Designing tridentate ligands for ruthenium(II) complexes with prolonged room temperature luminescence lifetimes

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Coordination complexes have been used extensively as the photoactive component of artificial photosynthetic devices. While polynuclear arrays increase the probability of light absorption, the incorporation of the stereogenic Ru(2,2′-bipyridine)$_3^{2+}$ motif gives rise to diastereomeric mixtures whereas the achiral Ru(2,2′:6′,2″-terpyridine)$_2^{2+}$ motif creates stereopure polynuclear complexes. Thus, polynuclear arrays composed of ruthenium(II) complexes of tridentate ligands are the targets of choice for light-harvesting devices. As Ru(II) complexes of tridentate ligands have short excited state lifetimes at room temperature (r. t.), considerable effort has been focused on trying to increase their r. t. luminescence lifetime for practical applications. This *tutorial review* will report on the sophisticated synthetic strategies currently in use to enhance the room temperature photophysical properties of Ru(II) complexes of tridentate ligands.

1 Introduction

Ruthenium(II) polypyridine complexes have been the focus of considerable attention over the last few decades.[1] Their rich photophysical properties make them attractive candidates for applications as photosensitisers in light-harvesting devices (LHDs) where they replace natural chromophores, such as chlorophyll-*a* and β-carotenoid in photosystem II (PSII). The Ru(II) complexes absorb energy in the visible region of the spectrum giving rise to a singlet metal-to-ligand charge-transfer (^{1}MLCT) excited state, which quickly produces a potentially emitting triplet excited state (^{3}MLCT). The ^{3}MLCT excited state may be sufficiently long-lived to transfer an electron or energy to a suitable acceptor depending on the complex under investigation. In PSII, the excited special pair rapidly transfers an electron through pheophytin to a plastoquinone due to the spatial arrangement of the chromophore and the electron acceptors.[2] Although duplicating the structure of PSII in a LHD would be extremely difficult, artificial systems capable of duplicating its function, that is, generating a charge-separated state, are of increasing interest.[3] In the absence of the fast electron transfer found in PSII, the excited state lifetimes of Ru(II) polypyridine complexes must be optimized to permit vectorial electron or energy transfer before excited state deactivation can occur.[3] The luminescence lifetimes may be fine-tuned by manipulating the properties of the excited states which are ultimately dependent on the ligands bonded to the Ru(II) ions.[4] As a greater mechanistic understanding of the processes involved in harnessing light energy may lead to LHDs that replace conventional non-renewable sources of energy with renewable solar energy sources,[5] the design and synthesis of new ligands and their Ru(II) complexes is of critical importance.[6]

The artificial counterparts for the chromophores of PSII have typically been based on the [Ru(bpy)$_3$]$^{2+}$ motif due to its relatively long-lived excited state at room temperature

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(1100 ns).[1] However, in larger polynuclear systems based on $[Ru(bpy)_3]^{2+}$, the stereogenic metal centres create diastereomers, and further substitution on the bpy ligands may lead to *facial* and *meridional* isomers.[7] Although methods to create enantiopure complexes based on $[Ru(bpy)_3]^{2+}$ have been developed,[8] attention has turned to synthetically more accessible complexes based on tridentate ligands such as 2,2′:6′,2″-terpyridine (tpy). $[Ru(tpy)_2]^{2+}$ has a relatively long luminescence lifetime in a rigid matrix at 77 K, however, at room temperature its excited state is essentially quenched with a lifetime of only 250 ps.[9] The rigid tridentate ligands create a greater distortion from ideal octahedral geometry in their Ru(II) complexes. Smaller N–Ru–N *trans* angles are found in coordinated tpy (158.6°) as compared to the analogous Ru(II) complexes with bpy (173.0°).[10,11] This gives rise to a weaker ligand field strength, which effectively reduces the energy of the dd metal-centred triplet state (^{3}MC) (Fig. 1).[12] A consequential decrease in the energy gap between the ^{3}MLCT and ^{3}MC is observed and the ^{3}MC is thermally accessible from the ^{3}MLCT, facilitating non-radiative decay back to the ground state (GS).

The excited state lifetime of Ru(II) complexes is dependent on the radiative and non-radiative rate constants as given by

$$\tau = \frac{1}{k^o + k^{o\prime}\exp(-E_a/RT)}$$

where $k^\circ = k_r + k_{nr}$, the sum of the radiative and non-radiative rate constants, respectively, and $k^{\circ\prime}$ relates to a thermally activated crossover process in which E_a is the activation energy barrier to the ^{3}MC state.[13] As Ru(II) polypyridine complexes are weakly emitting, the non-radiative decay constant is the more important factor of the two rate constants.[4] The two major pathways for non-radiative deactivation are through a direct contribution from the ^{3}MLCT state to the GS and through a thermally accessible ^{3}MC state back down to the GS. In order to reduce the overall non-radiative decay constant it is important to diminish the accessibility of the ^{3}MC state from the ^{3}MLCT state. However, if the ^{3}MLCT state is too low in energy, the excited state lifetime may be shortened even more by the direct contribution back to the GS according to the energy gap law.[1,3,4,13] Although tridentate ligands based on the tpy motif have overcome the problems associated with the chirality of $Ru(bpy)_3^{2+}$, it has come at the loss of their excellent photophysical properties.

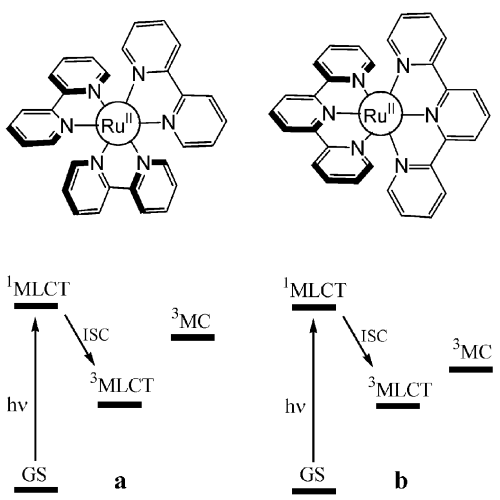

Fig. 1 (a) Photophysically appealing $Ru(bpy)_3^{2+}$ *versus* (b) synthetically appealing $Ru(tpy)_2^{2+}$.

