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Review

Synthesis and properties of mono- and oligo-nuclear Ru(II) complexes of tridentate ligands: The quest for long-lived excited states at room temperature

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Contents

Abstract

Manipulation of metal-to-ligand charge-transfer states of Ru(II) complexes incorporating tridentate ligands has been made possible through careful synthetic designs and has led to enhancement of the photophysical properties of various complexes. Light-harvesting mono- and oligonuclear complexes possessing these optimised photophysical properties are excellent candidates for applications in artificial photosynthetic devices. In this review, we summarise the synthetic methods used to improve the photophysical properties of Ru(II) complexes based on tridentate ligands and explore the application of these strategies to oligonuclear complexes incorporating Ru(II) metal centres. Current methods of improving the photophysical properties of $\mathrm{Ru(tpy)_2}^{2+}$-type complexes (tpy = 2,2′:6′,2″-terpyridine) concentrate on changing the coordination sphere of the metal ion by incorporating different heterocycles into the ligand or by expanding the tpy core.

Keywords: Ru(II); Mononuclear and oligonuclear complexes; Tridentate ligands; Room temperature luminescence lifetimes

1. Introduction

The development of artificial photosynthetic devices based on the fundamental processes of energy and electron transfer found in photosynthetic biosystems is an attractive goal [1,2]. Although many approaches to functional artificial photosynthetic devices exist, research over the past few decades has tended to focus on the two main components of photosystem II (PSII) in order to better understand, and eventually mimic, the natural process (Fig. 1) [3]. The first component is comprised of the light-harvesting antennae, in which secondary chromophores (SC) are used to absorb, collect and transfer light energy through to the primary chromophore (PC), which is the focal point of the energy transfer cascade [4–7]. The second component also contains the

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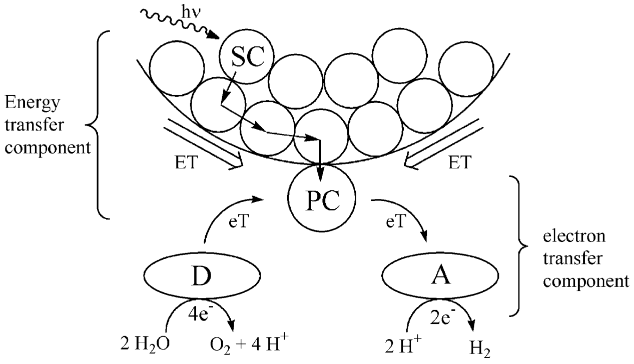


Fig. 1. The energy and electron transfer components of an artificial photosynthetic device—SC: secondary chromophore; ET: energy transfer; PC: primary chromophore; eT: electron transfer; D: electron donor; A: electron acceptor.

primary chromophore, but as the mediator of electron transfer reactions to an electron acceptor (A) and donor (D), where the electron and the corresponding electron hole are transferred in opposite directions [8,9]. The primary chromophore is necessarily accessible by both the energy and the electron transfer conduits.

In PSII, chlorophylls and carotenoids are the secondary chromophores, and they absorb and transfer solar energy toward the special pair, which plays the role of the primary chromophore. The excited special pair transfers an electron through to an acceptor, plastiquinone, which ultimately leads to the transfer of protons and electrons in order to produce ATP [10,11]. The electron hole in the reaction centre is replenished by a tyrosine residue, and then a manganese cluster, which leads to the oxidation of H_2O to O_2. In an artificial photosynthetic device, an electron would be transferred to an acceptor in order to generate H_2 from H^+ with the help of a suitable redox catalyst (Fig. 1) [12]. An electron donor (e.g. H_2O) would then be required to replace an electron in the reaction centre, thus regenerating the primary energy and electron reservoir [13].

Considering the benefits of producing hydrogen from water, considerable research effort has been directed to artificial photosynthetic systems, and there have been significant advances in the optimisation of the photophysical properties of non-natural chromophores for use in light-harvesting devices (LHDs) [14–18]. The inorganic systems involving d^6 metal polypyridine complexes show promise in this field due to their extended excited-state lifetimes, essential for efficient long-range electron transfer [14]. In general, polypyridine complexes of heavy d^6 metals can be excited in the visible region of the electromagnetic spectrum resulting in a metal-to-ligand charge transfer (MLCT) transition [15,16]. The singlet MLCT state rapidly undergoes inter-system crossing to the ‘triplet’ ^{3}MLCT on a time-scale of <100 fs before emission from the lowest energy excited state [17]. Ir(III), Rh(III), Os(II) and Ru(II) all have interesting properties when complexed to polypyridine ligands but it is the stability, ease of synthesis and relatively inexpensive starting materials which have favoured the intense research into Ru(II) complexes [18].

Ru(II) complexes based on bidentate bipyridine ligands have excellent photophysical properties and have been applied as chromophores in LHDs [14–18]. However, these complexes are chiral and building polynuclear systems based upon them can become exponentially problematic when trying to resolve isomers in a reaction mixture [12]. Despite the methods available for separating enantiomers in the substituted tris-bidentate complexes of 2,2′-bipyridine (bpy) [19], rapid synthesis of isomerically pure polynuclear systems is still difficult [20].

Over the last decade attention has turned to tridentate, achiral analogues based on 2,2′:6′:2″-terpyridine (tpy) [12]. Progress in the design and development of Ru(II) tpy-type complexes was initially limited by difficult ligand synthesis as tpy was first isolated in the 1930s by oxidative coupling of pyridine [21,22]. Current synthetic procedures either require metal-catalysed coupling of pyridyl rings or, more effectively, the central pyridine ring can be generated in a ring-forming reaction [23]. A multi-gram synthesis of tpy using two steps through a pyridyl-enaminone intermediate is a widely used route to unsubstituted tpy [24]. Recently, however, one-pot syntheses were reported using both solvent-less and solvent-assisted conditions [25]. 4′-Aryl substituted terpyridines are more readily synthesised and the classic approach requires the synthesis of a diketone intermediate through the condensation reaction of two equivalents of 2-acetylpyridine with an appropriate aryl aldehyde [23,26]. The synthesis has been well developed for both mononucleating ligands with a number of variable aromatic groups substituted in the 4′-position as well as dinucleating ligands [27,28].

Despite the improvements in the modern synthetic procedures to obtain tpy, the photophysical properties of the Ru(II) tpy-based complexes are poor. An excited-state lifetime of 0.25 ns is observed for $Ru(tpy)_2{}^{2+}$ at room temperature [29], inferior to that of $Ru(bpy)_3{}^{2+}$, which has a lifetime near 850 ns [30], albeit sufficient for incorporation in Gratzel-type cells [1]. The steric strain resulting from tridentate coordination reduces the ligand field strength of the tpy as compared to the bidentate-bpy analogues; consequently, thermal access to a metal-centred (MC), non-emissive state is enhanced at room temperature [31]. Ru(II) complexes of tridentate ligands with prolonged excited-state lifetimes would therefore be required in order to benefit from their achiral nature.

A number of different strategies have improved the photophysical properties of Ru(II) complexes of tridentate ligands [32]. Herein, we summarise the strategies developed for mononuclear systems and their application to the synthesis of oligonuclear complexes with extended excited-state lifetimes at room temperature (RT) [33,34]. As the scope of this area of research is very large, only RT luminescent mono- and oligonuclear Ru(II) complexes of tridentate ligands have been considered for the purpose of this review.

2. Mononuclear complexes of tridentate ligands

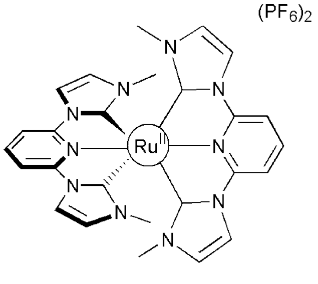
The synthetic procedures used to modify the properties of mononuclear, $Ru(tpy)_2{}^{2+}$-type complexes can be summarised in two ways: (a) methods involving a change in the coordination sphere that no longer retain the tpy ligand and (b) methods involving substitution on the tpy core that maintain the tpy ligand. For both examples the photophysical properties are enhanced by manipulating the energies of the MLCT or MC states, or a combination of the two, in order to maximize the energy difference between these two states.

2.1. Incorporating alternate heterocycles

Alternate heterocycles can replace the central and peripheral pyridyl rings in new tridentate ligands. A series of Ru(II) complexes based on carbenes were recently synthesised and shown to have very promising photophysical properties (Fig. 2, complex **1**) [35].

Carbenes are extremely good σ-donors and are, therefore, strongly bound to the metal centre, which consequently increases the energy of the MC states. The ^{1}MLCT states for carbene complexes such as **1** are excited at wavelengths between 340 nm and 380 nm, significantly blue-shifted compared to $Ru(tpy)_2{}^{2+}$ (475 nm). The excited-state lifetimes are enhanced considerably as Br-salts in aqueous solutions (3100 ns) as compared to PF_6 salts in acetonitrile (820 ns), which is very promising for practical applications. Alternative strong σ-donor ligands, using anionic triazole ligands, have been substituted at the peripheral position (Fig. 2, complex **2**). The heteroleptic complexes incorporating the triazole ligand destabilise the ground state, thereby lowering the energy of the ^{3}MCLT state. As a result the complexes emit at lower energy (~700 nm) and excited-state lifetimes can be extended to 77 ns. Protonation of the triazole rings results in quenching of the excited state as the protonated rings reduce σ-donating ability, and thereby reverses the process [36].

Cyclometallating ligands can also be effective in improving the σ-donating properties of the ligands: they can be synthesised by removal of the coordinating N-atom, by replacing a pyridine ring with a phenyl ring or by protecting the N-atom from metal-ion coordination. There are a number of cyclometallating systems in the literature and the synthetic procedures vary from one system to the next. One of the simplest ligand systems is 6-phenyl-2,2′-bipyridine (phbpy) [37]. The syntheses of its Ru(II) complexes are highly solvent dependent. Glacial acetic acid with a reducing agent (*N*-ethylmorpholine) favoured the synthesis of the bidentate coordinated complex as a deep red solution (Fig. 3, complex **3**).



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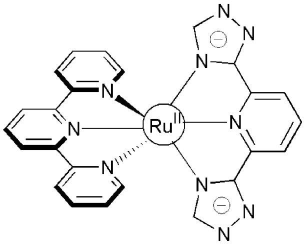

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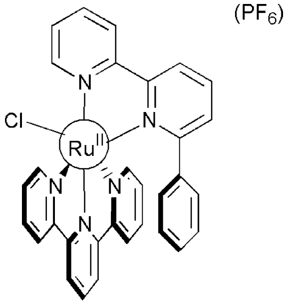
Fig. 2. Ru(II) complexes of strong σ-donors: carbene complex **1** and triazole complex **2** [35,36].



