The influence of ligand localized excited states on the photophysics of second and third row transition metal terpyridyl complexes: recent examples and a case study.

Jing Gu,[‡] Yong Yan,[‡] Brian J. Helbig, Zhuangqun Huang,[†] Tianquan Lian[†] and Russell H. Schmehl*

Department of Chemistry

Tulane University

New Orleans, LA 70118

[†] Department of Chemistry

Emory University

Atlanta, GA 30322

[‡] Chemical and Nanoscale Sciences

National Renewable Energy Laboratory

Golden, CO 80401

russ@tulane.edu

Abstract: The photophysical behavior of Ru(II) and Os(II) diimine complexes having complex aromatic hydrocarbon diimine ligands has received considerable attention as systems exhibiting intramolecular energy transfer to yield excited states with lifetimes much longer than the parent diimine complexes. Here we present a focused discussion of the photophysical behavior of transition metal complexes with modified terpyridyl ligands. The overview includes, as an example of approaches used to evaluate such systems, spectroscopic studies of a pair of Ru(II) mono- and bis- terpyridyl complexes modified with vinylpyrene (Pyr-v-tpy) to have ligand localized excited states that are equal to or lower than the energy of the known MLCT state of the parent complexes, $[\text{Ru}(\text{Mpt})_2]^{2+}$ and $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ (Mpt = 4'-tolyl-2,2',6',2''-terpyridine, dien = diethylenetriamine). The common observation is that the presence of Pyr-v-tpy serves to lengthen the excited state lifetime of the complex through interaction of MLCT and ligand localized (IL) states. For $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}$ the excited state lifetime increases by a factor of more than 10^4 relative to $[\text{Ru}(\text{Mpt})_2]^{2+}$. For $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$, the ^3IL state is close in energy to the MLCT state of the parent $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ and, while the transient absorption spectrum is significantly perturbed relative to $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$, the excited state decay rate changes by only a factor of four. The long-lived excited state is formed in less than a ps, indicating strong coupling of the MLCT and ligand localized manifolds.

Keywords: ruthenium; terpyridyl complexes; intraligand; transient absorption; diethylenetriamine; excited state lifetime; MLCT; ILCT.

Contents

1. Introduction

2. Approaches to influencing metal terpyridyl complex excited state lifetimes

2.1 *Minimizing excited state distortion*

2.2 *Influencing ligand field splitting*

2.3 *Inclusion of ligands with low energy excited states*

3. Case study of Pyr-v-tpy Complexes

3.1 *Ligand and complex syntheses*

3.2 *Electrochemistry*

3.3 *Absorption and luminescence spectra*

3.4 *Transient absorption studies*

4. Summary

1. Introduction:

The photophysical behavior of transition metal diimine and triimine complexes has been the focus of numerous investigations for more than 40 years[1-5]. In part the development of this area is driven by the potential of diimine complexes of Ru(II), Os(II), Re(I) and other metals to serve as visible light absorbing chromophores for light induced redox reactions[6-8]. The visible absorption of the dyes in this class of chromophores arises from metal-to-ligand charge transfer transitions (MLCT). The color can be tuned by varying the electron donating/withdrawing properties of the imine ligand(s) bound to the metal and, to a lesser extent, by changes in the spectator ligands. For the majority of these complexes the lowest energy allowed electronic transition is one involving a metal localized $d\pi$ orbital and an imine π^* orbital as acceptor. The emitting excited state has triplet MLCT character and the excited state lifetimes of these complexes are in the 10 ns to 2 μ s scale. In addition, the excited state nonradiative decay processes of 3 MLCT states follow the energy gap law[9-11]. A characteristic of many complexes in this group is that triplet ligand field (metal centered), 3 MC, states are close in energy to the 3 MLCT state and often relaxation is dominated by thermally activated internal conversion from the 3 MLCT to the 3 MC state that is followed by rapid (few ns) decay to the ground state (see Figure 1). This is especially true for Ru(II) complexes having a 2,2':6',2''-terpyridine (tpy) ligand.

An emphasis of recent work on terpyridyl containing dyes has been finding ways to extend their excited state lifetimes, thereby enhancing opportunities for using the complexes as sensitizers in photoredox reactions, especially in bimolecular photoredox reactions. This paper is intended to present a brief overview of select literature in this area and also to provide a case study of complexes having a terpyridyl vinyl pyrene ligand (Scheme 1) coordinated to Ru(II) in a homoleptic and a heteroleptic complex.

2. Approaches to influencing metal terpyridyl complex excited state lifetimes

In 2005, Hanan *et al.* wrote a review that provides a nice introduction to modified terpyridyl complexes that have extended lifetimes[12]. Various approaches have been employed including (a) decreasing excited state distortion, (b) altering the coordination environment to increase the energy of ligand field excited states, and (c) employing ligands that include separate chromophores with low energy, long-lived, ligand localized excited states. A review of pyrene containing complexes by Wolf and coworkers is a part of this issue of Coordination Chemistry Reviews and contains examples of long-lived terpyridyl pyrene complexes.

2.1 Minimizing Excited State Distortion: One avenue has been to design ligands and complexes for which the excited state distortion is particularly small, thereby diminishing nonradiative relaxation via channels other than the 0-0 transition. It has been observed that terpyridyl ligands with 4'-acetylide substituents (tpyCCR, R = aromatic hydrocarbon) form complexes of the type $[\text{Ru}(\text{tpy})(\text{tpyCCR})]^{2+}$ that have luminescent $^3\text{MLCT}$ excited states with lifetimes of several hundred nanoseconds[13,14]. The effect presumably results from increasing the delocalization of the $^3\text{MLCT}$ state, stabilizing the state relative to the ^3MC state and decreasing the excited state distortion. Other complexes falling into this category have ligands such as 4'-(5-X-pyrimid-2-yl)-2,2',2''-terpyridyl derivatives (X= Cl, Ph, CN) that achieve planarity of the pyrimidyl substituent with the central pyridyl ring of the terpyridyl through N(pyrimidyl)-H(pyridyl) H bonding interactions[15]. Very recently, Baitalik *et al.* investigated a series of 4'-polyaromatic-substituted terpyridine and 2,6-bis(benzimidazol-2-yl)pyridine Ru(II) complexes $[(\text{H}_2\text{pbbzim})\text{Ru}(\text{L1-L5})]^{2+}$, $\text{H}_2\text{pbbzim}=2,6\text{-bis(benzimidazol-2-yl)pyridine}$ (Figure 2)[16]. These compounds exhibited quite strong luminescence at room temperature with lifetimes in the range of 5.5–62 ns. The 4'-substitution group of center terpyridyl, as seen from figure 2, substantially enhanced electron delocalization and stabilized the LUMO, which is significantly ligand based. The lifetimes depended not only upon the nature of the

polycyclic aromatic moiety, but also the solvation environment attributed from imidazole N-H dissociation related anion induced lifetime quenching and/or enhancement.

