPh\(_5\)-Os, in which the metal complexes are linked via an oligophenylene bridge connected in meta position, are described. Electronic energy transfer from the excited ruthenium-based component (donor) to the osmium moiety (acceptor) has been investigated using steady state and time resolved spectroscopy. The results obtained for the meta substituted compounds are compared with the analogous systems in which the phenylene spacers are substituted in para position. The mechanism of energy transfer is discussed.

Chapter 3

3.1 Introduction

The investigation and understanding of energy transfer processes in metal complex-based systems has received a lot of attention because of fundamental and applied implications.\textsuperscript{1-13} A great effort has been devoted to the design and study of systems able to collect electronic energy and funnel it to a single chromophore (antenna systems) in order to mimic natural photosynthetic species.\textsuperscript{14-19} Besides the intrinsic absorption properties that the energy collectors must possess, a crucial aspect is the electronic interaction amongst the chromophores in order to have an efficient energy transfer. For systems in which the donor and acceptor pairs are covalently linked, through the so-called "bridging ligand", the structural and electronic properties of the connection play a major role.\textsuperscript{20-26} The possibility to tune the excited state electronic interactions between the donor and acceptor components is related to the spectroscopic properties of the chromophores involved in the photoinduced processes. In a through bond mechanism, the coupling is also strongly dependent on the properties of the bridging ligand.\textsuperscript{27-29} Therefore, the structural and electronic features of the bridge are key factors for the energy or charge transfer processes. The desire to have long range and vectorial photoinduced\textsuperscript{30} processes has pushed the development of systems containing long lived excited state donor units, such as ruthenium polypyridine derivatives, and rigid, modular, conjugated connectors.\textsuperscript{31-33} The acceptor unit must possess lower lying excited states. Often for energy transfer processes, luminescent moieties such as osmium polypyridine complexes have been employed.\textsuperscript{34-36} In many cases, the mechanism for the energy transfer reaction is hard to assign because of the difficulties to construct systems in which it is possible to vary only one parameter at the time, e.g. distance between the donor acceptor moieties, geometry or electronic nature of the bridging ligand, and the lack of easy calculation of the orbital overlap integral. Even in a Förster-type mechanism, in which it is possible to estimate the rate of the process by spectral data, the uncertainty related to the distance between the donor-acceptor units and the difficulties related to an accurate value of the orientation factor often prevent a final attribution of the mechanism.

It was also recently shown,\textsuperscript{37} for electron transfer processes, that even in a through bond interaction, the use of "conducting" spacers could lead to a different mechanism for the photoinduced processes. Going from small bridging ligands to larger systems containing many spacer units, the energy of the lowest unoccupied molecular orbital (LUMO) is lowered and the electronic coupling between the acceptor and the donor is enhanced. Such effect has been observed for systems containing polyphenylenevinylene units between a donor and an
By increasing the number of aromatic units, a switch from superexchange to hopping mechanism has been observed and a consequent reduction of the distance dependence on the rate of the process was reported.

When the bridging ligand consists of aromatic units, an interesting role is not only played by the number of spacers but also by the position of substitution, in order to connect the donor and acceptor moieties. In fact, substitution in ortho, meta, or para position on a phenyl ring could lead to different electronic coupling of the substituents as already demonstrated by Brédas et al. for phenylenevinylene derivatives.

Here we report on the synthesis of heterometallic dinuclear ruthenium/osmium trisbipyridine complexes linked by oligophenylene units (3 or 5) constituting the bridging ligand. In our systems, Ru-mPh₃-Os and Ru-mPh₅-Os, the central phenylene moiety is substituted in meta position (Chart 1). The photophysical properties have been investigated and electronic energy transfer from the excited ruthenium-based component to the osmium center is discussed. The role played by the meta connection, ‘loss in conjugation’, is shown by comparing the novel complexes with the correspondent para substituted compounds.

![Chart 1](image)

*Chart 1.* Schematic representation of the investigated complexes and their abbreviations. The correspondent para systems and the metal-metal distances are also shown.
3.2 Results and Discussion

All the structures of the complexes prepared and investigated, their abbreviations, and the metal-metal distances (r) are depicted in Chart 1. For comparison, the analogous para oligophenylene compounds are also shown. The homonuclear Ru-mPh$_3$-Ru complex has been prepared and studied because it represents an excellent model compound for the heterometallic complexes. It is interesting to notice that the meta substitution results in a shortening of the metal-metal distance due to the bending of the complexes.

3.2.1 Synthesis

The homometallic compound Ru-mPh$_3$-Ru, was synthesized from 1,3-phenylenebisboronic acid (11) and the ruthenium complex 1 in a one-step reaction (Scheme 1).

