From ruthenium(II) to iridium(III): 15 years of triads based on bis-terpyridine complexes

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In order to mimic the photosynthetic reaction centre and better understand photoinduced electron transfer processes, a family of compounds has been studied for the past 15 years. These are transition metal complexes, $M(tpy)_2$ where tpy is a $2,2':6',2''$ terpyridine based ligand, bearing on one side a donor group and on the other side an acceptor group. The resulting triad molecules or their two-component reference compounds (donor-$M(tpy)_2$ and $M(tpy)_2$-acceptor) can contain Ru, Os, Rh or Ir as the metal centre and both visible-light non absorbing groups and porphyrins as donor and acceptor groups. This *tutorial review* will briefly present the different systems studied and the reasons that led to the preparation of new systems with improved performances.

1 Introduction

Light, the primary source of energy on earth is both inexhaustible and free but can only be used and directly converted to chemical energy by photosynthetic organisms such as green plants and some bacteria. In some cases the mechanism of light conversion in photosynthetic bacteria has been fully elucidated. In *Rhodopseudomonas viridis*, the initial conversion of light into usable chemical energy occurs in the photosynthetic reaction centre (RC)[1] of the organism, the special pair (SP = a dimer of bacteriochlorophyl) being the primary electron donor. In its excited state, *SP is able to donate an electron to a neighbour bacteriochlorophyl

(B$_A$) inducing a multi-step electron transfer to a bacteriopheophytin (H$_A$) and then to a menaquinone (Q$_A$) and an ubiquinone (Q$_B$) (Scheme 1 *Rhodopseudomonas viridis*). Such a multi-step transfer increases the distance between the hole and the electron, leading to a potential gradient which is converted to a proton gradient across the membrane.[2]

One of the key features of the photosynthesis processes is the efficiency of charge separation: each absorbed photon leads to the transfer of an electron. In the purple bacteria the energy stored is about 1/3 of the energy absorbed, but this is the price to pay in order to obtain such an efficient mechanism. This optimisation can be explained, at least in part, by the rigid geometry and the

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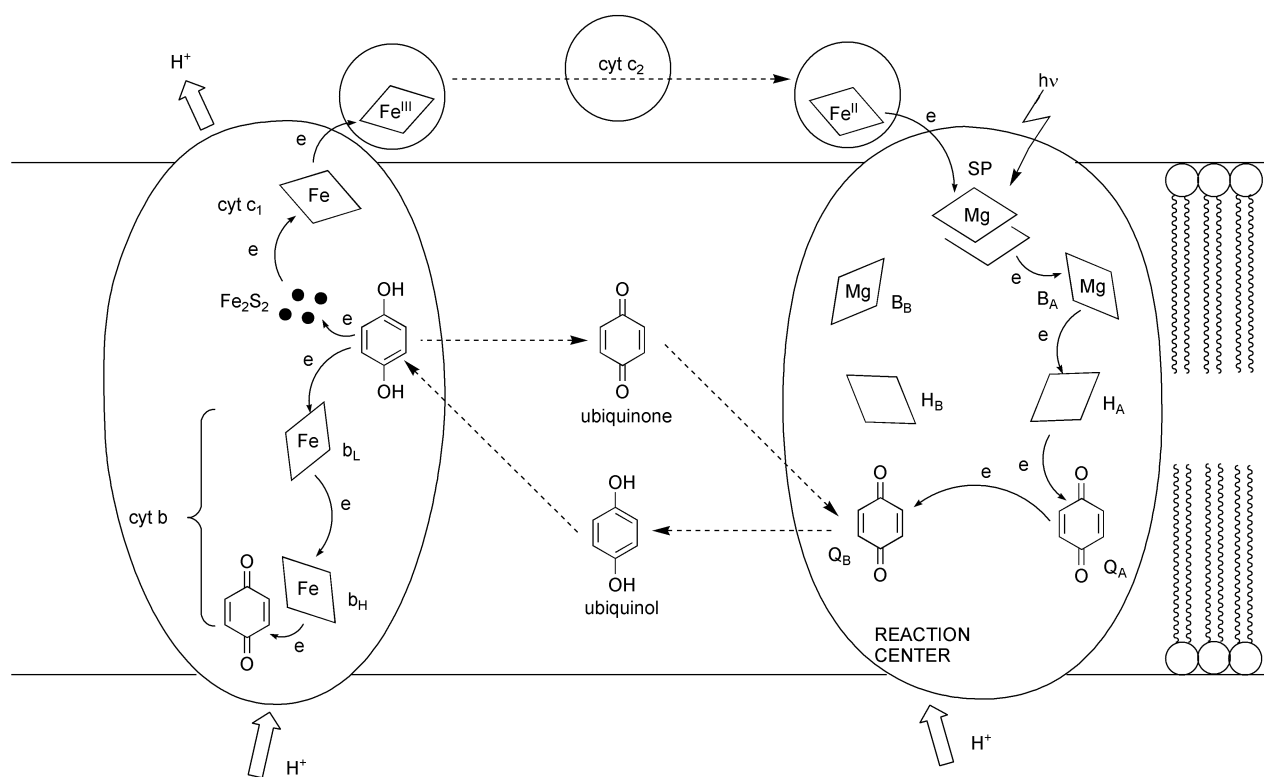
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Scheme 1 Schematic view of the electron pathway in the RC of the purple bacteria *Rhodopseudomonas viridis*.

arrangement of the different chromophores, electron acceptor, and donor groups, which allows facile transfer of the electron. Secondly, the arrangement of the various energy levels as well as redox properties of the groups prevents electron–hole recombination.

The design, synthesis and studies of RC models is important for improving our understanding of electron and energy transfer processes as well as to assess current theories.[3–5] As long-term objective, this may enable the use of light directly as an energy source to generate high energy-content molecules and chemicals of interest.

Over the last 20 years many RC models have been synthesised, which could be classified into three broad categories depending on the kind of photosensitizer used: (i) the photoactive centre (PAC) is a tetrapyrrole pigment (*i.e.* the biomimetic approach),[6–8] (ii) the PAC consists of an aromatic system,[9] or (iii) the PAC is a transition metal complex.[10–13]

One can consider a triad (*i.e.* a model with three components) as a convenient system for modelling a RC, as multi-step transfer of electrons can be induced. Different organisations of donor and acceptor groups and PAC in triads, and their photoinduced processes are summarised in Scheme 2.