Stilbene and ene-anisole moiety substitutions of the 4'-position of bis-terpyridine ligands give Ru(II) and Ir(III) complexes ($[\text{Ru}(\text{L11})_2]^{2+}$ and $[\text{Ir}(\text{L11})_2]^{2+}$, Figure 2) with prolonged excited state lifetimes and strong two photon absorption[17]. In all these complexes, increasing structural conjugation by pendent alkene or aromatic moiety leads to a red shift of the MLCT transitions. As consequences, expanded visible light absorption as compared to their parent complexes $[\text{M}(\text{tpy})_2]^{2+}$ (M=Ru, Ir) was also achieved. The dihedral angles in the Ir(III) complexes between the pyridyl and tolyl group are smaller compared to those of in the Ru(II) complexes, presumably resulting in a larger degree of π -delocalization across the ligand in the Ir(III) compounds. The Ir(III) compounds have green emission at room temperature with 1-2 μs lifetimes; the emission was explained by mixture of LC, MLCT and ILCT states. The related Ru(II) compounds have green emission with 2-3 ns lifetimes attributed to ligand localized excited states that decay rapidly to populate a non-emissive MLCT state at lower energy. Thus, in this case, the desired delocalization effect occurs for the Ru(II) complex, but has a marginal effect on the major thermally activated nonradiative decay pathway.

This approach can be also applied to the development of sensitizers for dye sensitized solar cells (DSSC). The extended π -conjugation of the terpyridine ligand could increase the molar extinction coefficient of the dye ruthenium molecules and expand their visible and NIR absorption. Two novel heteroleptic ruthenium polypyridyl examples ($[\text{Ru}(\text{L12})(\text{bpyCOOH})(\text{NCS})]^{1+}$, $\text{bpyCOOH} = 2,2'$ -bipyridine-4,4'-dicarboxylic acid, Figure 2), demonstrated by Giribabu *et al.*, utilizing a π -conjugated terpyridine ligand, a bipyridine ligand with carboxyl anchoring group to attach onto TiO_2 and a thiocyanate ligand to adjust the redox properties.

Photoelectrochemical characterization illustrated superior photovoltaic performance relative to most other related mono-thiocyanate complexes[18].

In addition, a combined concept of molecular switches and extended π -conjugated terpyridine ruthenium molecules has been studied by Vila *et al.*[19]. In this case intramolecular photoisomerization results in a decrease in conjugation and a corresponding *loss* of luminescence. Several mono- and dinuclear bisterpyridine ruthenium complexes ($[(\text{tpy})\text{Ru}(\text{L6-L9})\text{Ru}(\text{tpy})]^{4+}$ and $[(\text{tpy})\text{Ru}(\text{L10})]^{2+}$), covalently linked by a photoswitchable dimethyldihydropyrene (DHP) moiety, were synthesized (Figure 2). The conjugated DHP form of the complexes exhibits room temperature luminescence in the range of 649-660 nm with excited lifetime around 5 ns. However, the photoisomerized non-conjugated form of the DHP derivatives, achieved by irradiation with visible light ($\lambda \geq 490$ nm), resulted in a blue shift of the absorption spectra and loss of room temperature luminescence. In this instance, switching off of the extended conjugation through photoisomerization results in loss of the slightly extended luminescence lifetime.

An aromatically extended π -conjugation system having polyaromatic ring 4'-substituted 2,2':6',2''-terpyridine in various Ru (II) complexes ($[\text{Ru}(\text{L14})_2]^{2+}$, $[\text{Ru}(\text{tpy})(\text{L15})]^{2+}$, $[\text{Ru}(\text{tpy})(\text{L16})]^{2+}$, figure 3) has been studied by Draper and coworkers[20]. The fused moiety displays interesting electronic properties due the high degree of electron delocalization that also promotes a bathochromic shift of MLCT absorption and increases in the molar extinction coefficient. These complexes are non-emissive at room temperature, but are strong red emitters in frozen glasses at 77 K with lifetimes of more than 12 μs . However, the excited states of these systems with extended fused conjugation are only slightly longer lived than the terpyridyl complex precursor (11 μs) and the lack of room temperature luminescence suggests that there is a small effect of the extended aromatic systems on the excited state lifetime. In these complexes steric factors very likely inhibit delocalization in the excited state since the torsion angle cannot come anywhere near planarity with the

terpyridyl ring. McCusker and coworkers have illustrated the importance of excited state torsional motion to achieve extended conjugation in Ru(II) 4'-aryl-2,2'-bipyridyl complexes [21]. Unfortunately, the complex $[\text{Ru}(\text{tpy})(\text{L17})]^{2+}$, with a planarized extended aromatic structure, was not prepared and examined.

A series of platinum complexes with 4'-Ar-tpy ligand (Ar=4'-naphthyl, phenanthryl, anthryl and pyrenyl), candidates for optical limiting materials, has been developed (Figure 4)[22]. Guo et al. reported that the 4'-pyrenyl terpyridyl platinum complex has room temperature emission that stems from an admixture state of $^3\text{MLCT}$, $^3\text{ILCT}$ and $^3\pi,\pi^*$, states. All other compounds, with smaller aromatic substituents on the terpyridine ($[\text{Pt}(\text{L18-5})(\text{CC-ph})]^+$, $[\text{Pt}(\text{L18-6})(\text{CC-ph})]^+$ and $[\text{Pt}(\text{L18-7})(\text{CC-ph})]^+$), have $^3\text{MLCT}$ excited states. The pronounced extended excited state lifetimes of 2 μs and 300 μs observed at room temperature and 77 K, for the $[\text{Pt}(\text{L18-8})(\text{CC-ph})]^+$ complex, are much greater than those of the corresponding complexes of ligands 18-5, 18-6 and 18-7.

2.2 Influencing Ligand Field Splitting: Another approach to making terpyridyl complexes with long-lived excited state lifetimes is increasing the energy of the ^3MC state through ligand control. Scandola demonstrated this in the late 1990s in the heteroleptic complex $[(\text{tpy})\text{Ru}(\text{CN})_3]$ [23]. More recently McMillin's group has shown that, for $[(\text{X-tpy})\text{Ru}(\text{dmcb})(\text{CN})]^+$ complexes (dmcb = 4,4'-dicarboxymethyl-2,2'-bipyridine, X = electron donating and withdrawing substituents), the luminescence lifetime varies as a function of the emission energy, decreasing with decreasing emission energy, and decreasing energy gap between the $^3\text{MLCT}$ and ^3MC state, which decreases with increasing emission energy[24]. Baraldo and coworkers examined the behavior of related complexes having bridging NC ligand $[(\text{tpy})(\text{bpy})\text{Ru}(\text{II})(\mu\text{-NC})\text{Ru}(\text{II})(\text{L})_4\text{CN}]^x$ (L=py, x=2+ ; CN^- , x=2-)[25,26]. Luminescence is observed from the $[(\text{tpy})(\text{bpy})\text{Ru}(\text{II})(\text{NC})]$ chromophore of the bimetallic complexes in solution, with emission lifetimes that exceed, to a small degree, the lifetime of the parent monometallic complex [26]. Significant

contributions to this area have been made by the Endicott group over the years, especially with respect to understanding the photophysical behavior of multimetallic complexes [27-29].