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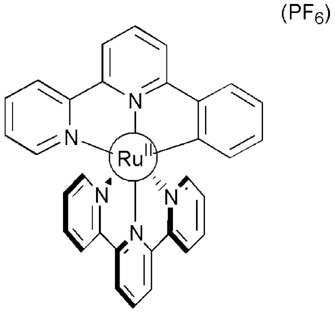

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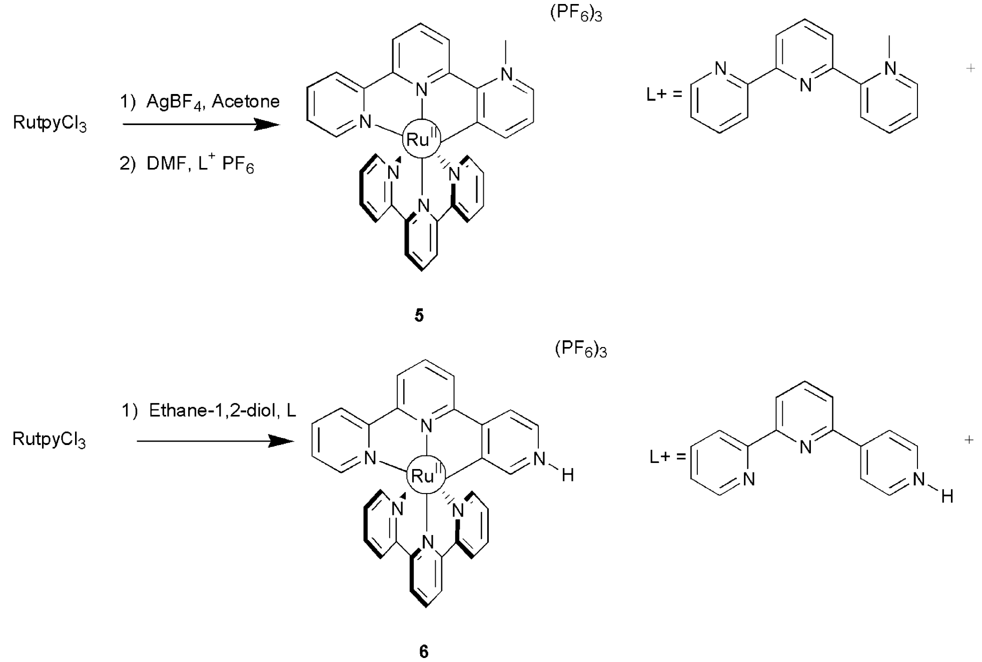
Fig. 3. Competition between bidentate and cyclometalling coordination [37].

However, using butan-1-ol resulted in a red/purple solution containing a 1:1 mix of cyclometallated and bidentate coordinated complexes which were separable by column chromatography. Methanolic reactions favoured the formation of the purple cyclometallated product in a 10:1 ratio (Fig. 3, complex **4**). Aqueous reactions almost exclusively favoured the formation of the same purple product but the reaction proceeded very slowly due to the poor solubility of the starting materials. The absorption spectrum of **4** displays a ^{1}MLCT band at ~500 nm. The enhanced σ-donating ability destabilises the ground state lowering the energy of the ^{1}MLCT state and consequently the ^{3}MLCT state. The complex $Ru(phbpy)(ttpy)^{2+}$ emits at 808 nm at room temperature with an associated excited-state lifetime of 60 ns [38].

Eliminating the possibility for *N*,*N*,*N* coordination by quaternising one of the peripheral N-atoms can facilitate the synthesis of cyclometallating complexes [39]. However, quaternisation of tpy is not straightforward and in order to obtain *N*-methyl-2,2′:6′,2″-terpyridinium hexaflurophosphate exclusively, methylation of tpy was carried out with trimethyloxonium tetrafluoroborate in DCM at reflux for 2 h followed by counter-ion exchange. Dechlorination of $Ru(tpy)Cl_3$ in acetone using $AgBF_4$ prevented the formation of the chlorinated bidentate complex (Scheme 1, complex **5**). The reaction of the solvated complex with the ligand salt in DMF afforded the cyclometallated product in 11% yield. In this system a reducing agent was not used as reactions carried out in the presence of *N*-ethylmorpholine resulted in ligand scrambling to yield significant amounts of $Ru(tpy)_2{}^{2+}$ and partial reduction of the Ru salt to metallic ruthenium. Similarly to the example above, a red-shift in the ^{1}MLCT band (505 nm) was observed in the absorption spectra on comparison to $Ru(tpy)_2{}^{2+}$ along with the presence of a second ^{1}MLCT band at 380 nm, although no emission was noted. Using 2,2′:6′,4″-terpyridine, *N*,*N*,*N* coordination is impossible and the synthesis of the cyclometallated analogue can be favoured using ethane-1,2-diol (Scheme 1, complex **6**) [40]. Using either glacial acetic acid or methanol with a reducing agent afforded a complex mixture of products. The ^{1}MLCT band in the electronic spectra is slightly blue-shifted on comparison to the phenyl-bipyridine and a higher energy MLCT band is observed at 354 nm associated with the π^* orbital of the cyclometallating ligand.



Scheme 1. Synthetic procedure favouring the synthesis of cyclometallating products [39,40].

Two 4′-methylthio-terpyridines also gave cyclometallated complexes with methylated 4- and 3-pyridyl groups as one of the metallated rings [41]. Refluxing the 4- and 3-pyridyl ligands in EtOH with Ru(tpy)Cl$_3$, and using triethylamine as a reducing agent, afforded the cyclometallating complexes in 85% and 76% yield, respectively. The absorption spectra of the complexes show low energy ^{1}MLCT bands at 480–495 nm, respectively, corresponding to the transition to the *N,N,N* coordinated tpy ligand while the higher energy transitions to the cyclometallated ligands appear as shoulders at 344 nm and 350 nm, respectively.

Sauvage and co-workers synthesised a family of substituted phenyl–phenanthroline-type ligands and their cyclometallated Ru(II) complexes [42]. In this family there are two competing factors governing the excited states. The rigidity of phenanthroline-type ligands increases steric strain at the metal centre, thereby lowering the energy of the MC states. However, the cyclometallating component improves σ-donating capability and transfers electron density onto the metal centre, thereby stabilising the MLCT states while destabilising MC states. The ^{1}MLCT bands are found at >500 nm in all of the complexes as a direct result of the MLCT stabilisation. Interestingly a prolonged excited-state lifetime was only observed for those complexes with substituted aromatic groups *ortho* to the coordinating N-atom on the phenanthroline ligand. This is considered to be a consequence of the stabilising inter-ligand π–π interactions between the R1 group and the phenanthroline ligand. Complex **7** (Fig. 4) has the longest lived excited state of a mononuclear Ru(II) complex (106 ns) for such a low energy emission (816 nm).

Introducing electron deficient heterocycles into the Ru(II) coordination sphere can stabilise MCLT states to a greater extent than MC states, thereby increasing excited-state lifetimes while retaining low energy absorption in the visible region of the spectrum.

Electron-deficient N-heterocycles have been introduced into both the peripheral and central positions of the tridentate ligand (Fig. 5, complexes **8–10**). An *N,N,N* coordinating analogue was synthesised with pyrazine rings in the peripheral position (Fig. 5, complex **8**) [43]. The homoleptic Ru(II) complexes were synthesised and the photophysical properties were studied in the solid state. An emission was observed at 667 nm with an associated lifetime of 18 ns.

Triazines were introduced into the central position of tridentate ligands and a family of hetero- and homoleptic complexes was synthesised with a range of substituted phenyl rings in the 4′-position of the triazine ring [44,45]. The triazine ligands function in two ways: a stabilisation of the MLCT singlet and triplet states results from the strong π-accepting nature of the triazine ring, and the ^{3}MLCT state is further stabilised due to a favourable co-planar configuration as a result of intra-molecular H-bonding interactions between the N-atoms on the triazine and the *ortho* annulated H atoms. The homoleptic triazine-based complexes, however, have shorter excited-state lifetimes than

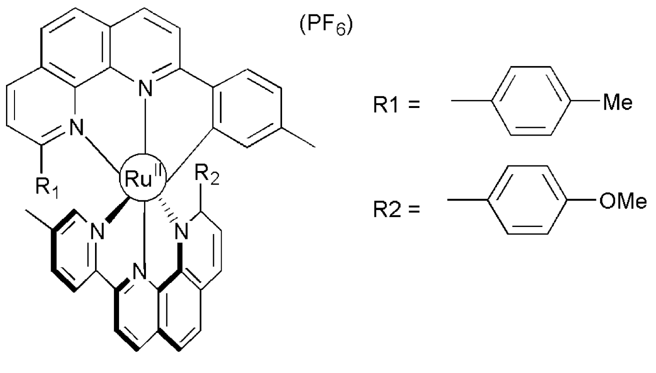


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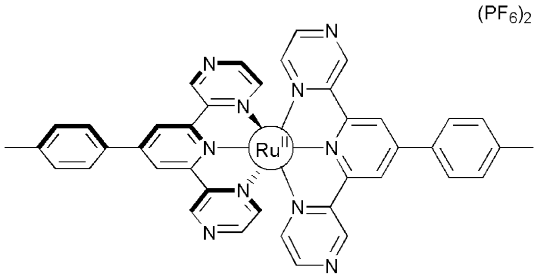
Fig. 4. Excited-state stabilisation through inter-ligand π–π interactions [42].



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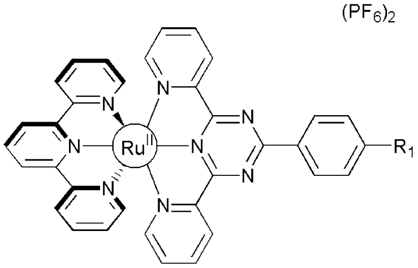

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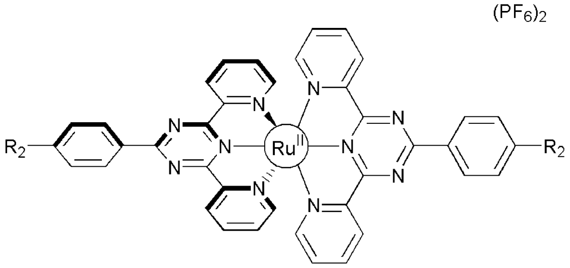

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Fig. 5. Electron-deficient analogues of tpy [43,44].

their heteroleptic triazine/tpy counterparts. The introduction of two triazine ligands reduces the energy of both the MC states as well as MLCT states and, therefore, thermal access of the MC state from the MLCT state is relatively facile. In contrast, the heteroleptic complexes have a tpy ligand increasing electron density at the metal centre. Consequently, triazine-based π^* orbitals are stabilised and these complexes emit at longer wavelength (732–754 nm) with lifetimes of 8–15 ns depending on the substituents.

2.2. Expanding the tpy core

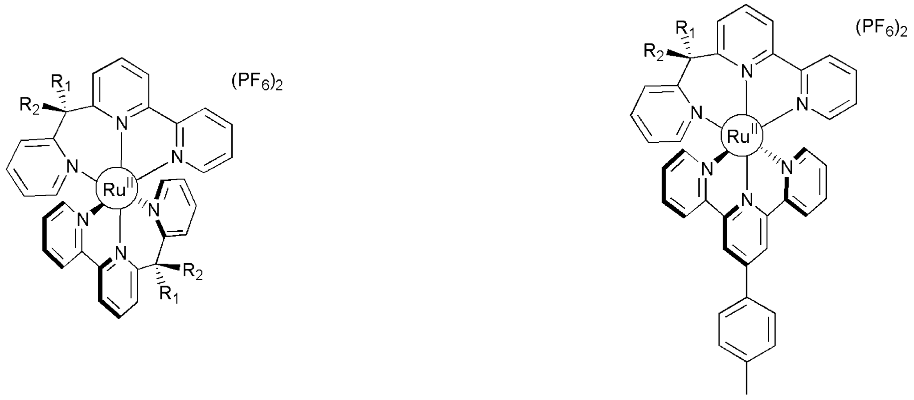
An efficient method to enhance photophysical properties of tpy-based ligands is to increase the bite angle and reduce steric strain in the ligand when bound to the Ru(II) centre. Introduction of a methylene spacer between the 2-pyridyl rings increases the bite angle and, therefore, the ligand field strength, with a consequent increase in the energy of the MC state (complex **11**, Fig. 6) [46]. The complexes are synthesised by using a Ru(II) starting material, typically $Ru(DMSO)_4Cl_2$, as the lability of DMSO ligands allows milder conditions to be used [47]. The ^{1}MLCT absorption band at 477 nm is very close to the parent compound $Ru(tpy)_2{}^{2+}$ although an additional band is observed at higher energy (415 nm) corresponding to a d–π^* pyridine transition. Complex **11** emits at room temperature and has an excited-state lifetime of 15 ns [48].