Scheme 1. Synthesis of the reference compound Ru-mPh$_3$-Ru; (a) DMF, K$_2$CO$_3$, Pd(PPh$_3$)$_4$, T= 80°C

The preparation of the heterometallic complexes was carried out via a multi-step procedure. Due to the low solubility of the polyphenylene units, the general procedure of preparing the free ligand was replaced by the so called ‘chemistry on the complex’.

Using such an approach, the metal complexes (3, 7 and 9) were linked via Suzuki cross-coupling reactions with phenylene units (12 and 13) in order to obtain the desired number of spacers (Scheme 2).
The last cross coupling with the bipyridine boronic acid (14) leads to the products 4 and 10 having a free chelating ligand to coordinate a second metal complex. This final complexation was performed in ethylene glycol with bpy\textsubscript{2}OsCl\textsubscript{2} under microwave irradiation (2 x 2 min, 450 W) to yield Ru-\textsubscript{mPh\textsubscript{3}}-Os and Ru-\textsubscript{mPh\textsubscript{5}}-Os. All the details of the synthesis and the characterization of the complexes are reported in the experimental section.

Scheme 2. Synthesis of Ru-\textsubscript{mPh\textsubscript{3}}-Os and Ru-\textsubscript{mPh\textsubscript{5}}-Os: (a) DMF, K\textsubscript{2}CO\textsubscript{3}, Pd(PPh\textsubscript{3})\textsubscript{4}, 90 °C, (b) ICl, CH\textsubscript{2}Cl\textsubscript{2}, 0 °C, (c) ethylene glycol, microwave irradiation, 450 W.
3.2.2 Photophysical properties

All the photophysical measurements were performed in aerated acetonitrile solution and the most relevant data are reported in Table 1.

Table 1. Room temperature absorption and emission data in acetonitrile solutions

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Absorption</th>
<th>Luminescence 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{max}$ (nm) ($c \times 10^3$ Lmol$^{-1}$ cm$^{-1}$)</td>
<td>$\lambda_{max}$ (nm)</td>
</tr>
<tr>
<td>Ru-mPh$_2$-Ru</td>
<td>290 (130), 326 (45), 455 (3.1)</td>
<td>626</td>
</tr>
<tr>
<td>Ru-mPh$_2$-Os</td>
<td>290 (141), 325 (56), 455 (31), 600 (3)</td>
<td>630</td>
</tr>
<tr>
<td>Ru-pPh$_2$-Os</td>
<td>290 (145), 333 (68), 455 (31), 600 (3)</td>
<td>629</td>
</tr>
<tr>
<td>Ru-mPh$_2$-Os</td>
<td>290 (130), 324 (46), 457 (34), 600 (3)</td>
<td>-</td>
</tr>
<tr>
<td>Ru-pPh$_2$-Os</td>
<td>290 (131), 342 (54), 457 (34), 600 (3)</td>
<td>620</td>
</tr>
<tr>
<td>Ru-pPh$_2$-Os</td>
<td>290 (126), 345 (57), 456 (31), 600 (2.9)</td>
<td>617</td>
</tr>
<tr>
<td>Ru-pPh$_2$-Os</td>
<td>290 (138), 347 (74), 457 (34), 600 (3.1)</td>
<td>621</td>
</tr>
</tbody>
</table>

