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Design, synthesis and excited-state properties of mononuclear Ru(II) complexes of tridentate heterocyclic ligands

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Artificial photosynthetic systems that contain light-harvesting coordination complexes may one day replace conventional non-renewable sources of energy with renewable solar energy sources. Light-Harvesting Complexes (LHC) are important components of natural photosynthetic systems and are also sought after in artificial systems as well. Polynuclear photoactive complexes are therefore very attractive, and those based on stereogenic $[Ru(2,2'\text{-bipyridine})_3]^{2+}$ are photophysically appealing, but difficult to obtain in a stereochemically pure form. On the other hand, polynuclear complexes based on the achiral $[Ru(2,2':6',2''\text{-terpyridine})_2]^{2+}$ motif are easy to synthesise, however, these complexes are devoid of attractive excited-state properties. Hence strategies to increase the r.t. excited-state lifetime of these complexes would be of practical importance in vectorial electron and/or electron transfer in various optoelectronic applications. This *tutorial review* will report on the sophisticated synthetic strategies currently in use to enhance the photophysical properties of mononuclear Ru(II) complexes of tridentate ligands at room temperature.

Key learning points

(1) You will learn why $[Ru(tpy)_2]^{2+}$-based complexes typically have poor photophysical properties when compared to $[Ru(bpy)_3]^{2+}$-type complexes.

(2) You will learn that although $[Ru(bpy)_3]^{2+}$-type complexes are more desirable for practical applications, their inherent chirality leads to diastereomers in polynuclear complexes.

(3) You will learn how to increase the excited-state lifetimes of $[Ru(tpy)_2]^{2+}$-based complexes using electron-donating and electron-withdrawing groups.

(4) You will learn various approaches to improve the photophysical properties of $[Ru(tpy)_2]^{2+}$-based complexes.

(5) You will learn recent strategies, *e.g.*, incorporation of carbene unit and bichromophoric effects, to prolong the r.t. excited-state lifetimes of $[Ru(tpy)_2]^{2+}$-based complexes.

1. Introduction

Energy and electron transfer as found in natural photosynthetic systems continues to inspire scientists and researchers around the world.[1] As metal–polypyridyl complexes can be used to absorb light in an analogous fashion to natural chromophores, such as chlorophyll-*b* and β-carotenoid in photosystem II (PSII), they are of particular interest. Among the d^6 metal complexes (where M = Re(I), Ir(III), Rh(III), Os(II), Ru(II)), Ru(II) complexes are often sought out as photosensitizers in light-harvesting devices (LHDs)[2] and red-emitting bio-sensors[3] due to their chemical robustness, ease of synthesis and relatively inexpensive Ru-starting material. Thus, Ru(II) complexes that mimic chromophores in PSII are highly desirable.

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Upon absorption of solar energy, the secondary chromophores in the peripheral Light-Harvesting Complexes (LHCs) of PSII transfer the excited-state energy efficiently to the "special pair" of chlorophylls in the reaction centre. Once excited, the special pair transfers an electron, through a series of electron-transfer steps, to plastoquinone, which ultimately leads to the production of ATP.[4] Thus, the Ru–polypyridyl chromophores could be used to mimic chromophores in the LHC or the special pair itself. Absorption of light leads to a singlet metal-to-ligand charge-transfer (^{1}MLCT) excited state, which produces a potentially emitting triplet metal-to-ligand charge-transfer excited state (^{3}MLCT) by spin-crossover (Fig. 1). To be applied in artificial photosynthetic systems, this excited state should possess a sufficiently long lifetime to permit efficient vectorial electron or energy transfer. Careful ligand design is necessary in this context as the ligands play a direct role in governing the energies of the related excited states that ultimately determine the excited-state lifetime.[5]

Considerable attention has focused on the development of LHDs with the photophysically appealing tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) motif due to its long-lived room temperature (r.t.) excited-state lifetime ($\sim$860 ns).[6] However, due to the inherent stereogenicity of the metal centre (Λ and Δ-enantiomers), the purity of polynuclear systems based on these chiral units becomes questionable due to the increasing number of diastereomers for larger polymers. Furthermore, when the complexity of *meridional* and *facial* isomerization is considered, the number of species present becomes daunting.[7] Much interest has thus focused on complexes based on tridentate ligands, for example, 2,2′:6′,2″-terpyridine (tpy), due to its achiral nature and higher symmetry (D_{2d} instead of D_3 in $[Ru(bpy)_3]^{2+}$), which allows rod-like linear arrays to be constructed upon suitable substitution at the 4′-position of tpy.[8] Although achiral complexes are synthetically accessible, $[Ru(tpy)_2]^{2+}$ has poor excited-state properties; the r.t. excited-state lifetime is only 0.25 ns with a quantum yield (Φ) of $\leq 5 \times 10^{-6}$,[9] a consequence of the deviation from ideal octahedral geometry around ruthenium in $[Ru(tpy)_2]^{2+}$ as compared to that in $[Ru(bpy)_3]^{2+}$. Moreover, due to the rigidity of the tpy ligand, which forms two five-membered chelate rings upon coordination to Ru(II), the N–Ru–N *trans* angle is only 158.6°. On the other hand, the N–Ru–N *trans* angle in $[Ru(bpy)_3]^{2+}$ is 173.0°.[10] Due to the distorted octahedral geometry of the N atoms around the ruthenium center, the overall tpy ligand-field strength is weak, so that the non-emissive dd metal-centered triplet state (^3MC) is in close equilibrium with the emissive ^3MLCT state. Hence a non-radiative decay *via* the ^3MC state to the ground state (GS or S_0) is facilitated upon its thermal population from the ^3MLCT state (Fig. 1).[11]

To enhance the excited-state properties of these achiral complexes the process of thermally induced non-radiative deactivation through the ^3MC state has to be reduced. The two primary pathways to reduce the non-radiative decay constant are (i) stabilization of the ^3MLCT state and (ii) destabilization of the ^3MC state; both of which increase the ^3MLCT-^3MC energy-gap. However, if the energy of the ^3MLCT state is very
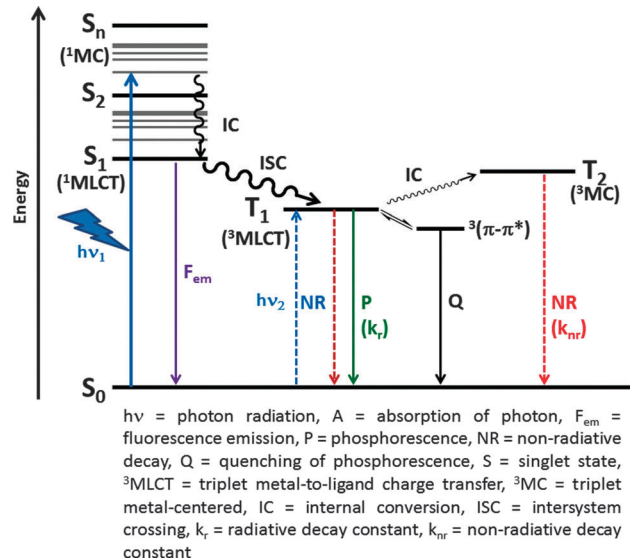

Fig. 1 Qualitative Jablonski diagram illustrating the electronic states of Ru(II) polypyridyl system and transitions among the states. The $^3(\pi–\pi\star)$ state of a secondary chromophore (if present) in this system is in equilibrium with the ^3MLCT state.

low, a direct radiative decay from the ^3MLCT state to the GS comes into play according to energy-gap law,[12] thus shortening the excited-state lifetime (Fig. 1).

In this review, the strategies used to synthesize different tridentate ligands, which govern the photophysical properties of their Ru(II) complexes, will be reported. In addition to the various strategies adopted to increase the ^3MLCT-^3MC energy-gap, an alternate pathway is to introduce auxiliary chromophore(s). If a functionalized complex has a triplet ($\pi–\pi\star$) state that is quasi-isoenergetic to its ^3MLCT state, the $^3(\pi–\pi\star)$ state repopulates the ^3MLCT state through a ^3MLCT-^3MC oscillating equilibrium, effectively acting as an energy reservoir (Fig. 1). We will review the strategies developed to date and highlight the most efficient in four

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sections. This review is strictly confined to homo- or hetero-leptic mononuclear Ru(II) complexes of tridentate ligands due to space constraints.[5,13]

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

2.1. Direct incorporation of an electron-withdrawing or electron-donating substituent onto tpy

Direct attachment of electron-withdrawing groups (EWGs) or electron-donating groups (EDGs) on the 4′-position of the central pyridyl ring has pronounced effects on the photophysical properties of Ru(II) complexes of type [Ru(tpy-X)(tpy-Y)]$^{2+}$ (where X or Y = EWG or EDG). The EWGs operate by stabilizing the ligand-based lowest-unoccupied molecular orbital (LUMO) with a minimal effect onto the metal-based highest occupied molecular orbital (HOMO), while the EDGs destabilize the HOMO without affecting the LUMO to a great extent. In both the cases, a concomitant red-shift in ^{1}MLCT and ^{3}MLCT maxima has been observed compared to the prototypical [Ru(tpy)$_2$]$^{2+}$ (^{1}MLCT and ^{3}MLCT maxima of [Ru(tpy)$_2$]$^{2+}$ are 475 nm and 629 nm, respectively). Substitution by EWGs shows the additional advantage of an increased ^{3}MLCT-^{3}MC energy gap due to stabilization of the LUMO, and subsequently lower thermal population of ^{3}MC states. The luminescence

lifetimes of these complexes are increased and dramatic improvements are observed for complexes with strong EWGs and also in complexes with both EWG and EDG.[8,9,14,15] The ligands for these complexes can be synthesized using recently developed single-step one pot condensation of (X/Y)-substituted arylaldehyde with two equivalents of 2-acetylpyridine in presence of aqueous ammonia (as a source of NH$_3$), to form the central pyridine ring.[5] The homo- or hetero-leptic complexation could be performed by heating 2:1 molar ratio of tpy-X/Y with RuCl$_3$ or Ru(DMSO)$_4$Cl$_2$ (DMSO = dimethylsulfoxide) and heating a suspension of equimolar amount of Cl$_3$Ru(tpy-X/Y) or its solvent adduct with opposite tpy-Y/X, generally in high boiling alcoholic solvents and in the presence of a reductant (Scheme 1).