Another system reported recently involves complexes for which both increasing energetic separation of the $^3\text{MLCT}$ - ^3dd energy gap *and* decreased distortion of the excited state are important. Complexes of 4'-(2-pyrimidinyl)- terpyridine and related derivatives (**L13**, Figure 2) are believed to have extended excited state lifetimes reflecting both these factors[15,30]. Very significant increases in the $^3\text{MLCT}$ luminescence lifetime were observed for $[(\text{tpy})\text{Ru}(\text{L13-3})]^{2+}$ and $[(\text{tpy})\text{Ru}(\text{L13-4})]^{2+}$ with pentafluorophenyl and cyano substituents on the pyrimidinyl substituted terpyridine ligand.

2.3 Inclusion of Ligands with Low Energy Excited States: A third approach, and the topic of the case study below, is the incorporation of complexes covalently linked to aromatic hydrocarbon substituents with triplet excited states lower in energy than the $^3\text{MLCT}$ state. Energy migration between the $^3\text{MLCT}$ state and the aromatic hydrocarbon localized triplet state (^3IL) occurs and, since the ^3IL state experiences weaker spin-orbit coupling than the $^3\text{MLCT}$ state, relaxation to the ground state is slower for the ^3IL state, often orders of magnitude slower[12,31-33]. A part of the reason this approach is effective is that the energy splitting between the lowest singlet excited state and the lowest triplet state is significantly larger for aromatic hydrocarbons ($> 10,000 \text{ cm}^{-1}$) than for metal complexes having MLCT excited states ($< 6,000 \text{ cm}^{-1}$)[34], thus the lowest energy absorption transition can be designed to be MLCT while the lowest energy excited state is the ^3IL . In effect, this represents selective development of bichromophoric molecules. We have exploited this in work on terpyridyl phenylene vinylene bridged (tpvpvpt) bimetallic complexes, $[(\text{tpy})\text{Ru}(\text{tpvpvpt})\text{Ru}(\text{tpy})]^{4+}$ (t = terpyridine; p=phenyl; v=vinyl)[35]. The ^3IL state of the tpvpvpt ligand is lower in energy than the $^3\text{MLCT}$ state and, while the complex and related derivatives are nonluminescent at room temperature, they exhibit strong

transient absorbance throughout the visible with a lifetime that increases as the energy gap between the $^3\text{MLCT}$ and the ^3IL states increases. Campagna, Hanan and coworkers illustrated this approach as well in the photophysical behavior of anthracenyl linked terpyridyl Ru(II) complexes[36,37] and other systems are mentioned in Hanan's 2005 review[12].

New examples have also been emerged to discuss this effect of inclusion of ligands with low energy excited states ligands in Ru terpyridinyl complexes. Zhang and coworkers have investigated 1-naphthyl, 1-pyrenyl and 9-anthracenyl 4'-substituted Ru bis-terpyridinyl complexes ($[\text{Ru}(\text{L3-5})(\text{tpy})]^{2+}$, $[\text{Ru}(\text{L3-5})_2]^{2+}$) [38]. The energy of ^3IL state of these ligands was carefully compared with that of the $^3\text{MLCT}$ states. Similar to Ru(II) bipyridyl complexes, they found that the ^3IL energy of naphthyl ligand was higher than the MLCT state of the mixed ligand complex while the pyrenyl ^3IL state is almost equivalent in energy and the anthracenyl is lower in energy than the $^3\text{MLCT}$ state. Hence, the first two complexes $[\text{Ru}(\text{L3})_2]^{2+}$ and $[\text{Ru}(\text{L4})_2]^{2+}$ behave very similarly to the parent complex because the lowest energy excited state is $^3\text{MLCT}$. The complexes therefore have very short excited state lifetimes and, as a consequence, very low $^1\text{O}_2$ generation quantum yields, In contrast, for the L5 containing complexes, which were reported to exhibit extremely high $^1\text{O}_2$ generation quantum yields (0.96 and 0.71 for $[\text{Ru}(\text{L5})_2]^{2+}$ and $[\text{Ru}(\text{L5})(\text{tpy})]^{2+}$ complexes, respectively), the lowest energy excited state is the anthracene-localized $^3\pi-\pi^*$ state. For that reason, the promising applications of this complex in $^1\text{O}_2$ involved processes were suggested, such as photodamage capabilities on DNA.

A large number of Pt(II) terpyridyl complexes with ligand localized excited states lower than or in equilibrium with $^3\text{MLCT}$ states have been prepared and thoroughly characterized by the Castellano group [39-43]. Examples of the complexes include especially derivatives of Pt(II) containing acetylide ligands with substituents having ^3IL states at energies beneath the $^3\text{MLCT}$ (Pt(II) - tpy π^*) excited state as shown in figure 5. The pyrene substituted terpyridine ligand (L5) mentioned above was also

investigated in Pt complexes ($[\text{Pt}(\text{L5})(\text{X})]^+$, $\text{X}=\text{Cl}$, Ph , CCPh , Figure 2) by Macmillin et al.[44]. It exhibits a very long-lived excited state, up to 45 μs in non-coordinating solvents, resulting from population of a low-lying $^3\pi-\pi^*(\text{pyrene})$ excited state, at least order of magnitude longer than other substitution groups: pyrrolidinyl or dimethylamines. This complex was compared with a (NNC) cyclometallated Pt complexes ($[\text{Pt}(\text{NNC})(\text{Py})]^+$, $\text{NNC}:6'$ -phenyl-2,2'-bipyridine and Py : pyridine, 4.8 μs in the same condition).

Excited state relaxation following excitation into the MLCT absorption and intersystem crossing to the $^3\text{MLCT}$ state is primarily determined by competition between (a) internal conversion from the $^3\text{MLCT}$ state to the ^3MC state and (b) internal conversion between the $^3\text{MLCT}$ and the ^3IL state, as shown in figure 1. Very long-lived excited states ($> 50 \mu\text{s}$) are observed for complexes in which the ^3IL state is lower in energy than the $^3\text{MLCT}$ state and the ^3MC state is significantly higher in energy than the $^3\text{MLCT}$ state[45]. Even when the $^3\text{MLCT}$ and ^3IL states are in equilibrium, the excited state lifetime observed is longer than the $^3\text{MLCT}$ lifetime in the absence of the ^3IL state, as the decay rate for equilibrated excited states is the weighted average of the relaxation rates of the two states[46].

We present here a comparison of the behavior of two complexes having a terpyridyl pyrene ligand (figure 6) with the comparable complexes lacking the pyrene : $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}/[\text{Ru}(\text{Mpt})_2]^{2+}$ and $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}/[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$. The combined result of redox properties, excited-state absorption and luminescence properties suggest that for the Mpt complexes the $^3\text{MLCT}$ state is deactivated by population of the ^3MC state and huge differences in excited properties arise upon inclusion of the pyrene (from the $^3\text{IL } ^3\pi-\pi^*$ state). In the second group the emission arises from $^3\text{MLCT}$ and the two complexes have very similar photophysical properties.