a- UV/visible absorption spectroscopy

The UV/visible absorption spectra of the meta and para complexes are shown in Figure 1. The spectra show intense absorption bands at 290 nm attributed to the $\pi-\pi^*$ transitions involving the bipyridine ligands coordinated to the metal ions. Also in the UV region (between 320 and 350 nm), intense bands are observed due to the $\pi-\pi^*$ transitions of the phenylene spacers. As expected, these bands shift to lower energy upon increasing the number of phenyls. In fact, the conjugation increases with the number of units until the effective conjugation length is reached. The absorption spectra of the para metal complexes show a very minor red-shift going from four to five phenylenes. This indicates that the effective conjugation length is already almost reached with five spacer units. It is interesting to note that the 320-350 nm bands for the meta complexes are blue shifted compared to the para analogs. This effect is again related to the conjugation of the phenylene bridge. It is known that for meta substitution the electronic coupling between adjacent phenyls is lower than for the correspondent para systems.
substituted complexes (Chart 1), one can imagine that the complexes with three, Ru-\textit{m}Ph\textsubscript{3}-Os and five Ru-\textit{m}Ph\textsubscript{5}-Os phenylenes are constituted by two "isolated" metal trisbipyridine parts, each substituted with two and three phenylene units respectively. Therefore, the absorption due to the \(\pi-\pi^*\) transitions located on the phenylenes, assuming that the \textit{meta} substituted phenyl acts as an insulator, should mirror this effect and a biphenyl-type absorption should be expected. The absorption maxima of the phenylene units for Ru-\textit{m}Ph\textsubscript{3}-Os and Ru-\textit{m}Ph\textsubscript{5}-Os are 325 nm and 333 nm, respectively, while for Ru-\textit{p}Ph\textsubscript{2}-Os, Ru-\textit{p}Ph\textsubscript{3}-Os and Ru-\textit{p}Ph\textsubscript{5}-Os they are 324 nm, 342 nm and 347 nm, respectively. Therefore, the \textit{meta} complexes (Ru-\textit{m}Ph\textsubscript{3}-Os and Ru-\textit{m}Ph\textsubscript{5}-Os) are more similar to the corresponding \textit{para} complexes containing only 2 and 3 phenylene spacers, respectively (Ru-\textit{p}Ph\textsubscript{2}-Os and Ru-\textit{p}Ph\textsubscript{3}-Os). The insulating effect of the \textit{meta} substitution was already described for other conjugated systems by Brédas \textit{et al.}\textsuperscript{38} and very recently for dinuclear complexes by Vos \textit{et al.}\textsuperscript{26}

![Figure 1. UV/visible absorption spectra of Ru-\textit{p}Ph\textsubscript{2}-Os (---), Ru-\textit{m}Ph\textsubscript{3}-Os (--), Ru-\textit{p}Ph\textsubscript{3}-Os (\ldots), Ru-\textit{m}Ph\textsubscript{5}-Os (---) and Ru-\textit{p}Ph\textsubscript{5}-Os (---) recorded in acetonitrile solutions.]

In the visible region, the \(^1\)MLCT bands of the ruthenium and of the osmium moieties are observed. The ruthenium band is centered at 450 nm while the transitions for the osmium-based component fall at lower energy, at about 480 nm (Figure 1). As for any osmium trisbipyridine compound, a weaker broad band around 600 nm (\(\varepsilon = 3000\ \text{Lmol}^{-1}\text{cm}^{-1}\)) is observed. Such absorption is due to spin-forbidden transitions from the ground to the lowest \(^3\)MLCT excited states. Because osmium is a heavy metal, these transitions are partially allowed due to the strong spin-orbital coupling.\textsuperscript{34} The MLCT transitions are not affected by \textit{meta} versus \textit{para} substitutions since, in any case, the electronic coupling between the terminal metal units is very weak.
Figure 2. UV/visible absorption spectra showing the isosbestic point at 446 nm for monomeric ruthenium (---) and monomeric osmium (---) proving that, at the excitation wavelength of 450 nm, 50% of the light is absorbed by the ruthenium moiety and 50% by the osmium moiety in the Ru-mPh3-Os (—) complex.

b- Steady state luminescence

All the compounds investigated show two broad structureless emissions centered at about 630 nm and at 750 nm from the two metal-based units (Figure 3).

Figure 3. Room temperature emission spectra of Ru-mPh3-Ru (---)(divided by 10), Ru-mPh3-Os (——) and Ru-mPh5-Os (---) in acetonitrile solutions. All the compounds have the same absorbance at the excitation wavelength (λex = 450 nm).

The high energy emission band is due to the ruthenium based component while the lower energy band is attributed to the osmium-based ^3MLCT emission. By comparison with
the homometallic compound (Ru-\(m\)Ph\(_3\)-Ru), it can be easily seen that the ruthenium centered emission in the heterometallic compounds is strongly quenched (more than ten times for Ru-\(m\)Ph\(_5\)-Os and more than one hundred times for Ru-\(m\)Ph\(_3\)-Os). Such a quenching is accompanied by a sensitization of the osmium emission that has the same emission quantum yield than the homometallic Os-pPh\(_{10}\)-Os (\(\phi = 4.2 \times 10^{-3}\)). This spectroscopic behavior can be easily interpreted as an efficient energy transfer from the excited ruthenium based component (donor) to the lowest excited state located on the osmium moiety (acceptor). In order to have a quantitative analysis of the process, the emission spectra were recorded by exciting at 450 nm, where 50% of the light excites the ruthenium component and 50% is absorbed by the osmium unit (in fact, from the absorption spectra of the homometallic and heterometallic compounds, an isosbestic point is obtained at 446 nm indicating that, at this wavelength, the light energy absorbed by the two chromophores is the same, see Figure 2). The residual ruthenium emission from the longest dinuclear compound has a much higher quantum yield than the shorter molecule. This is in good agreement with different distances between the donor-acceptor pair (21.4 Å for Ru-\(m\)Ph\(_3\)-Os and 28.2 Å for Ru-\(m\)Ph\(_5\)-Os, see Chart 1). By increasing the distance between the two metal centers, the electronic coupling decreases and the energy transfer is slowed down. However, as will be discussed in the next section, since a through-bond superexchange mechanism is responsible for the energy transfer process, the meta versus para position on the substitution of the phenylene units plays the most important role in reducing the electronic coupling between the metal units.