In this paper we will focus on systems based on $M(tpy)_2$ molecules (where M can be Ru, Os, Rh or Ir and tpy is 2,2′:6′,6″terpyridine) bearing a donor and an acceptor group. We will present and discuss different triad systems based on these complexes where $M(tpy)_2$ will act sometimes as a PAC and an electron relay and sometimes only as an electron relay.

2 Design of multicomponent systems

A possible way to achieve controlled photoinduced electron or energy transfer in multicomponent systems is to assemble the different building blocks in a well-designed geometric pattern, usually a linear one. Then introduction of rigidity in the system should lead to well known and defined distances and 3D arrangement of the building blocks. In addition, the different components must exhibit photochemical stability, and suitable
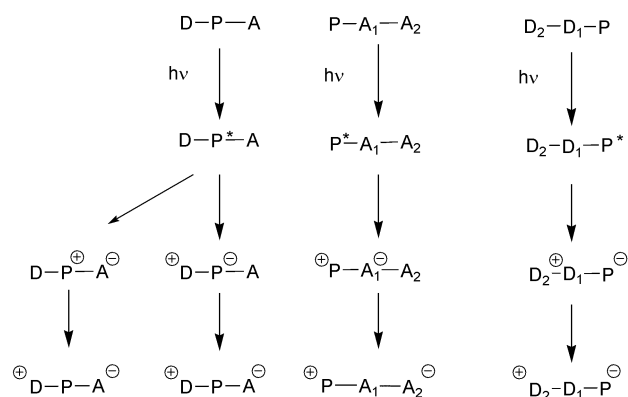
P: photosensitizer, A: acceptor, D: donor, A_1: primary acceptor, A_2: secondary acceptor, D_1: primary donor, D_2: secondary donor.

Scheme 2 Photoinduced processes in triads with different organisation of donor and acceptor groups and photosensitizer.

redox potential. Furthermore, the photosensitizer must absorb visible light leading to an excited state with a long lifetime and able to promote the electron transfer processes. Moreover, the oxidised and reduced forms of the donor and acceptor groups, respectively, should be chemically stable in order to avoid photochemical side-reactions in the charge separated state.

On the basis of their photochemical and photophysical properties, Ru(II) and Os(II) complexes of 2,2′-bipyridine (bpy) and related bidentate ligands are promising photosensitizers.[14,15] However the use of bidentate bpy-like ligands is less convenient than the use of tridentate tpy-type ligands. Indeed bpy leads to optical and geometrical isomers with no control over the geometry of the system (Fig. 1).[16]

Introduction of a tpy substituted at the 4′ position offers the possibility of designing systems in which donor and acceptor groups lie in opposite directions with respect to the chromophore (Fig. 1). In such systems the metal acts: (i) as a template to gather the donor and the acceptor groups, (ii) as an electron relay, (iii) when possible, as a photosensitizer.
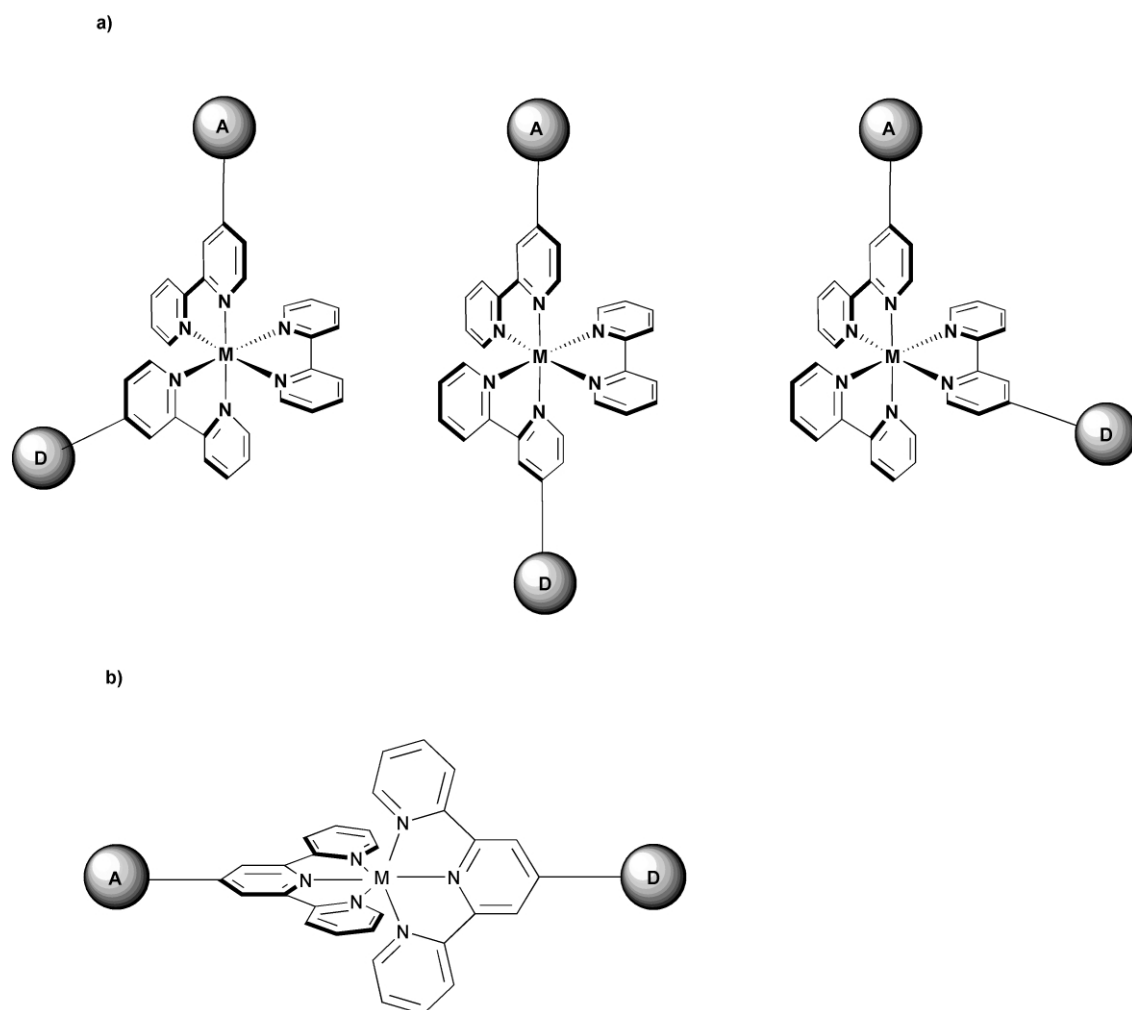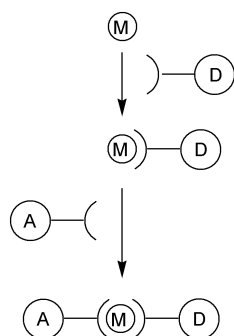
a)

b)

Fig. 1 a) Some isomers obtained with a system based on M(bpy)$_3$. b) The only geometrical isomer obtained with a system based on M(tpy)$_2$ where tpy are substituted in the 4′ position.