3. Case Study of Pyr-v-tpy Complexes:

3.1 Ligand and complex syntheses: The ligand Pyr-v-tpy was prepared from 4'-(4-methylphenyl)-2,2':6,2''-terpyridine by NBS bromination of the methyl, reaction of the bromide with triphenylphosphine and reaction of the phosphonium salt with pyrene-1-carboxaldehyde under Wittig conditions as shown in Scheme 1. The overall yield from the starting tolylterpyridine was approximately 20%. [Ru(Pyr-v-tpy)Cl₃] was prepared using a variation of literature methods.[47] [Ru(Pyr-v-tpy)(dien)]²⁺ was prepared by reaction of [Ru(Pyr-v-tpy)Cl₃] with excess diethylenetriamine in refluxing ethanol:water (v:v =1:1). The complex was purified by column chromatography on alumina and characterized by NMR, UV-Vis, cyclic voltammetry and ESI mass spectroscopy at high resolution (HRMS). The bis-terpyridine complex was prepared by reaction of [Ru(Pyr-v-tpy)Cl₃] with AgBF₄ in acetone to make the solvento complex which was further reacted with the pyr-v-tpy ligand. The complex was purified by column chromatography on alumina and characterized by the above techniques. ESI mass spectra were characterized by both exact mass, generally varying by less than 20 ppm from calculated mass, and the intensities of isotope distributions.

3.2 Electrochemistry: Cyclic voltammetry and Differential pulse voltammetry studies were performed on all of the compounds in acetonitrile with 0.1M tetrabutylammonium hexafluorophosphate as the supporting electrolyte (Supporting information Figure 11S and Figure 12S shows cyclic voltammograms for [Ru(Mpt)(dien)]²⁺ and [Ru(Pyr-v-tpy)(dien)]²⁺). All the redox potentials are reported relative to SCE, but the Fc/Fc⁺ couple was used as internal standard and a value of 0.4 V versus SCE was taken for the Fc/Fc⁺ couple in CH₃CN. Potentials are given in Table 1.[48] The ligand Pyr-v-tpy exhibits an irreversible oxidation of the pyrene moiety, similar to oxidation of Pyr-bpy and Pyr-v-bpy.[49,50]

[Ru(Mpt)(dien)]²⁺ and [Ru(Pyr-v-tpy)(dien)]²⁺ both exhibit multiple irreversible oxidation waves. Earlier work of Meyer et al. illustrated that cyclic voltammetry of

[Ru(bpy)₂(en)]²⁺ (en = ethylenediamine) is quasi-reversible and exhaustive electrolysis results in oxidation of the ethylenediamine to the coordinated imine, a four electron process.[51] For the dien complexes studied here, the first two irreversible oxidations are at 0.65 (0.85) V and 0.85 (1.15) V for the Mpt (Pyr-v-tpy) complexes. We have not investigated further or done spectroelectrochemical studies to assess the nature of the irreversible processes, but it is likely the pattern of behavior is similar to that of the en complex reported by Meyer. The third oxidative wave in cyclic voltammograms of the dien complexes is observed at 1.3 V for both and the wave very likely corresponds to Ru(III/II) reaction. [Ru(Pyr-v-tpy)(dien)]²⁺ has a fourth wave at 1.55 V corresponding to irreversible oxidation of the pyrene of Pyr-v-tpy [49].

Voltammetric analysis of [Ru(Pyr-v-tpy)₂]²⁺ revealed one reversible oxidation at 1.25 V. On the basis of earlier work by others on [Ru(Mpt)₂]²⁺, a wave at 1.26 V is assigned to the Ru(III/II) redox process [52]. The expected wave for oxidation of the coordinated pyrene was not observed, possibly being buried in solvent oxidation at the anodic limit.

All the complexes above have several overlapping quasi-reversible reduction waves corresponding to reduction of the tpy ligand(s).

3.3 Absorption and luminescence spectra: The room temperature absorption spectra of the complexes was measured in MeCN and absorption maxima and absorbivities were recorded in Table 1. Spectra of [Ru(Pyr-v-tpy)₂]²⁺, [Ru(Mpt)₂]²⁺ and [Zn(Pyr-v-tpy)₂]²⁺ (prepared *in situ*) are shown in Figure 7 and spectra of [Ru(Pyr-v-tpy)(dien)]²⁺, [Ru(Mpt)(dien)]²⁺ and [Zn(Pyr-v-tpy)₂]²⁺ are shown in Figure 8. The spectra for [Zn(Pyr-v-tpy)₂]²⁺ demonstrate the effect of divalent metal ion coordination on the electronic spectrum of the Pyr-v-tpy ligand without the inclusion of MLCT and ligand field transitions associated with the Ru metal center.

The UV transitions between 300 nm to 320 nm correspond to the intraligand terpyridine localized π - π^* transitions which are close in energy and relative

absorptivity to the transitions observed for bis-terpyridine ruthenium complexes.[1,23,35,53] In earlier work on Pyr-v-bpy complexes of Ru(II) [49], the ligand has a $\pi \rightarrow \pi^*$ ligand localized absorption at 342 nm. For the ligand Pyr-v-tpy the absorption maximum is significantly to the red at 390 nm. There are clear differences between the ligands, if the aromatic frameworks are compared: the Pyr-v-bpy ligand can be viewed as the pyrene vinyl moiety linked to a meta-substituted biphenyl while the Pyr-v-tpy ligand, having a phenyl between the vinyl and the terpyridine, appears more like 1,3,5-triphenylbenzene with the Pyr-v moiety in the para position of one of the phenyls (see fig. 6). Also, for the coordinated Pyr-v-tpy in $[\text{Zn}(\text{Pyr-v-tpy})_2]^{2+}$, which has no visible MLCT transitions, the ligand localized $\pi-\pi^*$ transition appears at 405 nm, suggesting some degree of pyrene to coordinated terpyridine charge transfer character. The same transition for both the Ru(II) complexes appears in the 370 - 400 nm range; the absorption maximum, however, is almost certainly influenced by overlap with MLCT transitions. Figure 8 shows that the $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ Pyr-v-tpy localized $\pi-\pi^*$ transition maximum is at 400 nm ($25,000 \text{ cm}^{-1}$) compared to 370 nm ($27,000 \text{ cm}^{-1}$) for $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}$.

The Ru(II) complexes have a weaker absorption further to the red with a maximum near 500nm ($20,000 \text{ cm}^{-1}$). For the closely related complex $[\text{Ru}(\text{tpy})_2]^{2+}$ this is assigned as a metal to ligand charge transfer (MLCT) transition.[12,14,54-56] The broad absorption of $[\text{Ru}(\text{tpy})(\text{dien})]^{2+}$ between 450nm-550nm is also most likely a MLCT transition. The dien ligand is weaker field than the Pyr-v-tpy and serves only as a sigma donor to the Ru(II) center; thus the expectation is that the MLCT absorption will be at lower energy than that for $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}$. Of interest is the fact that the MLCT absorption of $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ shows two partially resolved absorption transitions, differing somewhat from the single broad transition observed for $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$.