In this tutorial review, the synthetic strategies used to enhance the photophysical properties of Ru(II) complexes of tridentate ligands will be reported. The most popular approach has focused on manipulating the energy difference between the ^{3}MLCT and ^{3}MC states of the complex in order to minimise non-radiative decay through the ^{3}MC state to the GS. Destabilisation of the ^{3}MC state or stabilisation of the ^{3}MLCT state, or both, leads to a greater energy gap between the two states. However, stabilisation of the ^{3}MLCT also reduces the energy gap to the ground state which is the usual deactivation pathway for low energy emitting Ru(II) complexes. Alternatively, an additional chromophore may be introduced with a comparable triplet energy to the ^{3}MLCT excited state of the complex, which produces a bichromophoric effect and a substantial increase in the r. t. luminescence lifetime. In the following four sections, we will review the strategies developed to date and highlight the most efficient.

2 Ruthenium(II) complexes of functionalised 2,2′:6′,2″-terpyridine ligands

a) Direct incorporation of an electron withdrawing or electron donating substituent onto tpy

Complexes of the $[Ru(tpy\text{-}X)(tpy\text{-}Y)]^{2+}$ type were synthesised in which X and Y were a wide range of both electron withdrawing and electron donating groups on the 4′-position of the central pyridyl ring.[14] The complexes with electron withdrawing groups (EWGs) were shown to absorb at a lower energy due to greater stabilisation of the ligand-based lowest unoccupied molecular orbital (LUMO) as compared to the metal-based highest occupied molecular orbital (HOMO). The energy of the ^{3}MLCT state was consequently lowered and the thermal population of the ^{3}MC state was reduced. The luminescence lifetimes were increased and dramatic improvements were observed for complexes with strong EWGs: X = H, Y = SO_2Me: λ_{max} = 679 nm, τ = 36 ns; X = SO_2Me, Y = SO_2Me: λ_{max} = 666 nm, τ = 25 ns. A comparable red shift in the absorption bands was also observed when X or Y were electron donating groups (EDGs) as they destabilise the metal-based HOMO to a greater extent than they destabilise the ligand-based LUMO. However, the EDGs do not destabilise the ^{3}MC state to a great extent and non-radiative decay back to the GS was facilitated. The longest lifetimes were found for the complexes with mixed EDGs and EWGs: X = OH, Y = SO_2Me: λ_{max} = 706 nm, τ = 50 ns.

When electron withdrawing triarylpyridinium functionalised terpyridines are coordinated to Ru(II), the heteroleptic complexes have a low energy emission (670 nm) and an extended r. t. luminescence lifetime of 55 ns.[15] However, the introduction of a phenyl spacer between the tpy and the pyridinium group diminishes the effect of the electron withdrawing pyridinium substituent and the lifetime is reduced quite significantly to 580 ps, comparable to that of $Ru(tpy)_2^{2+}$. Attaching the relatively electron rich thiophene group directly

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to the tpy ligand also increases the r. t. luminescence lifetime of Ru(II) complexes, albeit to a lesser extent (<10 ns).[16]

Early pioneering work with acetylene substituents in the 4′-position of the coordinated tpy ligand demonstrated that long excited state lifetimes could be obtained.[17] The complexes have acetylene groups grafted directly onto the terpyridine core which enhances electron delocalisation and stabilises the ligand-based LUMO (Fig. 2).[17] The increase in the ^{3}MLCT–^{3}MC energy gap reduces the mixing of the ^{3}MLCT state with the ^{3}MC state. An increase in the number of acetylene units also decreases the emission energy and increases the lifetime of the excited state. The longest r. t. lifetime for acetylene-based complexes corresponds to the acetylene–pyrene complex (580 ns).[17] Although pyrene's triplet state (^{3}Pyr) is higher in energy than the ^{3}MLCT state, it may be populated from the ^{3}MLCT which effectively delays the emission. A similar effect may be responsible for the extended lifetime on the ferrocene-based acetylene complex (Fig. 2).[18] The strategy of using the equilibrium between triplet states to increase the luminescence lifetime will be discussed in section 3.

b) Co-planarity of aromatic groups on the tpy ligand

Phenyl substitution in the 4′-position of the tpy gives Ru(II) complexes with photophysical properties that cannot be explained simply in terms of electron donating or withdrawing ability. The Hammett parameter for a phenyl group is essentially the same as hydrogen, therefore, one would expect similar properties to those of $[Ru(tpy)_2]^{2+}$.[14] However, the MLCT absorption band (481 nm) and emission band (715 nm) are at a lower energy for $[Ru(Ph\text{-}tpy)_2]^{2+}$ as compared with $[Ru(tpy)_2]^{2+}$, which absorbs and emits as 475 and 629 nm, respectively. The ^{3}MLCT state is stabilised by the phenyl substituent to a greater extent than the ^{1}MLCT, an effect that has been observed in a number of similar systems.[19,20] In the ground state, the phenyl ring twists away from the central pyridine ring due to unfavourable steric interactions between the hydrogens *ortho* to the inter-annular bond (Fig. 3). In the excited state, there is a change in the dihedral angle between the phenyl ring and the central pyridine ring to give a co-planar arrangement. Consequently, the ^{3}MLCT excited state is more stabilised by extended electron delocalisation than the GS. The complex $[Ru(Ph\text{-}tpy)_2]^{2+}$ and its triphenyl-tpy analogue have r. t. luminescence lifetimes of approximately 4 ns.[19] A similar effect is noted for $[Ru(p\text{-toluyl-}tpy)_2]^{2+}$ (0.95 ns).[7] Femtosecond absorption spectroscopy has been used to study a few related systems.[21]