A general procedure for the synthesis of these kinds of compounds can be summarised by a sequence (Scheme 3) where at

Scheme 3 General synthetic strategy for the synthesis of systems based on M(tpy)$_2$. The arc of circle symbolises a tpy fragment.

first one tpy is introduced on a chloride salt of the desired metal, followed by addition of a second tpy, usually under harsher conditions due to the difficulty of removing the chloride. Of course this synthetic strategy and the photophysical study can be only envisaged if the metal complexes are resistant to ligand exchange processes, *i.e.* if there are no scrambling reactions.

In addition, the single building blocks (*i.e.* the donor group D, the acceptor group A and the metal centre M(tpy)$_2$) and dyads (*i.e.* D-M(tpy)$_2$ and M(tpy)$_2$-A) have to be synthesised; their study is actually of great help to understand the behaviour of the triad under irradiation.

In order to have a good model for the RC, the components of the arrays should be "independent", *i.e.* it should be possible to describe the system in terms of states localised on the individual components which retain their properties, so that intramolecular processes can be described as processes occurring between states localised on the different components of the complex system. For this reason particular attention has to be paid to the geometry and the nature of the linker between each component.

3 Systems based on Ru(ıı) and Os(ıı)

For these complexes, the acceptor is a methylviologen (MV^{2+}) group with a phenothiazine (PTZ) group as a donor. Due to synthetic problems with the latter group, a more stable triarylamine, di-*p*-anisylamine (DPAA) has been chosen.[17] Other attempts were also performed using a ferrocene (Fc) moiety as a donor group.

3.1 Synthesis

The general method described above is ineffective for the synthesis of complexes bearing a MV^{2+} group because of the instability of this group in the conditions of the subsequent reactions. Instead, a statistical procedure using a "Ruthenium blue solution", a Ru(ıı) precursor prepared *in-situ*, and one equivalent of each tpy permits the ruthenium based triad to be obtained.

General reaction conditions for Os(ıı) compounds are well-known to be harsher than for ruthenium due to the extreme inertia of the Os(ııı)–Cl bond. Fortunately, milder conditions can be used when starting with a potassium-osmate compound, in which the osmium is in the +vı oxidation state, and allow a stepwise

procedure. The introduction of a tpy bearing a Fc moiety onto ruthenium or osmium follows the previously described general procedure.

Three triads were synthesised (Fig. 2) and their photophysical properties investigated under visible light irradiation together with those of the model species (*i.e.* D, A, M(tpy)$_2$, D-M(tpy)$_2$, M(tpy)$_2$-A).

3.2 Processes under visible light irradiation

In general, the study of model systems (*i.e.* dyads and single components) is necessary to understand the mechanism of the more complicated triad systems. It should be recalled that the identification of convenient models is not always trivial, see below.

In these systems, excitation in the spin-allowed MLCT bands of the metal complex leads to population of the lowest energy ^{3}MLCT level after inter-system crossing. At 155 K, the lifetime of the isolated photosensitizers Ru(ttpy)$_2^{2+}$ and Os(ttpy)$_2^{2+}$ are 800 ns and 540 ns respectively (ttpy is 4'-*p*-tolylterpyridine which is a more suitable model for the triads than a simple tpy due to the addition of a phenyl ring). At room temperature the ruthenium complex has a very short lifetime (less than 1 ns) due to the distortion of the

octahedral geometry, resulting in an available low-lying metal-centred (MC) state that favours non-radiative decay of the excited states. This prevents its detection by conventional steady state luminescence spectroscopy and nanosecond transient absorbance; the experiments were therefore performed at low temperature to be able to use all the spectroscopic tools and compare the Ru(II) and Os(II) cases.

For the Ru based D–P–A triad (D = DPAA, A = MV^{2+}), the photoinduced processes are summarised in Fig. 3. The excitation of the photosensitizer leads to a quenched luminescence lifetime of 15 ns as in the corresponding P–A dyad which, compared to a lifetime of 800 ns for the model, yields an electron transfer rate of 6.6×10^7 s^{-1}. The transient spectrum obtained in the triad after excitation of P is different from what is obtained upon excitation of the same unit in P–A, in that the rise of the DPAA$^+$ radical cation absorption band was detected with a lifetime of 18 ns. Therefore after the formation of the first charge separated state, D–P$^+$–A$^-$, the fully charge separated state, D$^+$–P–A$^-$, is formed and subsequently decays with a lifetime of 27 ns.

For the Os-based triad, the first electron transfer quenching process leading to D–P$^+$–A$^-$ takes place with $k = 6.7 \times 10^8$ s^{-1} ($\tau = 1.5$ ns) (Fig. 4). As can be seen from the energy level scheme,