Simple substitution of electron-donating and electron-withdrawing substituents can be very efficient in manipulating the MLCT states relative to the MC states [49,50]. The relative energies of the ^{1}MLCT and ^{3}MLCT states of $Ru(tpy)_2{}^{2+}$-type complexes are shown in Table 1, Fig. 7. Although substitution of H with Cl in the 4′-position slightly improves the

Table 1
Spectroscopic and photophysical data of the complexes in deaerated acetonitrile solution (298 K) unless otherwise stated

Complex	R1	R2	Ref.	Absorption ^{1}MLCT, λ_{max} (nm)	Luminescence, 298 K	
					λ_{max} (nm)	τ (ns)
15	$MeSO_2$	$MeSO_2$	[49]	486	666	25.0
16	Cl	Cl	[49]	480	653	0.2
17	H	H	[29]	474	629	0.25
18	Ph	Ph	[49]	487	715	1.0
19	H	$MeSO_2$	[49]	482	679	36.0
20	OH	$MeSO_2$	[49]	490	706	50.5
21	Cl	EtO	[49]	484	668	0.2
22	OH	Ph	[49]	488	675	0.4
23	$MeSO_2$	NMe_2	[49]	500	~800	–
24	Cl	NMe_2	[49]	497	746	–
25	CN	H	[50]	480	701	75
26	Cl	H	[50]	478	651	0.7
27	CN	CN	[50]	490	680	50.0
28	tph	tph	[51]	498	664	8.5[a]
29	tph	H	[51]	486	664	5.9[a]
30	tphCl	tphCl	[52]	490	680 ± 15	8.5[a]
31	tphBr	tphBr	[52]	502	680 ± 15	27.2[a]
32	tphBr	tphtpy	[52]	504 (580 sh)	680 ± 15	30.7
33	tph–tph	tph–tph	[53]	514	710	–
34	fur	fur	[53]	500	660	–
35	Pyrrol	Pyrrol	[53]	507	665	–

[a] Air equilibrated solutions.



	R1	R2	λmax abs	λmax EM	τ, ns
11	H	H	477	655	15
12	H	H	486	655	1.4
13	CH_3	OCH_3	482	~650	0.47
14	CH_3	OH	482	~650	0.14

Fig. 6. Increasing the bite angle in tpy-based Ru(II) complexes **11**–**14** [48].

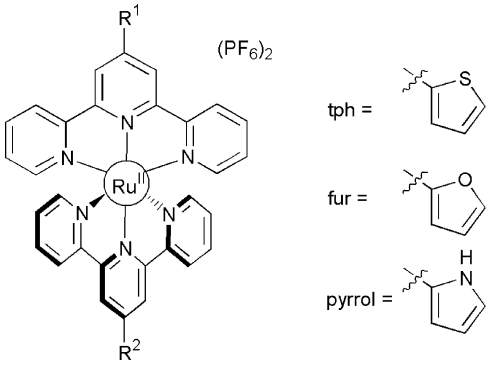
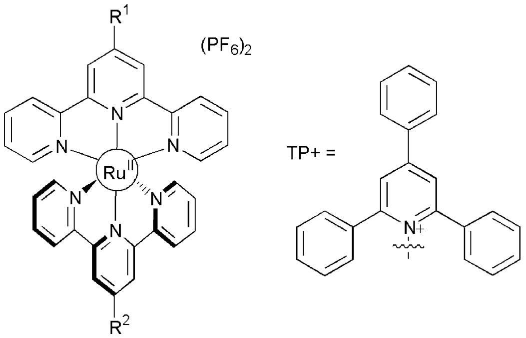


Fig. 7. Direct substitution on the 4′-position of tpy.

photophysical properties, substitution with stronger electron-withdrawing groups, such as CN and $MeSO_2$, can stabilise the ligand-centred π^* orbitals to a greater extent than the MC state. Consequently, the excited states are longer lived (25 ns and 50 ns, respectively). Further prolongation of excited-state lifetimes may be obtained with heteroleptic complexes. In the presence of strong electron-donating ligands, the lowest energy ^{3}MLCT state resides on the electron-deficient ligand and higher energy MC states are retained due to the presence of the electron-donating ligand. Excited-state lifetimes can be increased up to 75 ns at room temperature for **25**.

Five-membered heterocyclic rings introduced into the 4′-position of tpy, e.g. thiophene, furane and pyrrole, have the effect of extending delocalisation and stabilising ^{3}MLCT states, thereby increasing the energy difference with the non-emissive MC state (Fig. 7). This process is discussed in more detail in the next section.

A family of triarylpyridinium (TP^+) funtionalised tpy and phenyl-tpy Ru(II) complexes have been synthesised and the photophysical properties explored (Fig. 8) [54]. Simple incorporation of the triarylpyridinium component into the non-luminescent $Ru(tpy)_2{}^{2+}$ parent complex modifies its photophysical properties and the excited-state lifetimes are significantly extended at room temperature for the monosubstituted complex (55 ns) and for the disubstituted complex (27 ns). This enhancement results from an inductive intramolecular electronic effect increasing the energy gap between the ^{3}MLCT and ^{3}MC states. Complexes incorporating a phenyl spacer between the tpy and acceptor components see a very subtle improvement in the excited-state lifetimes in the subnanosecond region.



	R1	R2	λmax EM	τ, ns
36	H	TP+	670	55
37	TP+	TP+	644	27
38	Ph-Me	PhTP+	—	0.74
39	PhTP+	PhTP+	—	0.82

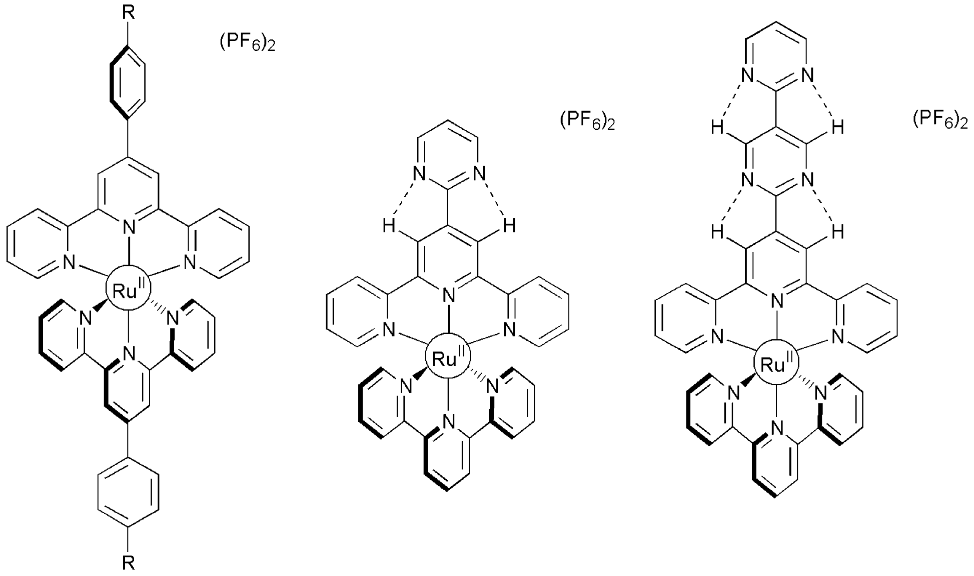
Fig. 8. Triarylpyridinium functionalized $Ru(tpy)_2{}^{2+}$ complexes [54].

2.3. Increasing delocalisation in the excited state

Aromatic substitutents can be introduced on to the tpy backbone prior to complexation; however, there are cases where this is not possible and a 'chemistry-on-the-complex' methodology is used to access the desired products [55]. Lifetimes may be prolonged by substituting an aromatic ring in the 4′-position, e.g. **40**, $Ru(ttpy)_2^{2+}$ (ttpy = 4′-toluyl-2,2′:6′:2″-terpyridine). However, this enhancement cannot be explained simply in terms of electron-donating/accepting ability using Hammett parameters as the values of ρ for H and Ph substitutents are essentially equal. The aromatic groups can conjugate with the low-lying π^* level of tpy, thereby extending delocalisation and stabilising ^{3}MLCT states relative to non-emissive ^{3}MC states [56]. This effect is pronounced in systems where the pendant ring favours a co-planar arrangement through intra-molecular H-bonding interactions as is observed with 4′-(2-pyrimidyl)-terpyridine ligands (Fig. 9) [57]. The emission energies of complexes **41** and **42** are significantly lower than the parent complex due to the extended delocalisation in the excited state.

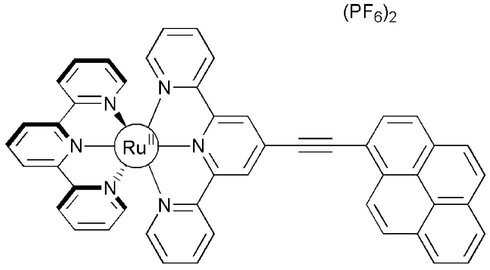
A whole family of complexes based on substituted 4′-phenyl-tpy ligands exists; however, their excited-state lifetimes do not vary much from the archetypical compound **40** (Fig. 9). The synthetic approaches to the ligands are all fundamentally the same, based on Chichibabin- and Krohnke-type syntheses involving substituted benzaldehydes, 2-acetylpyridine and an ammonium source [26]. The photophysical properties were determined in ethanol for complexes of type **40**, for which R = Me, OMe and Cl [58]. Excited-state lifetimes were 4.5 ns, 4.8 ns and 11 ns depending on whether toluyl, methoxyphenyl or chlorophenyl groups were substituted on the 4′-position of tpy. Reported differences in the excited-state lifetime of complex **40** for R = Me may be attributed to a change of solvent (acetonitrile or ethanol) or a change in the counter-ion (PF_6^- or Br^-) [12,58].

Early work by Ziessel and Harriman and co-workers has shown that incorporation of an electron-withdrawing ethynyl scaffold in the 4′-position of the central pyridine ring can dramatically prolong excited-state lifetimes by lowering the energy of the MLCT states and consequently decoupling the MC states [59,60]. The complexes are synthesised by the reaction of one equivalent of the ligand with either using $Ru(tpy)Cl_3$ with a dechlorinating agent and an alcoholic solution or more commonly Ru(II) starting material, typically $Ru(DMSO)_4Cl_2$ [47]. The photophysical properties have been studied with a number of substituents on the ethynyl group and the substitutent dependence explored [61–65]. The excited-state lifetime at room temperature for mononuclear ethynyl-based complex **43** is 580 ns (Fig. 10). The triplet state of ethynyl-pyrene moiety is higher in energy than the ^{3}MLCT state associated with the complexes and the prolonged excited-state lifetime is attributed to a high degree of π–π^* orbital mixing between the ^{3}MLCT state and the triplet state associated with the ethynyl-pyrene moiety [62,66]. A model complex incorporating a phenyl ring in place of the pyrene substituent has a significantly shorter excited-state lifetime of 44 ± 3 ns with a ^{3}MLCT emission band centred around 680 nm [60]. A structurally similar complex has been synthesised with a thiophene-ethynyl residue between the tpy and ethynyl-pyrene moieties [67]. An intraligand charge-transfer state (^{3}ILCT) state is the lowest energy emitting state at room temperature with an intrinsic excited-state lifetime 2.5 ± 0.2 μs. There are many examples of ethynyl-based oligonuclear systems and these will be discussed in more detail in a later section.



