2018

Structure-Property Relationships for a Series of Ruthenium(II) Polypyridyl Complexes Elucidated through Raman Spectroscopy

Luke O'Neill
Technological University Dublin, Luke.oneill@tudublin.ie

Laura Perdisatt
Technological University Dublin

Christine O'Connor
Technological University Dublin

Recommended Citation

O'Neill, L. et al (2018) Structure-Property Relationships for a Series of Ruthenium(II) Polypyridyl Complexes Elucidated through Raman Spectroscopy, Journal of Spectroscopy Volume 2018, Article ID 3827130, 11 pages. doi:10.1155/2018/3827130

Hindawi
Journal of Spectroscopy
Volume 2018, Article ID 3827130, 11 pages
https://doi.org/10.1155/2018/3827130

Research Article

Structure-Property Relationships for a Series of Ruthenium(II) Polypyridyl Complexes Elucidated through Raman Spectroscopy

Luke O'Neill,[1] **Laura Perdisatt**,[2] **and Christine O'Connor**[3]

[1]*FOCAS Research Institute, Dublin Institute of Technology, Kevin St., Dublin 8, Ireland*
[2]*FOCAS Research Institute/School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin St., Dublin 8, Ireland*
[3]*School of Food Science and Environmental Health, Dublin Institute of Technology, Cathal Brugha St., Dublin 1, Ireland*

Correspondence should be addressed to Luke O'Neill; luke.oneill@dit.ie

Received 13 December 2017; Revised 5 June 2018; Accepted 10 October 2018; Published 1 November 2018

Academic Editor: Vincenza Crupi

A series of ruthenium polypyridyl complexes were studied using Raman spectroscopy supported by UV/Vis absorption, luminescence spectroscopy, and luminescence lifetime determination by time-correlated single photon counting (TCSPC). The complexes were characterised to determine the influence of the variation of the conjugation across the main polypyridyl ligand. The systematic and sequential variation of the main polypyridyl ligand, 2-(4-formylphenyl)imidazo[4,5-f][1,10]phenanthroline (FPIP), 2-(4-cyanophenyl)imidazo[4,5-f][1,10]phenanthroline (CPIP), 2-(4-bromophenyl)imidazo[4,5-f][1,10]phenanthroline (BPIP), and 2-(4-nitrophenyl)imidazo[4,5-f][1,10]phenanthroline (NPIP) ligands, allowed the monitoring of very small changes in the ligands electronic nature. Complexes containing a systematic variation of the position (*para*, *meta*, and *ortho*) of the nitrile terminal group on the ligand (the *para* being 2-(4-cyanophenyl)imidazo[4,5-f][1,10]phenanthroline (*p*-CPIP), the meta 2-(3-cyanophenyl)imidazo[4,5-f][1,10]phenanthroline (*m*-CPIP) and 2-(2-cyanophenyl)imidazo[4,5-f][1,10]phenanthroline (*o*-CPIP)) were also characterised. Absorption, emission characteristics, and luminescence yields were calculated and correlated with structural variation. It was found that both the electronic changes in the aforementioned ligands showed very small spectral changes with an accompanying complex relationship when examined with traditional electronic methods. Stokes shift and Raman spectroscopy were then employed as a means to directly gauge the effect of polypyridyl ligand change on the conjugation and vibrational characteristics of the complexes. Vibrational coherence as measured as a function of the shifted frequency of the imizodale bridge was shown to accurately describe the electronic coherence and hence vibrational cooperation from the ruthenium centre to the main polypyridyl ligand. The well-defined trends established and elucidated though Raman spectroscopy show that the variation of the polypyridyl ligand can be monitored and tailored. This allows for a greater understanding of the electronic and excited state characteristics of the ruthenium systems when traditional electronic spectroscopy lacks the sensitivity.

1. Introduction

A significant amount of research has been invested into the development of potential novel inorganic therapeutics [1–3]. Since the platinum-based drug *cis*-platins serendipidous discovery, the development of primary and secondary structural analogues has increased exponentially; however, only some of have received FDA worldwide approval, i.e., carboplatin and oxaliplatin. Although the potential is undeniable, several shortcomings within these platinum drugs regarding their clinical efficacy, limited activity against common types of cancers, the drug resistance phenomena which has lowered the impact of these drugs, and a range of deplorable side effects, has limited their potential usage [4]. To this end, ruthenium-based drugs have been proposed as an alternative. To date, several different ruthenium(II) and (III) complexes have exhibited good antitumour and anti-metastatic properties [5–7]. Both ruthenium compounds NAMI-A and KP1019 have successfully completed phase I clinical trials and have commenced to phase II [8].