In order to evaluate the rates of the energy transfer process, time-resolved emission and transient absorption spectroscopy were performed on the complexes.

c- Time resolved spectroscopy

The luminescent excited state lifetimes of all the complexes were determined by single photon counting or streak camera techniques and the results are summarized in Table 1. For Ru-\(m\)Ph\(_5\)-Os, the ruthenium based component, monitored at 600 nm, has a much shorter excited state lifetime (\(\tau = 14\) ns) than the reference dinuclear complex, Ru-\(m\)Ph\(_3\)-Ru (\(\tau = 205\) ns). Such fast decay of the luminescent state is in good agreement with the emission quantum yield of the ruthenium moiety that is 10 times lower than the quantum yield of the homometallic compound. For the Ru-\(m\)Ph\(_3\)-Os complex, the excited state lifetime of the ruthenium component (\(\tau = 780\) ps) is even shorter than for the Ru-\(m\)Ph\(_5\)-Os complex. The
luminescent excited state of the ruthenium component is quenched by the low-lying excited state of the osmium component (see Figure 4a) that for the Ru-\textit{m}Ph\textsubscript{3}-Os is populated with a time constant, risetime, of 700 ps (Figure 4b). The excited osmium unit then decays within 43 ns to the ground state in both complexes (the same excited state lifetime was also found for \textit{para} substituted complexes). The energy transfer process for both complexes is thermodynamically allowed ($\Delta G = -0.38$ eV, see Figure 4a). As expected, the rate of the energy transfer depends on the distance between the two chromophores. The rate is about 20 times faster for the shorter complex Ru-\textit{m}Ph\textsubscript{3}-Os than for Ru-\textit{m}Ph\textsubscript{5}-Os (see Table 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{(a): Simplified energy scheme of the states involved in the processes. (b): Decay of the ruthenium-based component (780 ps) and risetime (700 ps) monitored on the osmium-based component, for Ru-\textit{m}Ph\textsubscript{3}-Os in air-equilibrated acetonitrile ($\lambda_{ex} = 324$ nm).}
\end{figure}

A comparison with the \textit{para} substituted complexes Ru-\textit{p}Ph\textsubscript{3}-Os and Ru-\textit{p}Ph\textsubscript{5}-Os reveals that the photoinduced processes are, at least, one order of magnitude slower for the \textit{meta} complexes. Such behavior already suggests that a Förster-type energy transfer mechanism can be ruled out. In fact, the spectral overlap for the ruthenium-osmium pair is reasonably good, and of course is the same for both series of complexes since the absorption of the acceptor and the emission properties of the donor are not affected by the substitution position of the phenylene spacer. On the other hand the distance between the donor and acceptor pairs in the case of the \textit{meta} complexes is smaller than the correspondent \textit{para} compounds due to the bending of the bridging ligand (see Chart 1). Therefore, for a pure Förster energy transfer process, on the basis of distance dependence and spectral overlap integral, the rates of the \textit{meta} complexes should be faster than for the linear \textit{para} analogues.

The energy transfer rate \textit{via} a Förster-type mechanism can in fact be calculated using equation 1:

$$k_{en} = \frac{1}{\tau''} (\frac{R0}{r})^6$$

(Eq1)

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where $\tau^*$ is the decay time of the donor without acceptor, $R_0$ is the critical Förster radius and $r$ is the donor-to-acceptor distance\textsuperscript{49} (see Chart 1).

To calculate the Förster distance $R_0$, the simplified equation (2) can be applied:

$$R_0^6 = \frac{(8.8 \times 10^{-25} K^2 \Phi^6)}{(n^4 \tau^* k_{on})} \quad \text{with} \quad J_F = \int F(v) \epsilon(v) v^4 dv \quad (\text{Eq2})$$

where $n$ is the refractive index of the medium, $\Phi^6$ is the quantum yield of the donor in the absence of the acceptor, $K$ is the orientation factor (considered as 2/3) and $J_F$ is the overlap integral of the donor emission and the acceptor absorption.