Results of TD DFT calculations for the 20 lowest singlet excited states relative to the geometry-optimized ground state, using methods essentially identical to those of

others, prove problematic for these complexes. For instance, for $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}$ the absorption near 500 nm arises from the a transition that, according to the TD DFT results (see Fig. 13S) is an intraligand charge transfer (ILCT) absorption, despite the fact that the wavelength and band shape are similar to those observed for the MLCT transition of $[\text{Ru}(\text{Mpt})_2]^{2+}$. In this particular case the ILCT transition may have a charge separation distance great enough that a significant under estimation of the energy in TD DFT may result [57]. For $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ the longest wavelength transition (shoulder) is also calculated to be predominantly HOMO-1 (Pyr-v-tpy π) to LUMO (Pyr-v-tpy π^*) (Fig. 14S). However, given the similarity in energy and bandshape of the lowest energy absorption transitions to the definitive MLCT transition of $[\text{Ru}(\text{tpy})_2]^{2+}$, it is more appropriate to assign the lowest energy allowed absorption transition as MLCT.

Fluorescence is observed from the Pyr-v-tpy ligand at 500 nm, significantly to the red of pyrene fluorescence (373 nm), indicating strong perturbation of the excited state. Emission maxima, quantum yields and lifetimes in deaerated solution are listed in Table 1 for the ligand and the Ru(II) complexes. Luminescence was not observed, either at room temperature or 77 K for $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}$. This is in contrast to $[\text{Ru}(\text{Mpt})_2]^{2+}$ which lacks room temperature luminescence, but exhibits strong emission at 77 K with a maximum at 628 nm ($15,900 \text{ cm}^{-1}$) and a lifetime of 4.5 μs . DFT results for the geometry optimized triplet of $[\text{Ru}(\text{Pyr-v-tpy})_2]^{2+}$ indicate the state reflects ILCT (Fig. 13S) character relative to the ground state, while the $[\text{Ru}(\text{Mpt})_2]^{2+}$ excited state is clearly of MLCT origin.

Both $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ and $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ exhibit broad, featureless luminescence in solution at room temperature at $13,600$ and $12,900 \text{ cm}^{-1}$, respectively (figs. 9, 10). These emission maxima fall between those measured by Endicott and coworkers for $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$ (en = ethylenediamine) and $[\text{Ru}(\text{bpy})(\text{en})_2]$ at $14,350 \text{ cm}^{-1}$ and $12,600 \text{ cm}^{-1}$, respectively. The luminescence of these en complexes was evaluated in considerable detail and has been assigned as originating from an MLCT

excited state for $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$, [27,58,59] consistent with the TD DFT results that indicate the lowest energy triplet state arises from a HOMO ($d\pi$) to LUMO (π^*) transition (Fig. 14SA). The energy of the lowest triplet state determined by TD DFT, the energy difference between the geometry optimized ground and lowest triplet states, and the observed emission maximum agree within 500 cm^{-1} ($< 5\%$, table 2). For $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$, TD DFT results indicate some degree of MLCT character in the transition associated with populating the triplet state (Fig. 14S), although the transition is largely intraligand charge transfer from the pyrene to the terpyridine. Here again, there is good agreement of the experimental triplet energy from the luminescence maximum and the energies calculated using TD DFT and the energy difference of the DFT geometry optimized ground state and lowest triplet state. (the 0-0 energy; table 2). Nonetheless, the similarity of the luminescence spectra of the two dien complexes and the relation of the observed emission energies relative to those of $[\text{Ru}(\text{bpy})_2(\text{en})]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{en})_2]^{2+}$ suggest that the observed luminescence is of primarily MLCT origin for all the complexes. Transient absorption spectral data, however, suggest a Pyr-v-tpy ligand localized state does indeed contribute significantly to an excited state for $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ that is thermally equilibrated (*vide infra*). The luminescence lifetimes of the two complexes are in the 100-400 ns time range, with the Pyr-v-tpy complex having the longer lifetime. Observed radiative decay rate constants, calculated from luminescence lifetimes and quantum yields, are between 5000 and 9000 s^{-1} for the two complexes, much lower than typical MLCT radiative decay constants for Ru(II) diimine complexes (generally at least $50,000 \text{ s}^{-1}$). [1,5] Since the experimental radiative decay rate constant is from a triplet excited state, $k_{r,\text{exp}}$ actually equals $\eta_{\text{isc}}k_r$ and it is possible that the low measured radiative decay constants simply represent inefficient population of the emitting $^3\text{MLCT}$ state. 77 K Emission maxima and lifetimes were obtained in ethanol : methanol (v:v = 4:1) for the two dien complexes and the maxima are also listed in Table 1. The low temperature spectra of both $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ and

[Ru(pyr-v-tpy)(dien)]²⁺ have narrower bandwidths relative to the room temperature emission and both also lack vibrational structure. The fact that no emission spectral shift is observed between room temperature solution and the frozen matrix contrasts the observed behavior for [Ru(bpy)₂(en)]²⁺ and [Ru(bpy)(en)₂]²⁺; however, the data for the dien complexes are reported for two different media and, based upon results of others, it is highly likely that the solvent will influence the energy of the MLCT emission. We have not yet explored solvent effects on emission for these complexes [27,59].

3.4 Transient absorption studies: The transient behavior for the parent complex, [Ru(tpy)₂]²⁺, has been reported by a number of groups and the excited state lifetime is under 1 ns in solution at room temperature. A recent paper by Damrauer et al. illustrates that the transient absorption spectrum of [Ru(tpy)₂]²⁺ is similar to that of [Ru(bpy)₃]²⁺, with a strong excited state absorption between 350 and 400 nm, bleaching of the MLCT absorption and weak absorption to the red of 500 nm[60]. All of the complexes studied here have much longer excited state lifetimes and very different transient absorption spectra. Spectra were obtained in acetonitrile solution from < ps to 1.5 ns and separately, from 10 ns until the transient signal decayed to zero. No net photochemistry was observed for the complexes in the pulsed laser experiments.

The transient spectra of [Ru(Pyr-v-tpy)₂]²⁺ in the nanosecond and ultrafast time domains are shown in figure 11. The spectrum differs completely from that of [Ru(Mpt)₂]²⁺ as it lacks any absorbance below 500 nm and has strong, broad excited state absorption between 550 and 800 nm. The spectrum exhibits little change from the earliest times observed (~ 1 ps) to the end of the triplet decay over 20 μs later. The DFT geometry optimized triplet state suggests the state has a mix of Pyr-v-tpy ILCT and pyrene localized π-π* character (not MLCT). This assignment is also consistent with the observation of an excited state lifetime that is much longer than the other Ru(II) terpyridyl chromophores.