R = Me, **40**	**41**	**42**
λmax_{abs} 490 nm	λmax_{abs} 486 nm	λmax_{abs} 489 nm
λmax_{em} 640 nm	λmax_{em} 675 nm	λmax_{em} 690 nm
τ, ns 0.95 ns	τ, ns 8 ns	τ, ns 43 ns

Fig. 9. Extending delocalisation in tpy-based complexes [12,57].



Complex	λmax_{EM}	τ, ns
43	698	580

Fig. 10. Introduction of an ethynyl-pyrene moiety to extend excited-state lifetimes [62].

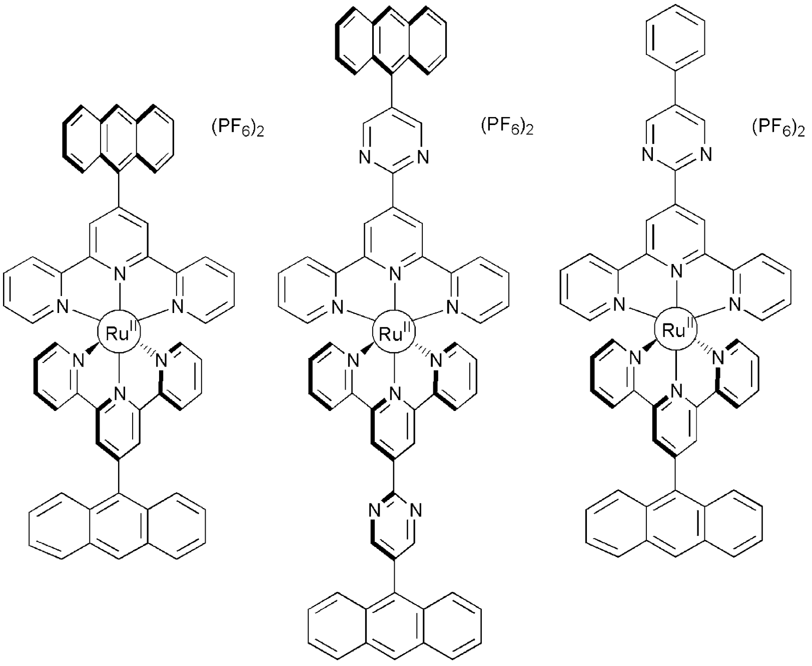
2.4. Bichromophoric approaches

The excited-state lifetimes of mononuclear complexes can be improved by incorporating additional chromophores with excited states isoenergetic to the ^{3}MLCT of the Ru(II) complexes [68,69]. In designing such systems it is important to have the components electronically independent of one another so as to maintain the individual properties of the various chromophores. There are many examples of bichromophoric systems based on the bidentate analogues that have ^{3}MLCT states isoenergetic to 'triplet' pyrene states [68,70]. Conversely, the homoleptic Ru(II) complex with anthracene attached to tpy does not emit at RT as the triplet state of anthracene (^{3}An) quenches the luminescence as it is the lowest energy state and is non-emissive [71]. However, a very efficient multi-component system was produced using the terpyridine-pyrimidyl ligands discussed above [72,73]. The ^{3}An state of an anthracene moiety and the ^{3}MLCT state associated with Ru(II) complexed to a pyrimidyl-terpyridine ligand are almost isoenergetic. A perpendicular arrangement of the anthracene ring relative to the pyrimidine ring is sterically favoured so the individual energetics of both components are retained, giving rise to a bichromophoric effect. Anthracene can also be substituted on the opposite side of the coordination sphere from the terpyridine-pyrimidyl ligand and the bichromophoric system can be effective over a longer distance [73]. Both complexes **45** and **46** have bi-exponential decays due to direct emission of the ^{3}MCLT state followed by a longer-lived emission after the reversible population of the ^{3}An state (Fig. 11).

3. Oligonuclear complexes

Some of the methods available to improve the photophysical properties of mononuclear complexes at room temperature have been discussed. The way in which these properties are conveyed in polynuclear systems is extremely important for applications in light-harvesting devices.

There have been very significant advances in the synthesis and characterisation of oligonuclear complexes based on mixed-metal systems in particular, but for the purpose of this review, only Ru(II) oligonuclear complexes of tridentate ligands are



44
Excited state quenched

45
λ_{max}(em) = 675 nm
τ = 5.8ns, 1806ns

46
λ_{max}(em) = 670 nm
τ = 25ns, 1052ns

Fig. 11. Bichromophoric systems employing anthracene substituents [72,73].

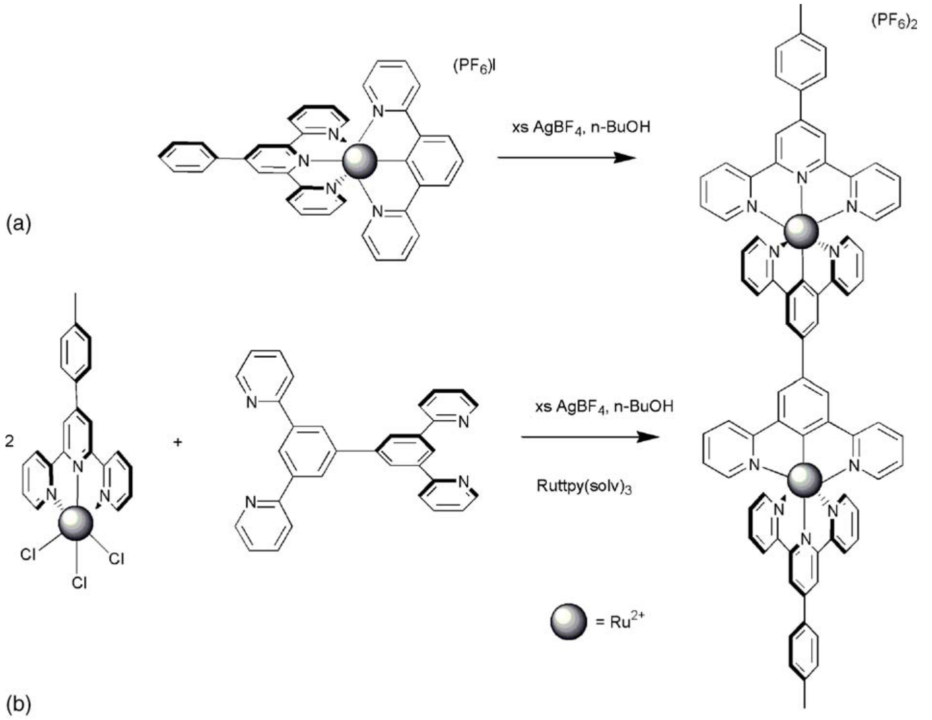
considered. The oligonuclear systems can be divided into three categories: (1) linear metallorods, (2) polymers and (3) dendritic systems.

3.1. Linear metallorods

On advancing to oligonuclear complexes, there are only a few examples of complexes involving a change in the tpy *N*,*N*,*N* coordination sphere and they are based on cyclometallating ligands [74]. Complex **47** was first described by the oxidative coupling of a mononuclear cyclometallated complex (Scheme 2a) [74]. A direct synthetic approach was then developed, and it resulted in fewer side products compared to the synthesis of complexes **3–7** as the cyclometallating component was in the central position and the formation of bidentate coordinated products was not favoured. Nonetheless, complex **47** is only weakly emissive at room temperature with a lifetime of 4 ns [75]. This is an improvement over the mononuclear complex as the σ-donating ability of the cyclometallating ligands destabilise the MC states and reduce thermal activation of these states at room temperature. However, the low energy emission (798 nm) is subject to faster deactivation according to the energy gap law [76].

The photophysical properties, and more specifically the excited-state lifetimes, depend upon the extent of electronic communication in the oligonuclear species. There have been examples of studies in which the extent of electronic communication is studied as a function of distance between chromophoric sites in metallorod-type structures [77]. In turn, the extent of electronic communication is highly dependent on the nature of the bridging ligand. For applications in light-harvesting devices, electron transfer may need to be efficient over long distances [14]. However, some degree of localisation is necessary to retain a multi-component supramolecular system with individual redox and excited-state processes associated with each component. If the excited states are highly localised, the photophysical properties of the mononuclear components predominate. An early example of this effect in linear metallorod complexes is observed in Fig. 12, using ttpy as the terminal ligand and tpy bridging ligands with a variable number of phenyl spacers [28,78]. The complexes were synthesised by dechlorinating RuttpyCl$_3$ with Ag salts and adding half an equivalent of the bridging ligand in refluxing DMF [79].

In complex **48** the metal centres are extremely close and extensive electronic coupling is observed. As a consequence the complex absorbs at significantly lower energy (650 nm). This complex emits at 826 nm at RT with an intrinsic excited-state lifetime of 100 ns. The low energy emission results in shorter excited-state lifetimes than otherwise expected due to direct relaxation back to the ground state according to the energy gap law [76]. According to the Robin Day Classification, complex **48** is considered to be type III due to a large comproportionation constant ($K_c = 10^5$) [79]. The ^{1}MLCT absorption bands are at 520 nm and 499 nm for complexes **49** and **50**, respectively. Complex **49** emits at room temperature at 720 nm and its excited-state lifetime is 570 ns with an additional improvement in quantum yield. The low energy absorption and emission, and the prolonged exited state lifetimes indicate enhanced delocalisation. Despite being electronically more localised than complex **48**, two cathodic peaks can be resolved for complex **49** although the comproportionation constant remains relatively small. Incorporating a phenyl spacer in complex **50** between the two metallic centres reduces the extent of electronic coupling.



47

Scheme 2. (a and b) Synthesis of binuclear complexes of cyclometallating ligands [74].

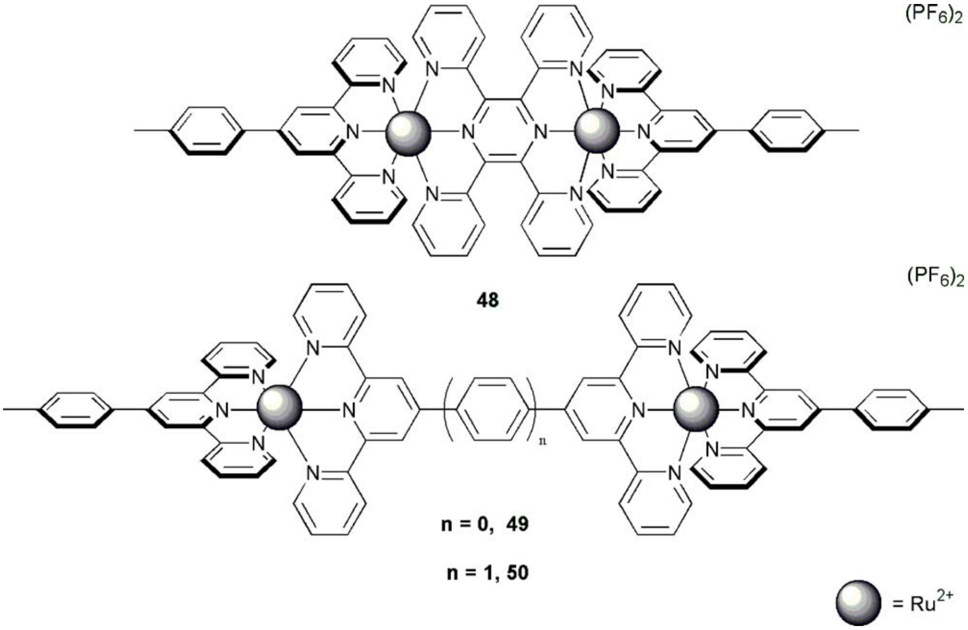


Fig. 12. Binuclear complexes used to assess the effects of extending delocalisation in polynuclear systems [77,78].