From the experimental spectroscopic data, $R_0$ was estimated to be about 36 Å in our systems. In such a case, the energy transfer rate, calculated by the Förster-type mechanism, can be estimated to be $1.2 \times 10^8 \text{ s}^{-1}$ and $2.4 \times 10^7 \text{ s}^{-1}$ for Ru-$m$Ph$_3$-Os and Ru-$m$Ph$_5$-Os, respectively.

The experimental values obtained for the meta systems (see Table 1) are very different from the calculated ones ($1.3 \times 10^9 \text{ s}^{-1}$ for Ru-$m$Ph$_3$-Os and $6.7 \times 10^7 \text{ s}^{-1}$ for Ru-$m$Ph$_5$-Os). Such discrepancies for the energy transfer rates could be explained by the large uncertainty in the estimation of the metal to metal distance in metal complexes in which the lowest excited state is an MLCT involving the bridging ligand. In fact, upon excitation of the donor moiety, the exciton is not localized on the bipyridine but it extends to the phenylene units present as substituents on one of the bipyridine (see also next section of the transient spectroscopy). Therefore, the distance calculated using simple molecular modeling does not reflect the real situation in systems in which delocalization plays a major role. Nevertheless the same argument applies for the para substituted compounds and can be easily seen that the distance between the two metal centers is much smaller in the meta substituted complexes (21.4 Å for Ru-$m$Ph$_3$-Os vs. 24.0 Å for Ru-$p$Ph$_3$-Os and 28.2 Å for Ru-$m$Ph$_5$-Os vs. 32.5 Å for Ru-$p$Ph$_5$-Os) (see Chart 1). Thus, since the lowest excited state is for both families of complexes the same, it is clear that the electronic factors related to the substitution on the phenylene rings must play a major role by influencing the electronic coupling between the two chromophores and therefore the orbital overlap, important for the Dexter mechanism.\textsuperscript{49} A closer analysis of the excited state levels of the bridging ligands suggests that the energy of such states is too high to mix with the donor or acceptor levels. Their direct involvement in the energy transfer process can only be expected in a superexchange mechanism. In such regime, the attenuation factor $\beta$ can be calculated knowing the distance between the two metal units ($r = r' - r_0$, see ref 50) and the rates for the processes ($k_{en}$) using equation (4) derived
from equation (3):

\[ k_{en} = k_{en}(0)\exp(\beta(r' - r_0)) \]  

(Eq3)

\[ \ln(k_{en}) = -\beta r + c, \text{ where } c \text{ is a constant} \]  

(Eq4)

Plotting the logarithm of \( k_{en} \) versus the distance leads to a \( \beta \) value of 0.44 Å\(^{-1}\) (Figure 5). This value is in excellent agreement with the \( \beta \) value obtained for polyphenylene units and for the para complexes (0.50 Å\(^{-1}\)) (Figure 5). It is also interesting to notice that the rates decrease exponentially with increasing distance, as expected in a superexchange regime.\(^{51-53}\)

In previously reported dinuclear systems containing a meta-substituted phenylene bridging ligand, the energy transfer processes were attributed to a Förster-type mechanism.\(^{26}\) In fact, for such systems the lowest excited state involved the peripheral bipyridine since the chelating site residing on the bridging ligand was an electron reach moiety.

**Figure 5.** Logarithm of the energy transfer rate versus donor-acceptor distance (□: para substituted complexes, ○: meta substituted complexes). Attenuation factors \( \beta \) are evaluated by linear fit.

A further confirmation of the energy transfer process and of the involvement of the bridging ligand in the photoinduced excitation was obtained by sub-picosecond absorption transient spectroscopy (Figure 6). For the model complex, **Ru-mPh3-Ru**, in which no energy transfer is possible, upon light excitation (\( \lambda_{exc} = 450 \) nm) the MLCT state is formed resulting in the formation of the radical anion of the bipyridine, visible at about 370 nm and of the bleaching in the visible region 420-480 nm (Figure 6b). A broad absorption band is also observed in the visible region of the spectrum attributed to the partial delocalization of the charge on the phenylene units attached to the bridging bipyridine ligand.\(^{46}\)
Electronic energy transfer and electron transfer in dinuclear metal complexes

Figure 6. Sub-picosecond transient absorption spectra of a) Ru-*Phj-Os and b) Ru-*Phj-Ru, recorded in air-saturated acetonitrile at room temperature (λex = 450 nm). The increment between each frame is 100 ps. Sub-picosecond transient absorption spectra of Ru-*Phj-Os (—) and Ru-*Phj-Ru (---) 800 ps after the laser pulse (λex = 450 nm) are shown in c).