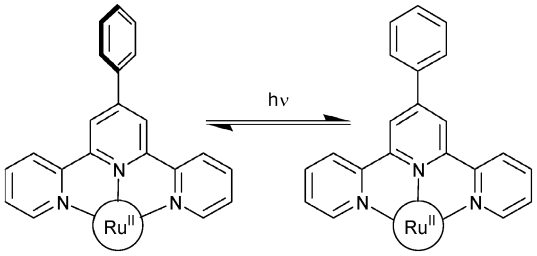
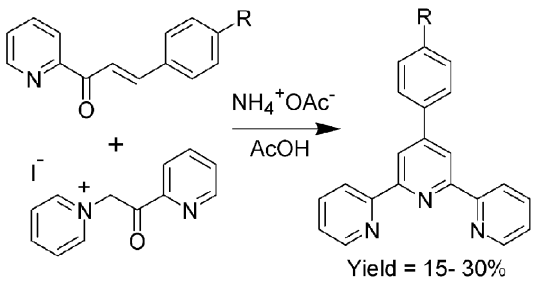


Fig. 3 Non-planar (left) and co-planar (right) 4′-phenyl-tpy complexes of Ru(II).[19]

A general synthetic approach has been optimised for the synthesis of such ligands in which the substituents are introduced prior to the condensation reaction (Scheme 1).[22] Those substituents that are not accessible through this route, may be synthesised by functionalisation of 4′-*p*-toluyl-2,2′:6′,2′-terpyridine. Electron withdrawing substituents may be substituted on the pendant phenyl ring which further stabilises the ligand LUMO.

Further studies to improve the effect of co-planar aromatic rings have been carried out by employing a pyrimidyl spacer in place of a phenyl ring. The 2-pyrimidyl substituent lies co-planar to the central terpyridine ring as a result of the intramolecular hydrogen bonding between the N lone pairs on



Scheme 1 Synthesis of substituted phenyl-terpyridine ligands.[22]

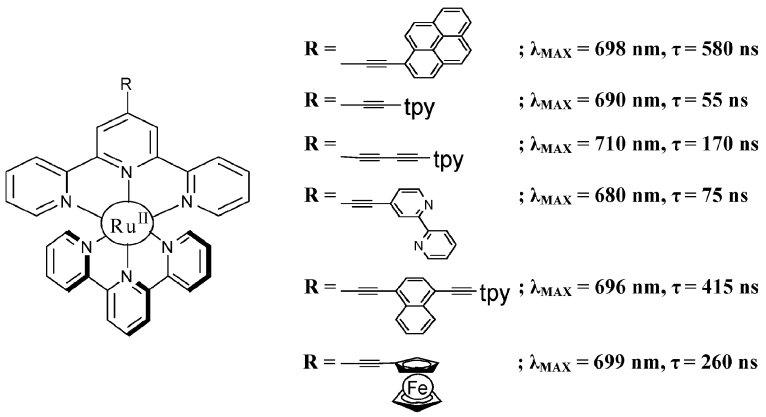


Fig. 2 Photophysical data for acetylene-substituted $Ru(tpy)_2^{2+}$ complexes.[17,18]

the pyrimidine and H atoms on the central pyridine ring (Fig. 4).

Further stabilisation of the LUMO can be achieved through substitution of electron withdrawing groups in the 5-pyrimidyl position.[23] The synthesis involved multiple steps to initially obtain the 4′-amidinate-2,2′:6′,2″-terpyridine, which is further reacted with substituted trimethinium cations (Scheme 2). The heteroleptic Ru(II) complexes were synthesised with a range of electron withdrawing groups (Scheme 2).[23] The parent complex, where R = H, has a r. t. luminescence lifetime of 8 ns and all other substituents improve on this value. The cyano-substituted heteroleptic complex has a relatively long-lived r. t. excited state (200 ns). A combination of efficient electron delocalisation over the entire ligand and the electron withdrawing nature of the cyano group contribute to the stabilisation of the ^{3}MLCT state.

3 Bichromophoric systems

The most successful strategy developed to date is the bichromophore approach, in which an organic chromophore with a non-emissive triplet state is similar in energy to an emissive ^{3}MLCT state and an equilibrium is established between the two states.[24] When a perpendicular arrangement of the organic ligands is favoured on steric grounds, orbital mixing is minimised, which maintains the independence of the two chromophoric units, and consequently favours emission from the ^{3}MLCT state. In some cases, mixing of the organic chromophore triplet state and the ^{3}MLCT state leads to emission from an intraligand state, nonetheless a longer lived excited state is usually obtained.[13] This strategy has been applied extensively to Ru(II) complexes of bidentate ligands to which pyrene is commonly introduced as the additional chromophore.[25,26] As pyrene's triplet state is higher in energy than the ^{3}MLCT state of tpy-based Ru(II) complexes, and anthracene's triplet state (^{3}An) is lower in energy (E^{00} = 1.85 eV, 671 nm),[27] the bichromophore approach has not been widely applied to Ru(II) complexes of tridentate ligands. The parent Ru(II) complex has a ligand (tpy-An) consisting of an anthracene moiety directly connected to the 4′-position of terpyridine (Fig. 5).[28] However, $[Ru(tpy\text{-}An)_2]^{2+}$ is not luminescent at room temperature as the energy of the ^{3}MLCT state is significantly higher in energy than the non-emissive ^{3}An state and irreversible energy transfer occurs thereby quenching the excited state.

In order to have efficient energy equilibration in bichromophoric systems, complexes and chromophores with isoenergetic triplet states are required. The pyrimidyl-terpyridine

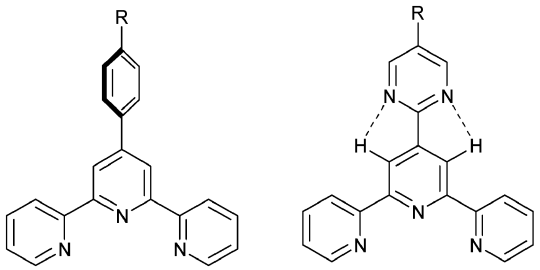


Fig. 4 Introducing co-planar substituents onto the terpyridine through intramolecular hydrogen bonding.[23]