In 2009, an article by Gianferrara et al. categorised metal anticancer compounds based on their mode of action, which

could be divided into five different classes: [9] (1) the metal has a functional role, (2) the metal has a structural role, (3) the metal is a carrier for main ligands that are delivered *in vivo*, (4) the metal compound behaves as a catalyst *in vivo*, and (5) the metal compound is photoactive.

Fundamental studies into the mode of action of anticancer agents are essential. Hence, this requires structure-property relationships to be formulated, starting with the explanation of small changes, which can then be applied to the larger more complex systems for the advantageous properties of ruthenium complexes as novel inorganic therapeutics to fully realise the processes, which govern the reactivity of the complexes, must be clearly established.

Many research teams have embraced the phenanthroline (phen) structure into the synthesis of a variety of polypyridyl ligands with different end group positions in the phenyl ring, developed on from the planar ligand; 2-phenyl-imidazo[4,5-f]1,10-phenanthroline (PIP) consists of a basic phenyl ring. Increasing the surface area of the phen polypyridyl ligand has seen to increase the DNA binding affinity of the complex [8]. Promising activity has been observed for these phen functionalised ligands as ruthenium-based complexes, and Liu et al. synthesised a similar series of these style ligands, *p*-MOPIP with the OMe group (2-(4-methoxyphenyl)imidazo [4,5-f][1,10]phenanthroline) (R_1 (*para*) position on the phenyl ring), *p*-HPIP with the OH group 2-(4-hydroxyphenyl)imidazo[4,5-f][1,10]phenanthroline, and *p*-NPIP with the NO_2 group (2-(4-nitrophenyl)imidazo[4,5-f] [1,10]phenanthroline) [10]. In the last decade, trends in medicinal chemistry are moving away from high-throughput approaches to drug discovery (i.e., those where vast databases of molecules are screened against a biological target) towards structure-based drug discovery (i.e., those where the drug design is based on specific structural information about a biological target) [4].

Establishing the structure-property relationships is a crucial aspect in several other potential applications for which ruthenium-based complexes are at the forefront of research too, e.g., concentrators for solar cells, oxygen sensors and photoactive drugs [11–13].

Research into optimisation of electronic and emissive characteristics in ruthenium complexes, in which the auxiliary ligand is systematically changed, has shown a well-defined relationship between the absorption and emission wavelengths and the electronic effect of the auxiliary ligand as measured by the electronic redox potential [14]. The relationship between the luminescence yield and lifetime establishes that the dominant effect of the auxiliary ligands being systematically changed is a manipulation in the nonradiative decay rate. These structure-property relationships have also been previously shown to exist in organic polymeric and oligomeric systems.

Well-defined relationships have been established showing a well-defined relationship with the vibrational coherence and the luminescence yield with Stokes shift, integrated Raman intensity, and electronic gap [15–18].

To this end, coordination compounds of Ru(II) were synthesised with the following nitrogen donor ligands, 2, 2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 2, 2′-biquinoline (biq). The step-by-step substitution of the functional group on the polypyridyl ligand allows analysis with essentially a single variable, changing the electron affinity of the terminal group on the polypyridyl ligand. The effect of the systematic change on the complexes properties is investigated using a series of ruthenium complexes with the end-group terminations that varied from 2-(4-formylphenyl)imidazo[4,5-f][1,10]phenanthroline [*p*-FPIP], 2-(4-cyanophenyl)imidazo[4,5-f][1,10]phenanthroline [*p*-CPIP], and 2-(4-bromophenyl) imidazo[4,5-f][1,10]phenanthroline [*p*-BPIP] to 2-(4-nitrophenyl)imidazo[4,5-f][1,10]phenanthroline [*p*-NPIP]. The nature and influence of the end-group position was also investigated.

This article presents a study originating in the electronic band gap transitions but extended to the Stokes shift, and thus, the vibrational nature of the complexes is introduced. The study shows that systematic structural variations made to the polypyridyl ligand can be described in terms of the effect on the vibrational coherence across the complex. This variation in the vibrational properties of the complexes can be directly measured via Raman spectroscopy. The vibrational decoupling will allow for quantitative structure-property relationships to be formed and optimisation of the preferred avenue of decay leading to maximising the radiative decay, i.e., luminescence. Hence, the study is aimed at establishing structure-property relationships for both electronic and vibrational characteristics in these systems. Structure-property relationships will aid the smart design of complexes which absorb and emit in required spectral windows. The potential for control and optimisation of luminescence yield and lifetime is also extremely desirable for applications such as photoactive therapeutics, solar cell dyes, and oxygen sensor research where the excited state characteristics are extremely important, and elongation of the luminescence lifetime without compromising the yield is paramount.