The incorporation of a positively-charged pyridinium moiety at the 4′-position of a tpy unit has the pronounced effect of stabilizing the ligand-based LUMO in its heteroleptic Ru-complex, as evidenced by a red-shifted ^{3}MLCT emission maximum (775 nm) and long lifetime (125 ns) in [Ru(tpy)(MePy-tpy)]$^{3+}$ (MePy-tpy = 4′-methylpyridinium-2,2′:6′,2″-terpyridine).[16] Heteroleptic Ru(II) complexes of metal–organic rotaxane frameworks (MORFs) containing interlocked alkylpyridinium-tpy and crown ethers also exhibit red-shifted ^{3}MLCT maxima (788–850 nm) with improved excited-state lifetimes (9–24 ns).[5] Molecular dyads of Ru(II)-chromophores and expanded pyridinium acceptors (Fig. 2) have a low-energy emission (670 nm) and extended r.t. luminescence lifetime of 55 ns,[17] although, the first generation pyridinium acceptor with a phenyl
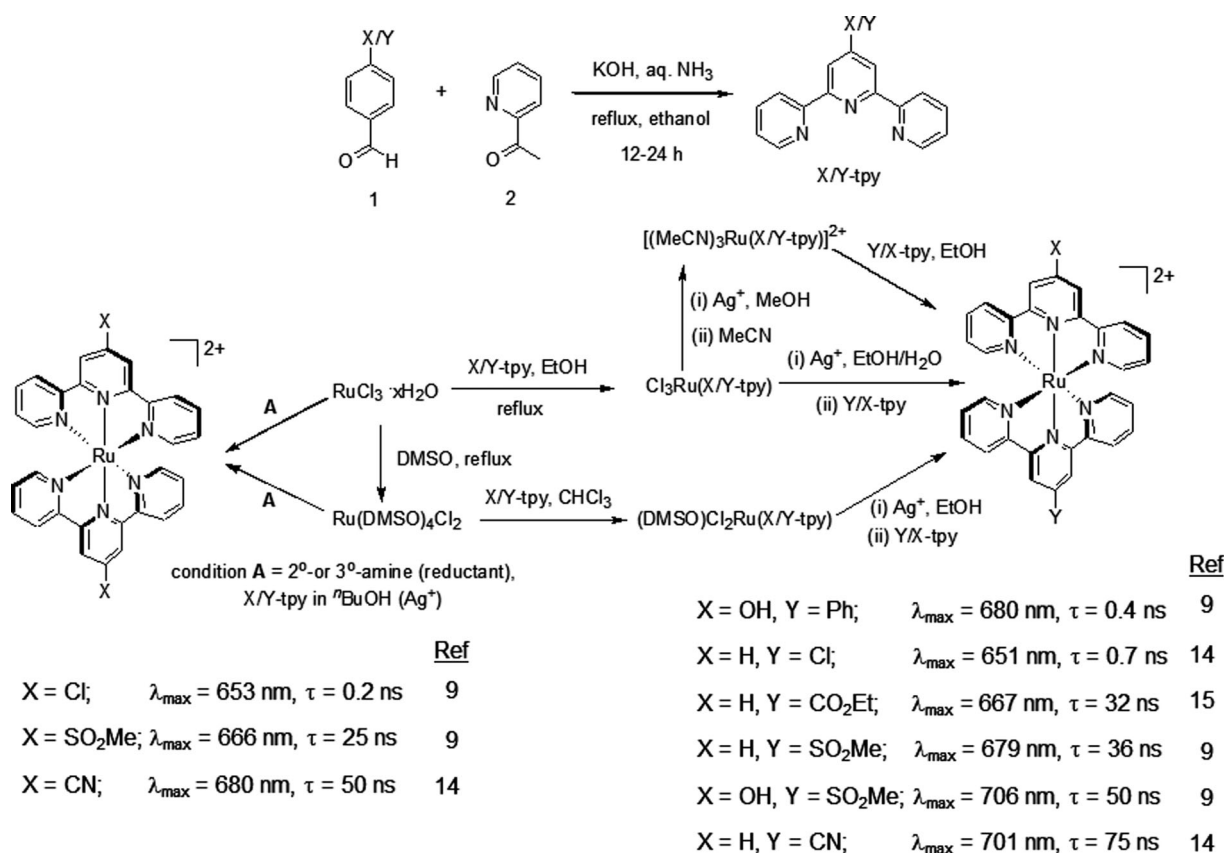
Scheme 1 General syntheses of substituted 2,2′:6′,2″-terpyridines (tpy-X/Y) and their homo- and hetero-leptic Ru(II) complexes with their photo-physical data.[9,14,15]

1st generation dyad, λ_{max} = 685 nm, τ = 15 ns

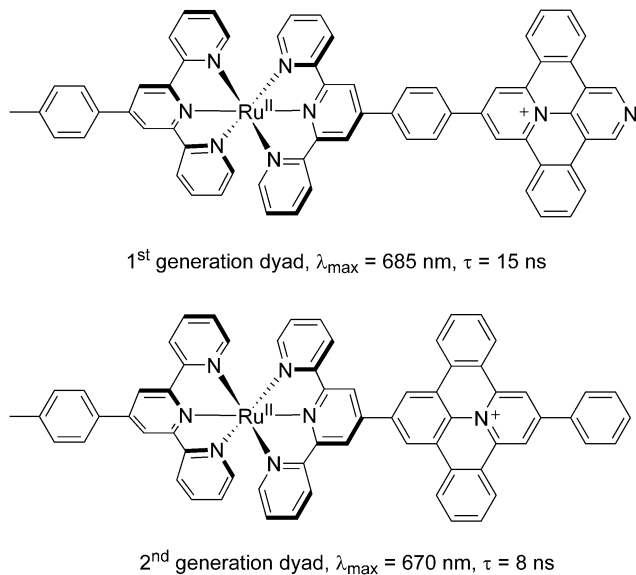2nd generation dyad, λ_{max} = 670 nm, τ = 8 ns

Fig. 2 Photophysical data for donor–acceptor dyad Ru(II) complexes.[17]

spacer and second generation pyridinium acceptor exhibit reduced lifetimes of 15 ns and 8 ns, respectively, this is nonetheless two orders of magnitude higher than that of Ru(tpy)$_2$$^{2+}$.

2.2. Incorporation of extended π-conjugation onto tpy

2.2. (A) Incorporation of extended π-conjugation onto tpy with acetylene as spacer. The enhanced electronic delocalization between a tpy unit and an aryl group, that are connected together by alkynyl linkers, grafted directly at the 4′-position of the tpy unit or at the 4,4′′-position(s) of the peripheral pyridyl groups of tpy unit,[18,19] greatly stabilizes the ligand-based LUMO of Ru(II) polypyridyl complexes and thus results in a higher ^{3}MLCT-^{3}MC energy gap. The subsequent effect is a decrease in emission energy and an increase in the lifetime of the excited state. These

effects are proportional to the number (n) of alkynyl unit(s) when two tpy units are connected in a back-to-back fashion 2(n = 1; λ_{max} = 690 nm, τ = 55 ns; n = 2; λ_{max} = 710 nm, τ = 170 ns). The longest r.t. lifetime for acetylene-based complexes corresponds to the acetylene–pyrene complex (580 ns), which is due to thermal population of the alkyne–pyrene's triplet state (^{3}Alk–Pyr) from the ^{3}MLCT state of the tpy, thus delaying the emission by a "reservoir" effect. A similar effect may be responsible for the extended lifetime of the ferrocene- and terthiophene-based acetylene complexes (Fig. 3).[20,21]

2.2. (B) Direct incorporation of extended π-conjugation onto tpy. The recent fruitful approach of attaching substituted imidazole unit at the 4′-position of tpy to increase the r.t. lifetime of the excited state takes advantage of extended π-delocalization.[22] Attachment of a ferrocenyl group to tpy lowers the energy of the ligand-based LUMO and establishes an equilibrium between the ferrocene's triplet state and the Ru-to-tridentate ligand ^{3}MLCT state, which results in a dramatic enhancement in r.t. lifetime of the corresponding complex (Fig. 4).[23]