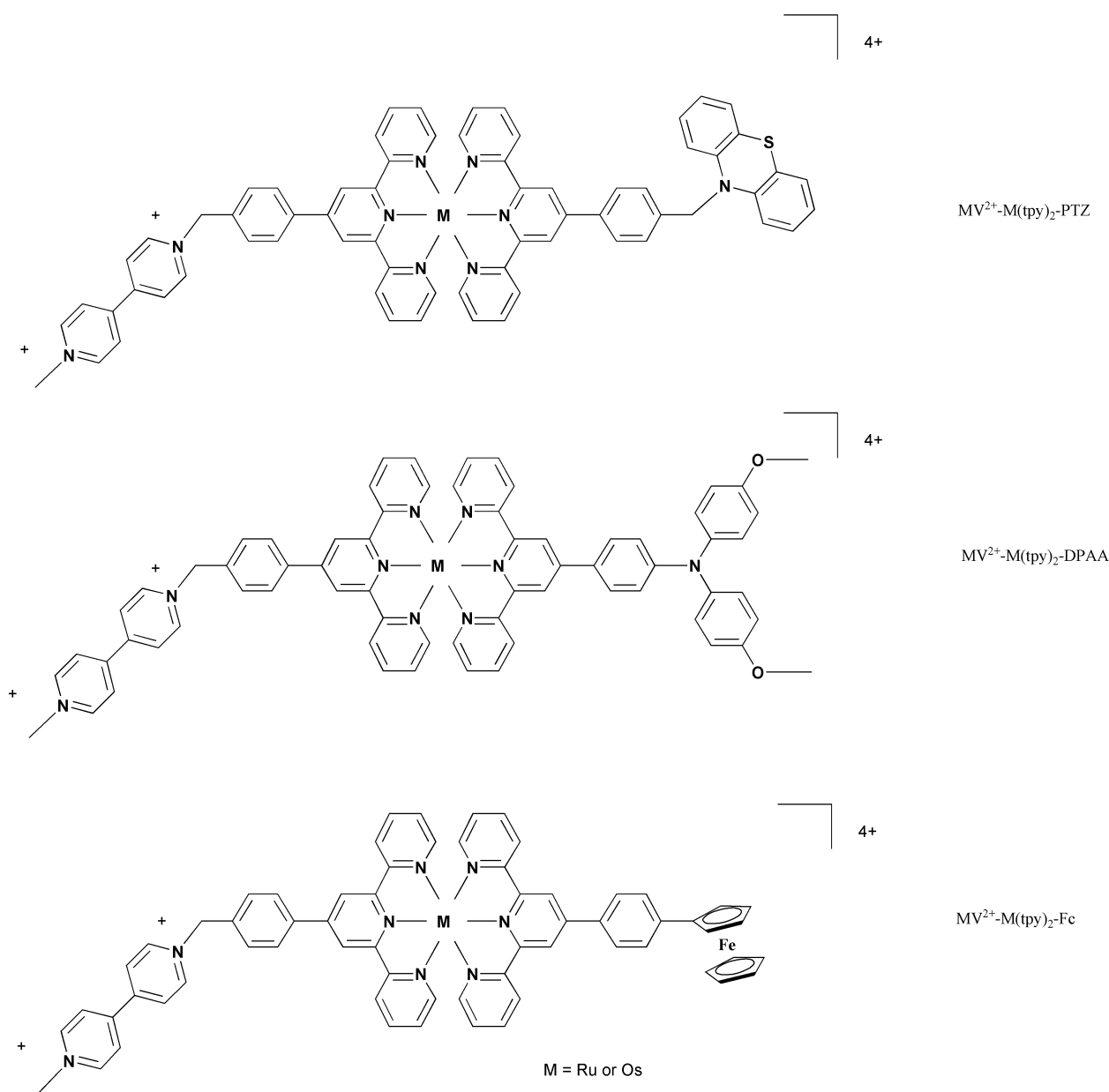Fig. 2 Triads using Ru(tpy)$_2$ and Os(tpy)$_2$ as photoactive centres.
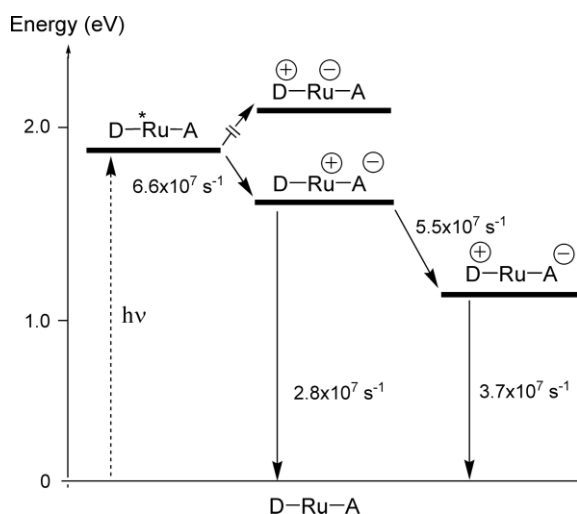
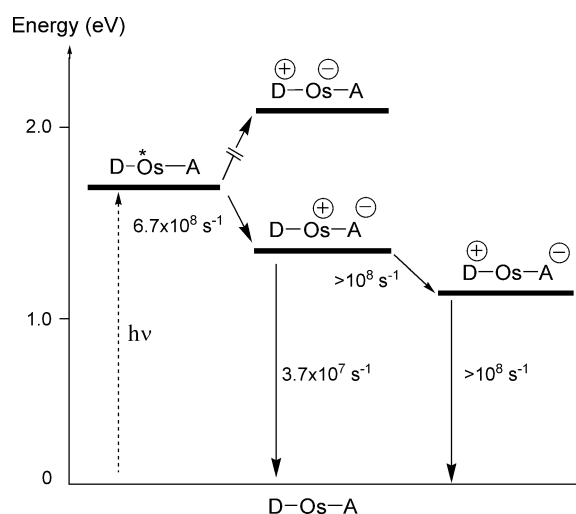**Fig. 3** Schematic energy-level diagram of DPAA–Ru–MV^{2+} in butyronitrile at 155 K.

Fig. 4 Schematic energy-level diagram of DPAA–Os–MV^{2+} in butyronitrile at 155 K.

derived from spectroscopic and electrochemical data, electron transfer from the donor to the oxidised photosensitizer is thermodynamically feasible. Since D$^+$ absorption band is not detected in the transient spectra, it can be concluded that the deactivation of D–P$^+$–A$^-$ *via* D$^+$–P–A$^-$ is faster than the rate of back electron transfer in the dyad (k = 3.7 × 10^7 s^{-1}) and that the subsequent charge recombination of the fully CS state D$^+$–P–A$^-$ is faster than the experimental resolution (*ca.* 10 ns), placing for the last two reactions a lower limit of 10^8 s^{-1}.