The mononuclear complexes incorporating ethynyl substituents are effective in prolonging excited-state lifetimes and the application of this methodology to bi- and oligo-nuclear complexes is very efficient [59]. Ziessel and Harriman and coworkers have synthesised and analysed the properties of a range of binuclear Ru(II) complexes in which the extent of electronic coupling is studied as a function of distance and substituents (Fig. 13) [80].

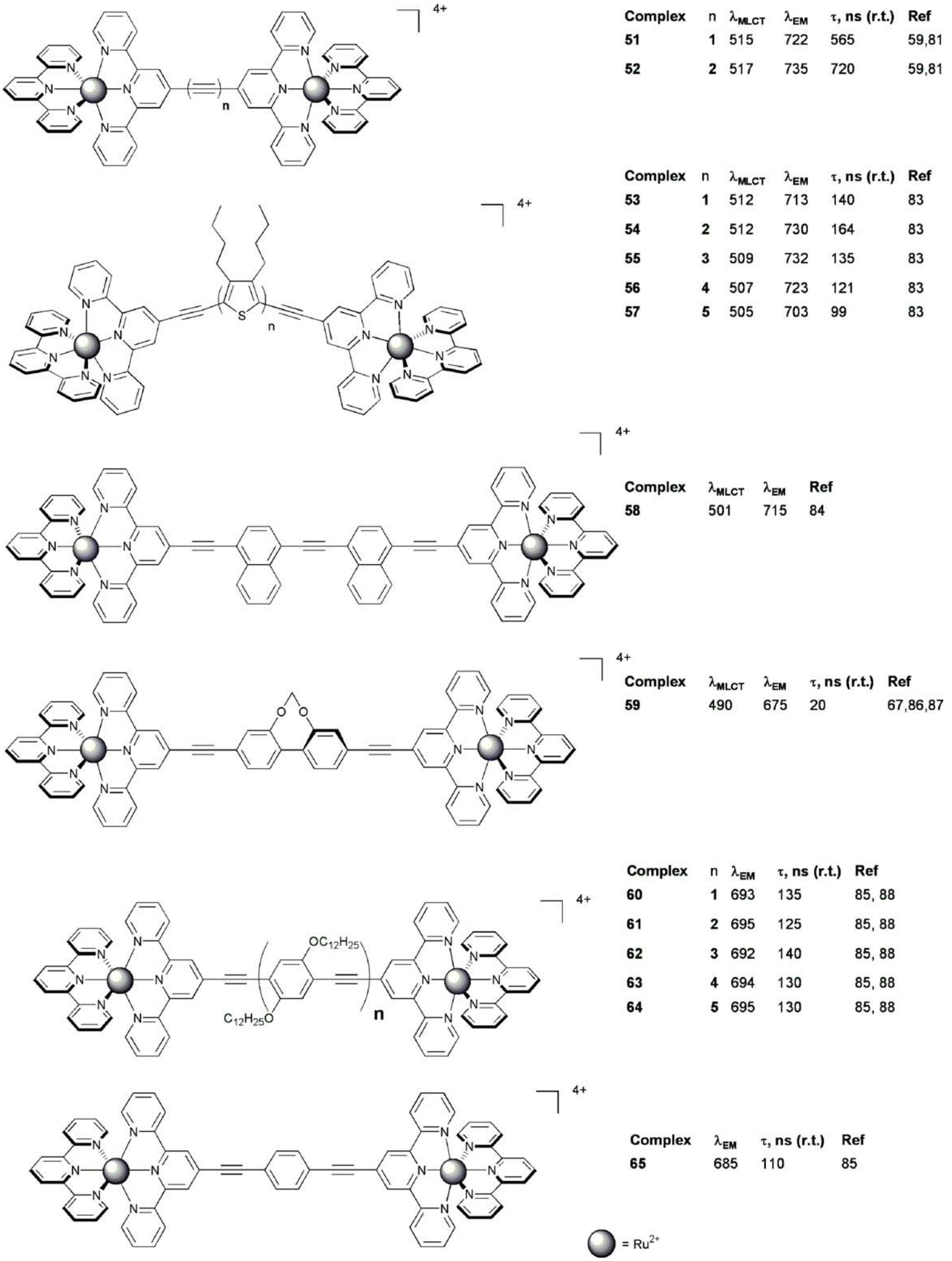
Attachment of ethynyl groups directly to the central tpy ring for complexes **51** and **52** was shown to prolong excited-state lifetimes significantly compared to the parent complex $\mathrm{Ru(tpy)_2}^{2+}$ [59]. However, the quantum yields for emission from the triplet manifold for the dimers are significantly less than unity and surprisingly less than their mononuclear counterparts [81]. There may be more than one triplet state in this complex and, therefore, access of the lowest energy ^{3}MCLT state could be via a higher ^{3}MLCT associated with a $d\pi$–π^* (terminal) tpy transition. The lower energy state has significantly more ‘triplet’ character than the higher energy state. An equilibrium is believed to exist between these two MLCT states, which leads to population of the lower MLCT state, a process restricted by spin rules which will compete with direct emission from the higher energy state with greater ‘singlet’ character. These complexes could be polymerised by reductive electrolysis although the photophysical properties of the new polymers were not discussed [82].

3,4-Dibutylthiophene substituted bridging ligands have been synthesised and incorporated onto ethynyl-tpy backbones (complexes **53–57**) [83]. The photophysical properties as a function of the number of thiophene groups ($n = 1$–5) have been investigated. Comparisons were made to mononuclear controls and the ^{1}MLCT absorption bands lie between 498 nm and 512 nm, depending on the number of thiophene units. In the binuclear complexes the lowest energy absorption (512 nm) was observed for the complex where $n = 1$. Small shifts to higher energy were observed as the number of thiophene fragments increased. The electronic delocalisation is most efficient for the complex where $n = 1$ and diminishes as the number of thiophene fragments increase. The photophysical properties can be finely tuned by varying the solubilising substituent on the thiophene residue. A structurally similar complex to **53** with a 3-dodecylthiophene unit bridging ethynyl-tpy backbones is also room temperature luminescent with an emission band centred at 705 nm and an excited-state lifetime of 320 ns [66].

The synthesis of complex **58** is shown in Scheme 3 in which a naphthalene moiety is grafted onto an ethynyl-tpy ligand. The Pd-catalysed Sonagashira reaction is employed to introduce the ethynyl-based Ru(II) complexes onto the organic frame [84]. The complex emits at relatively low energy even though insertion of aromatic substituents has previously resulted in a blue-shift in the emission spectrum [85]. The naphthalene substituents appear to increase electronic coupling between metal centres although a full photophysical analysis was not provided.

In a recent study to observe the temperature dependence on intramolecular energy transfer between Ru(II) and Os(II) centres a homonuclear Ru(II) dimer was synthesised using ethynylated-biphenylene tpy-based bridges [67,86,87]. A dialkoxy strap was attached to the biphenylene unit in order to restrict rotation around the connecting bond and favour a co-planar conformation, thus enhancing delocalisation and electronic communication. The Ru(II) dimer had a lifetime of 25 ns at room temperature. There are a large number of similar substituted-biphenylene-type ligands although the unsubstituted biphenylene dimer is unknown.

Complexes **60–64** were synthesised with a variable number of ethylene, di-alkoxy benzene groups between Ru(II) centres [85,88]. The photophysical properties were shown to be independent of the number of ethylene, di-alkoxy benzene spacers and the complexes had excited-state lifetimes associated with



Complex	n	λ_{MLCT}	λ_{EM}	τ, ns (r.t.)	Ref
51	**1**	515	722	565	59,81
52	**2**	517	735	720	59,81

Complex	n	λ_{MLCT}	λ_{EM}	τ, ns (r.t.)	Ref
53	**1**	512	713	140	83
54	**2**	512	730	164	83
55	**3**	509	732	135	83
56	**4**	507	723	121	83
57	**5**	505	703	99	83

Complex	λ_{MLCT}	λ_{EM}	Ref
58	501	715	84

Complex	λ_{MLCT}	λ_{EM}	τ, ns (r.t.)	Ref
59	490	675	20	67,86,87

Complex	n	λ_{EM}	τ, ns (r.t.)	Ref
60	**1**	693	135	85, 88
61	**2**	695	125	85, 88
62	**3**	692	140	85, 88
63	**4**	694	130	85, 88
64	**5**	695	130	85, 88

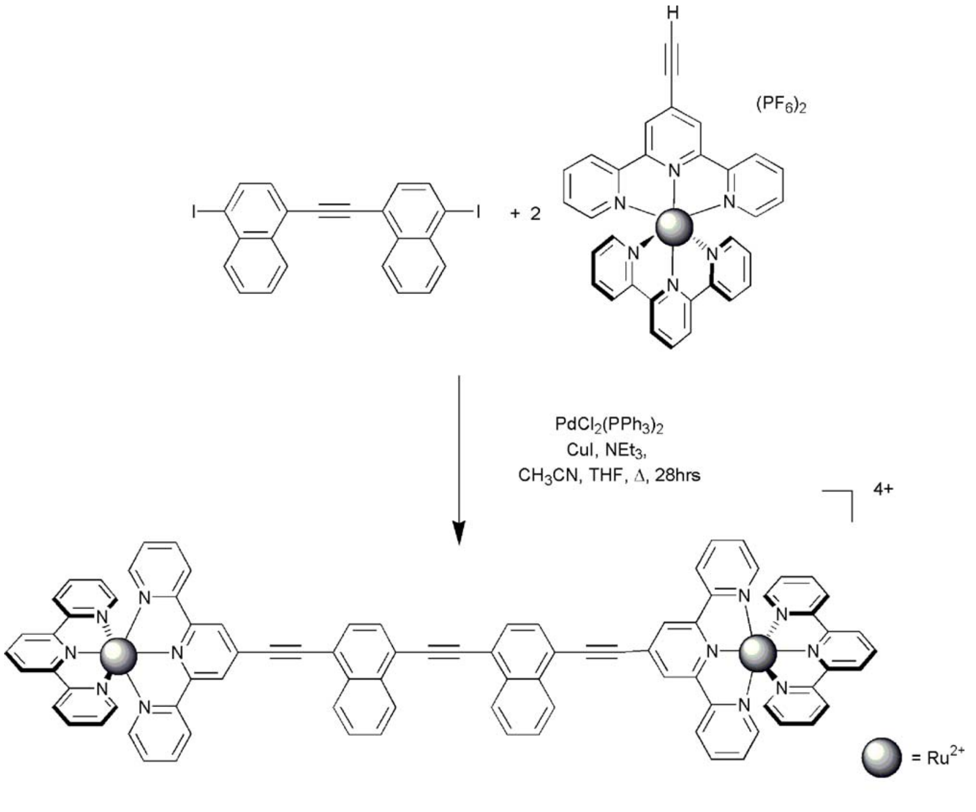
Complex	λ_{EM}	τ, ns (r.t.)	Ref
65	685	110	85

Fig. 13. Examples of binuclear ethynyl–terpyridine complexes.

ethynyl-substituted tpy Ru(II) complexes. The results indicated that despite the attempts to increase delocalisation and lower the energy of the bridging ligand, the lowest energy excited state resided on a terminal ligand. The interspersed aromatic rings are considered to disrupt electronic coupling along the molecular axis and serve to raise the triplet energy of the connector. The Ru(II) complex with the unsubstituted phenylene-terpyridine spacer has a shortened excited-state lifetime of 110 ns and a slightly higher energy triplet state [85].