2. Experimental

The ruthenium complexes investigated, shown in Figure 1, were $[Ru(bpy)_2L]^{2+}$, $[Ru(phen)_2L]^{2+}$, and $[Ru(biq)_2L]^{2+}$, where L is the main ligand with differing functional group terminations (L = 2-(4-formylphenyl)imidazo[4,5-f][1,10] phenanthroline (*p*-FPIP), 2-(4-nitrophenyl)imidazo[4,5-f] [1,10]phenanthroline (*p*-NPIP), 2-(4-bromophenyl)imidazo [4,5-f][1,10]phenanthroline (*p*-BPIP), 2-(4-cyanophenyl)imidazo [4,5-f][1,10]phenanthroline (*p*-CPIP), 2-(3-cyanophenyl) imidazo[4,5-f][1,10]phenanthroline (*m*-CPIP), and 2-(2-cyanophenyl)imidazo[4,5-f][1,10] phenanthroline (*o*-CPIP).

Synthesis of the ruthenium complexes shown in Table 1 have been described elsewhere [19, 20]. The complexes were prepared in an acetonitrile solution. Concentration-dependent studies were undertaken to ensure the samples were unaffected by aggregation. Absorption spectroscopy was carried out using a PerkinElmer Lambda 900 UV/VIS/NIR absorption spectrometer. The luminescence measurements were performed using a PerkinElmer LS55 luminescence spectrometer. These measurements were used to calculate luminescence yields.

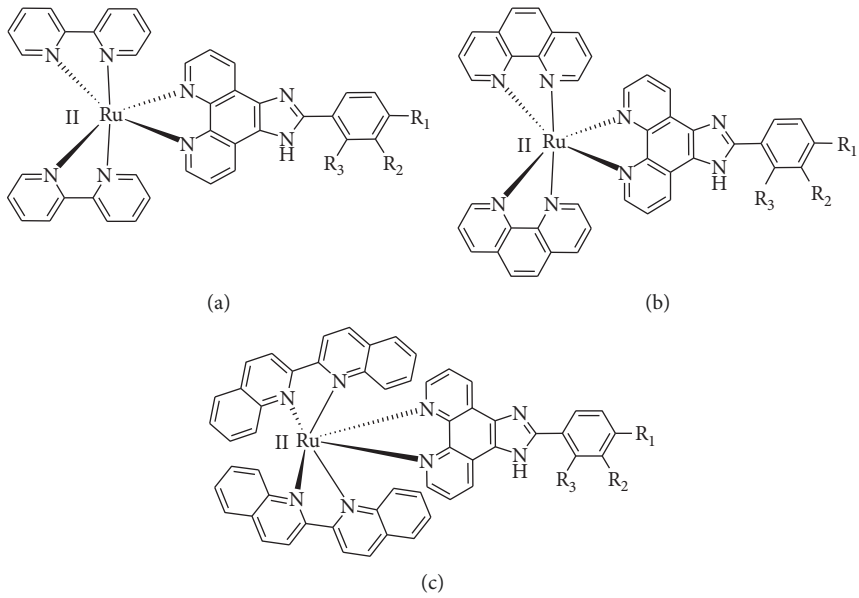

Figure 1: Ruthenium complexes: (a) $[Ru(bpy)_2L]^{2+}$, (b) $[Ru(phen)_2L]^{2+}$, and (c) $[Ru(biq)_2L]^{2+}$, where L is FPIP, NPIP, BPIP, and CPIP with R groups being CHO, NO_2, Br, and CN for the ligands, respectively.

Table 1: R groups for each main polypyridyl ligand.

Ligand names	R_1	R_2	R_3
p-FPIP	CHO	H	H
p-BPIP	Br	H	H
p-NPIP	NO_2	H	H
p-CPIP	CN	H	H
m-CPIP	H	CN	H
o-CPIP	H	H	CN

The electron affinity for the terminal group is taken from the literature and used to gauge the electronic state of the main ligand as the only parameter being varied. The electron affinity can be defined as the tendency of a chemical species to acquire electrons and thereby be reduced. Hence, it is a measure of the tenancy of the main ligands to contribute electrons across the Ru centre.

Luminescence lifetimes of aerated samples were measured using a computer-controlled time-correlated single photon counting (TCSPC) Spectrometer FL900 from Edinburgh Instruments. A nanosecond nF900 flashlamp excitation source using deuterium gas at a pressure of ~0.40 bar provided the fluorescence excitation pulses at 300 nm. A Peltier-cooled Hamamatsu R955 side-window photomultiplier tube (PMT) was used in an orthogonal geometry. All decay curves were corrected using a deconvolution with the instrument response function obtained using a scattering solution. The profile of the instrument response pulse had a FWHM of ~1 ns which was the detection limit of the system. All samples were run using a variation in concentrations from 10^{-4} M to 10^{-9} M at 300 K in HPLC-grade acetonitrile, and in all cases, the lifetime was found to be concentration independent within 0.1 ns.