2.3. Co-planarity of aromatic groups on the tpy ligand

A direct and relatively unexplored approach of introducing co-planar aromatic rings to improve the π-delocalization of the GS employs a pyrimidyl spacer attached to the 4′-position of the tpy unit. The collective effect of electrostatic interactions between the N atoms of the 2-pyrimidyl substituent and the H atoms of the central pyridine ring renders the 2-pyrimidyl substituent coplanar to the central terpyridine ring (inset crystal structure of similar ligand in Scheme 2). Further stabilization of the ^{3}MLCT state can be achieved through substitution of electron-withdrawing groups in the 5-pyrimidyl position.[5] The syntheses of these types of ligands include transformation of a cyano group to amidinate to obtain 4′-amidinate-2,2′:6′,2′′-terpyridine, which is subsequently reacted with R-substituted vinamidium cations to form the R-substituted pyrimidyl ring at
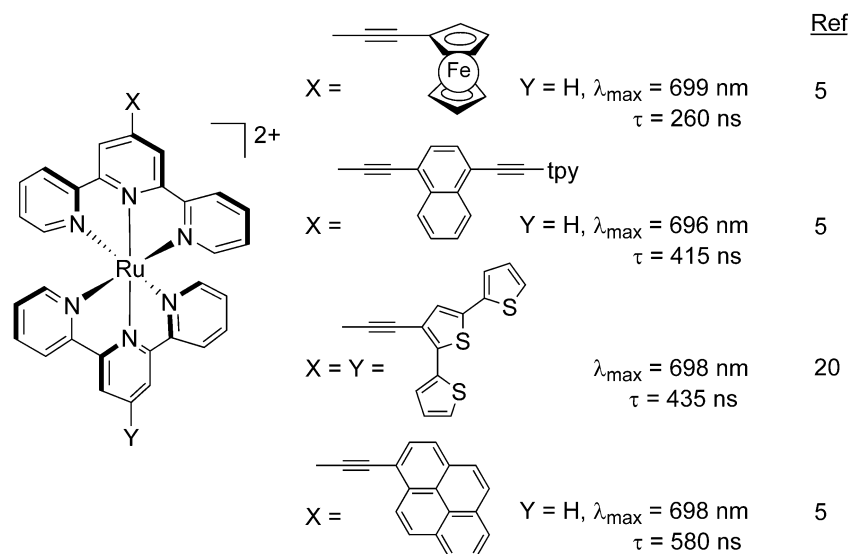

Fig. 3 Photophysical data for acetylene-substituted [Ru(tpy)$_2$]$^{2+}$ complexes.[5,20]

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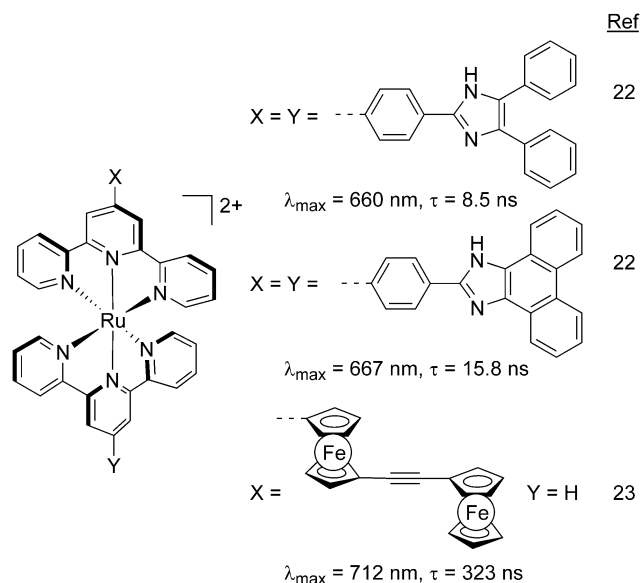
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Fig. 4 Photophysical data for 4′-tpy-substituted $[Ru(tpy)_2]^{2+}$ complexes.[22,23]

the 5′-position (Scheme 2). The homo- and hetero-leptic Ru(II) complexes were synthesized following Scheme 1.[24] All of the complexes exhibit red-shifted ^{3}MLCT maxima and improved r.t. lifetime of excited-state compared to those of $[Ru(tpy)_2]^{2+}$. A relative comparison among the photophysical properties of homoleptic complexes, when R = X = Me and R = X = CN suggests that the EDG do not destabilize the ^{3}MC state to a great extent and non-radiative decay back to the GS is facilitated, while the stabilization of the ^{3}MLCT state is more pronounced with EWG(s), thus leading to higher a ^{3}MLCT-^{3}MC energy-gap and much improved r.t. excited-state lifetimes.
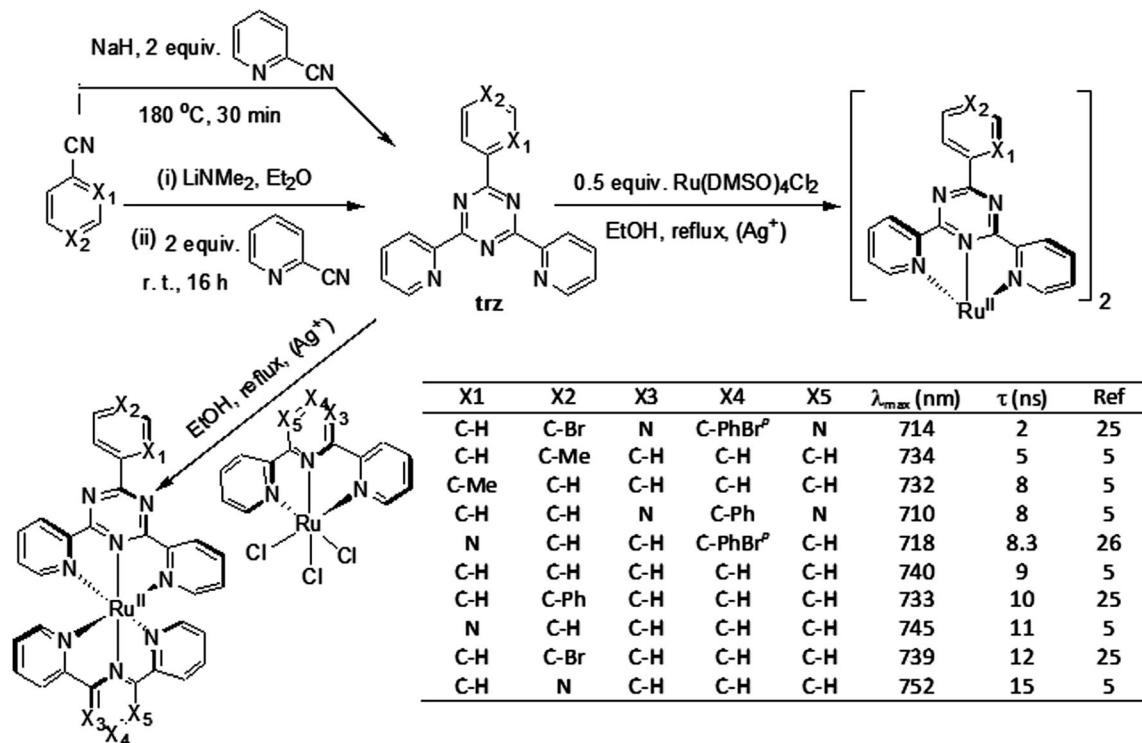
3. π Electron accepting ability

3.1. Introduction of a 2,4(dipyrid-2′-yl)triazine (dpt) unit

The stabilization of the ^{1}MLCT state and consequently the ^{3}MLCT state can be achieved by introduction of a better π-accepting triazine core in place of the central pyridine ring in a tpy unit. The operating coulombic C–H$^{δ+}$–N$^{δ−}$ interactions, as discussed in Section 2.3, are also responsible for overall ligand planarity and subsequently further stabilization of the emissive ^{3}MLCT state. A series of 2,4(dipyrid-2′-yl)triazine (dpt) ligands containing EDGs and EWGs were synthesized by cyclo-trimerization of nitrile groups either (a) in the presence of catalytic amount of NaH at high temperature or (b) via orga-nolithium intermediate under milder conditions (Scheme 3). The homoleptic complexes $[Ru(dpt)_2]^{2+}$ and the heteroleptic complexes $[Ru(dpt)(tpy)]^{2+}$ were synthesized by standard proce-dures (Scheme 3). Concomitant with the bathochromic shift of the ^{1}MLCT maxima in $[Ru(dpt)_2]^{2+}$ and $[Ru(dpt)(tpy)]^{2+}$ as compared to that in $[Ru(tpy)_2]^{2+}$, the ^{3}MLCT emission maxima of these homo- or hetero-leptic complexes are also considerably red-shifted compared to that in $[Ru(tpy)_2]^{2+}$.[5,25,26] The hetero-leptic complex $[Ru(dpt)(tpy)]^{2+}$, with a 4-pyridyl group as a substituent in dpt unit, emits at 752 nm, with an associated r.t. excited-state lifetime of 15 ns. The homoleptic complexes have shorter excited-state lifetimes as compared to those of heteroleptic complexes, presumably due to facilitated non-radiative decay due to solvent interaction with the non-coordinated nitrogen atoms on the triazine ring and the weaker ligand field splitting generated by triazine ligands. Although the homoleptic Ru(II) complex of 4′-phenyl substituted dpt units exhibits a longer r.t. excited-state lifetime of 8 ns, and a longer wavelength emission (λ_{max} = 710 nm) compared to $Ru(tpy)_2^{2+}$, homoleptic Ru(II) complexes with other substituents,
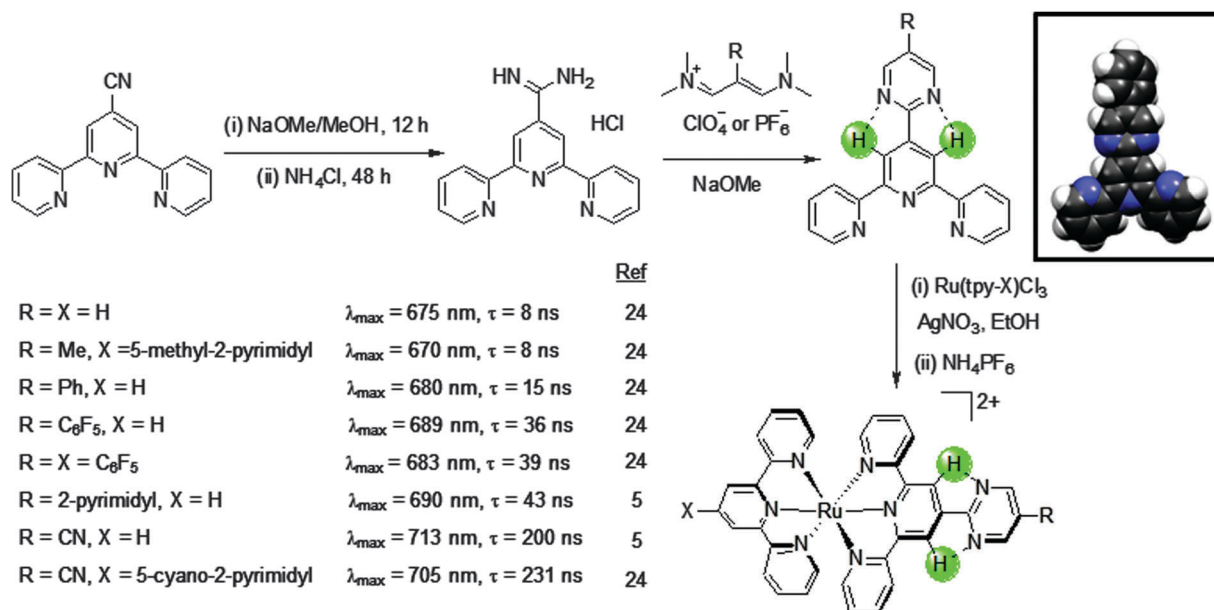
Scheme 2 Syntheses of a variety of substituted pyrimidyl terpyridine heteroleptic Ru(II) complexes and their r.t. excited-state lifetimes (solid-state structure of the ligand (R = Ph) in inset shows the planar arrangement of the central pyridine and the 2-pyrimidyl units).[5,24]