The introduction of an Fc moiety is interesting since the redox couple Fc$^+$/Fc is chemically and electrochemically reversible in several solvents. Unfortunately, photophysical investigation on D–P and D–P–A compounds (where D is Fc, P is Ru(ttpy)$_2$ or Os(ttpy)$_2$ and A is MV^{2+}) have shown that the existence of low lying MC excited states localised on Fc can efficiently quench *P by energy transfer. It should be noticed that while in the previous cases electron transfer and hence quenching of *P is blocked in rigid glasses, as expected on the basis of the destabilisation of CS state by the solidification of the solvent, in the Fc case quenching of the *P is efficient also in the glass.

Currently, three systems have been obtained. However, using a ferrocene as donor, problems arise due to energy transfer, and for PTZ there is chemical and photochemical instability. For D–P–A (D = DPAA, A = MV^{2+}) where Os(ttpy)$_2$ is used, the fully charge separated state could not be detected because of its short lifetime and poor accumulation. Only for the Ru-based triad, a lifetime of 27

ns could be determined for the charge separated state (CS) at 155 K in a propionitrile–butyronitrile mixture.

4 Systems including porphyrins

Since the ^{3}MLCT level of Ru(tpy)$_2$$^{2+}$ is higher than for Os(ttpy)$_2$$^{2+}$, an higher amount of energy for performing useful functions can be stored in the former complex, so it has been preferred as photosensitizer in the subsequent development of the project.

Several models of the photosynthetic centre contain porphyrins, indeed the RC itself contain several porphyrin-like pigments. It may be interesting to couple the properties of a porphyrin with the properties of a metal centre. While several multicomponent systems incorporating porphyrins attached to a transition metal complex have been reported,[18] only recent use has been made of the potential ability of the metal to act as a gathering centre for porphyrins.[19–21]

In this type of system, use of visible light leads both to the excitation of the complex centre and of the porphyrin unit; selectivity can be achieved and the processes are generally different upon excitation of the different units. In order to fulfil most of the requirements necessary to perform long range charge separation, a free base or a zinc (II) porphyrin was used as donor group and a gold(III) porphyrin as acceptor.

In each case, a tpy bearing a porphyrin is first synthesised and then coordinated on the metal centre. After the coordination reaction, metalation of the free base with zinc gives the corresponding compound. In the case of gold, the metalation of the porphyrin is performed before complexation since gold porphyrins are extremely stable towards demetalation.

4.1 System using an etio-porphyrin

The presence of alkyl groups on the tetrapyrrolic donor increases the electron donating ability of the singlet excited state (^{1}*PZn or ^{1}*PH$_2$) and thus favours electron transfer to the central Ru(ttpy)$_2$ unit. On the contrary, the four aryl groups on the gold porphyrin increase the accepting properties of this system (Fig. 5).

Preliminary studies on systems containing one of the previously mentioned porphyrins with a metal bis-tpy core have shown that the insertion of a phenyl ring between the porphyrin and the tpy slows down the electron transfer processes. Comparison of systems using a Ru or a Rh metal centre suggest that ruthenium is the better choice as the forward and backward electron transfers are faster in the case of rhodium.

The photophysical properties of each compound have been measured using picosecond transient absorption and emission spectroscopy.[22] Upon excitation of the metal complex centre, triplet energy transfer to the donor appended porphyrin rapidly quenches the excited state of the central ruthenium bisterpyridyl unit. The triplet-excited state of the gold porphyrin is unreactive toward electron or energy transfer processes.

Excitation into the free base moiety produces the corresponding excited singlet state that transfers an electron to the adjacent ruthenium. As one can see in the corresponding scheme (Fig. 6), the two energy levels, corresponding to the singlet state of the free base porphyrin and the first charge separated species, are very close, and consequently charge transfer is expected to be highly reversible. A second forward electron transfer is expected to be competitive with the back transfer which would lead directly to the ground state. More interestingly, a third way of deactivation can take place where the reduction of the gold porphyrin by the ruthenium(II) bisterpyridyl radical anion gives the fully charge separated state, PH$_2$$^+$–Ru–PAu$^-$. This process occurs with a rate constant of 5.6 × 10^8 s^{-1} at room temperature forming the species with a quantum yield of 0.27, and a lifetime of 75 ns in acetonitrile.

The same experiments performed on the triad containing zinc etio-porphyrin as a donor (Fig. 7) leads to a fully charge separated state with a yield of 0.60 and a lifetime of 33 ns. This shorter lifetime may be due to the smaller energy gap for the zinc
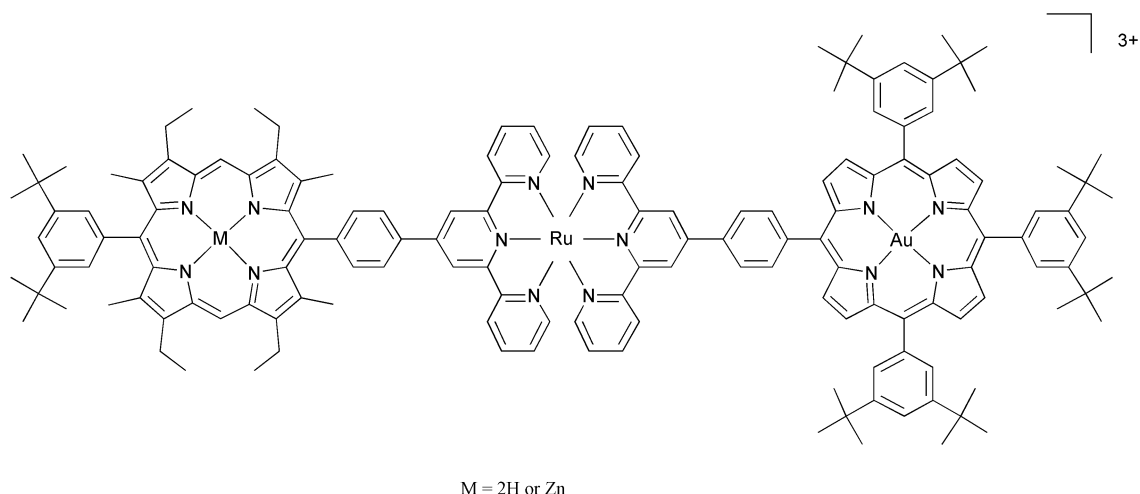
M = 2H or Zn