Raman spectroscopy was performed using a Horiba Jobin-Yvon Labram HR800 UV confocal Raman imaging microscope system. A solid-state (785.1 nm/3 mW) laser source was used. The light was imaged to a diffraction-limited spot via the objective lens of an Olympus BX40 microscope. All experiments were carried out at room temperature (300 K).

2.1. Results: Part I—Effect of Changing Electron Affinity of the Terminal Group. The normalised absorption and emission spectra of $[Ru(phen)_2L]^{2+}$ in acetonitrile can be seen in Figures 2(a) and 2(b), respectively. The principle absorption of ruthenium complexes is made up of two main features at ~300 nm and at ~460 nm corresponding to the ligand centred (LC) and a metal to ligand charge transfer (MLCT) absorption, respectively [21–23]. It can be seen as expected that there is a gradual systematic bathochromic shift of the important MLCT transition as the electron affinity of the functional group located on the polypyridyl ligand is increased. The luminescence spectra for the ruthenium complexes in Figure 2(b) exhibit the same trend.

It would be expected that the systematic introduction of more electron withdrawing groups attached to the polypyridyl ligand follows a well-defined trend, starting with the lowest wavelength BPIP to the longest wavelength NPIP via the electronically intermediate aldehyde (FPIP) and nitrile (CPIP) groups [24]. Changes in excited state geometry, vibrational coherence, and electronic delocalisation can play a major role in determining the excited state condition [25, 26].

The electron withdrawing from the functional group at the termination site will lead to the polypyridyl ligand attracting electrons from the metal centre and hence acting to delocalise the electron density. It can be clearly seen form Table 2 that the emission maxima behaves in a similarly well-defined manner as the absorption maxima.

Unlike in the absorption however magnitude of the wavelength shift in emission maxima with the introduction

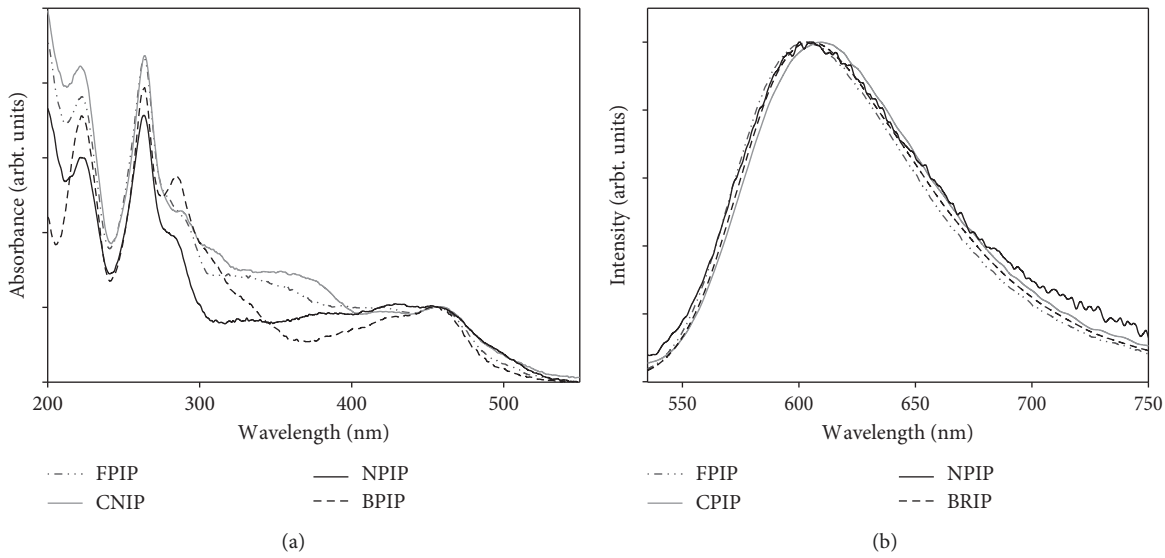

Figure 2: UV/Vis absorption (a) and luminescence (b) spectra of ruthenium complexes in acetonitrile with incremented termination group electronegativity for $[Ru(phen)_2L]^{2+}$.

Table 2: Electronic data for ruthenium complexes aerated in acetonitrile at 275 K.

	UV/Vis λ_{max} (nm)				Luminescence λ_{max} (nm)			
	p-NPIP 21.5	*p*-CPIP 15.9	*p*-FPIP 14.9	*p*-BPIP 6.2	*p*-NPIP 21.5	*p*-CPIP 15.9	*p*-FPIP 14.9	*p*-BPIP 6.2
EA (eV)								
Bpy	466	460	460	458	628	622	614	612
Phen	463	458	456	453	607	606	605	603
Biq	553	551	550	549	755	752	750	749

of the more electronegative functional groups, from BPIP to NPIP, cannot be explained solely as linear combination of the functional group and auxillary ligand electronic effects. From complexes BPIP to NPIP in the phenanthroline series, a shift of 4 nm is observed; however, in the bipyridine, it increases to 16 nm and then back to a relatively small shift of 6 nm for the biquinoline complexes. It is evident from this behaviour that a more complex relationship is at work here, than the first evidenced by the absorption spectra. It has been previously shown that the luminescence is greatly affected by the polypyridyl ligand [25, 27] and as such direct substitution to the terminal ring causing planarity effects and polarity alternation/interference [28]. This delocalisation will lead to a larger effective conjugation length and hence a bathochromic shift for the absorption and luminescence features [29]. As such, it is expected that the luminescence would exhibit a differing and more complex effect than the absorption with functional group change.