Interestingly, a differential spectrum obtained by superimposition of the spectra of the Ru-*Phj-Ru and Ru-*Phj-Ru under identical experimental conditions shows that, for the meta substituted complex, the visible band is less intense. Even more interestingly, the bipyridine radical anion band is blue-shifted by about 10 nm (centered at 370 nm and 380 nm for Ru-*Phj-Ru and Ru-*Phj-Ru, respectively) as expected for less conjugated systems.

The transient spectrum for the Ru-*Phj-Os complex shows more intriguing features (Figure 6a). In fact, the bleaching due to the formation of the excited state of the ruthenium evolves over time, forming a new band at very close energy. Furthermore, the broad absorption between 550 and 700 nm is now less pronounced and a clear bleaching in the 600-700 nm
region is observed. In order to identify better such small spectral changes, we have performed the same measurement on isoabsorptive solutions of the homometallic \( \text{Ru-}m\text{Ph}_3\text{-Ru} \) and the heterometallic \( \text{Ru-}m\text{Ph}_3\text{-Os} \) compounds under identical experimental conditions (Figure 6c). The spectra shown in Figure 6c were recorded after 800 ps and they clearly show that the MLCT bleaching band due to the ruthenium moiety excitation in the mixed metal complex has a broader and distinguishable feature at 490 nm. From the absorption spectrum (Figure 1), a strong overlap of the ruthenium based component and the osmium transitions between 430 and 490 nm are observed, which prevents a full separation of the two bands. The formation of the osmium excited state can also be evidenced by the bleaching at about 600 nm due to the spin-forbidden MLCT band (see also absorption spectrum, Figure 1). The kinetics for the disappearance of the ruthenium excited state (880 ps) and formation of the osmium luminescent state (800 ps) are in good agreement with what was measured by emission spectroscopy. Therefore, we can conclude that a fast energy transfer \((1.3 \times 10^9 \text{ s}^{-1})\) is observed for the complex \((\text{Ru-}m\text{Ph}_3\text{-Os})\). However, this energy transfer depends on the phenylene substitution as showed by the faster energy transfer rate for the \(\text{para}\) complexes (60 times faster than for the \(\text{meta}\)).

### 3.3 Conclusion

We have prepared and characterized two new heterometallic complexes containing ruthenium and osmium trisbipyridyl moieties connected by an oligophenylene bridge with a central \(\text{meta}\) substituted unit. Their photophysical properties have been investigated using steady state and time resolved spectroscopy. We have shown that energy transfer takes place from the excited ruthenium-based component to the lowest excited state localized on the osmium unit. The rates of the photoinduced processes strongly depend on the distance between the two chromophores. By comparison with the \(\text{para}\) substituted analogue complexes, it has been demonstrated that the bridging ligand plays a key role. In particular, due to the \(\text{meta}\) substitution, the electronic coupling between the energy donor and acceptor moieties decreases. Therefore, slower energy transfer processes have been observed, compared with the \(\text{para}\) substituted complexes, even though the metal-metal distance between the ruthenium and osmium components is smaller for the \(\text{meta}\) than for the \(\text{para}\) compounds. On the basis of these results and by comparison between the Förster calculated rates and the experimental findings, we have attributed the energy transfer to a superexchange mechanism.

We believe that our results are of interest not only for a full understanding of the role played
by key factors such as distance, nature and geometry of the bridging ligands, but also for the
design of systems in which a partial and tunable energy transfer process could lead to
interesting effects such as white light generation from blue and red metal complexes.  

3.4 Experimental part

All chemicals were purchased from Acros or Aldrich and were used as received. All
solvents for the synthesis were purchased and used in analytic grade. For the spectroscopy,
spectroscopic grade solvents were used. Compounds 1, 5 and 14 were synthesized
according to literature procedures. All the purification by chromatography were performed
with a water, methanol, acetonitrile and NaCl mixture (1:4:1:0.1%) (magic mixture).  

Synthesis of Ru-mPhi-Ru

In a 100 mL Schlenk flask, 1 (50 mg, 0.048 mmol), 11 (4 mg, 0.024 mmol) and
K₂CO₃ (40 mg, 0.290 mmol) were mixed in DMF (15 mL) and the solution was degassed. To
the solution, Pd(PPh₃)₄ (6 mg, 0.005 mmol) was added. The reaction was stirred at 80 °C
under nitrogen during 16 hours. The DMF was removed under vacuum and the solid was
purified by column chromatography (silica gel) using magic mixture as eluant. The organic
solvents were evaporated and the complex was precipitated from water by adding NH₄PF₆ (50
mg). The precipitate was filtered, washed with water and diethyl ether and extracted using
acetonitrile. The solvent was evaporated and the orange solid was dried at 80 °C overnight
under vacuum. Yield: 50% (M = 1945.12 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.83 (m, 
2H), 8.74 (m, 2H), 8.59-8.47 (m, 8H), 8.18-7.95 (m, 21H), 7.94-7.66 (m, 15H), 7.50-7.42 (m, 
5H), 7.40-7.30 (m, 5H).