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X1	X2	X3	X4	X5	λ_{max} (nm)	τ (ns)	Ref
C-H	C-Br	N	C-PhBr^p	N	714	2	25
C-H	C-Me	C-H	C-H	C-H	734	5	5
C-Me	C-H	C-H	C-H	C-H	732	8	5
C-H	C-H	N	C-Ph	N	710	8	5
N	C-H	C-H	C-PhBr^p	C-H	718	8.3	26
C-H	C-H	C-H	C-H	C-H	740	9	5
C-H	C-Ph	C-H	C-H	C-H	733	10	25
N	C-H	C-H	C-H	C-H	745	11	5
C-H	C-Br	C-H	C-H	C-H	739	12	25
C-H	N	C-H	C-H	C-H	752	15	5

Scheme 3 Syntheses of tridentate dpt-based ligands and its homo- and hetero-leptic Ru(II) complexes with photophysical data.[5,25,26]

such as, 1-naphthyl, 9-phenanthryl, 1-pyrenyl are non-emissive due to the weaker ligand-field strength of dpt unit compared to the tpy unit, which results in non-radiative deactivation *via* the [3]MC state.[27]

3.2. Introduction of a central diazine unit

Ligands containing differently substituted pyrazine or pyrimidine rings in place of a central pyridine ring in tpy have been synthesized (2,3,5,6-tetrakis(2-pyridyl)pyrazine (**tpp**), 4-chloro-2,6-bis(2-pyridyl)pyrimidine (**cpp**)) and their homo- and heteroleptic complexes with the Ru(II)(tpy)-core were also prepared (Fig. 5, top).[28] All of the complexes display better photophysical properties than that of [Ru(tpy)₂]²⁺, although the sharp decrease in excited-state lifetime of the **cpp** analogue is presumably due to the overly stabilized [3]MLCT state, which deactivates to the ground state as described by the energy-gap law.

3.3. Introduction of peripheral diazine units

Attaching two pyrazine heterocycles in the 2,6-positions of a 4-substituted pyridine ring to furnish different types of tridentate ligands should also improve the π accepting ability of these ligands. Indeed, the corresponding homoleptic Ru(II) complex of 4-*p*-tolyl-2,6-bis(2-pyrazinyl)pyridine exhibits a red-shifted [3]MLCT maximum (667 nm) with a longer r.t. excited-state lifetime (18 ns in the solid state).[5] The deactivation of its r.t. emission is presumably due to strong interaction of the lone pair of the pyrazine N atoms with the solvent.

4. Increasing the energy of the [3]MC state

4.1. σ-Donating ability

Sigma-donor ligands operate by interacting with the metal-based d orbitals, with a minimal effect on the π* orbitals of the ancillary ligand attached to the metal in a heteroleptic complex; thus giving fine control over the HOMO–LUMO gap. Since the interaction destabilizes the HOMO, the overall effect of incorporating σ-donor ligands in Ru(II)–polypyridyl complexes is the lowering of [1]MLCT energy, and consequently, the [3]MLCT energy as well. In addition, the strong donating nature of the ligands destabilizes the [3]MC state, thus, the effective surface crossing from the [3]MLCT state to the [3]MC state is reduced, which in turn, results in a longer excited-state r.t. luminescence lifetime. However, if the [3]MLCT state is too low in energy, non-radiative decay directly to the GS may occur according to the energy gap law. A few major ways of increasing the σ-donor strength of the tridentate ligand are described in the following sections.

4.1. (A) σ-Donating ability of cyclometallating ligands. The anionic nature of cyclometallating ligands makes them appealing as they are strong σ-donors, which significantly increase the [3]MLCT-[3]MC energy gap in their heteroleptic Ru(II) complexes with tpy. Although the excited state is typically quite short lived due to the energy gap law, it is still possible for rapid photo-injection into the conduction band of TiO₂ semi-conductors with efficient photoelectric current conversion (efficiency up to 12% in test cells). Thus, the visible light absorbing Ru(II)
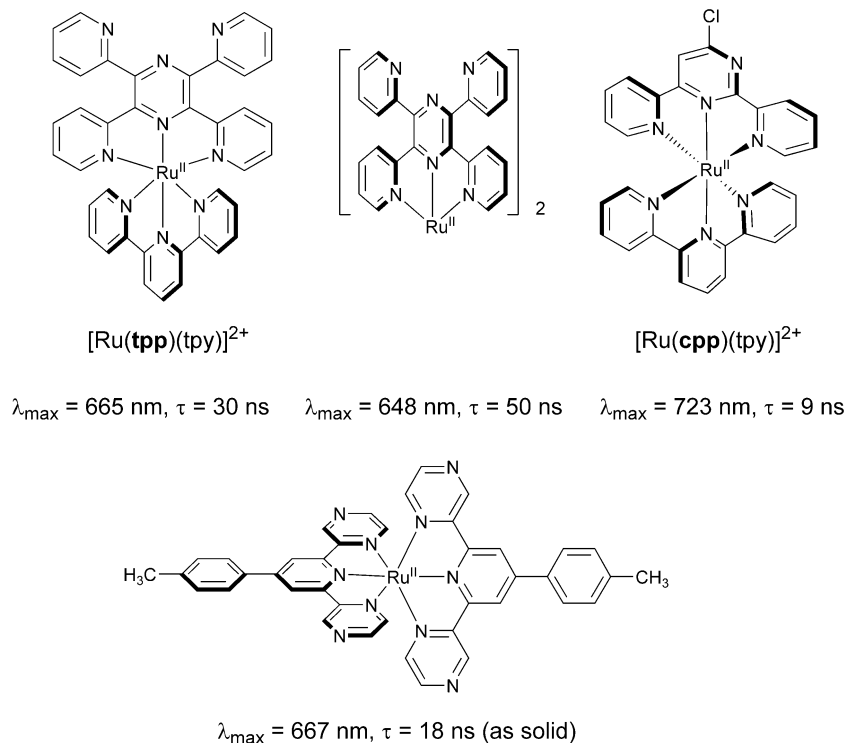
Fig. 5 Hetero- and homo-leptic Ru(ɪɪ) complexes of tridentate ligands containing central diazine units (top). Homoleptic Ru(ɪɪ) complex of 2,6-dipyrazinylpyridine (bottom).[5,13]

cyclometallated complexes have been incorporated into 'next generation' dye-sensitized solar cells (DSSCs).[29] These cyclometallating ligands bind in either N^C^N or N^N^C coordination modes, thus replacing a Ru–N bond with a Ru–C bond. Several strategies have been adopted to develop various types of cyclometallating ligands, for example, (a) quaternization of a tpy-N (or 4′-methylthiotpy-N) atom by trimethyloxonium tetrafluoroborate so that the quaternized N atom is no longer available for coordination, thereby giving a [(N^N^C)Ru(tpy)]+ complex,[5] (b) coupling of a 3-bromo-2,2′-bipyridine with 4-trimethylstannylpyridine to furnish 2,2′:6′,4″-terpyridine, which exhibits a N^N^C tridentate binding mode,[30] (c) attachment of 2,2′-bipyridine with thiophene to afford 6-(2-thienyl)-2,2′-bipyridine which can bind by either N^N^S or N^N^C coordination mode, depending on the pH of the reaction media,[31] (d) incorporation of a phenyl ring into tpy instead of the peripheral or central pyridyl ring to force N^N^C or N^C^N coordination, respectively.[38] Although several homo- and hetero-leptic Ru(tpy) complexes with these kinds of ligands have been synthesized, their luminescence properties have rarely been reported.

The strongly-donating cyclometallating ligands interact with the metal-based $T_2[d(Ru)]$ orbitals, thereby increasing the energy of the HOMO. As the ³MLCT state lies on the non-cyclometallated ligand, a significant amount of red-shift (743–807 nm) is observed in the r.t. emission energy of a series of weakly emissive [(N^N^C)Ru(tpy)]+ or [(N^C^N)Ru(tpy)]+ type of complexes compared to that of [Ru(tpy)₂]²⁺.[32] The poor emission properties, as revealed by the relatively low r.t. excited-state lifetime of [Ru(p-tolyl-tpy)(dpb)]+ (where **dpb** = 2,6-dipyridylbenzene) of

4.5 ns at 784 nm, is possibly due to the small ³MLCT-GS energy gap, which facilitates non-radiative decay from the ³MLCT state to GS.