In summation, a reduction in the absorption and emission energy is observed with the changing of the functional group on the polypyridyl ligand from the bromo (BPIP), to the aldehyde (FPIP) to the nitrile (CPIP) and then the nitro- (NPIP-) based ligands. However, of particular interest is the variation in the magnitude of the wavelength shift with the systematic changing of the electronic withdrawing properties of the functional group for differing auxillary ligands (phenanthroline, bipyridine, and biquinoline). The systematic tuning of the band gap with the auxiliary ligands was most effective in the complexes with the greater electronegativity of the terminal functional group of the polypyridyl ligand, [14] and tuning was well defined approaching a linear dependence on the reduction potential of the auxiliary ligand. However, it is apparent when considering the functional group variation on the polypyridyl ligand that this is not a simple one-parameter effect. The effect of changing the electronic susceptibility of the functional group is highly influenced by the available electron density at the Ru centre afforded by the attached auxiliary ligands.

This magnitude of the effect on luminescence maxima of varying the functional group from BPIP to NPIP cannot be reconciled by treatment of the functional group change alone, and the interaction of the auxiliary ligand and the functional group is paramount in determining the extent of the electronic change.

With the Stokes shift, a manifestation of both electronic and vibrational effects, it was an ideal entry point to explore the potential for vibrational spectroscopy as a direct tool to correlate structural and vibrational effects with electronic changes. The stokes shift was calculated, taken as the difference between the absorption maximum and the emission maximum [30–32]. The $[Ru(phen)_2L]^{2+}$ complexes show a variation in Stokes shift with changing of the terminal group from BPIP to NPIP of 4 nm, the $[Ru(bpy)_2L]^{2+}$ showing the largest variation with systematic functional

group change (8 nm), and $[Ru(biq)_2L]^{2+}$ the smallest variation (3 nm).

In Figure 3, the Stokes shift is shown as a function of the electronic nature of the terminal group on the polypyridyl ligand. The Stokes shift combines aspects of both the electronic and vibrational nature of the complexes. It can be readily observed that the Stokes does indeed vary in a well-defined manner with electron affinity, but not all complexes behave in a similar manner. The $[Ru(phen)_2L]^{2+}$ series shows a decrease in the Stokes shift as the electron affinity is increased, and conversely the $[Ru(bpy)_2L]^{2+}$ shows a concomitant increase with electron affinity of the terminal group. The $[Ru(biq)_2L]^{2+}$ series is least affected by electronic change on the polypyridyl ligand only showing a minimal increase in Stokes shift with increasing electron affinity.

From analysis of the Stokes shift, with origins in both electronic and vibrational coherence, it can be seen that systematic changing of the polypyridyl ligand is effective in the tuning of the electronic band gap, but the Stokes shift relationship again relays a more complex dependence. The effects, both vibrational and electronic, cannot be wholly described by the electron density changes induced by the functional group alone. The differing behaviour, albeit still well defined, of the Stokes shift with increasing electronegativity of the functional group leads to the possibility that the vibrational changes incurred with the systematic variation of the end-group polarity are hugely different to that previously illustrated for changing auxiliary ligands wherein the end-group contribution became negligible [14].

For the systematic changing of the auxiliary ligand, it was shown that the Stokes shift was inversely proportional to the nonradiative rate for all complexes. As seen earlier, the variation of the functional group does not show the same magnitude of effect across all ruthenium complexes studied. This would lend itself to the inference that the electronic nature and by extension the electronic delocalisation can be considered in terms of a modified push-pull effect where the ability of the ruthenium centre to donate electrons and the ability of the polypyridyl ligand to accept electrons must be accounted for. When working at extremes of the electron donated (the auxiliary ligand) or electron-accepting ability (the polypyridyl ligand), there will always be a saturation point where an increase in either will cease to have a noticeable effect on the electronic delocalisation. As such, linear behaviour as a function of either the auxiliary ligand or the functional group alone cannot be expected to reconcile the spectral changes. Both extremes, fully delocalised and fully localised electron densities situated on the complex would negate any influence on functional group change.