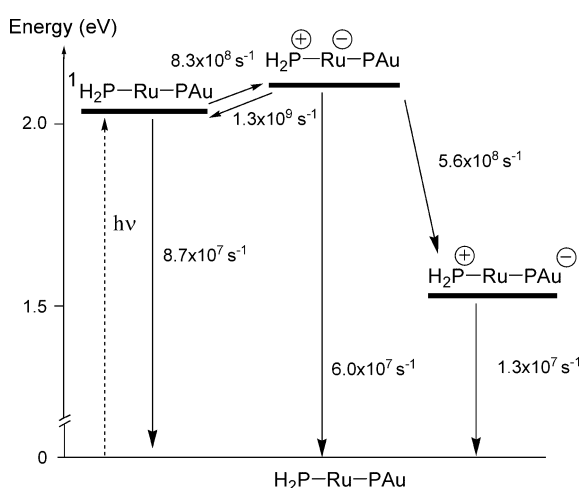**Fig. 5** System using an etio-porphyrin as photoactive centre.

Fig. 6 Schematic energy-level diagram of PH$_2$–Ru–PAu, where PH$_2$ is an etio-porphyrin, in acetonitrile at room temperature.
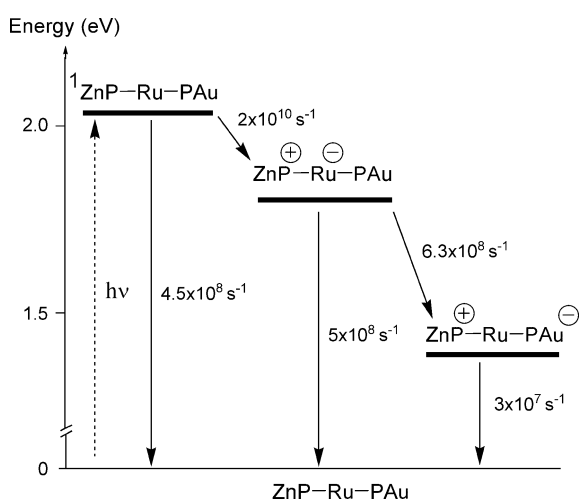

Fig. 7 Schematic energy-level diagram of PZn–Ru–PAu, where PZn is an etio-porphyrin, in acetonitrile at room temperature.

porphyrin-containing triad, with charge recombination not occurring so deep in the Marcus inverted region as for the free-base porphyrin-containing triad.

4.2 Tetra-aryl porphyrin as donor

In the previously described systems, the fully charge separated state is formed over a centre-to-centre distance of 30 Å between each porphyrin through a two-step electron transfer, and not through the direct transfer from one porphyrin to the other. This is due to the poor ability of ruthenium in promoting electronic coupling between the extreme components. In order to try to achieve a direct electronic coupling between the extreme units, the distance between the electron donor and electron acceptor was reduced to 21 Å. Furthermore the very fragile etio-porphyrin was substituted by the more robust tetra-aryl porphyrin. The triad studied now contains a free base tetra-aryl porphyrin as a donor, a ruthenium(II) bis-terpyridyl as a gathering unit, and a gold tetra-aryl porphyrin as an acceptor, with both porphyrins directly attached to the terpyridine ligand (Fig. 8).[23–25] It should be recalled that, being the *tetra-aryl* porphyrin a weaker donor than the corresponding *etio* one, the thermodynamic of the system could be altered.

Photoinduced processes occurring after excitation of the free base porphyrin are summarised in Fig. 9. After excitation into the free base porphyrin moiety, which leads to the singlet excited state, an initial energy transfer occurs to the triplet state of the central metal complex. This state deactivates rapidly ($k > 5 \times 10^{10}$ s^{-1}) through two pathways: energy transfer to either the triplet state of the free base or to the triplet of the gold porphyrin. These two processes are shown to occur in the model dyads; in the triad, from the experimental ratio of the porphyrin triplet yields, Φ^3PAu/Φ^3PH$_2$, the relative efficiency of the energy transfer steps is calculated to be four in favour of the gold porphyrin triplet. The lifetime of the triplet localised on the gold porphyrin is the same as in the model dyad and the single molecule, $\tau = 1.4$ ns, showing that this state is not participating in any process. The triplet lifetime of the free base porphyrin is slightly reduced with $\tau = 20 \mu$s compared to 40 μs in the dyad and 200 μs in the single molecule, very likely for the effect of heavy ruthenium ion on the intersystem crossing rate.

It has been found that, in spite of the coupling of the components in this system, it can still be described in terms of intramolecular processes between states localised on individual components which retain their properties with small perturbations. The energy transfer step between the singlet of the free base and the triplet of the Ru complex, which should be formally forbidden for spin conservation rules, is made possible by the perturbation brought about by the heavy ruthenium ion.

5 Iridium(III) as gathering metal

5.1 Why iridium(III)?

Very often Ru(II) based complexes are found to be involved in energy transfer processes that are competitive to electron transfer processes, because of the presence of relatively low-lying energy levels (especially Ru to tpy charge transfer located at 2 eV in comparison with the energy of ^{1}*PH$_2$ around 1.95 eV and ^{1}*PZn, around 2.05 eV). To avoid quenching of the primary singlet