The effect of enhanced π-delocalization in cyclometallated Ru–polypyridyl complexes greatly stabilizes the ³MLCT state, dramatically increasing the r.t. excited-state lifetime. Complexes with cyclometallating ligands with substitution by aromatic groups in the position *ortho* to the coordinating N atom, for *e.g.*, [Ru(**mappy**)(**dtp**)]+ (where **mappy** = 2-p-anisyl-9-(4-methyl-2-pyridyl)-1,10-phenanthroline and **dtpH** = 2,9-bis(p-tolyl)-1,10-phenanthroline), and several of their derivatives exhibit r.t. low-energy ³MLCT emission maxima (778–816 nm) with longer excited-state lifetimes (70.5–106 ns) at r.t. compared to that of [Ru(tpy)₂]²⁺.[33]

Cyclometallated [(N^C^N)Ru(tpy)]+-complexes containing fused benzimidazolyl (**Mebib**)[34] or substituted triazole units[35] also exhibit improved r.t. excited-state lifetimes due to a combination of favourable effects of σ-donation (Fig. 6), which counteracts the unfavourable effects of steric strain in these complexes and increases π-delocalization.

4.1. (B) Alternative N-heterocycles as strong σ donors. Attaching different N-heterocycles in the 2,6-positions of a pyridine ring affords tridentate heterocyclic ligands that fine-tune the ³MLCT-³MC energy gap in their homo- or hetero-leptic Ru(ɪɪ) complexes. The increased N content in these ligands enhances σ-donation onto the metal (due to resonance effects) and thus destabilizes the metal-based ³MC state. Three different approaches have been adopted to develop σ-donating neutral tridentate ligands with increased N content.
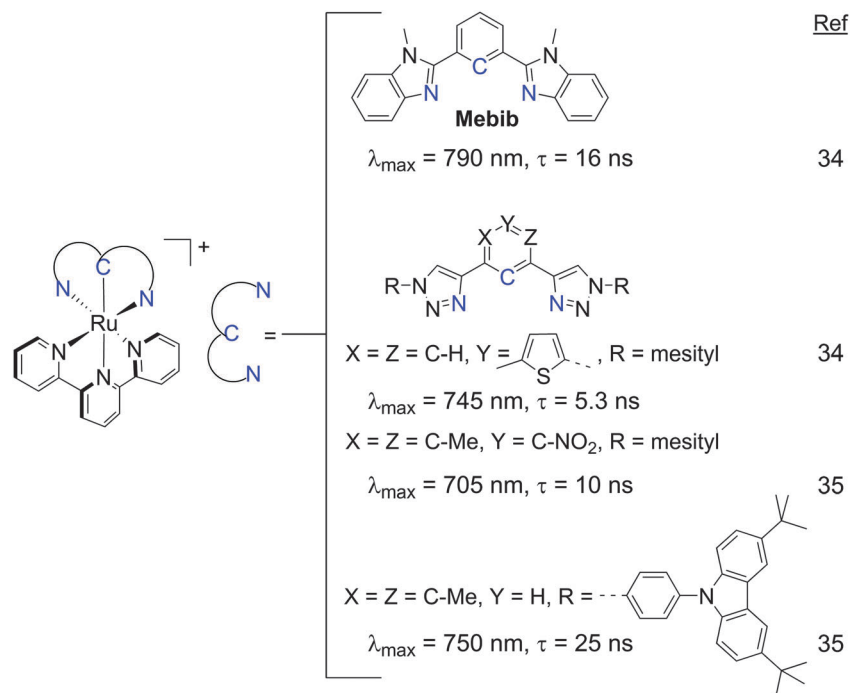
Ref

Mebib

λ_{max} = 790 nm, τ = 16 ns   34

X = Z = C-H, Y = [thiophene] , R = mesityl   34

λ_{max} = 745 nm, τ = 5.3 ns

X = Z = C-Me, Y = C-NO$_2$, R = mesityl

λ_{max} = 705 nm, τ = 10 ns   35

X = Z = C-Me, Y = H, R = [carbazolyl-phenyl]

λ_{max} = 750 nm, τ = 25 ns   35

Fig. 6 Ru–polypyridyl complexes with various cyclometallating ligands.[34,35]

4.1. (B.i) Pyridine ring attached with fused benzimidazolyl ring containing two N. In a typical approach, the bis(benzimidazolyl)-pyridine (**bip**) and bis(*N*,*N*′-dimethylbenzimidazolyl)pyridine (**Mebip**)[34] can be synthesized by condensation of 1,2-pheny-lenediamine and *N*-methyl-1,2-phenylenediamine, respectively, with pyridine-2,6-dicarboxylic acid in polyphosphoric acid at elevated temperature ($\sim$200 °C). The heteroleptic complexes can be synthesized as shown in Scheme 1. The complexes exhibit r.t. luminescence at lower energy associated with a longer excited-state lifetime (Fig. 7). The unfavorable consequences of increased steric strain due to the fused benzene rings in **bip** are countered by the favorable σ-donation due to increased N content. A linear relationship with positive slope of $\ln(k_{nr})$ *vs.* E_{em}^{max} clearly indicates that the predominant pathway of non-radiative decay *via* ^{3}MLCT-to-^{3}MC surface crossing has been efficiently reduced with increasing electron withdrawing influence of the substituent at 4′-position of tpy.[36,37]

4.1. (B.ii) Pyridine ring attached with anionic triazole and tetrazole rings containing three N and four N atoms, respectively. The deprotonation of triazole or tetrazole rings in the tridentate core of 2,6-bis([1,2,4]triazol-3-yl)pyridine and 2,6-bis([1,2,3,4]-tetrazol-5-yl)pyridine, respectively, leads to neutral heteroleptic Ru(tpy)-complexes that have improved photophysical properties. Although anionic triazole ligands donate more electron density towards the metal as compared to neutral ligands, their use remains relatively unexplored due to complications in the purification of Ru-complexes having different substitutional isomers. Nonetheless, by increasing the σ-electron density a red-shift is observed in the r.t. ^{3}MLCT emission maxima (in an average of $\sim$70 nm compared to that of [Ru(tpy)$_2$]$^{2+}$) with a much improved excited-state lifetime (24–77 ns).[5]

[Ru(X,X-**bip**)(Y-tpy)]$^{2+}$

Ref

X = Me, Y = H	λ_{max} = 790, τ = 30 ns	34
X = H, Y = C$_6$H$_4$(Me)^p	λ_{max} = 675, τ = 14.8 ns	36
X = H, Y = C$_6$H$_4$(CH$_2$Br)^p	λ_{max} = 688, τ = 34 ns	36
X = H, Y = C$_6$H$_4$(CH$_2$CN)^p	λ_{max} = 690, τ = 36.9 ns	36
X = H, Y = C$_6$H$_4$(CHBr$_2$)^p	λ_{max} = 696, τ = 50 ns	36
X = H, Y = C$_6$H$_4$(CH$_2$PPh$_3$Br)^p	λ_{max} = 691, τ = 42.5 ns	36
X = H, Y = C$_6$H$_4$(CHO)^p	λ_{max} = 700, τ = 57.5 ns	36
X = H, Y = [pyrene-imidazolyl-phenyl]	λ_{max} = 681, τ = 55.5 ns	37
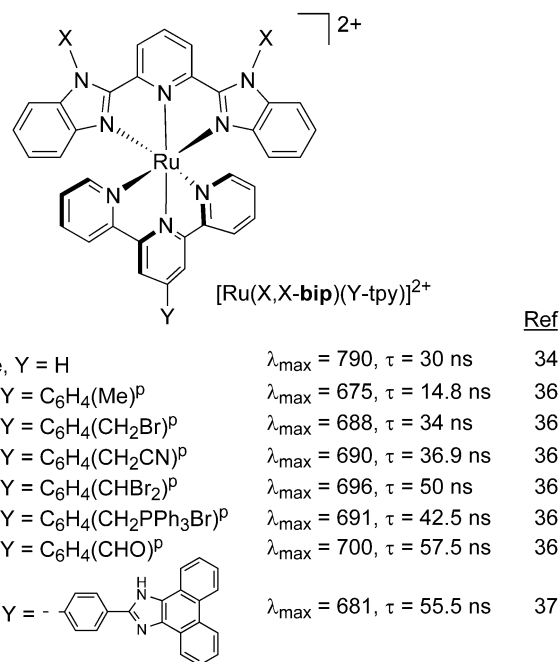
Fig. 7 Ru–polypyridyl complexes with σ-donating bis(benzimidazolyl)-pyridine (**bip**) ligands.[34,36,37]

4.1. (B.iii) Incorporation of carbene unit. The most recent and powerful way to destabilize the ^{3}MC state and thus separate the ^{3}MLCT from the ^{3}MC state is the incorporation of strong σ-donating and π-accepting mesoionic carbene into the tridentate ligand. The multistep synthesis of these carbene ligands includes synthesis of neutral 2,6-bis(substituted-triazolyl)pyridine

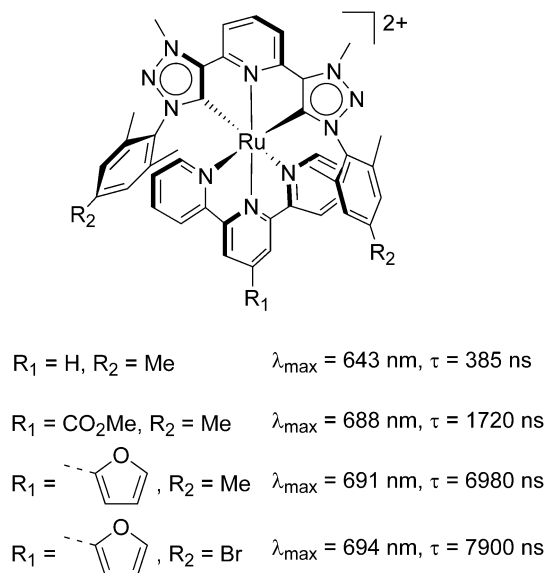R_1 = H, R_2 = Me λ_{max} = 643 nm, τ = 385 ns