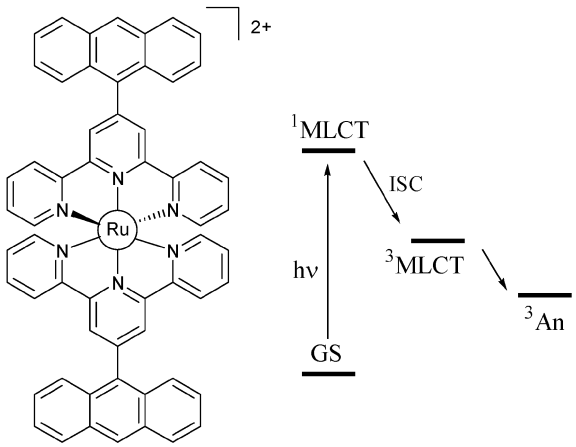
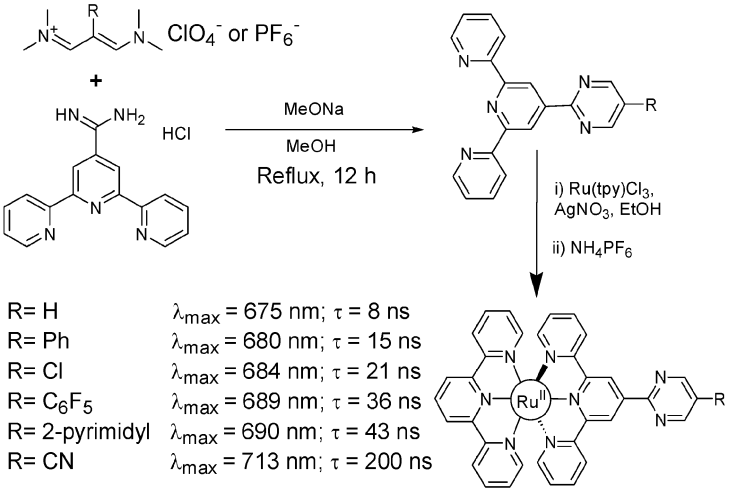


Fig. 5 Quenching of the ^{3}MLCT excited state of $[Ru(tpy\text{-}An)_2]^{2+}$ due to the low lying non-emissive ^{3}An state.[28]



Scheme 2 Synthesis of a variety of substituted pyrimidyl terpyridine heteroleptic Ru(II) complexes and their r. t. excited state lifetimes.[23]

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complexes can be used to fine-tune the ^{3}MLCT energy (Scheme 2). The anthracene moiety can then be grafted directly onto the 5-pyrimidyl position of the pyrimidyl-terpyridine ligand (Fig. 6). The terpyridine-based complex with a 5-(9-anthryl)-pyrimid-2-yl substituent has a ^{3}MLCT energy lower than that of the complex in Fig. 5.† The ^{3}MLCT and the ^{3}An states are now nearly isoenergetic and hence equilibration can occur. The homoleptic complex $[Ru(tpy\text{-}pm\text{-}An)_2]^{2+}$ exhibits biexponential radiative decay back to the GS, with an initial r. t. luminescence lifetime of 6 ns followed by a longer lived component with an r. t. excited state lifetime of 1806 ns (Fig. 6).[29] The first component is attributed to the ^{3}MLCT state based on the pyrimidyl-terpyridine unit, and the second component arises from the equilibrium with the ^{3}An state which repopulates the ^{3}MLCT state after the initial emission. The heteroleptic complex $[Ru(tpy\text{-}pm\text{-}An)(tpy)]^{2+}$ also exhibits dual exponential decay with a short-lived first component (5.5 ns) and a longer lived second component (402 ns). In these complexes, the anthracene lies nearly perpendicular to the plane of the pyrimidine ring and, therefore, maintains its own excited state properties. This is an important feature as the secondary chromophore should contribute its independent properties to the final assembly.

In all of the bidentate and tridentate bichromophoric systems synthesized to date, the organic chromophore has always been on the same ligand that is involved in the ^{3}MLCT state. Very recently, it has been shown that these two excited states do not have to be involved with the same ligand. The anthryl-terpyridine and pyrimidyl-terpyridine ligands may be synthesized separately and their heteroleptic complexes prepared (Fig. 7). Even though the spatial separation of the two chromophores exceeds 1 nm, the ^{3}An and the ^{3}MLCT states are almost isoenergetic, which allows equilibration between the two states. A dual exponential decay of the excited state gives two lifetimes at r. t.; 25 ns and 1052 ns (Fig. 7).[30]

Two multicomponent systems were reported with a 9-anthryl group introduced into the tridentate ligand (Fig. 8).[31] The absorption and emission energy of the ^{1}MLCT and ^{3}MLCT states are at significantly longer wavelengths as compared with $Ru(tpy)_2^{2+}$. For the methylated complex (Fig. 8, left), the ^{1}MLCT and ^{3}MLCT bands are at 530 and 730 nm, respectively, and its r. t. luminescence lifetime is 60 ns. The non-methylated complex (Fig. 8, right) has similar absorption (510 nm) and emission energies (715 nm),

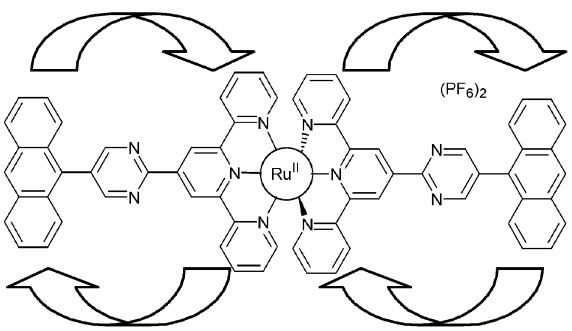


Fig. 6 The bichromophoric effect in $[Ru(tpy\text{-}pm\text{-}An)_2]^{2+}$: energy transfer from the ^{3}MLCT to the ^{3}An state and back is very efficient.[29]

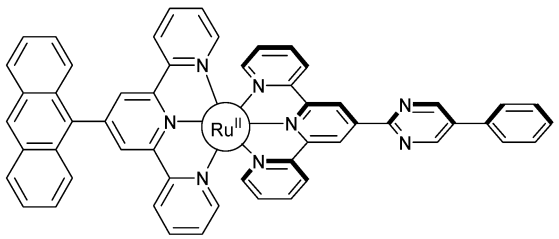


Fig. 7 Prolonging r. t. excited state lifetimes through a long-range multi-chromophore approach.[30]