General procedure for the synthesis of complexes 2, 6, and 8

In a 100 mL Schlenk flask, complex-PhX (X = Br or I) (1, 5, 7) (1 eq), 1-
trimethylsilylphenylboronic acid (12 or 13) (1.3 eq) and K₂CO₃ (7 eq) were mixed in DMF
(10-15 mL) and the solution was degassed. A catalytic amount of Pd(PPh₃)₄ was added (0.1
eq). The reaction was heated overnight at 90 °C under nitrogen. The DMF was removed under
vacuum. The solid was purified by column chromatography (silica gel) using magic mixture
as eluant. Finally, the orange solid was dried at 80 °C overnight under vacuum.
2. Yield: 87% (M = 1160.06 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.82 (m, 1H), 8.75-8.72 (d, 3J = 8.4 Hz, 1H), 8.56-8.52 (m, 4H), 8.13-8.06 (m, 5H), 8.01-7.98 (d, 2H), 7.98-7.95 (d, 3J = 8.1 Hz, 2H), 7.90-7.81 (d, 4H), 7.80-7.76 (m, 6H), 7.70-7.64 (m, 1H), 7.63-7.59 (d, 3J = 7.5 Hz, 1H), 7.53-7.47 (t, 3J = 7.5 Hz, 1H), 7.46-7.40 (m, 6H), 0.33 (s, 9H).

6. Yield: 68% (M = 1083.94 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.82 (m, 1H), 8.75-8.72 (d, 3J = 7.5 Hz, 1H), 8.57-8.52 (m, 4H), 8.15-8.06 (m, 5H), 8.03-8.00 (d, 3J = 8.1 Hz, 2H), 7.93-7.88 (m, 3H), 7.87-7.68 (d, 3J = 6.4 Hz, 8H), 7.65-7.63 (dd, 3J = 7.5 Hz, 4J = 1.5 Hz, 1H), 7.55-7.52 (d, 3J = 7.5 Hz, 1H), 7.47-7.40 (m, 5H), 0.34 (s, 9H).

8. Yield: 90% (M = 1236.14 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.83 (m, 1H), 8.76-8.70 (d, 3J = 8.1 Hz, 1H), 8.58-8.53 (m, 4H), 8.16-8.04 (m, 5H), 8.04-8.02 (d, 3J = 8.7 Hz, 2H), 8.00-7.98 (m, 1H), 7.97-7.95 (d, 3J = 8.4 Hz, 2H), 7.90 (m, 4H), 7.85-7.68 (m, 13H), 7.63-7.60 (d, 3J = 7.5 Hz, 1H), 7.47-7.40 (m, 5H), 0.33 (s, 9H).

General procedure for the conversion of the trimethylsilyl group into iodo, (derivatives 3, 7 and 9)

In a 100 mL round bottom flask, 2, 6 or 8 (1 eq) was solubilized in CH₂Cl₂ (45 mL) and the solution was cooled to 0 °C. Iodine chloride (4 eq) in CH₂Cl₂ (5 mL) was then added slowly. The reaction was stirred for 1.5 h at 0 °C, then 2.5 h at room temperature. The reaction was quenched with a 1M solution of Na₂S₂O₅ in water (50 mL). The organic phase was washed with water and the solvent was removed under vacuum. The complex was solubilized in magic mixture, the volume of solvent reduced and the complex was precipitated by adding NH₄PF₆ (50 mg). The orange solid was dried for 3 h under vacuum at 60 °C.

3. Yield: 96% (M = 1137.65 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.81 (m, 1H), 8.75-8.70 (d, 3J = 7.8 Hz, 1H), 8.57-8.51 (m, 4H), 8.16-8.04 (m, 6H), 8.02-7.99 (d, 3J = 8.1 Hz, 2H), 7.89-7.86 (d, 3J = 7.8 Hz, 2H), 7.85-7.70 (m, 9H), 7.52-7.40 (m, 5H), 7.56-7.33 (d, 3J = 7.8 Hz, 1H).