Dinuclear complexes have been synthesised with free coordinating sites in the presence and absence of ethynyl substituents (Fig. 14).

Complex **67** has a significantly shorter excited-state lifetime as compared to **66** although the emission energies are



58

Scheme 3. Sonogashira coupling on the complex to access naphthalene–acetylene groups [84].

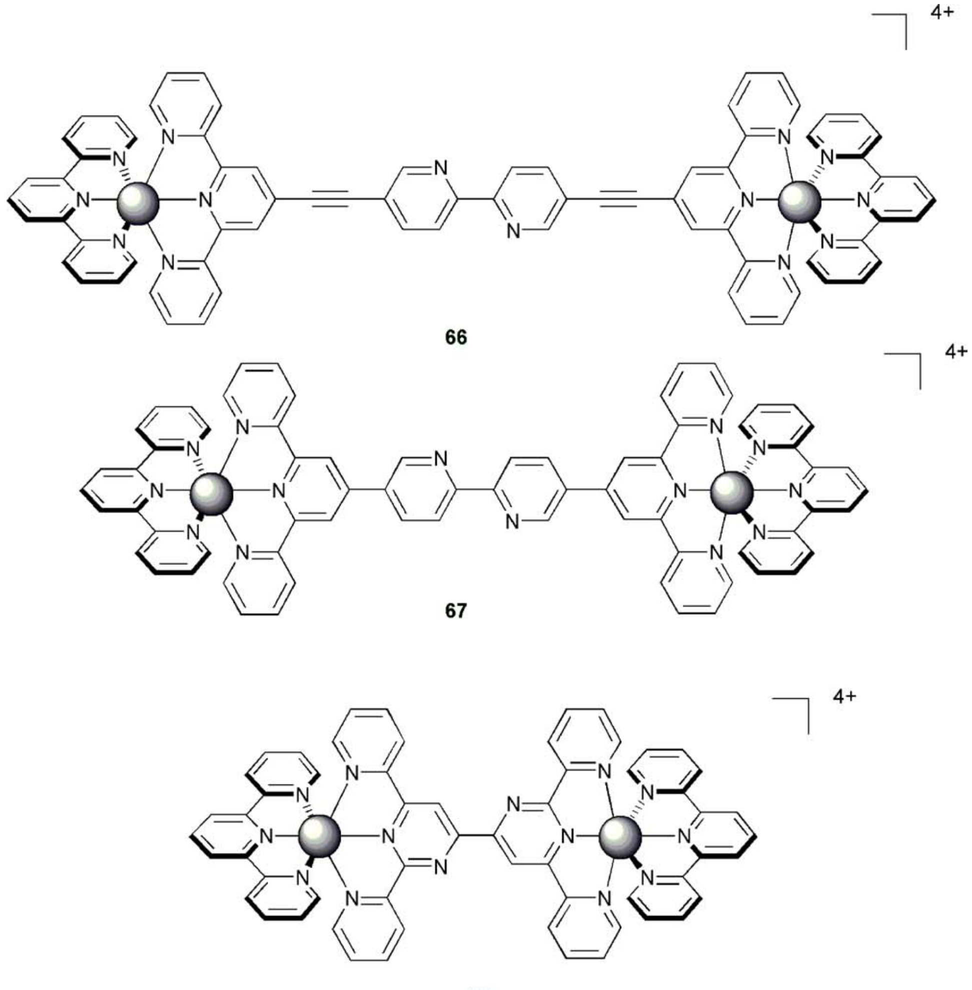
very similar [89,90,92]. The central aromatic unit can be substituted in **66** and the photophysical properties are only slightly affected when a phenyl spacer is used in place of bipyridine. This suggested only a small degree of mixing between π^* orbitals localised on the aromatic unit and those on the acetylene-tpy moiety [89]. A complex structurally similar to **66** has been synthesised where a 2,2′-bipyrimidine link is substituted for bpy. This complex has comparable photophysical properties with an emission at 705 nm at room temperature with an excited-state lifetime of 60 ns [93]. Complex **68** has been synthesised with a bridging tetrapyridyl-dipyrimidine unit [91]. The complex emits at very low energy (819 nm) with an excited-state lifetime of 420 ns at room temperature. The excited state is unusually long-lived for such a low energy emission due to a combination of factors. The acceptor orbitals of the emissive ^{3}MLCT state are lowered in energy due to the additional nitrogen in the bridging ligand and a second stabilisation of the ^{3}MLCT state is observed as a result of the favourable co-planar interaction of the bridging ligand in the ground state. Both effects contribute to reducing the efficiency of the MC deactivation pathway.

Bi- and tri-nuclear Ru(II) complexes were synthesised with terpyridine ligands linked through thiophene spacers (Fig. 15) [94]. Comparisons were made to the monometallic complex with one Ru(II) tpy moiety coordinated to one thiophenyl substituted terpyridine ligand. This complex emits at 664 nm with a lifetime of 5.9 ns. The ^{3}MLCT states of the bi- and trinuclear complexes are obviously stabilised relative to the monometallic complex and emit at significantly longer wavelengths with prolonged excited-state lifetimes due to the increased energy difference between the non-emitting MC states and the lowest energy ^{3}MLCT states.

Azo groups have been used as linkers between tpy ligands [95]. Complex **71** in Fig. 16 is non-emissive at room temperature as well as at 77 K. This is an unprecedented result in consideration of the extended delocalisation in this system in addition to the electron-withdrawing nature of the azo group. The authors noted that the quenching of the excited state could have a number of contributions: (a) internal conversion and relaxation according to the energy gap law; (b) isomerisation and twisting at the N–N bond; (c) population of the ligand localised triplet state from the ^{3}MLCT followed by relaxation to the ground state; (d) interaction of the bridging azo N-atoms with solvent molecules facilitating non-radiative decay to the ground state [95].

A trinuclear triangular complex was synthesised incorporated ethynyl–terpyridine-based ligands with phenyl spacers (Scheme 4) [96]. A ^{1}MLCT band was observed in the electronic spectra at 496 nm. This is consistent with localised mononuclear complexes although emission properties have not been reported.

Trinuclear linear Ru(II) complexes incorporating phenylene-vinylene terpyridine systems have been synthesised (Fig. 17) [97]. Both complexes are emissive at room temperature although



66

67

68

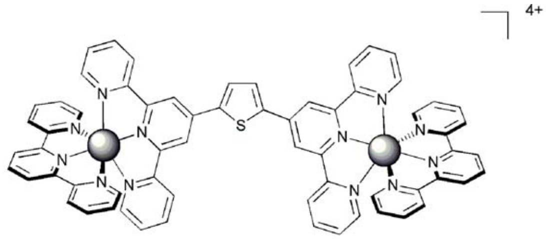
Complex	λ_{MLCT}	λ_{EM}	τ, ns (r.t.)
66	495	678	100
67	490	680	5
68	567	819	420

● = Ru^{2+}

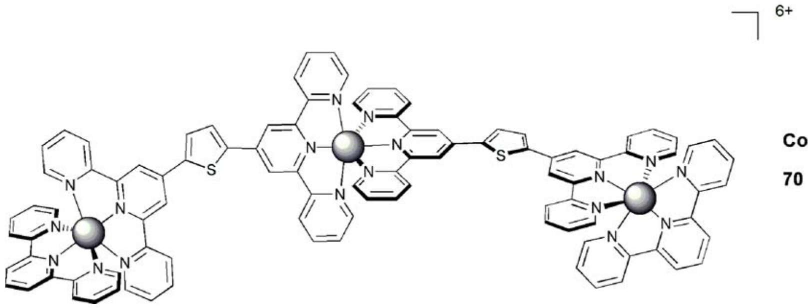
Fig. 14. Introducing free coordination sites in the bridging ligand [89–91].

the associated parameters differ quite significantly. Complex **74** emits at lower energy compared to **73** as a result of the extended delocalisation associated with the additional phenylene-vinylene moiety. The excited-state lifetime of **73** is considerably shorter than **74** and the emitting state of **73** is assigned to a ^{3}MLCT state. The emitting state of **74** is believed to have ^{3}IL character with significant charge transfer character [98]. Interestingly, a complex similar in structure to **73** but with a central Fe(II) ion is still emissive, albeit with a much shorter excited-state lifetime [97].

Di- and tri-nuclear rack-type complexes have been synthesised and their photophysical properties studied (Fig. 18) [99–102]. The dinuclear complex **75** has a ^{1}MLCT absorption band in the visible region of the electromagnetic spectrum. The higher energy band is assigned to the ^{1}MLCT band to the tpy ligand and the lower energy bands correspond to a ^{1}MLCT band to the first and second LUMO's of the bridging ligand. Both complexes presented in Fig. 17 are emissive at room temperature. Complex **75** emits at significantly lower energy than complex **76** [101,102]. The polypyridyl ligand in **75** is held in a more rigid conformation on coordination to Ru(II) as compared to the bridging ligand in **76**. The co-planar arrangement favours extended delocalisation and stabilises the ligand-based LUMO to a greater extent thereby lowering the energy of the ^{3}MLCT state. A trinu-

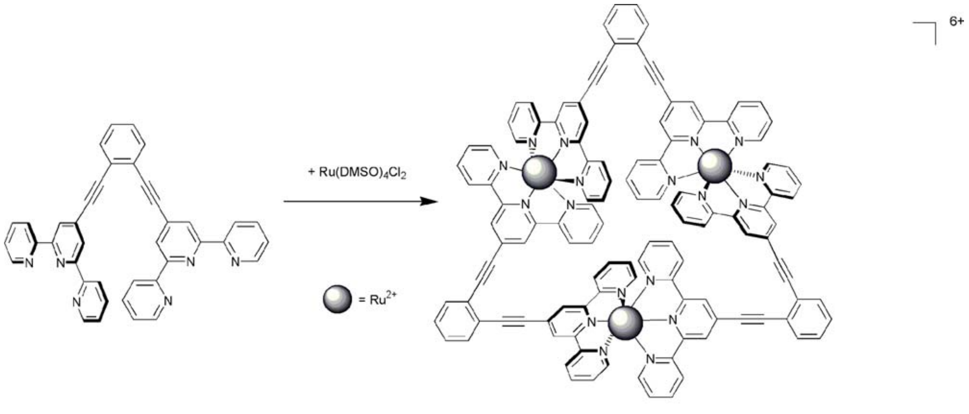


Complex	λ_{MLCT}	λ_{EM}	τ, ns (r.t.)
69	517	738	340



Complex	λ_{MLCT}	λ_{EM}	τ, ns (r.t.)
70	532	736	330

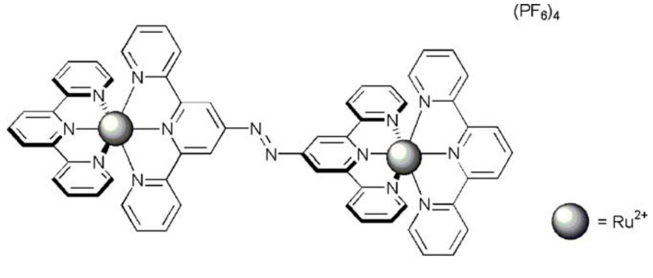
Fig. 15. Ru(II) complexes of thiophene linked terpyridine-bridging ligands [94].