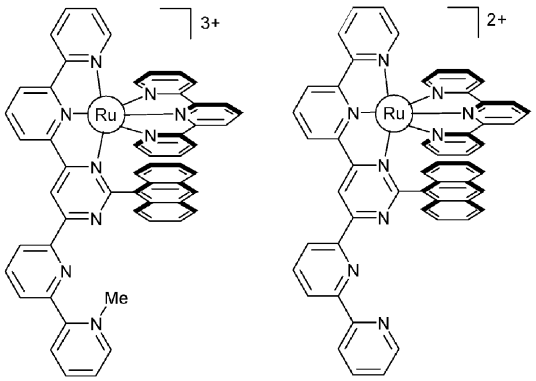
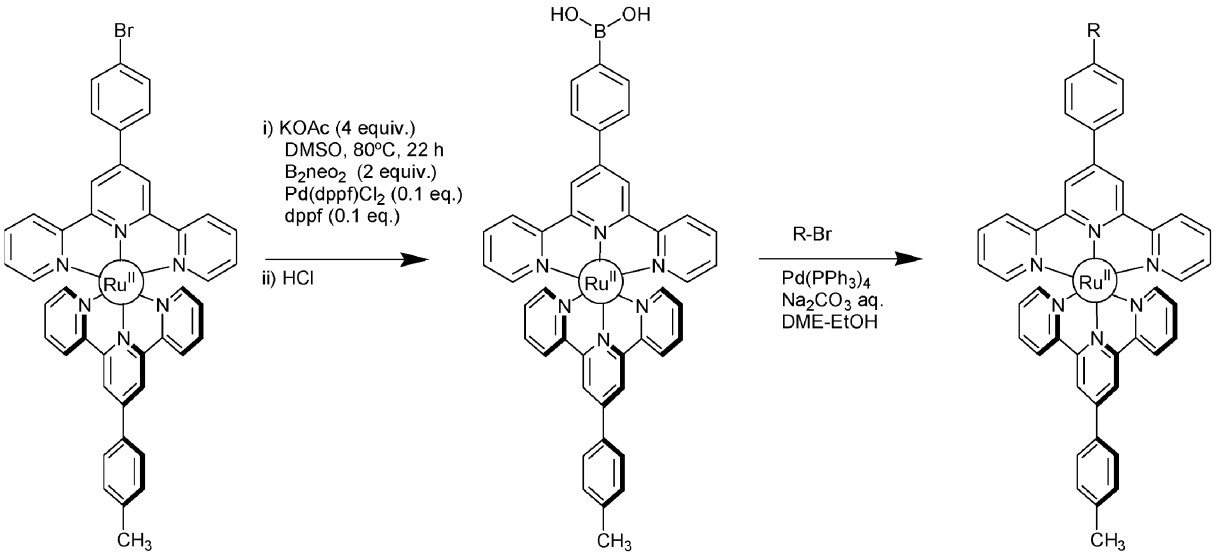


Fig. 8 Multi component systems that contain Ru^{II} polypyridine and anthracene chromophores.[31]

but a shorter r. t. excited state lifetime (30 ns). The emission energy is lower than the energy of the ^{3}An state, which should preclude a bichromophoric effect, suggesting that another process may be operating. The longer lifetime may be a result of the interligand π–π interactions which stabilises the ^{3}MLCT state (*cf.* section 4).

More versatile methods have been investigated to incorporate a wider range of organic groups into metal complexes, *e.g.*, the Suzuki–Miyaura cross-coupling reaction with an aryl halide, an arylboronic acid and a Pd(0) catalyst. The conventional synthetic approach for Ru(II) polypyridines is to couple the appropriate organometallic reagent to the halide functionalised Ru(II) complex.[32] However, an alternative approach is to introduce the organometallic reagent onto the complex itself.[33] The Pd(0)-catalysed reaction of a 4′-(*p*-bromophenyl)-tpy complex of Ru(II) with bis(neopentylglycolato)diboron (B_2neo_2), followed by hydrolysis of the corresponding boronate ester gave the boronic acid directly on the complex (Scheme 3).

The cross-coupling reactions with a range of aryl halides were carried out using $Pd(PPh_3)_4$ and Na_2CO_3 in DME–EtOH (Scheme 3). The coupling reactions are not as efficient as the reactions starting with halosubstituted complexes, however, this alternative approach should allow for the synthesis of complexes that would otherwise not be accessible. Although the complexes prepared by this approach are only weakly



Scheme 3 Synthesis of boronic acid on the metal complex followed by Pd-catalysed coupling reactions.[33]

emitting, there is considerable potential for new ligands and complexes to be obtained.

4 Increasing the energy of the ^{3}MC state

a) σ-Donating ability

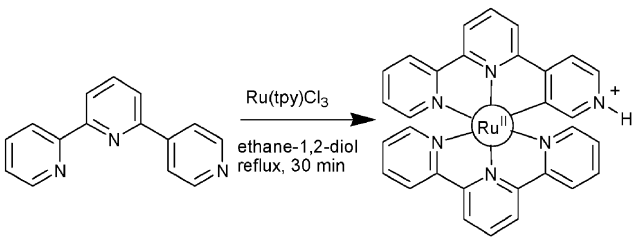
As strong σ-donor ligands typically destabilise metal-based orbitals while having a minimal effect on the π* orbitals of the second tridentate ligand in a heteroleptic complex, they have a great influence over the energies of the molecular orbitals involved in MLCT processes. Consequently, strong σ-donor ligands lower the energy of the ^{1}MLCT and the ^{3}MLCT states effectively reducing surface crossing to the ^{3}MC state. However, if the ^{3}MLCT state is too low in energy, non-radiative decay directly to the GS may occur. The two major ways of increasing σ-donor strength are by cyclometallation and by introducing strong σ-donor heterocycles into the tridentate ligand.

i) Cyclometallation. Cyclometallated complexes are attractive synthetic targets as replacement of a Ru–N bond with a Ru–C bond will modify the redox and photophysical properties of the complex and, therefore, offer an alternative means to fine-tune orbital energies. Cyclometallating ligands are strong σ-donors and significantly increase the energy gap between the ^{3}MLCT and the ^{3}MC state for heteroleptic complexes with one ligand bound in an N,N,N mode and the cyclometallated ligand in either a N,N,C or N,C,N coordination mode. There are two general synthetic approaches to introduce a cyclometallating group into the Ru(II) coordination sphere: (1) quaternise a nitrogen atom and force insertion of Ru in to a CH bond and (2) remove a nitrogen atom from the ligand to eliminate the possibility of N,N,N coordination.