The transient UV-Vis spectra of $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ and $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ are shown in Figures 12 and 13. While the similarity of the behavior of the luminescence spectra and decays suggest the two complexes may have lowest triplet excited states of MLCT origin, differences in the transient absorption spectra suggest the behavior may be more complex. Each of the complexes poses peculiarities to be addressed. For $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ the transient spectrum is distorted at long wavelengths (> 750 nm) because of luminescence from the complex. The spectral features of the ultrafast absorption carry over in the nanosecond spectrum and exhibit a maximum at 420 nm that is similar to the transient of $[\text{Ru}(\text{tpy})_2]^{2+}$, assigned as absorption of the tpy anion associated with the MLCT state [60]. Evolution of the transient is peculiar; the ground state bleaching initially apparent at 500 nm is gone by 100 ns ($\tau = 115$ ns), leaving only absorption in the blue and absorption between 575 and 725 nm. Despite this change in bandshape, the decay observed is a single exponential. We are investigating the transient behavior of this complex in greater detail (possible deprotonation of the dien ligand of the MLCT state).

$[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ exhibits much cleaner transient behavior, with the initially formed transient species in the ps time domain appearing to carry through the entire decay with a lifetime that is reasonably close to that measured by luminescence. The spectrum differs significantly from that of the Mpt complex, with no net absorbance observed in the 350-450 nm range and strong excited state absorbance in the red with a maximum of 750 nm. It is possible that bleaching of the strong absorption transition of the Pyr-v-tpy ligand in the 400 nm region completely obscures possible excited state absorption of a contributing MLCT state, possibly in equilibrium with the ligand localized state. The DFT results for the geometry optimized triplet excited state, however, suggest that, while the lowest emitting triplet state of $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$ is the MLCT state, the lowest triplet state of $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ is a mix of a Pyr-v-tpy ILCT transition and a MLCT (Fig. 14S). Given the fact that the ultrafast spectrum of this complex (Fig. 13) in no way

resembles the spectrum of $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$, it is likely excitation is directly into a potential surface that has mixed MLCT/ILCT character. To investigate these two complexes further, we intend to look at the temperature dependence of the luminescence lifetime between 77 K and room temperature and the transient absorbance at temperatures near room temperature; it may be that interaction between the MLCT and ILCT state in $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$ can be better defined.

4. Summary: Recent research on the photophysical behavior of transition metal terpyridyl complexes of Ru(II) and Pt(II) was presented with an emphasis on understanding factors that influence radiative and nonradiative decay. In addition a case study of the photophysical behavior of a pair of Ru(II) terpyridyl complexes modified to have ligand localized excited states that are equal to or lower than the energy of the known MLCT state of the parent complexes was undertaken. The common observation is that the presence of the modified terpyridyl ligand (Pyr-v-tpy) served to lengthen the excited state lifetime of the complex in a way similar to that observed for Ru(II) bipyridine complexes. For $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$, the ligand localized triplet state is close in energy to the MLCT state and, while the transient absorption spectrum is significantly perturbed relative to $[\text{Ru}(\text{Mpt})(\text{dien})]^{2+}$, the excited state decay kinetics change by only a factor of four. Future study of the temperature dependence of the transient spectral decay should shed light on thermally activated nonradiative decay pathways and coupling of the low energy triplet states of $[\text{Ru}(\text{Pyr-v-tpy})(\text{dien})]^{2+}$, possibly including metal centered excited states.

Acknowledgements:

RHS wishes to thank the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG-02-96ER14617). TL is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Solar Photochemistry Program (DE-FG02-12ER16347). We also thank the National Science Foundation (grant CHE0619770) for funding the ESI mass spectrometer. J.G. thanks the IBM

-
- 1 Corporation for a fellowship in Computational Science administered through the
 - 2 Tulane Center for Computational Science.
 - 3

1

2 **Scheme 1:** Synthetic route for 4-((1-pyrenylvinyl)phenyl)-2,2':6',2''-terpyridine

Table 1. Spectroscopic properties and potentials for one electron oxidation of ligand and complexes in acetonitrile.

compounds	$\lambda_{\max}^{\text{abs}}, \text{nm}$ (log ϵ)	$E^{\circ}(\text{ox})\text{V}$ vs. SCE	$\lambda_{\max}^{\text{em}}, \text{nm}$ (298 k)	$\lambda_{\max}^{\text{em}}, \text{nm}$ (77 k)	$\tau_{\text{em}}^{\text{a}}, \text{ns}$ (298 k)	$\tau_{\text{em}}, \text{ns}$ (77 k)	$\tau_{\text{TA}}^{\text{b}}, \text{ns}$ (298 k)	Φ_{em} (298 k)
Pyr-v-typ	400(4.39)		497	470				
[Ru(Pyr-v-typ)(dien)] ²⁺	314(4.16) 390(4.12) 494(3.80)	0.85, 1.15, 1.30, 1.55	773	753	391	1120	298	0.0017
[Ru(Mpt)(dien)] ²⁺	314(4.04) 508(3.57)	0.65, 0.85, 1.30	733	736	105	1200	114	<0.001
[Ru(Mpt) ₂] ²⁺	304(4.00) 490(3.80)	1.26 ^c	---	650 ^d	< 1	4500	4.5 ^d	NA
[Ru(Pyr-v-typ) ₂] ²⁺	316(4.04) 388(4.12) 498(3.80)	1.25	NA	NA	NA	NA	8360	NA
[Zn(Pyr-v-tpy) ₂] ²⁺	405(4.22)	---	721	630	---	---	---	---

^aSamples were degassed with N₂ in MeCN for 10 min. ^bLifetimes measured from TA at 500 nm. ^cFrom Ref. 32

^dFrom Ref. 48.

Table 2 Calculated and experimental values for hydrocarbon, ligand and complex singlet-triplet energy gaps and comparison with experimental values. Energies based upon the difference in the values obtained for the geometry optimized structures for the ground state singlet and triplet states (see text) as well as the energies obtained from TDDFT calculations on the geometry optimized singlet state, all in CH₃CN with a correction of -2000 cm⁻¹ in all of the complexes.