It has been previously shown for auxiliary ligand change that the Stokes shift can be seen as a crude measure of the nonradiative decay [14, 16–18]. A well-defined relationship would reinforce the idea that the vibrational coherence is a dominant effect and suggests the potential for tailoring the electronic and the vibrational (nonradiative decay) characteristics of the complexes. To further investigate the potential for such tailoring even with the complex nature of the spectral variations, the luminescence yield and lifetimes have been calculated as a means to elucidate the effect on the excited state lifetimes and yield, shown in Table 3.

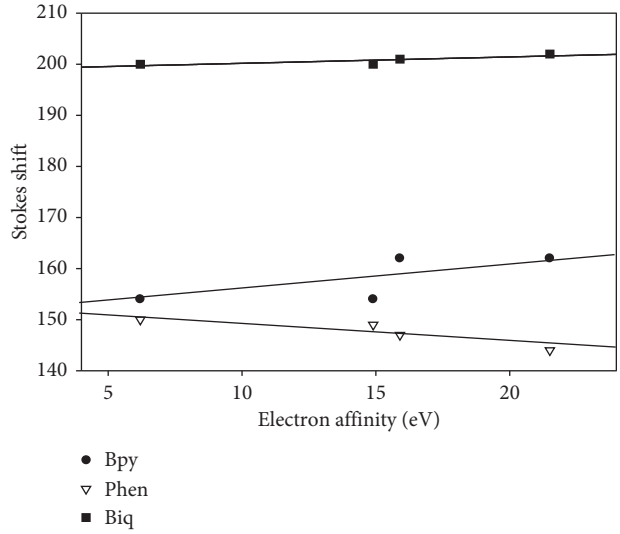

Figure 3: Stokes shift plotted as function of the electron density of the polypyridyl ligand terminal group.

A well-defined relationship is observed between the Stokes shift and luminescence yield, and a graph of the $[Ru(bpy)_2L]^{2+}$, $[Ru(phen)_2L]^{2+}$, and $[Ru(biq)_2L]^{2+}$ series is plotted as shown in Figure 4. A linear fit to the data points is presented as a guide for the eye; the slope indicates the effect of the changing of the polypyridyl ligand (L) from BPIP-FPIP-CPIP-NPIP.

The variation of luminescence yield with Stokes shift approaches a linear behaviour; however, the point of interest is the variation of the slope. With the Stokes shift taken as a crude measurement of the nonradiative rate, it would therefore be expected that all complexes would have a similar relationship as only the functional group is changing; however, the variation of slope indicates that the effect for the substitution of more electron-withdrawing functional ligands has a differing effect dependent on the attached auxiliary ligand. This variation of slope cannot be explained solely by considering the variation of the electronic nature of the dominant auxiliary ligands as determined by the reduction potential [7]. The slope varies from positive for the $[Ru(phen)_2L]^{2+}$ to slightly negative for the $[Ru(biq)_2L]^{2+}$ to a furthermore negative slope for the $[Ru(bpy)_2L]^{2+}$ with the reduction potential of the auxiliary ligand given a variation which should be in the order of phenanthroline, bipyridine, and biquinoline, respectively.

The variation in the slope further displays characteristics that are not in keeping with a simple linear solution and mirror those shown earlier. These variances can be reconciled by considering the complexes as a function of polarity interference/alternation as mentioned earlier or can be viewed as a modified version of the donor-acceptor push-pull system [33, 34]. The interaction along the conjugated backbone can be separated into two distinct and at times opposing factors. It has been shown that a series of "push-pull" oligomers can be systematically examined with

Table 3: Luminescence data for ruthenium complexes aerated in acetonitrile.

	Luminescence lifetimes (ns)				Luminescence yield* $\times 10^{-2}$			
	p-NPIP 21.5	*p*-CPIP 15.9	*p*-FPIP 14.9	*p*-BPIP 6.2	*p*-NPIP 21.5	*p*-CPIP 15.9	*p*-FPIP 14.9	*p*-BPIP 6.2
EA (eV)								
Bpy	72	125	138	156	0.12	3.9	3.7	4.5
Phen	33	107	103	120	0.78	3.2	3.0	3.9
Biq	2.7	3.2	4.6	10.0	0.30	1.8	1.6	2.1

*Relative to 0.095 measured for $[Ru(bpy)_3]^{2+}$.