The first approach can be more difficult to control and quaternisation of tpy has been found to be synthetically more difficult than expected. *N*-Methyl-2,2′:6′,2″-terpyridine hexafluorophosphate could be obtained by the reaction of trimethyloxonium tetrafluoroborate in DCM at reflux for 2 hours.[34] Its complexation to $RuCl_3$ then required optimisation of the cyclometallated product over the N,N-bidentate complex in which the vacant coordination site is occupied by a chloride ligand. Although the solvent system plays a vital role in determining the major product, the solvent effect changes from ligand to ligand and was difficult to predict. Quaternisation of 4′-methylthio-terpyridine proceeded more smoothly than for 2,2′:6′,4″-terpyridine and 2,2′:6′,3″-terpyridine ligands using CH_3I in DCM.[35]

The second approach, removing a nitrogen from the tpy core, is more commonly employed to synthesise cyclometallated complexes. One pyridyl ring of tpy may be replaced by a pyridine ring substituted in a different position, such as 2,2′:6′,4″-terpyridine, in which it is impossible to obtain an N,N,N coordination mode (Scheme 4).[36]

A red shift is observed for the energy of absorption in the ^{1}MLCT band as compared to $[Ru(tpy)_2]^{2+}$ as would be expected. The HOMO is raised in energy and consequently the HOMO–LUMO energy gap is reduced, as the ^{3}MLCT lies on the non-cyclometallated ligand. Although the effect of one of the non-radiative decay pathways has been reduced, the cyclometallated complex is still only weakly emissive at room temperature (λ_{max} = 790 nm) as the ^{3}MLCT to GS energy gap is very small and non-radiative decay through this alternate route is possible.



Scheme 4 Cyclometallation induced protonation of 2,2′:6′,4″-terpyridine.[36]

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Cyclometallating ligands have also been developed in which a phenyl ring is incorporated into tpy instead of the peripheral or central pyridyl ring to force N,N,C or N,C,N coordination, respectively. The majority of work on mononuclear systems has focused on 6-phenyl-2,2′-bipyridine (bpy-Ph) to obtain an N,N,C coordination motif.[37] The synthesis of the heteroleptic complex, $[Ru(tpy)(bpy\text{-}Ph)]^+$, is highly solvent dependent and a solvent with a high dielectric constant was required to favour the cyclometallated product. The signature for these complexes is the particularly high field signal in the ^1H NMR corresponding to the proton adjacent to the cyclometallating carbon. Complexes incorporating the cyclometallating bpy-Ph ligand all display a red shift of the ^1MLCT band in the visible region due to the destabilisation effect of metal-based orbitals although emission data for the ^3MLCT was not reported.[37]

Substituting peripheral rings in complexes containing the N,N,C mode can lead to optimisation of the synthesis of the cyclometallated product over the bidentate N,N side-products. Significant improvements in the photophysical properties of Ru(II) complexes may also be observed with substitution on peripheral rings. In the case of complexes displaying the N,N,N coordination mode, *ortho* substitution on peripheral rings leads to greater ring-strain and, therefore, greater distortion from the ideal octahedral coordination geometry. The weaker ligand field strength leads to a lower ^3MC state energy and thermally activated surface crossing onto the latter, from which non-radiative decay readily occurs. However, the favourable effects of σ-donation counteract the unfavourable effects of steric strain in cyclometallated complexes.[38] Substitution with aromatic groups in the position *ortho* to the N can also stabilise the ^3MLCT state. A crystal structure of $[Ru(mappy)(dtp)]^+$ (Fig. 9), indicates significant interligand π–π interactions which enhance the delocalisation of the ^3MLCT state and as a result increase the r. t. excited state lifetime to 107 ns.[38]

In contrast to the growing number of publications for Ru(II) complexes with N,N,C coordination, the number of reported N,C,N mononuclear complexes are relatively few. The N,C,N coordination mode has been obtained using the ligand di-1,3-(2-pyridyl)benzene (dpb) which gives the heteroleptic cyclometallated complex $[Ru(ttpy)(dpb)]^+$ when reacted with $Ru(ttpy)Cl_3$.[39] The λ_{max} of luminescence at 784 nm is significantly lower in energy than for $[Ru(tpy)_2]^{2+}$.[40] The luminescence lifetime is 4.5 ns, an 18-fold increase on the excited state lifetime of $[Ru(tpy)_2]^{2+}$. A number of functionalised analogues have been synthesised as synthetic intermediates in the construction of higher nuclearity complexes although their photophysical data are not available.[41] In addition to incorporating phenyl rings in the terpyridine core, thiophene has been introduced to direct the formation of cyclometallated products.[42] The ligand 6-(2-thienyl)-2,2′-bipyridine can be used to increase the σ-donating ability through cyclometallation, or alternatively, to decrease the σ-donating ability through an N,N,S coordination mode. It is interesting to note that the mode of coordination is pH dependent and may be modulated (Fig. 10). However, the effects of changing coordination modes on the photophysical properties were not reported.[43]

ii) Alternative N heterocycles as strong σ-donors. The σ-donor strength of the ligand may be increased while maintaining an N,N,N coordination mode by changing the nitrogen containing heterocycle in the tridentate ligand. Deprotonated triazole and tetrazole rings have been incorporated into the tridentate core with great success as the negatively charged ligands are more efficient σ-donors than the neutral terpyridine-based ligands.[44] The electron density is driven onto the Ru(II) centre which increases the energy gap between the ^3MC and ^3MLCT states. A mixture of isomers is obtained by introducing a triazole ring due to the inequivalence of N1 and N3 (Fig. 11). The reaction of $Ru(tpy)Cl_3$ with a 2,6-bis([1,2,4]triazol-3-yl)pyridine ligand yielded all three isomers which were isolated through a combination of column chromatography and semi-preparative HPLC (Figs. 11a–c). Previous studies on bidentate analogues had shown that the reaction can be directed to favour one isomer over others by introducing sterically demanding substituents in the C5 position. When the reaction was carried out using 2,6-bis(5-phenyl-[1,2,4]triazol-3-yl), the products in Fig. 11b and Fig. 11c were isolated and could be separated by column chromatography. In order to eliminate the formation of isomers, the symmetric ligand 2,6-bis([1,2,3,4]tetrazol-5-yl)pyridine was also employed. This was reacted with $Ru(tpy)Cl_3$ to obtain the heteroleptic complex without the need for column chromatography. All of the complexes are luminescent at room temperature in ethanol and their excited state lifetimes range from 20 to 80 ns. On protonation of the non-coordinated N's on the heterocyclic rings, the σ-donating strength is diminished and the excited state is quenched.