R_1 = CO_2Me, R_2 = Me λ_{max} = 688 nm, τ = 1720 ns

R_1 = [furan], R_2 = Me λ_{max} = 691 nm, τ = 6980 ns

R_1 = [furan], R_2 = Br λ_{max} = 694 nm, τ = 7900 ns

Fig. 8 Ru–polypyridyl complexes with σ-donating carbene ligands and their photophysical data in EtOH : MeOH (80 : 20, v/v) at r.t.[38]

precursors with C^N^C cores formed by reacting 2,6-diethynylpyridine and substituted-arylazides in presence of Cu(I)-salt. These precursors were then dimethylated in presence of Me_3OBF_4, followed by the addition of fresh Ag_2O to form the respective carbene ligands as their Ag(I)-salt. The transmetallation reaction of these Ag(I)-activated C^N^C carbenes and cis-[Ru(tpy-R_1)(DMSO)Cl_2] (where R_1 = H, CO_2Me, 2-furyl positioned at the 4′-position of tpy) under mild condition provided the heteroleptic complexes as BF_4 salts. The long τ values of these complexes are governed by the increased separation between the emissive ^{3}MLCT and deactivating ^{3}MC state at r.t. due to high σ-donation by the neutral-carbene moieties (Fig. 8). This fact is also supported by the 77 K emission data, where the compounds exhibit excited-state lifetime of 13–18 μs, which is comparable to that of [Ru(tpy)_2][(PF_6)_2] (τ = 11 μs) at this temperature. The exceptionally long lifetime of the complex substituted by Br at ambient temperature is believed to be due to inductive effect operating on the carbene ligand.[38]

4.2. Expanding the chelate ring

Ligand-field splitting is amplified with a hexacoordinated metal ion in octahedral (or near octahedral) geometry as opposed to a distorted octahedral geometry. Following this argument, approaches have been made to reduce the angular strain formed between the Ru(II) ion and the tridentate ligands, which raises the energy of the ^{3}MC state. This section can be sub-categorized into four other sections, and has seen the greatest interest by researchers in the last decade.

4.2. (A) Single unit expansion to form one six-membered chelate ring. Flexible ligands were synthesized by introducing a sp^3 hybridised carbon-spacer between the N-heterocyclic rings and the 2,2′-bipyridine unit and their complexation reactions with [RuCl_3] or [(p-tolyl-tpy)RuCl_3] have been performed (Fig. 9). In a general approach, these flexible ligands can be synthesized by coupling 2-N-heterocyclic arylbromide with 6-cyano-2,2′-bipyridine in presence of ^{n}BuLi to furnish a bipyridyl-N-heterocyclic-ketone, which can be subsequently reduced to form the sp^3-C. Although the heteroleptic [(p-tolyl-tpy)Ru(bpy-CMe_2-py)] was found to be very weakly emissive, other complexes exhibit slightly improved r.t. luminescence excited-state lifetime with red-shifted emission maxima.[39,40]

4.2. (B) Double unit expansion to form two six-membered chelate rings with broken π-conjugation. The coordination geometry around ruthenium can approach octahedral by incorporating two –NMe– units between the pyridine rings.[41] The resulting tridentate ligand affords two six-membered chelate rings upon complexation. The N,N′-dimethyl-N,N′-dipyridin-2-yl-pyridine-2,6-diamine (**ddpd**) ligand can be synthesized by base-catalyzed nucleophilic substitution of 2,6-dibromo-pyridine by N-methylpyridin-2-yl-amine or by taking advantage of C–N bond forming reaction between 2,6-dibromopyridine and N-methylpyridin-2-yl-amine. The corresponding hetero-leptic complexes were synthesized following complexation reaction in Scheme 1 by microwave-assisted heating. The **ddpd** N_cis–Ru–N_cis bite angles expands up to 87–88°, which is very close to ideal 90° octahedral bite angle, resulting in effective σ-overlap of metal d orbitals ("^ne_g") with the lone pairs of the

X = -CH_2-
λ_{max} = 655 nm, τ = 15 ns

X = -CMe_2-
λ_{max} = 650 nm, τ = 0.3 ns

λ_{max} = 650-700 nm,
τ = ~ 0.1 ns

X = -CH_2-, Y = -CO-
λ_{max} = 810 nm^a
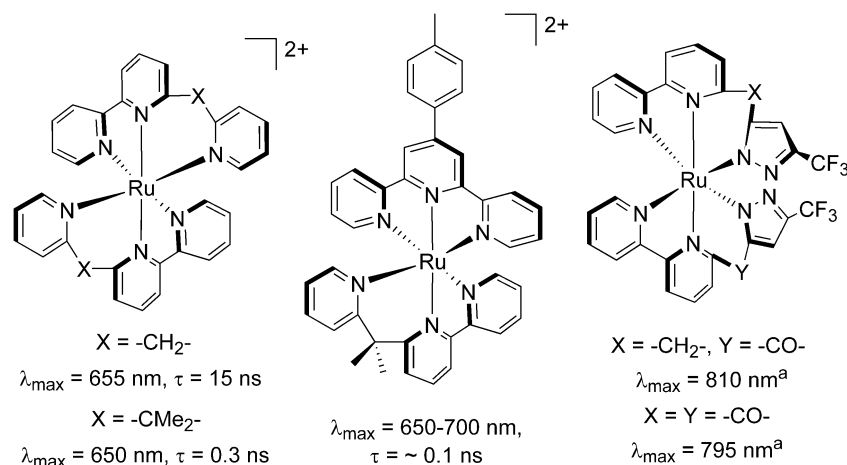
X = Y = -CO-
λ_{max} = 795 nm^a

Fig. 9 Increasing ligand field strength by alleviating steric strain in tridentate ligands.[39,40] ^{a} As solid, no τ is reported.[40]

ddpd nitrogen donor atoms. Due to this optimal overlap, the energy of the metal-based ^{3}MC state increases, thus prolonging the excited-state lifetime at r.t. for these complexes. The added 'push–pull' effect by N donors in the **ddpd** moiety and EWGs in the tpy moiety, respectively, also decreases the HOMO–LUMO gap, resulting in the low-energy ^{3}MLCT emission (Fig. 10).

Another photophysically appealing Ru(II) complex containing two tridentate ligands is the homoleptic Ru(II) complex of 2,6-bis-(2-pyridylmethylketone)pyridine (**bpmkp**), which exhibits r.t. excited-state lifetime up to 3.3 μs in deaerated acetonitrile solution, albeit the ^{3}MLCT maxima shift to a higher-energy region (608 nm) compared to that of [Ru(tpy)$_2$]$^{2+}$. The homoleptic Ru(II) complex of the ligand 2,6-bis(2-pyridylmethylketone)pyridine could be obtained by reaction of 2,6-bis(2-pyridylmethyl)pyridine (**bpmp**) and Ru(DMSO)$_4$Cl$_2$ at 100 °C in *N,N'*-dimethylformamide (DMF). This reaction leads to coordination of the two **bpmp** ligands with one Ru(II) ion, accompanied by simultaneous oxidation of the methylene groups of the **bpmp** ligand to the corresponding diketone ligand. Any attempt to react 2,6-bis(2-pyridylmethyl-ketone)pyridine directly with Ru(DMSO)$_4$Cl$_2$ failed to yield the homoleptic complex. Nonetheless, the almost perfect octahedral geometry around Ru(II)-ion, where N$_{cis}$–Ru–N$_{cis}$ and average N$_{trans}$–Ru–N$_{trans}$ bite angles are 89.58(12)° and 178.48(12)°, increases the ^{3}MLCT-^{3}MC energy gap in such a way that the complex also exhibits a r.t. excited-state lifetime up to 1.36 μs in air-equilibrated acetonitrile solution.[42]

4.2. (C) Double unit expansion to form two six-membered chelate rings with extended π-conjugation. Considerable attention has focused on attaching quinoline, quinoxaline or 7-azaindole groups on to suitably substituted 2,6-dibromo-pyridine to give tridentate ligands that are able to form two six-membered chelate rings with extended π-conjugation and almost linear N$_{trans}$–Ru–N$_{trans}$ bite angle upon coordination (Fig. 11).[43] Several homo- and hetero-leptic Ru-complexes with these ligands have been synthesized. The complexes containing meridional 2,6-di(quinoline)pyridine (**dqp**) as tridentate ligands, and the ester-substituted versions exhibit exceedingly long r.t. excited-state lifetime in MeOH–EtOH mixtures. The relatively short r.t. excited-state lifetime of homoleptic Ru(II) complex of 2,6-di-(quinoxalin-5-yl)pyridine (**dqxp**) is presumably due to the higher stabilization of the ^{3}MLCT state compared to that of the homoleptic Ru(**dqp**)$^{2+}$ complex, so that the direct deactivation to the ground state is viable, although the ^{3}MC state remains high in energy due to near-octahedral geometry and consequently larger ligand-field splitting.[44,45]

4.2. (D) Double unit expansion to form two six-membered chelate rings with guanidine backbone. We recently adopted a mixed strategy in which both the effects, for example, (i) destabilization of metal-based ^{3}MC states due to increased σ-donor ability and (ii) improved ligand-field strength with decrease in angular strain around ruthenium by forming two six-membered chelate rings. Incorporation of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-α]pyrimidine (**H-hpp**) in the 2,6-positions of a pyridine ring gives 2,6-di(**hpp**)pyridine (diguani-dylpyridine or **dgpy**) and subsequent complexation with Ru(Ph-tpy)Cl$_3$ in 1:1 molar ratio affords the heteroleptic complex (Scheme 4). The [Ru(Ph-tpy)(**dgpy**)]$^{2+}$ complex is a NIR-emitter with long r.t. excited-state lifetime and high quantum yield (Φ). These properties are useful for vectorial electron and energy transfer processes in solution or at semiconductor interfaces and also in biological applications as luminescent sensors in cell-imaging systems.[46]