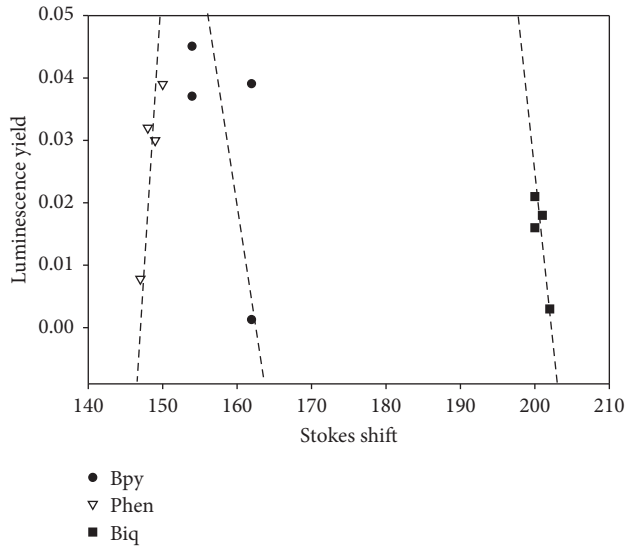

Figure 4: Luminescence yield versus peak Stokes shift for Ru(II) complexes (dotted lines are a linear guide for the eye).

a particular reference to alternate combinations of donor and acceptor end terminations.

The proposed effect of the functional group substitution on the polypyridyl ligand in these ruthenium complexes can be considered from a similar viewpoint as shown Figure 5.

Figure 5 shows a graphical representation for the proposed push-pull dynamic. The phenanthroline ligands (Figure 5(a)) contribute the least electron density to the central ruthenium moiety. This electron deficiency allows the changing functional group from Br (push) to NO_2 (pull) to mediate the conjugation length. The biquinoline ligand on the other hand has a huge associated electron density and as such contributes most to the central ruthenium moiety diminishing any effect the changing of the functional group may have. In essence, this push-pull effect determines whether the complexes behaves polymeric in nature as is the case with the biquinoline complexes where the terminal group does not influence the effective conjugation. On the other extreme, the phen complexes, due to a lesser electron density, act akin to oligomeric systems as the functional groups control the effective conjugative and hence the vibrational coherence.

The bipyridine and biquinoline auxiliary ligand with their greater associated electron densities than phen allowing the establishment of a great degree of electronic coherence across the polypyridyl ligand and as such variation of the polarity of the end group results in a pseudopolymeric regime. It has been shown that the bipyridine and biquinoline when attached as auxiliary ligands work to strengthen and planarise the polypyridyl ligand, hence restricting torsional effects facilitating pi electron delocalisation. This planarisation and delocalisation of pi electrons can be evidenced in the switching from a pseudo-oligomeric to a pseudopolymeric behaviour. The slope of the linear fits shows that the electronic nature of the functional group has a major impact on the relationship between the Stokes shift and luminescence yield, and a small variation in Stokes shift results in a large change in luminescence yield. The sensitivity of the luminescence yield to changes in the Stokes shift would point towards the changing of the functional group having a larger contribution to vibrational rather than a purely electronic effect.

In ascertaining that the functional group change has a great influence on the vibrational characteristics rather than the electronic, it was decided to directly examine the vibrational changes in the complexes via Raman spectroscopy. The Raman spectra of a series of complexes can be seen in Figure 6. The imidazole ring stretch of the polypyridyl ligand was examined for changes in vibrational nature with the systematic change of polypyridyl ligand end group as this provides the co-operative bridge for vibrational coherence.

This vibrational mode was chosen as it is unique to the polypyridyl ligand, and conjugation and vibrational coherence across this bridging ring will determine the extent of the effective conjugation. The imidazole ring also provides a large contribution to rotational freedom, and as such, the planarization of this ring structure will have a large effect on the polypyridyl ligand on a whole. This allows variations in both the planarity and electron delocalisation to be manifested in changing stretching frequency of this unique ring structure. The electronic nature of both the auxiliary ligands and polypyridyl functional group will considerably affect the electron density across the imidazole ring and therefore the vibrational frequency.

It is anticipated that direct measurement of relative conjugation across the imidazole bridge via Raman spectroscopy will elucidate both the complex relationship shown earlier and shortcoming of the energy gap law [35–37] when considering monomer to polymeric structures [38, 39].

Figure 7 shows the linear variation of the luminescence yield as a function of the variation of the frequency of the imidazole ring stretch of the polypyridyl ligand. As seen previously for the electronic properties, the bipyridine- and biquinoline-terminated complexes exhibit a similar activity