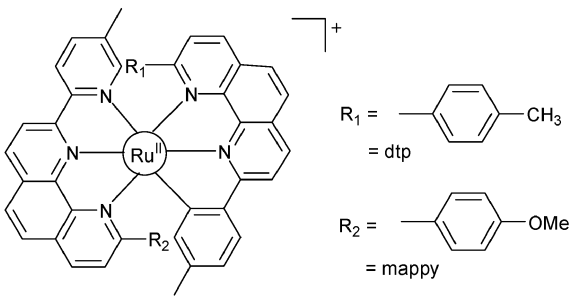


Fig. 9 Cyclometallated complex $[Ru(mappy)(dtp)]^+$.[38]

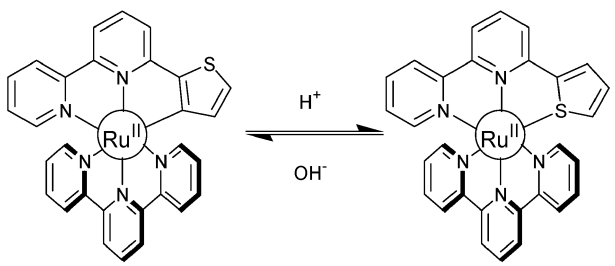


Fig. 10 Reversible cyclometallation of a thiophene-bipyridine ligand.[43]

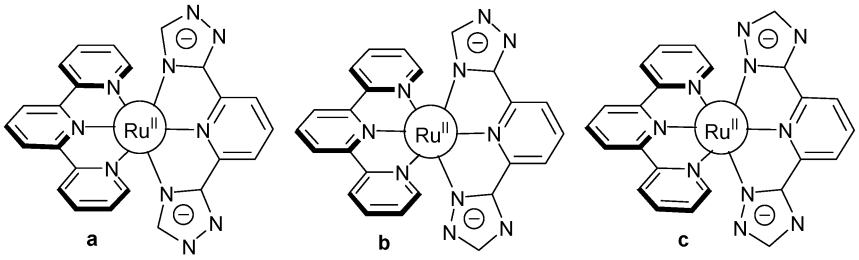
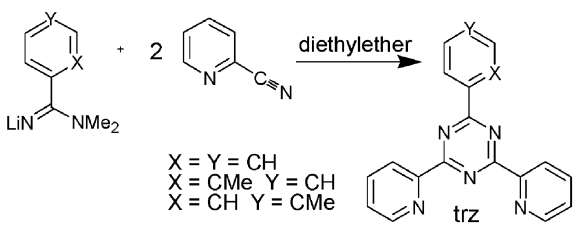


Fig. 11 Three isomers of a triazole-based Ru(II) complex.[44]

b) Decreasing the steric strain in the tridentate ligand

Another way to increase the ligand field strength is to reduce the angular strain in the tridentate ligands, which in turn increases the energy of the metal-based orbitals. A more flexible ligand was made by introducing a methylene spacer between two of the pyridine rings in tpy (Fig. 12).[45] The r. t. luminescence lifetime for the homoleptic complex incorporating the 6-(2-picolyl)-2,2′-bipyridine ligand is 17–18 ns, 70 times greater than that of $[Ru(tpy)_2]^{2+}$.



Scheme 5 Synthesis of tridentate triazine-based ligands.[46]

5 π Electron accepting ability

It has been shown that σ-donor strength can manipulate the energy levels associated primarily with the metal-based orbitals of these complexes. Another approach is to use better π accepting ligands to reduce the energy of the ^{1}MLCT state and consequently the ^{3}MLCT state. The central pyridyl ring of terpyridine can be replaced by a triazine ring while maintaining a N,N,N coordination mode. An efficient synthetic methodology has been developed for a range of triazine-based ligands (Scheme 5).[46]

The homoleptic complexes $[Ru(trz)_2]^{2+}$ and the heteroleptic complexes $[Ru(trz)(tpy)]^{2+}$ were synthesised by standard procedures.[46] The electronic absorption spectra contain ^{1}MLCT absorption bands which are red-shifted compared to the λ_{max} of $[Ru(tpy)_2]^{2+}$ due to the greater π accepting nature of the tpz ligands. The emission energy is significantly lowered as compared to that of $[Ru(tpy)_2]^{2+}$. The heteroleptic complex $[Ru(trz)(tpy)]^{2+}$, with a phenyl group in the pendant position, emits at 740 nm, 2385 cm^{-1} lower in energy than $[Ru(tpy)_2]^{2+}$ and has a lifetime of 9 ns. The stabilisation of the ^{3}MLCT state is also a result of the increased planarity arising from intramolecular H-bonding between the N atoms on the triazine ring with the hydrogens on the pendant phenyl ring. The homoleptic complexes have shorter excited state lifetimes, presumably due to facilitated non-radiative decay due to solvent interaction with the non-coordinated nitrogen atoms on the triazine ring.[46]

The synthesis and characterisation of a related system in which a pyrazine ring is in the central position have been carried out. In addition to polynuclear complexes, the ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine has been used in the synthesis of the mononuclear heteroleptic (tpy) and homoleptic complexes (Fig. 13).[47] Both complexes show some degree of stabilisation of the ^{3}MLCT state with red-shifted emissions at 665 and 648 nm and enhanced luminescence lifetimes of 30 and 50 ns for the hetero- and homoleptic complexes, respectively.