[Ru(R$_1$,R$_2$-tpy)(R$_3$-**ddpd**)]$^{2+}$

[Ru(**bpmkp**)$_2$]$^{2+}$

λ$_{max}$= 608 nm, τ = 3.30 μs[42]

	λ$_{max}$ (nm)	τ (ns)	Ref
R$_1$ = CO$_2$Et, R$_2$ = H, R$_3$ = H	729	722	41
R$_1$ = CO$_2$Et, R$_2$ = H, R$_3$ = NH$_2$	762	149	41
R$_1$ = R$_2$ = CO$_2$Me, R$_3$ = H	744	841	41
R$_1$ = R$_2$ = CO$_2$Et, R$_3$ = NH$_2$	788	136	41
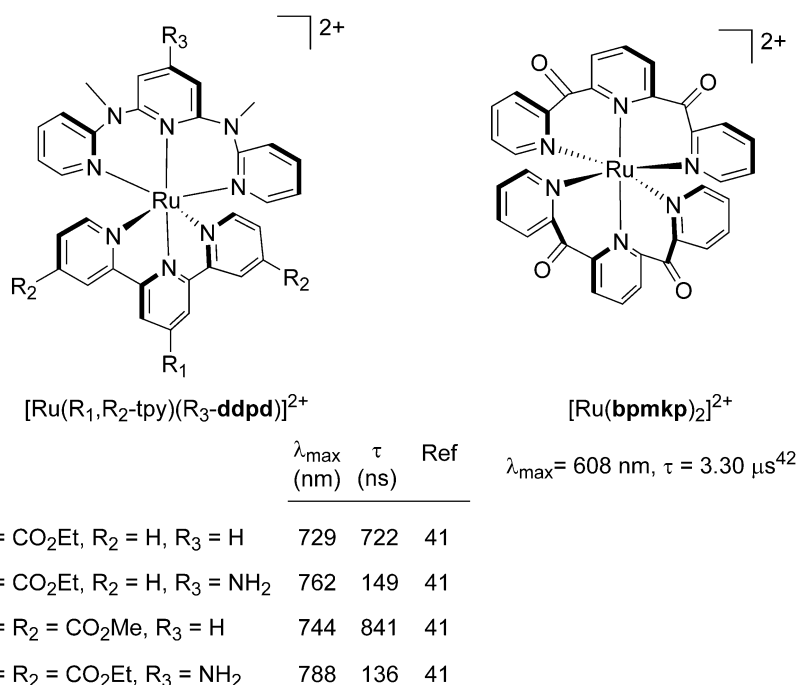
Fig. 10 Increasing ligand field strength by alleviating steric strain in tridentate ligands.[41,42]

$[Ru(dqp)_2]^{2+}$

	λ_{max} (nm)	τ (μs)	Ref
$R_1 = H, R_2 = H$	700	3	44
$R_1 = H, R_2 = Br$	693	2.9	45
$R_1 = H, R_2 = PhBr$	690	3	45
$R_1 = R_2 = PhMe$	694	2.3	45
$R_1 = H, R_2 = CO_2Et$	706	4.3	45
$R_1 = R_2 = CO_2Et$	693	5.5	45

$[Ru(dqxp)_2]^{2+}$
$\lambda_{max} = 715$ nm, $\tau = 255$ ns

$\lambda_{max} = 713$ nm, $\tau = 1570$ ns
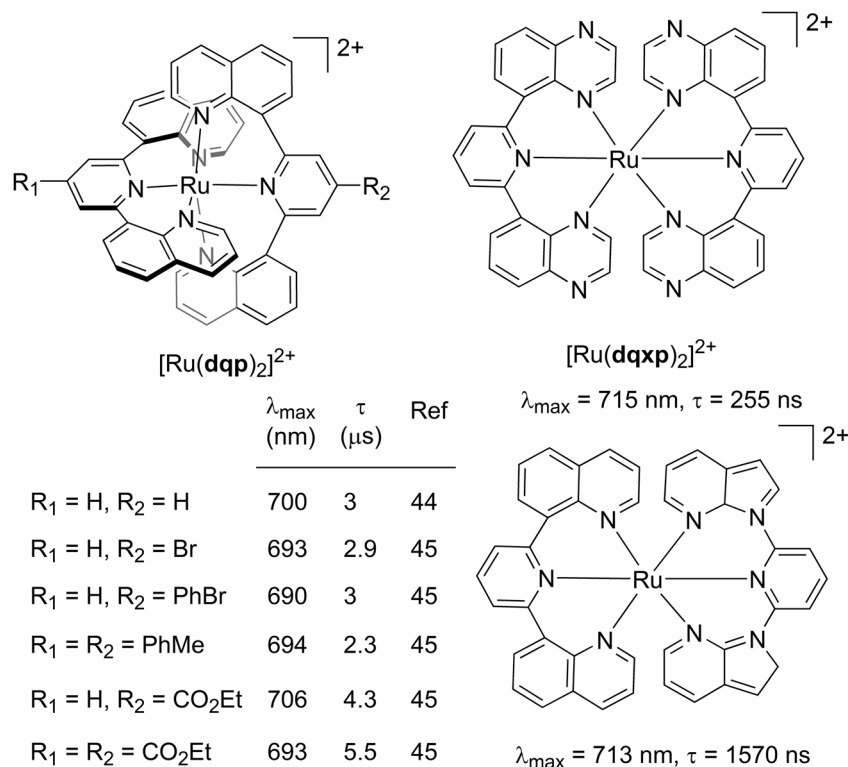
Fig. 11 Increasing ligand field strength by alleviating steric strain in tridentate ligands.[44,45]

$[Ru(Ph\text{-}tpy)(dgpy)] [(PF_6)_2]$
$\lambda_{em} = 901$ nm, $\tau = 129$ ns, $\Phi = 1 \times 10^{-3}$
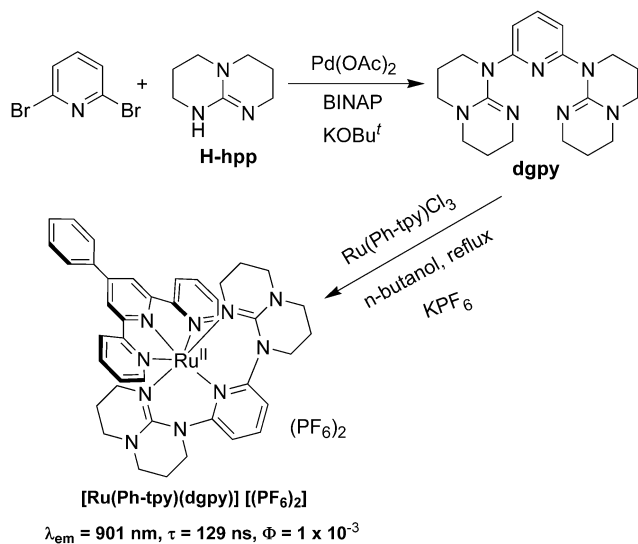
Scheme 4 Strong σ-donor ligand **dgpy** and its heteroleptic Ru(II) complex.[46]

5. Bichromophoric systems

The most successful method that has been adopted so far is the incorporation of an organic chromophore onto the tpy unit. The necessary criterion in this bichromophoric approach is that the newly-introduced auxiliary chromophore should have a triplet state that is quasi-isoenergetic with the emissive ^{3}MLCT state. This will permit reversible inter-component excited-state

energy transfer between the equilibrating ^{3}MLCT and $^3(\pi-\pi\star)$ state of the chromophore, so that the organic chromophore basically acts as an energy reservoir to repopulate the emissive ^{3}MLCT state, with an overall effect of 'delaying' the emission giving longer excited-state lifetimes. The successful incorporation of aromatic hydrocarbons, such as pyrene, naphthalene and anthracene, onto the tpy backbone supports this fact (Fig. 12). The most widely-used auxiliary chromophore is the anthracene (or its substituted derivatives) as its triplet state (^{3}An) is lower in energy ($E^{00} = 1.85$ eV, 671 nm) compared to the ^{3}MLCT energy of tpy-based Ru(II) complexes, whereas pyrene's triplet state (^{3}Pyr) is higher in energy ($E^{00} = 2.10$ eV, 590 nm).[47,48] Despite this mismatch in energy, incorporation of pyrene and naphthalene moieties onto tpy do indeed prolong the r.t. excited-state lifetimes of their corresponding homo- or hetero-leptic complexes (top-left and top-middle complexes in Fig. 12). A dual emission feature is due to the fact that the first component of emission with an associated excited-state lifetime of 1.5–2.1 ns is attributed to the ^{3}MLCT state based on the tpy or phenyl-terpyridine units and the second component arises from the equilibrium with ^{3}Pyr or ^{3}Np (triplet naphthalene) which repopulate the ^{3}MLCT state after the initial emission.[49]

The parent homoleptic Ru(II) complex, $[Ru(tpy\text{-}An)_2]^{2+}$, which consists of an anthracene moiety directly connected to the 4′-position of terpyridine, is not luminescent at room temperature. This is due to the fact that 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 ^{3}MLCT excited state. The complexes with ligands containing a phenyl or 2-pyrimidyl spacer between the 4′-position of a dpt or tpy unit, respectively, and the (substituted)anthracene exhibit prolonged r.t. excited state lifetimes. It was found that the incorporation of phenyl-dpt or 2-pyrimidyl-tpy spacers render the ^{3}An state nearly isoenergetic to the emissive ^{3}MLCT state and hence the ^{3}MLCT-^{3}An equilibrium is now more facile. The mono-exponential decay in the r.t. excited state lifetime of the Ru(II) complexes containing dpt core (top-right complexes in Fig. 12) may be explained as an emission from a triplet intraligand state, resulting from the mixing of triplet ^{3}MLCT and ^{3}An state.[25] Homo- or hetero-leptic Ru(II) complexes of 4′-[5-(9-anthryl)-pyrimid-2-yl]tpy and tpy or 5-chloro-pyrimid-2-yl-tpy (bottom-left and bottom-middle complexes in Fig. 12) exhibit a first relatively short-lived r.t. excited-state lifetime associated with the ^{3}MLCT state of pyrimidyl-tpy and a second fairly long-lived, particularly for the homoleptic complex, 'delayed' excited-state lifetime resulting from its repopulation from the ^{3}An state.