Ligand/ Complex	DFT ^a $\Delta E(S_0-T_1)$, cm ⁻¹	TD DFT $\Delta E(S_0-T_1)$, cm ⁻¹	$\Delta E(\text{Exp.})$, ^b cm ⁻¹	Transition (DFT orbitals)
Pyrene	16,900	---	16,900	$\pi-\pi^*$
Pyr-v-ph	13,600	---	---	$\pi-\pi^*$
Pyr-v-bpy	13,700	---	---	$\pi-\pi^*$
[Ru(Mpt)(dien)] ²⁺	13,900	13,400	13,600	MLCT (HOMO – LUMO)
[Ru(Pyr-v-tpy)(Mpt)] ²⁺	13,200	13,900	NA	MLLCT (HOMO – 1 to LUMO)
[Ru(Pyr-v-tpy)(dien)] ²⁺	13,100	13,300	12,900	MLLCT (HOMO – LUMO)

a. 0-0 energy (from geometry optimized S₀ and T₁)

b. 77 K luminescence maxima; FWHM of spectra averages 700 cm⁻¹

Figure 1 Energy level diagram for the pyrene-vinyl-terpyridine ruthenium complexes

Figure 2. Structural formulae of 4'-substituted terpyridine ligands

11

$R_1 = \text{H, OMe}$

12

R_4

12-1

12-2

13

$R = \text{H, 13-1}$
 $\text{CH}_3, \text{13-2}$
 $\text{C}_6\text{H}_5, \text{13-3}$
 CN, 13-4

Figure 3. Structural formulae of benzene-fused ligand

14

15

16

17

Figure 4. Structural formulae of platinum terpyridine compounds

Figure 5. Additional Pt(II) terpyridyl complexes with acetylide derivative ligands.

Figure 6 Representation of structures of the Pyr-v-tpy ligand and complexes

Figure 7 UV absorption spectra in CH₃CN of (A) [Ru(Pyr-v-tpy)₂]²⁺ and (B) [Ru(Mpt)₂]²⁺ (—) and [Zn(Pyr-v-tpy)₂]²⁺ (---)

Figure 8 UV absorption spectrum in CH₃CN of (A) [Ru(Pyr-v-tpy)(dien)]²⁺ and (B) [Ru(Mpt)(dien)]²⁺ (—) and [Zn(Pyr-v-tpy)₂]²⁺ (—). Calculated (TDDFT) maxima and relative intensities for [Ru(Pyr-v-tpy)(dien)]²⁺ are included in (A).

Figure 9 Luminescence spectra of $[(\text{Mpt})\text{Ru}(\text{dien})]^{2+}$ (A. In CH_3CN solution at room temperature following excitation at 520 nm. B. 77k emission spectrum of the complex in $\text{EtOH}:\text{MeOH}=4:1(\text{v}:\text{v})$)

Figure 10 Luminescence spectra of $[(\text{Pyr-v-tpy})\text{Ru}(\text{dien})]^{2+}$ (A.) In CH_3CN solution at room temperature following excitation at 520 nm. (B.) 77k emission spectrum of the complex in EtOH: MeOH=4:1(v:v))

Figure 11. Transient difference spectra of $[(\text{Pyr-v-tpy})_2\text{Ru}]^{2+}$ in CH_3CN solution at room temperature between $< 1\text{ ps}$ and $1\mu\text{s}$ following excitation at 500 nm . The middle frame contains the spectra obtained at 860 ns , $3.1\text{ }\mu\text{s}$, $6.0\text{ }\mu\text{s}$, $10.1\text{ }\mu\text{s}$, $15.1\text{ }\mu\text{s}$, $20.6\text{ }\mu\text{s}$. The lower frame shows the UV-Vis spectrum of the complex in acetonitrile.

Figure 12 Transient difference spectra of [(Mpt)Ru(dien)] in CH₃CN solution at room temperature between < 1 ps and 1.5 ns (A), and at times of 44 ns, 100 ns, 140 ns, and 180 ns (B) following excitation at 500 nm. Lower trace (C) shows uv-vis spectrum of the complex in acetonitrile.

Figure 13 Transient difference spectra of $[(\text{Pyr-v-tpy})\text{Ru}(\text{dien})]^{2+}$ in N_2 degassed CH_3CN solution at room temperature between 1 ps and 1.5 ns (A) and at times of 90 ns, 170 ns, 250 ns, and 370 ns (B) following excitation at 500 nm. Lower trace (C) shows uv-vis spectrum of the complex in acetonitrile.

References

1. A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Vonzelewsky, *Coord. Chem. Revs.*, 84 (1988) 85.
2. R. Ziessel, M. Hissler, A. El-Ghayoury and A. Harriman, *Coord. Chem. Revs.*, 178 (1998) 1251.
3. V. Balzani and A. Juris, *Coord. Chem. Revs.*, 211 (2001) 97.
4. P.A. Anderson, F.R. Keene, T.J. Meyer, J.A. Moss, G.F. Strouse and J.A. Treadway, *J. Chem. Soc., Dalton Trans.*, (2002) 3820.
5. S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini and V. Balzani, *Photochemistry and photophysics of coordination compounds: Ruthenium* (2007). 117.
6. J.P. Sauvage, J.P. Collin, J.C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola and L. Flamigni, *Chem. Revs.*, 94 (1994) 993.
7. J.H. Alstrum-Acevedo, M.K. Brennaman and T.J. Meyer, *Inorg. Chem.*, 44 (2005) 6802.
8. M.H.V. Huynh, D.M. Dattelbaum and T.J. Meyer, *Coord. Chem. Revs.*, 249 (2005) 457.
9. J.V. Caspar, E.M. Kober, B.P. Sullivan and T.J. Meyer, *J. Am. Chem. Soc.*, 104 (1982) 630.
10. J.V. Caspar and T.J. Meyer, *J. Phys. Chem.*, 87 (1983) 952.
11. E.M. Kober, J.V. Caspar, R.S. Lumpkin and T.J. Meyer, *J. Phys. Chem.*, 90 (1986) 3722.
12. E.A. Medlycott and G.S. Hanan, *Chemical Society Reviews*, 34 (2005) 133.
13. U. Siemeling, J.V. der Bruggen, U. Vorfeld, B. Neumann, A. Stammler, H.G. Stammler, A. Brockhinke, R. Plessow, P. Zanello, F. Laschi, F.F. de Biani, M. Fontani, S. Steenken, M. Stapper and G. Gurzadyan, *Chem. Eur. J.*, 9 (2003) 2819.
14. A. Harriman, A. Mayeux, A. De Nicola and R. Ziessel, *Phys. Chem. Chem. Phys.*, 4 (2002) 2229.
15. Y.Q. Fang, N.J. Taylor, G.S. Hanan, F. Loiseau, R. Passalacqua, S. Campagna, H. Nierengarten and A. Van Dorsselaer, *J. Am. Chem. Soc.*, 124 (2002) 7912.
16. D. Maity, S. Das, S. Mardanya and S. Baitalik, *Inorg. Chem.*, 52 (2013) 6820.
17. L.S. Natrajan, A. Toulmin, A. Chew and S.W. Magennis, *Dalton Trans.*, 39 (2010) 10837.
18. L. Giribabu, T. Bessho, M. Srinivasu, C. Vijaykumar, Y. Soujanya, V.G. Reddy, P.Y. Reddy, J.-H. Yum, M. Graetzel and M.K. Nazeeruddin, *Dalton Trans.*, 40 (2011) 4497.
19. N. Vila, G. Royal, F. Loiseau and A. Deronzier, *Inorg. Chem.*, 50 (2011) 10581.
20. A. Graczyk, F.A. Murphy, D. Nolan, V. Fernandez-Moreira, N.J. Lundin, C.M. Fitchett and S.M. Draper, *Dalton Trans.*, 41 (2012) 7746.
21. N.H. Damrauer and J.K. McCusker, *JPC,A*, 1999, 103, 8440-46, *J. Phys. Chem., A*, 103 (1999) 8440.
22. F. Guo and W. Sun, *J. Phys. Chem. B*, 110 (2006) 15029.