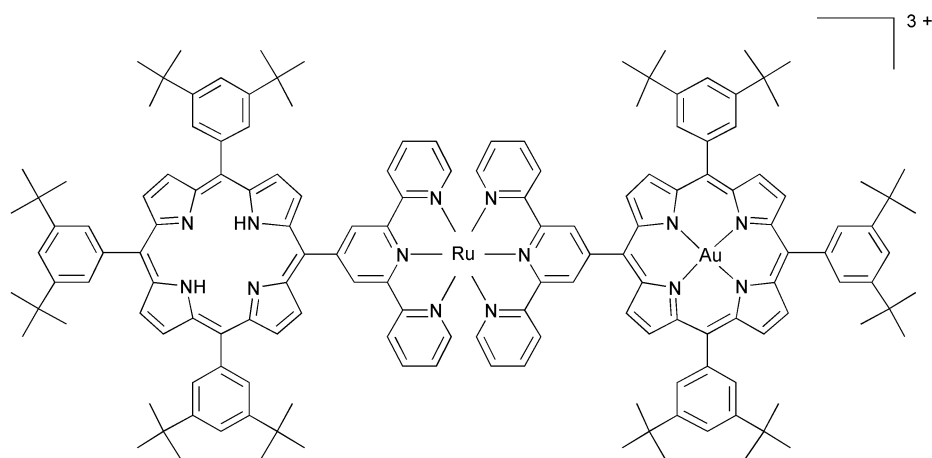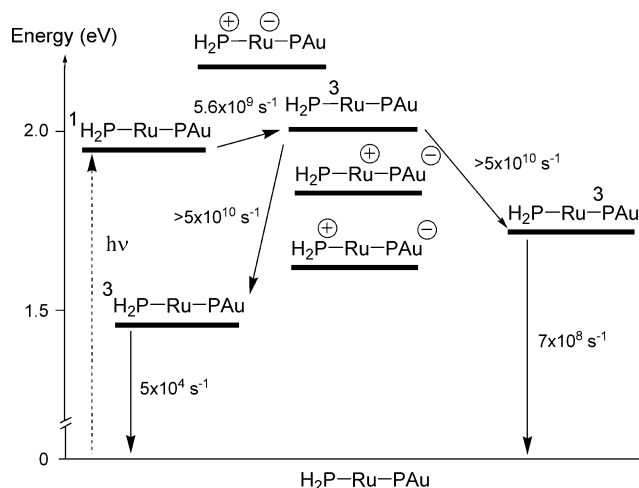Fig. 8 Highly coupled system PH₂–Ru–PAu where PH₂ is a tetra-aryl porphyrin used as photoactive centre.

Fig. 9 Schematic energy-level diagram of PH₂–Ru–PAu, where PH₂ is a tetra-aryl porphyrin, in butyronitrile at room temperature.

porphyrin excited state by the ^{3}MLCT of the templating metal centre, this centre should not possess a lower, or nearly isoenergetic excited state. An additional reason to replace Ru is that the lowest lying excited state ^{3}MLCT undergoes a fast deactivation with a lifetime shorter than 1 ns, leaving little time for the excited state to use this energy. In fact, in the case of long-range processes, the intrinsic deactivation of the templating unit becomes competitive with transfer process. Therefore the need for a different metal complex, was evident. The new metal should: (i) coordinate two tpy

in order to preserve the linear geometry, (ii) inhibit scrambling of the tpy units, implying kinetically inert coordination sphere, (iii) not possess low lying excited states in order to prevent quenching by energy transfer, (iv) possess suitable electrochemical properties with regards to the Zn or free base, and gold porphyrins, which allowed it to act as electron relay. Iridium(III) seems to be the answer, with apparently very few other alternatives.

Investigation of Ir(III) bis-terpyridyl complexes required development of new synthetic routes with milder conditions[26] than previously described in literature[27] for such compounds. Following studies of their properties, the complexes seem to be good candidates for replacing the Ru(tpy)₂.

Two triads were then synthesised using zinc or free base tetra-aryl porphyrin as a donor and photoactive centre, an Ir(tpy)₂ as a primary acceptor, and a gold tetra-aryl porphyrin as a secondary acceptor (Fig. 10).[28,29]

5.2 Photoinduced processes

The energy level diagrams for the triad containing the free base (in acetonitrile) and the triad containing the zinc porphyrin (in dichloromethane and in toluene) are shown in Figs. 11, 12 and 13.

It was shown that irradiation of the free base porphyrin in the PH₂–Ir dyad and PH₂–Ir–PAu triad led to quenching of the luminescence of the porphyrin, reducing the lifetime of the singlet state from 8.3 ns to 30 ps at room temperature in acetonitrile. Such a process does not occur in butyronitrile glass at 77K where the lifetime of the singlet remains 11 ns. The deactivation can be
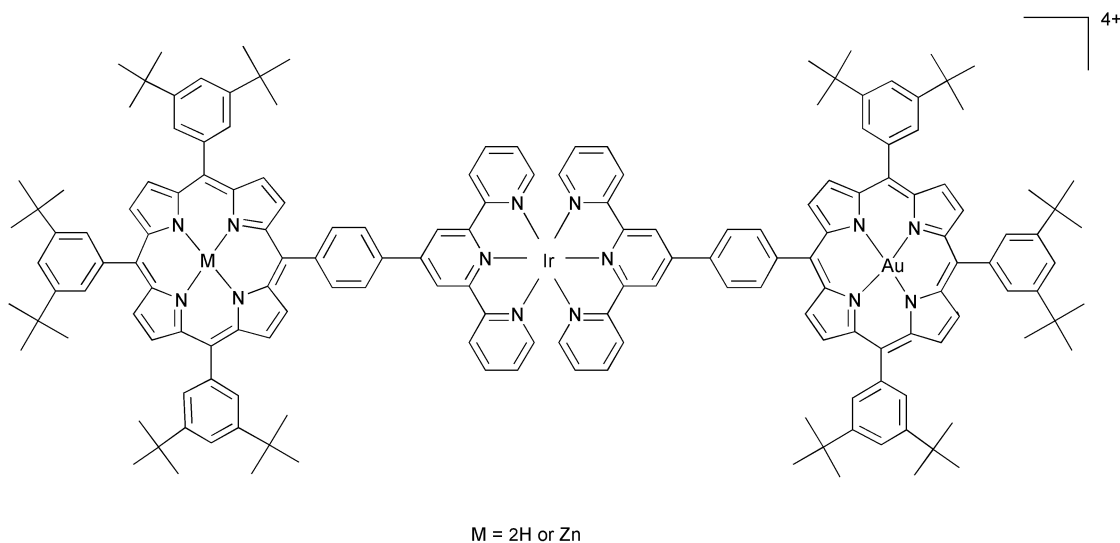

M = 2H or Zn
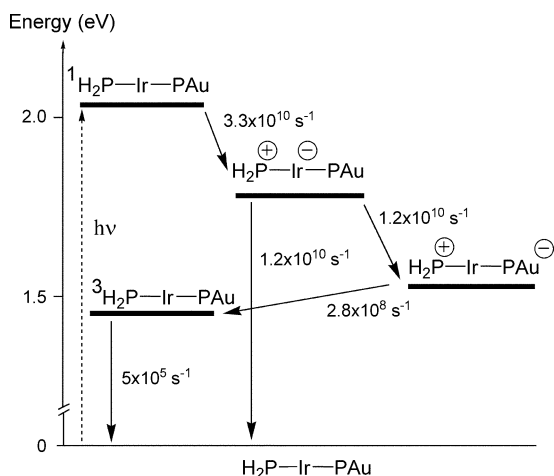
Fig. 10 Triads using Iridium(III) as gathering metal.