The longest r.t. excited-state lifetime from a Ru(II)-bis(tridentate) complex (bottom-right complex in Fig. 12), reported to date gains mixed advantage of (i) relieved angular strain by forming two π-delocalized six-membered rings around Ru(II)-ion and (ii) the bichromophoric effect, rendering it luminescent with a secondary excited-state lifetime of 42 μs at r.t in degassed acetonitrile. This extremely long lifetime is due to near quantitative reversible electronic energy transfer between the ^{3}MLCT and ^{3}An states. The excited-state equilibration is essentially complete in less than 400 picoseconds with an average of 94% of energy being stocked on the organic energy reservoir, as revealed by ultrafast time-resolved spectroscopies.[50]

6. Summary and outlook

In this tutorial review, different strategies to synthesize new tridentate ligands with different electronic and steric properties and their mononuclear homo- or hetero-leptic Ru(II) complexes have been presented. Various approaches to enhance the r.t. excited-state lifetime of these complexes, based on judicious design of ligands, are also discussed. To date, the most efficient means of prolonging r.t. luminescence lifetimes is through a combination of the bichromophoric approach and the effect of
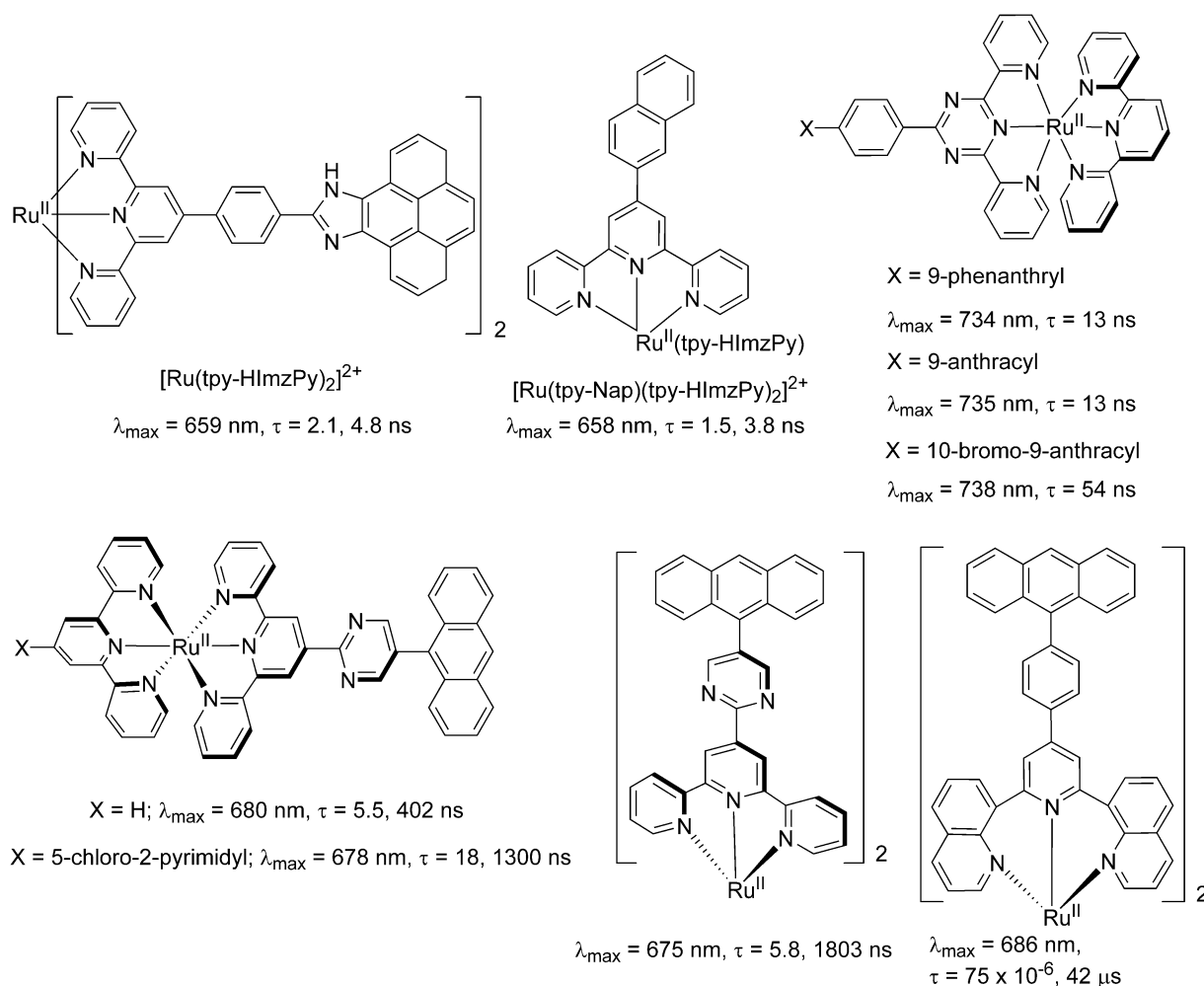

[Ru(tpy-HImzPy)$_2$]$^{2+}$
λ_{max} = 659 nm, τ = 2.1, 4.8 ns

[Ru(tpy-Nap)(tpy-HImzPy)$_2$]$^{2+}$
λ_{max} = 658 nm, τ = 1.5, 3.8 ns

X = 9-phenanthryl
λ_{max} = 734 nm, τ = 13 ns
X = 9-anthracyl
λ_{max} = 735 nm, τ = 13 ns
X = 10-bromo-9-anthracyl
λ_{max} = 738 nm, τ = 54 ns

X = H; λ_{max} = 680 nm, τ = 5.5, 402 ns
X = 5-chloro-2-pyrimidyl; λ_{max} = 678 nm, τ = 18, 1300 ns

λ_{max} = 675 nm, τ = 5.8, 1803 ns

λ_{max} = 686 nm,
τ = 75 × 10^{-6}, 42 μs

Fig. 12   Bichromophoric Ru(II) complexes of tridentate ligands.

λ_{max} = 686 nm, τ = 42 μs

λ_{max} = 694 nm, τ = 7.9 μs λ_{max} = 693 nm, τ = 5.5 μs
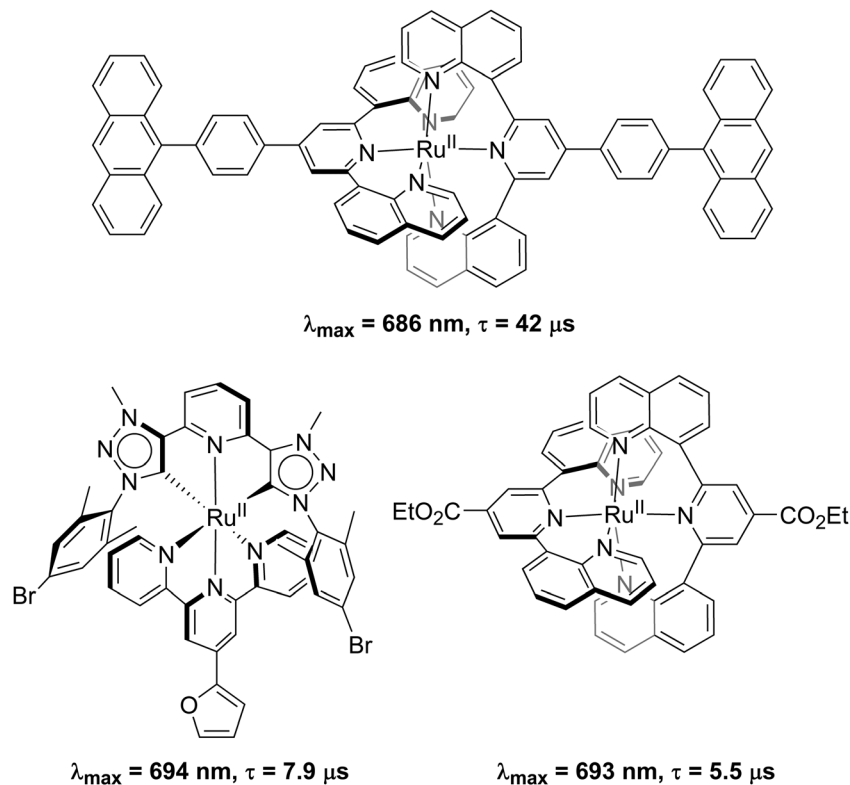
Fig. 13 Top three Ru(II) complexes of tridentate ligands with the longest r.t. excited-state lifetimes.

reducing the angular strain around the metal ion. The incorporation of strong σ-donor tridentate ligands in the form of **dgpy** or NHC is also reasonably promising. Fig. 13 gives a summary of the mononuclear tridentate complexes with the longest reported r.t. excited-state lifetimes. Although the optimization of the photophysical properties of Ru(II) complexes of tridentate ligands is still a developing area of polypyridine chemistry, it is clearly apparent from the survey of recent literature that the luminescence lifetimes of Ru(II) complexes of tridentate ligands can further be improved using a combination of the strategies outlined herein. Considering recent interest in polymers containing ruthenium complexes of tridentate ligands in LHD and DSSC applications, these new ways to synthesize r.t. luminescent ruthenium complexes with long excited-state lifetimes bode well for future applications.

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