7. Yield: 88% (M = 1213.77 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.83 (m, 1H), 8.76-8.70 (d, 3J = 8.4 Hz, 1H), 8.58-8.53 (m, 4H), 8.16-8.05 (m, 5H), 8.04-8.02 (d, 3J = 8.7 Hz, 2H), 7.98-7.95 (d, 3J = 8.4 Hz, 2H), 7.90-7.70 (m, 12H), 7.47-7.40 (m, 8H), 0.33 (s, 9H).
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9. Yield: 96% (M = 1289.85 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.83 (m, 1H), 8.76-8.70 (d, ²J = 8.1 Hz, 1H), 8.58-8.53 (m, 4H), 8.16-8.06 (m, 5H), 8.04-8.02 (d, 2H), 8.00-7.94 (m, 3H), 7.92-7.90 (m, 4H), 7.88-7.85 (m, 2H), 7.84-7.72 (m, 8H), 7.70-7.54 (m, 4H), 7.47-7.40 (m, 5H).

Synthesis of 4 and 10

In a 100 mL Schlenk flask, 3 or 9 (1 eq), 14 (1.4 eq) and K₂CO₃ (7 eq) were mixed in DMF (10-15 mL) and the solution was degassed. A catalytic amount of Pd(PPh₃)₄ was added (0.1 eq) and the reaction was stirred at 90 °C under nitrogen. The DMF was removed under vacuum. The solid was purified by column chromatography (silica gel) using magic mixture as eluant. Finally, the orange solid was dried at 80 °C overnight under vacuum.

4. Yield: 73% (M = 1242.03 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.81 (m, 1H), 8.80-8.70 (m, 4H), 8.59-8.47 (m, 5H), 8.18-8.06 (m, 5H), 8.04-7.89 (m, 9H), 7.87-7.70 (m, 10H), 7.69-7.61 (m, 2H), 7.50-7.41 (m, 6H).

10. Yield: 78% (M = 1394.23 g.mol⁻¹); ¹H NMR (CD₃CN): δ (ppm) = 8.83 (m, 1H), 8.80-8.70 (m, 4H), 8.59-8.47 (m, 5H), 8.18-8.06 (m, 5H), 8.04-7.86 (m, 19H), 7.82-7.69 (m, 8H), 7.68-7.61 (m, 2H), 7.50-7.41 (m, 6H).

General way for the preparation of bimetallic Ru-ₙPhₙ-Os complexes

Bpy₂OsCl₂.6H₂O (1 eq) and 4 or 10 (1 eq), in ethylene glycol (5 mL), were homogenized in an ultra-sonic bath. Subsequently, the solution was irradiated at 450 W for 2 min in a modified microwave oven and, after a cooling down period, for another 2 min. After evaporating most of the ethylene glycol under vacuum, the complex was solubilized in water then NH₄PF₆ (50 mg) was added to precipitate the complex. The green precipitate formed was filtered and re-extracted with acetonitrile. The compound was purified by column chromatography (silica gel) using magic mixture as eluant. The solution was concentrated under vacuum. Then, the product was precipitated by adding NH₄PF₆ (50 mg) to the aqueous solution. The precipitate was filtered over Celite, washed with water and diethylether and re-extracted with acetonitrile. The dark-green product was dried at 80 °C under vacuum overnight.
**Ru-mPh₃-Os.** Yield: 29% (M = 2034.53 g.mol⁻¹); MS (ESI, m/z): 873.15 (M⁺ –PF₆⁻), 532.77 (M⁺ – 2PF₆⁻), 369.59 (M⁺ – 3PF₆⁻); 'H NMR (CD₃CN): δ (ppm) = 8.83 (m, 2H), 8.74 (m, 2H), 8.59-8.47 (m, 8H), 8.18-8.01 (m, 14H), 7.99-7.94 (m, 4H), 7.92-7.66 (m, 18H), 7.50-7.40 (m, 5H), 7.41-7.30 (m, 5H).

**Ru-mPh₅-Os.** Yield: 61% (M = 2186.73 g.mol⁻¹); MS (ESI, m/z): 948.67 (M⁺ –PF₆⁻), 583.79 (M⁺ – 2PF₆⁻), 401.85 (M⁺ – 3PF₆⁻); 'H NMR (CD₃CN): δ (ppm) = 8.83 (m, 2H), 8.72 (m, 2H), 8.59-8.47 (m, 8H), 8.18-8.06 (m, 10H), 8.04-7.84 (m, 19H), 7.82-7.68 (m, 15H), 7.50-7.42 (m, 5H), 7.40-7.30 (m, 5H).

### 3.5 References


Electronic energy transfer and electron transfer in dinuclear metal complexes


Electronic energy transfer and electron transfer in dinuclear metal complexes