72

Scheme 4. Synthesis of triangular phenylene-based Ru(II) complex [96].

clear complex analogous to **75** has been synthesised and is also luminescent at room temperature at considerably lower energy as compared to **75**, and represents the lowest energy emitter at room temperature for oligonuclear Ru(II) complexes based on tridentate ligands (920 nm, 40 ns) [98].



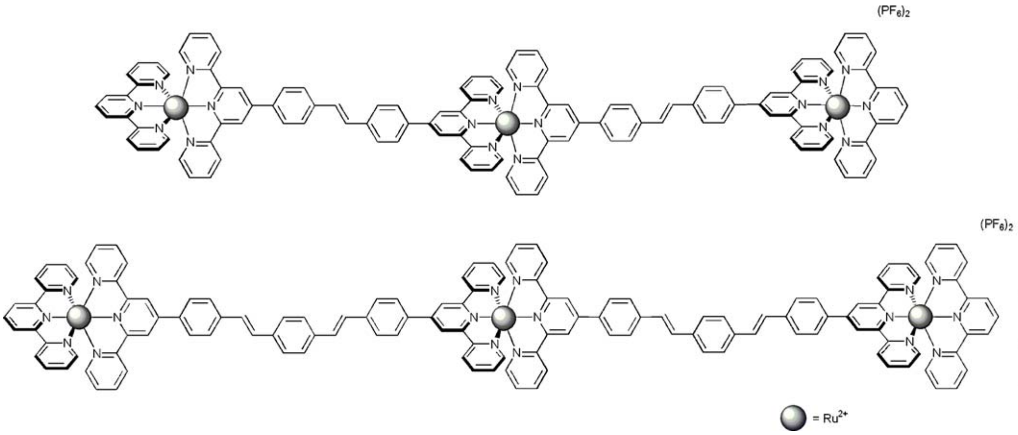
71

Fig. 16. Ru(II) binuclear complexes with azo-terpyridine linkers [95].

3.2. Polymers

Complexes of higher nuclearity can be synthesised by using polymerisation methods. There have been a number of reviews on both the synthesis and the properties of metallopolymers incorporating tridentate tpy-type ligands amongst others [103,104]. The complexes may either be incorporated into the side chains or into the polymer backbone. Energy or electron transfer processes may occur in both types but through different mechanisms: outer-sphere for polymers with branched Ru(II) tpy complexes and inner sphere for polymers with the complexes grafted into the polymer backbone. For efficient electron/energy transfer the latter type is more favourable although the synthesis can be more difficult. Within the latter type the distance between Ru(II) centres can be very long with bridging insulating organic groups and the photophysics are rarely discussed.

A family of mono-, di- and polynuclear complexes incorporating chiral-terpyridine moieties has been synthesised [105].



73

λ_{LUM} = 670 nm

τ = 10 ns

74

λ_{LUM} = 700 nm

τ = 320 ns

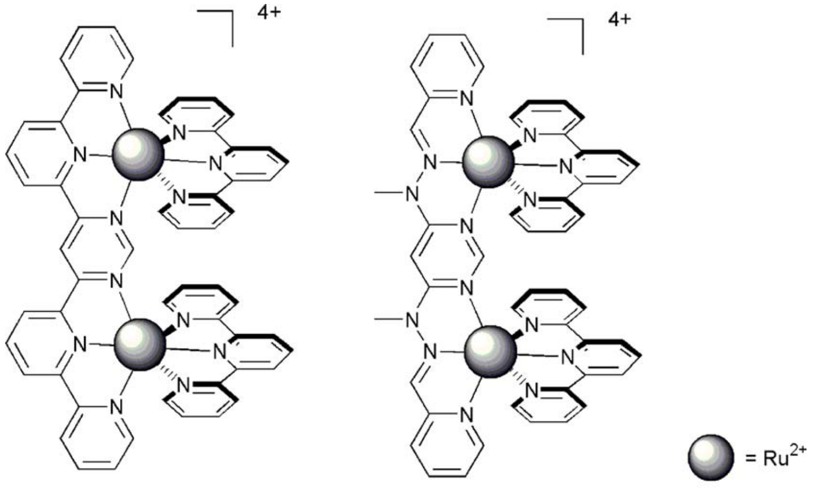
Fig. 17. Complexes incorporating a phenylene-vinylene terpyridine bridging ligand [97].

Generally, the use of materials which give rise to chiral complexes is avoided. However, in using enantiomerically pure starting ligands the synthesis of Ru(II) complexes of these ligands gives rise to enantiopure polymers using a flexible spacer **77** and a rigid spacer **78** (Fig. 19).

Evidence suggested that for both of the chiral metallopolymers, the number of monomeric units is between 40 and 60. The ^{1}MLCT bands observed in the absorption spectra are at 475 nm and 503 nm for **77** and **78**, respectively. Excited-state lifetimes for both polymers are 0.36 ns and 1.1 ns, respectively, only slightly longer than the parent complex, $Ru(tpy)_2{}^{2+}$. The polymers were synthesised from the $Ru(DMSO)_4Cl_2$ precursor in ethanol. A structurally similar achiral rigid polymer could be synthesised from $Ru(BF_4)_3$ following dechlorination of $RuCl_3$ (**79**, Fig. 19) [106]. The reaction with the bridging ligand was carried out in DMA to give a polymeric material with an approximated degree of polymerisation of 36,000 g mol^{-1}. The UV–vis spectra of the monomer, dimer and polymer are all characteristic of the parent complex and the electrochemical data support very little electronic communication amongst the Ru(II) centres.

3.3. Dendrimers

As with the metallorods, nearly all dendritic systems incorporate the tpy core and there are few examples of alternate heterocycles. There are two approaches to construct dendritic systems: a convergent approach and a divergent approach. The divergent approach involves sequential addition of monomeric building blocks to a branching centre. The convergent approach involves



75

λ_{LUM} = 855 nm

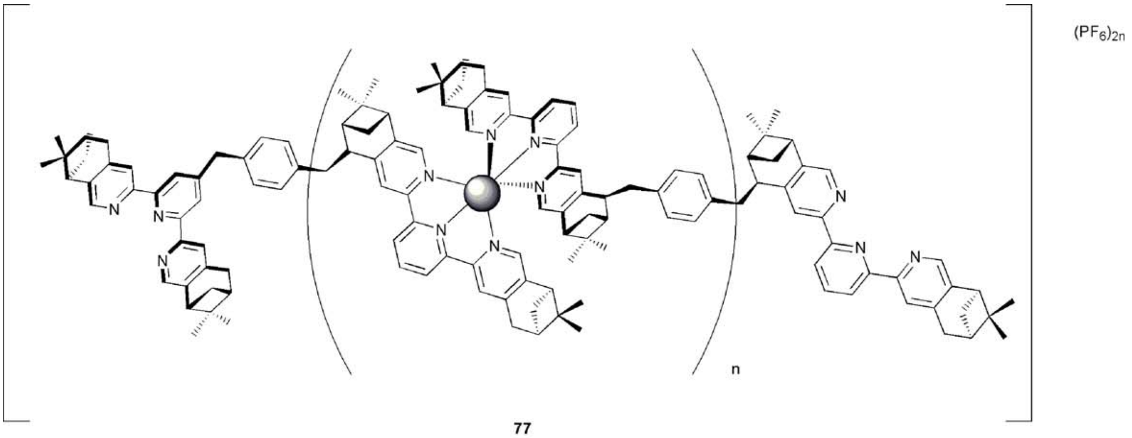
τ = 77 ns

76

λ_{LUM} = 758 nm

τ = 30 ns

Fig. 18. Dinuclear Ru(II) rack-type complexes [101,102].



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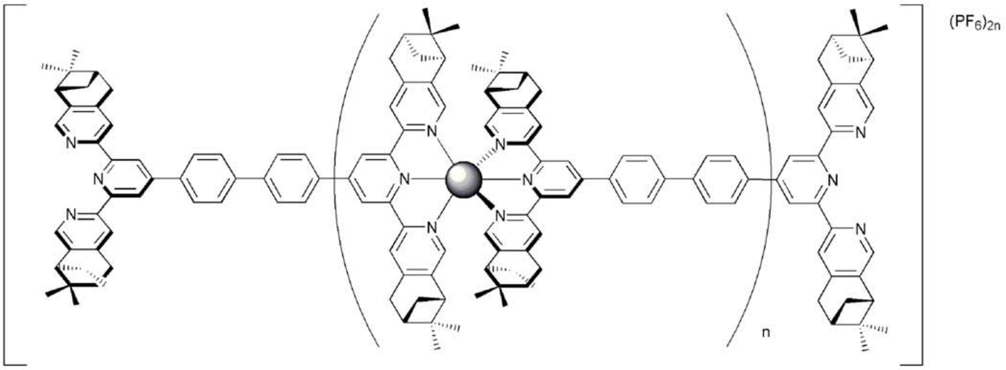

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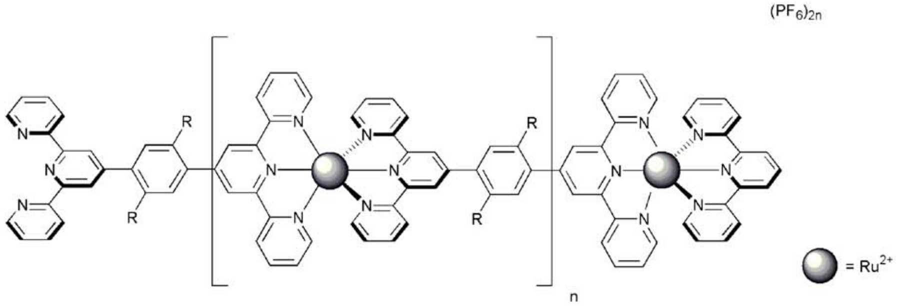
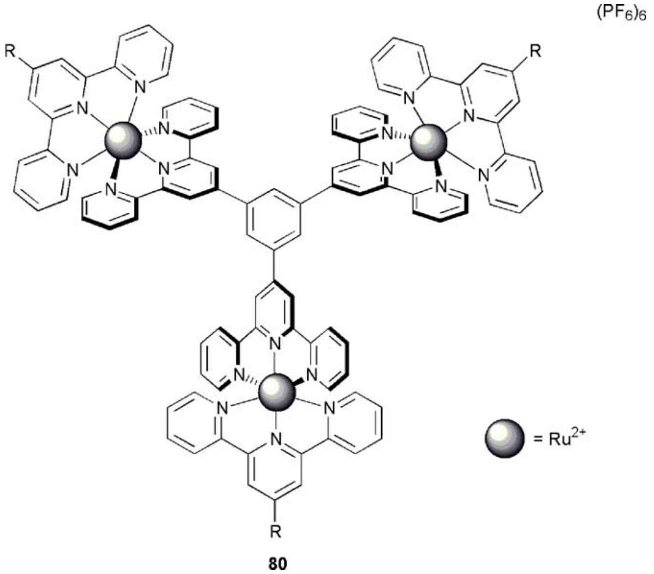


79

Fig. 19. Chiral and achiral Ru(II) tpy containing polymers [105,106].

synthesis from the periphery to a central point. Newkome et al. published a detailed structural and synthetic review in 1999 on metallodendrimers and dendrimers incorporating tridentate tpy ligands. Dendrimers were first synthesised by the same group although photophysical properties were not discussed [107,108]. Another large fourth generation dendrimer was synthesised incorporating 64 $Ru(tpy)_2{}^{2+}$ centres using peptide coupling procedures [109], although the Ru(II) metal centres are attached to the periphery of an organic dendrimer. For light-harvesting device applications efficient energy or electron transfer is essential and long distances in combination with insulating organic groups would not favour such applications. For light-harvesting applications incorporation of the Ru(II) complex into the branching core would be more favourable. Balzani et al. have synthesised a number of dendritic systems incorporating Ru(II) centres with bidentate ligands in the core and the photophysical properties were studied [30].