-
23. M.T. Indelli, C.A. Bignozzi, F. Scandola and J.P. Collin, *Inorg. Chem.* , 37 (1998) 6084.
 24. M.A. Bork, H.B. Vibbert, D.J. Stewart, P.E. Fanwick and D.R. McMillin, *Inorg. Chem.* , 52 (2013) 12553.
 25. A. Cadranel, P. Albores, S. Yamazaki, V.D. Kleiman and L.M. Baraldo, *Dalton Trans.*, 41 (2012) 5343.
 26. A. Cadranel, B.M.A. Troselj, S. Yamazaki, P. Albores, V.D. Kleiman and L.M. Baraldo, *Dalton Trans.*, 42 (2013) 16723.
 27. Y.-J. Chen, P. Xie, J.F. Endicott and O.S. Odongo, *J. Phys. Chem. A*, 110 (2006) 7970.
 28. C.N. Tsai, M.M. Allard, R.L. Lord, D.W. Luo, Y.J. Chen, H.B. Schlegel and J.F. Endicott, *Inorg. Chem.* , 50 (2011) 11965.
 29. C.N. Tsai, M.M. Allard, R.L. Lord, D.W. Luo, Y.J. Chen, H.B. Schlegel and J.F. Endicott, *Inorg. Chem.* , 51 (2012) 3921.
 30. Y.Q. Fang, N.J. Taylor, F. Laverdiere, G.S. Hanan, F. Loiseau, F. Nastasi, S. Campagna, H. Nierengarten, E. Leize-Wagner and A. Van Dorsselaer, *Inorg. Chem.* , 46 (2007) 2854.
 31. A.I. Baba, J.R. Shaw, J.A. Simon, R.P. Thummel and R.H. Schmehl, *Coord. Chem. Revs.*, 171 (1998) 43.
 32. X.Y. Wang, A. Del Guerzo and R.H. Schmehl, *J. Photochem. Photobiol. C-Photochem. Rev.*, 5 (2004) 55.
 33. E.A. Medlycott and G.S. Hanan, *Coord. Chem. Revs.*, 250 (2006) 1763.
 34. M. Montalti and S.L. Murov, *Handbook of photochemistry* (Boca Raton: CRC/Taylor & Francis, 2006).
 35. X.Y. Wang, A. Del Guerzo, H. Tunuguntla and R.H. Schmehl, *Res. Chem. Intermed.*, 33 (2007) 63.
 36. J.H. Wang, Y.Q. Fang, L. Bourget-Merie, M.I.J. Polson, G.S. Hanan, A. Juris, F. Loiseau and S. Campagna, *Chem. Eur. J.*, 12 (2006) 8539.
 37. J.H. Wang, G.S. Hanan, F. Loiseau and S. Campagna, *Chem. Commun.*, (2004) 2068.
 38. H.-Y. Ding, X.-S. Wang, L.-Q. Song, J.-R. Chen, J.-H. Yu, L. Chao and B.-W. Zhang, *J. Photochem. Photobiol.*, A, 177 (2006) 286.
 39. A. Chakraborty, J.C. Deaton, A. Haeferle and F.N. Castellano, *Organometallics*, 32 (2013) 3819.
 40. V. Prusakova, C.E. McCusker and F.N. Castellano, *Inorg. Chem.* , 51 (2012) 8589.
 41. M.L. Muro, A.A. Rachford, X.H. Wang and F.N. Castellano, *Topics in Organometallic Chemistry*, 29 (2010). 159.
 42. A.A. Rachford, S. Goeb, R. Ziessel and F.N. Castellano, *Inorg. Chem.* , 47 (2008) 4348.
 43. F.N. Castellano, I.E. Pomestchenko, E. Shikhova, F. Hua, M.L. Muro and N. Rajapakse, *Coord. Chem. Revs.*, 250 (2006) 1819.
 44. D.P. Lazzaro, P.E. Fanwick and D.R. McMillin, *Inorg. Chem.* , 51 (2012) 10474.

-
45. T.A. Grusenmeyer, J. Chen, Y. Jin, J. Nguyen, J.J. Rack and R.H. Schmehl, *J. Am. Chem. Soc.* , 134 (2012) 7497.
 46. J.N. Demas, *Excited state lifetime measurements* (New York: Academic Press, 1983).
 47. G.R. Newkome, T.J. Cho, C.N. Moorefield, R. Cush, P.S. Russo, L.A. Godinez, M.J. Saunders and P. Mohapatra, *Chem. Eur. J.*, 8 (2002) 2946.
 48. E. Amouyal and M. Mouallembahout, *J. Chem. Soc., Dalton Trans.*, (1992) 509.
 49. J. Gu, J. Chen and R.H. Schmehl, *J. Am. Chem. Soc.*, 132 (2010) 7338.
 50. J.A. Simon, S.L. Curry, R.H. Schmehl, T.R. Schatz, P. Piotrowiak, X.Q. Jin and R.P. Thummel, *J. Am. Chem. Soc.* , 119 (1997) 11012.
 51. G.M. Brown, T.R. Weaver, F.R. Keene and T.J. Meyer, *Inorg. Chem.* , 15 (1976) 190.
 52. R.P. Thummel, V. Hegde and Y. Jahng, *Inorg. Chem.* , 28 (1989) 3264.
 53. J.A. Treadway, B. Loeb, R. Lopez, P.A. Anderson, F.R. Keene and T.J. Meyer, *Inorg. Chem.* , 35 (1996) 2242.
 54. A. Amini, A. Harriman and A. Mayeux, *Phys. Chem. Chem. Phys.* , 6 (2004) 1157.
 55. A.C. Benniston, G. Chapman, A. Harriman, M. Mehrabi and C.A. Sams, *Inorg. Chem.* , 43 (2004) 4227.
 56. S. Welter, N. Salluce, A. Benetti, N. Rot, P. Belser, P. Sonar, A.C. Grimsdale, K. Mullen, M. Lutz, A.L. Spek and L. De Cola, *Inorg. Chem.* , 44 (2005) 4706.
 57. A. Dreuw and M. Head-Gordon, *J. Am. Chem. Soc.*, 126 (2004) 4007.
 58. D.S. Seneviratne, M.J. Uddin, V. Swayambunathan, H.B. Schlegel and J.F. Endicott, *Inorg. Chem.* , 41 (2002) 1502.
 59. P. Xie, Y.-J. Chen, M.J. Uddin and J.F. Endicott, *J. Phys. Chem. A*, 109 (2005) 4671.
 60. P.J. Vallett and N.H. Damrauer, *J. Phys. Chem. A*, 117 (2013) 6489.