Energy (eV)

Fig. 11 Schematic energy-level diagram of PH$_2$–Ir–PAu in acetonitrile at room temperature.
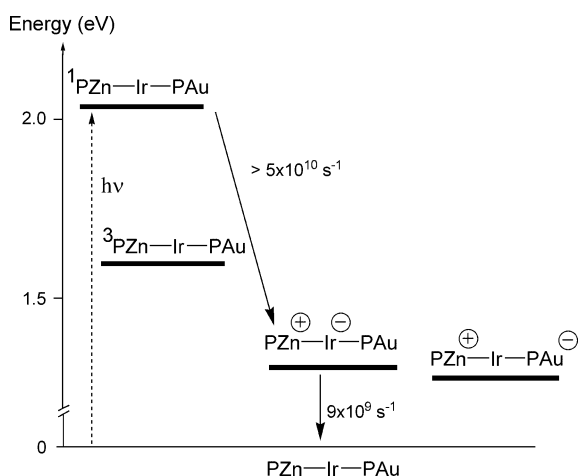
Energy (eV)

Fig. 12 Schematic energy-level diagram of PZn–Ir–PAu in dichloromethane at room temperature.
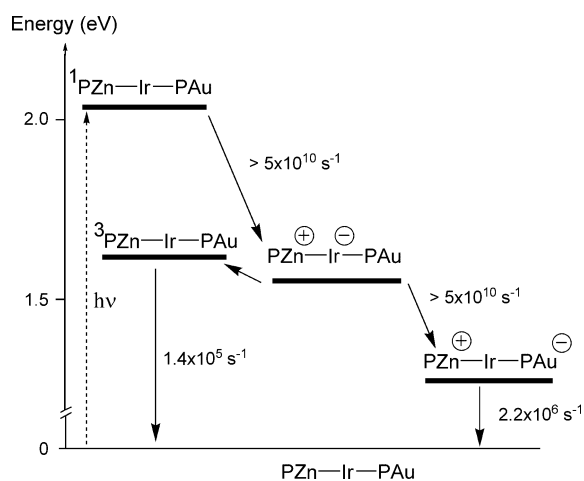
Energy (eV)

Fig. 13 Schematic energy-level diagram of PZn–Ir–PAu in toluene at room temperature.

attributed to an electron transfer from the singlet state of the free base to the central Ir(tpy)$_2$ core, the electron being localised on a tpy ligand. On the other hand, in each compound containing a PAu moiety (model PAu, dyad PAu–Ir, and triad PAu–Ir–PH$_2$) excitation of the PAu part leads to the triplet state of the gold porphyrin which decays with a lifetime of 1.4 ns without reacting with other compounds. Deactivation of the first charge separated state is faster in the triad (40 ps) than in the PH$_2$–Ir dyad (75 ps). In

the dyad deactivation can occur by recombination to the ground state whereas in the triad the deactivation can occur through a further electron transfer process leading to the completely charge-separated state PH$_2$+–Ir–PAu$^-$. This fully charge-separated state is formed with an efficiency of 0.5 and decays with a lifetime of 3.5 ns quantitatively through the triplet state of the free base porphyrin, as shown by the yield determined for the free base porphyrin triplet (Fig. 11).

In the case of PZn, to avoid demetalation of the porphyrin unit, which are unstable upon irradiation in nitrile solvent, dichloromethane or toluene were used to solubilise the PZn containing products. In dichloromethane, after quenching of the ^{1}PZn the only charge separated state detected was PZn+–Ir$^-$$^-$–PAu. which deactivates directly to the ground state with a lifetime of 110 ps, as the corresponding state in the model dyad PZn+–Ir$^-$ (Fig. 12).

In toluene, after a very fast quenching of the ^{1}PZn ($\tau < 20$ ps), a species with a band at 670 nm and a lifetime of 450 ns is detected and assigned to the fully charge separated state PZn+–Ir–PAu$^-$ (Fig. 13).

The difference in behaviour of the triad in CH$_2$Cl$_2$ or toluene can be explained by the effect of the polarity of the solvents on the stabilisation of the different states. The states PZn+–Ir$^-$$^-$–PAu, PZn+–Ir–PAu$^-$, and the ground state are more destabilised in the less polar toluene. However, the first species, PZn+–Ir$^-$$^-$–PAu, is expected to be more destabilised than PZn+–Ir–PAu$^-$ with respect to the ground state. This would increase the driving force of the second electron transfer, which should then be able to compete with recombination.

In these systems, the photoactive centre is a porphyrin and the iridium acts only as a gathering metal and electron relay. It was shown during preliminary photochemical studies on iridium compounds that the excited state of Ir(tpy)$_2$ can also act as a promising photosensitizer. Indeed it is high in energy (about 2.5 eV) and possesses a lifetime on the micro second scale. This is the motivation behind our current investigation of new compounds where Ir(tpy)$_2$ will act as a photoactive centre in addition to a gathering metal and electron relay.

6 Conclusion

In conclusion, M(tpy)$_2$ based systems are interesting models of the RC. While M(tpy)$_2$ complexes are not as luminescent as M(bpy)$_3$, the systems based on the former display well-defined control over the geometry, and may enable the design of multinuclear compounds.[30,31]

Some other recent work should be mentioned based on M(tpy)$_2$ compounds, *viz.* other compounds using Ru(tpy)$_2$ as PAC,[32] Ir(tpy)$_2$ as luminescent label for proteins[33] or anions sensor.[34]

Despite the progress towards artificial RC's over the 30 past years, charge separated states produced by Nature still live millions of times longer than the artificial systems based on M(tpy)$_2^{n+}$. It is noteworthy that those obtained when C$_{60}$ is the terminal acceptor are also extremely long-lived, due to the small reorganisation parameter, λ,[5] of this acceptor. It is thus tempting to combine M(tpy)$_2$ motif with C$_{60}$, in analogy to what has already been done for other dipyridyl Ru (II) complexes.[35]

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