The heterocycles in the peripheral position may also be modified. Introducing pyrazine heterocycles into the tridentate ligand should improve the π accepting ability of these ligands. The 2,6-dipyrazinylpyridine ligand was synthesised using a well developed condensation reaction (Scheme 6).[48] Lifetime studies were carried out in the solid state and the complexes were shown to be weakly emitting at room temperature (τ = 18 ns). The excited state is longer-lived than that of the

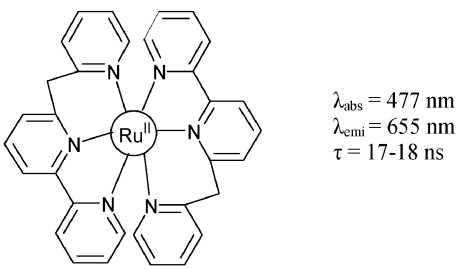


Fig. 12 Increasing ligand field strength by alleviating steric strain in tridentate ligands.[45]

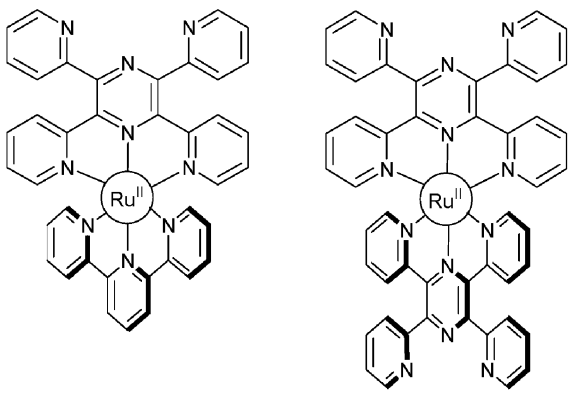


Fig. 13 Hetero- and homoleptic Ru(II) complexes of 2,3,5,6-tetrakis(2-pyridyl)pyrazine.[47]

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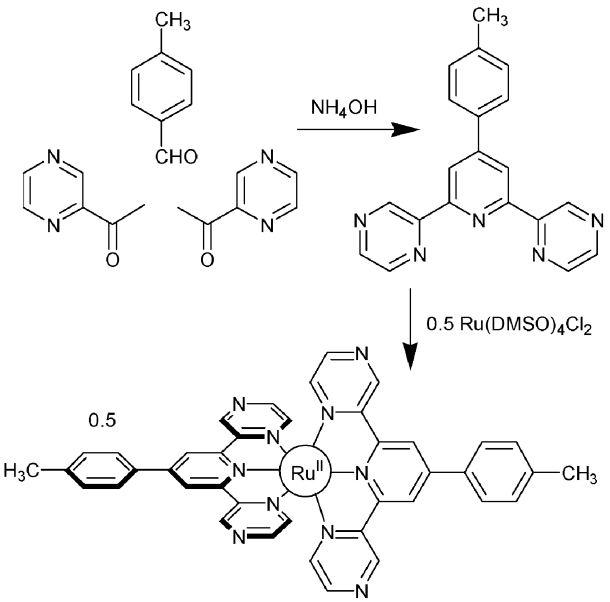

Scheme 6 Synthesis of 2,6-dipyrazinylpyridine and its Ru(II) complex.[48]

tolylterpyridine analogue $[Ru(ttpy)_2]^{2+}$ in the solid state (τ = 10.95 ns).

6 Summary and outlook

The optimisation of the photophysical properties of Ru(II) complexes of tridentate ligands is still a developing area of polypyridine chemistry. In this review, the different approaches currently used to synthesise new ligands and complexes as well as to enhance the r. t. excited state lifetimes of mononuclear complexes have been summarised. To date, the most efficient means of prolonging r. t. luminescence lifetimes is through a bichromophoric system in which emission from the ^{3}MLCT excited state is delayed by equilibration with an isoenergetic triplet state of another chromophore. Fig. 14 gives a summary of the mononuclear tridentate complexes with the longest reported r. t. excited state lifetimes. It is clearly apparent from the current literature that considerable potential exists to increase the luminescence lifetimes of Ru(II) complexes of tridentate ligands using a combination of the strategies outlined herein. Considering the recent interest in polyruthenium dendrimers and polymers containing tridentate ligands,[49,50] the ability to make them r. t. luminescent bodes well for future applications.

Note added in proof: A new bis-carbene tridentate ligand forms a Ru(II) complex with the longest reported luminescence lifetime (3100 ns in H_2O).[51]

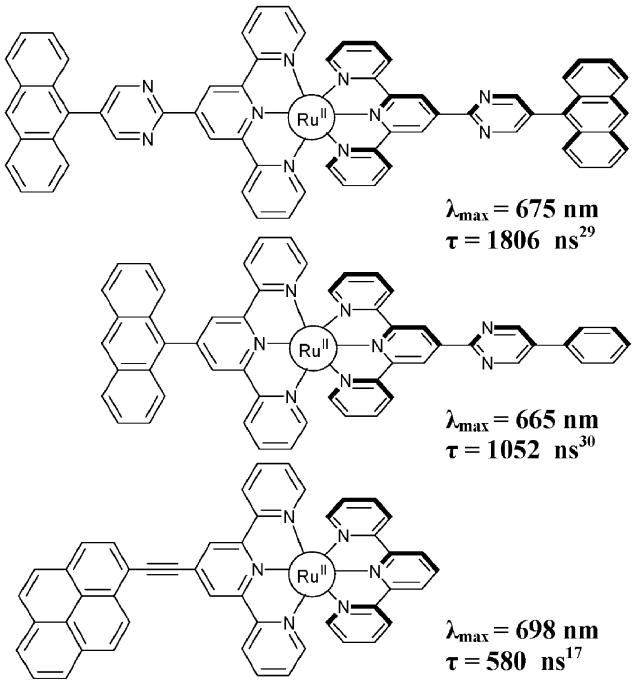

Fig. 14 Top three complexes with the longest r. t. excited state lifetimes.

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† The chloro-pyrimidyl-terpyridine complex from Scheme 2 was coupled with 9-anthrylboronic acid using a Pd(0) catalyst to generate $[Ru(tpy\text{-}pm\text{-}An)_2]^{2+}$.[29]

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