Simple tpy-based first generation dendrimers were synthesised using 1,3,5-tris(4′-terpyridyl)-benzene as a multi-topic ligand (Fig. 20) [110].

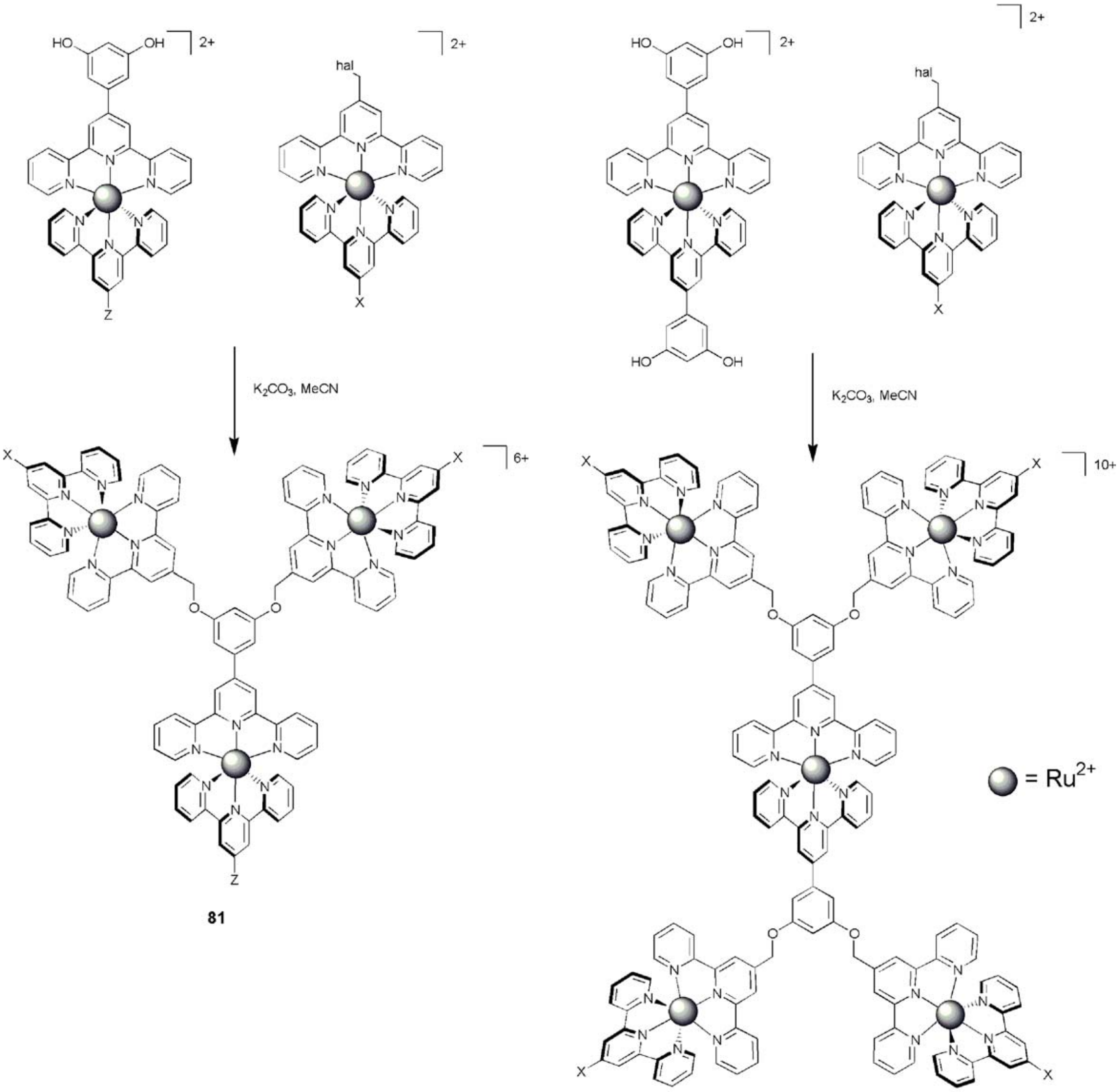


80

Fig. 20. A first generation dendrimer based on a tris-tridentate ligand [110].

The ligand could be synthesised by adapting a previously established procedure and the Ru(II) complexes were obtained by refluxing the ligand with three equivalents of substituted Ru(tpy-R)Cl_3 in methanol in the presence of *N*-ethylmorpholine. The complexes were obtained in 12–25% yield, where R = H, OH, OEt, Cl, Ph, NMe_2, SMe and SO_2Me. The absorption spectra for all complexes had a red-shifted MLCT band (487–507 nm) as compared to the parent complex. This is believed to be a result of the steric crowding around the central benzene spacer reducing conjugation in the structure [111].

A recent approach took advantage of the reaction of free ligands or coordinated ligands containing a nucleophilic substituent with a complex containing an electrophilic ligand to covalently link two metal centres (Scheme 5) [112]. Complexes **81** and **82** have ^{1}MLCT absorption bands at 480 nm and 485 nm, respectively. The absorption spectra appear as superimpositions of the mononuclear complexes indicating very poor electronic coupling between Ru(II) centres resulting from the insulating character of the ether tethers. The complexes emit from their



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Scheme 5. Synthesis of trinuclear V-shaped and pentanuclear X-shaped complexes [112].

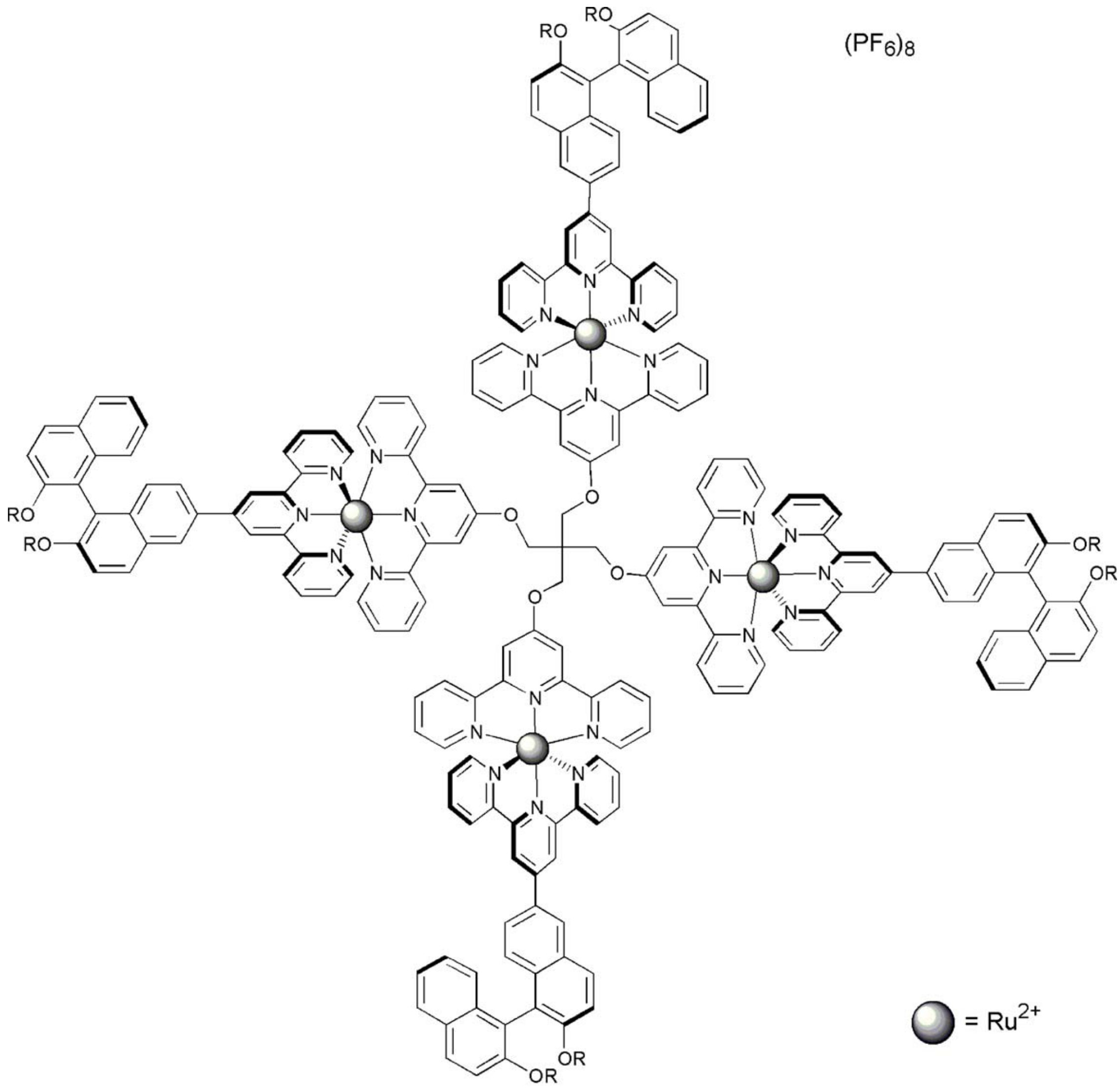

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Fig. 21. Synthesis of a chiral binaphthyl-substituted first generation dendrimer [115].

lowest lying ^{3}MLCT state at 640 nm and 662 nm, respectively; however, the lifetimes are very short and of the same order of magnitude as the mononuclear complexes.

The muliti-nucleating ligand tetrakis(2,2′:6′,2″-terpyridinyl-4′-oxymethyl)methane has also proved to be a synthetically useful multi-topic ligand for the synthesis of dendrimers [113]. Using a divergent approach, the Ru(II) centres could be added stepwise and the final generation resulted in a dendritic complex with 16 Ru(II) centres with an overall charge of 32+. The photophysical properties were not discussed and the complexes are presumably non-emissive at room temperature resulting from the insulating nature of the ether linker and, therefore, the inherent properties of the parent complex are retained.

The same ligand was applied to the synthesis of chiral Ru(II) dendrimers with binaphthyl substituents on tpy (Fig. 21) [114]. All of these complexes are non-emissive at room temperature and the UV–vis spectra are characteristic of mononuclear complexes indicating very little electronic coupling between metal centres [115].

4. Conclusions

The design and synthesis of mononuclear Ru(II) complexes with extended excited-state lifetimes has been extensively researched. There have been some elegant studies of binuclear complexes using ethynyl-substituted tpys and 4′-phenylterpyridines giving rise to excellent supermolecules for energy and electron transfer studies. Apart from these notable exceptions, there are a large number of mononuclear complexes with favourable photophysical properties which have not yet been applied to binuclear and oligonuclear systems. In the binuclear complexes presented herein, there are examples of complexes in which the excited-state lifetimes have been increased dramatically on comparison to the mononuclear complexes. In these cases, the properties of the monometallic complex are no longer observed and efficient electronic delocalisation results in new properties associated with the supermolecule. In dendritic systems, ligand synthesis seems to be the limiting factor. Nucleophilic substitution reactions currently applied to the synthesis of terpyridine-dendrimers are efficient in building up large molecules although the presence of the insulating ether linkage and the nature of the tpy ligands afford multi-component systems with poor photophysical properties. Clearly there is room for further research into light-harvesting oligo- and poly-nuclear complexes of tridentate ligands based on the improvements in the photophysical properties of the mononuclear complexes outlined herein.

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