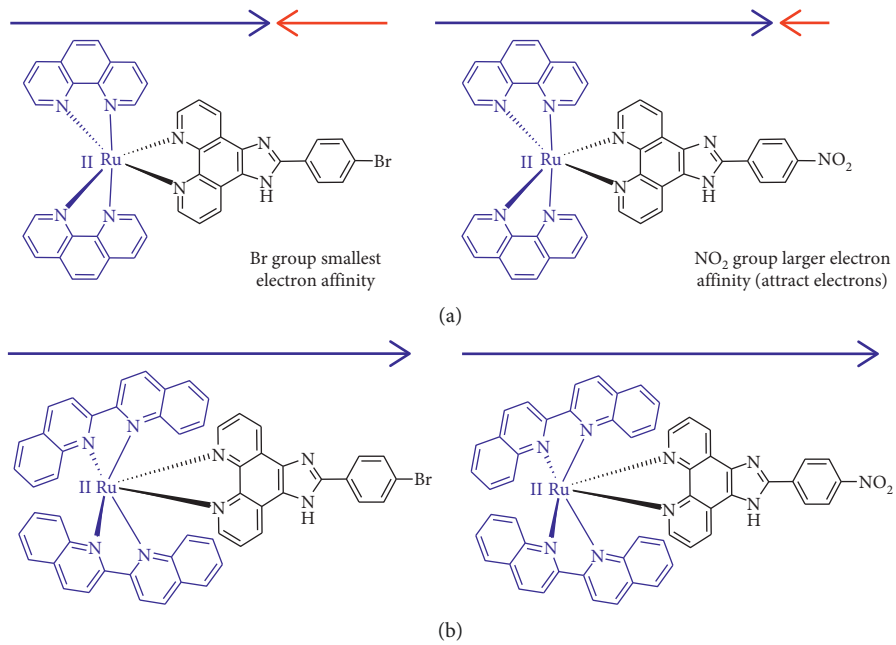

FIGURE 5: Graphical representation of the "donor-acceptor" description of electron density with end-group variation, showing Br to NO_2 for phen (a) and biq (b). Blue arrows indicate the electron delocalisation, and red arrows indicate the ability of the functional group to push back against the delocalisation.

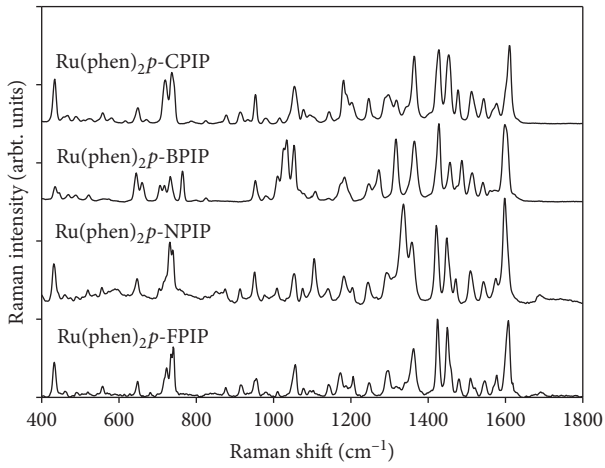

FIGURE 6: Solid-state Raman spectra of $[Ru(phen)_2L]^{2+}$ recorded at 273 K and 785 nm.

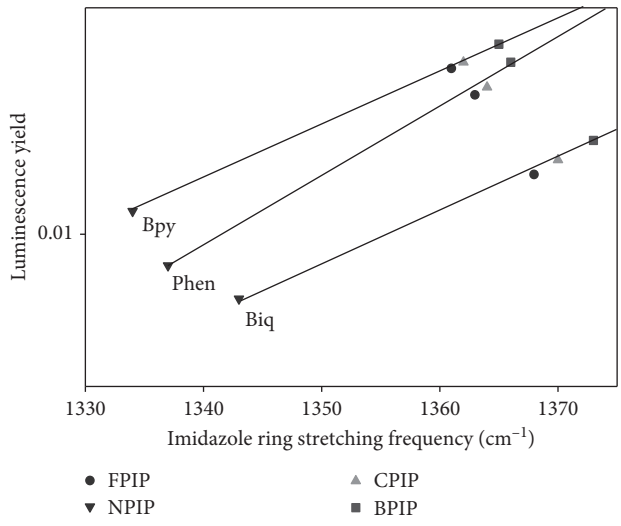

FIGURE 7: Imidazole stretching frequency against the luminescence yield. Linear fit is a guide for the eye.

profile. The phen series shows a linear behaviour but with significantly increased slope.

It is evident that there is a concomitant increase in luminescence yield with increasing ring stretching frequency. This behaviour is diametrical opposed to the behaviour seen when the ruthenium series are examined as a function of auxiliary ligand change where a reduction in the stretching frequency resulted in an increase in luminescence yield [14].

This behaviour can be reconciled by considering that the imidazole ring frequency is a conduit for electronic delocalisation to the functional group. As stated earlier, the substituted benzene ring at the end of the polypyridyl ligand has a large effect in determining the electronic and luminescence properties of the complex due to the lowest unoccupied molecular orbital (LUMO) location being centred on the polypyridyl ligand.

In the variation of the auxiliary ligand with the unchanging polypyridyl functional group, any increase in frequency of the imidazole ring stretch can be attributed to an increase of electron density available across the conduit and thus resulting in a concomitant increase in electronic density/conjugation of the terminal substituted benzene ring. Thus, an increase in frequency results in a decrease in

yield, and the increased electron density facilitated greater vibrational coherence. However, when considering the variation of the functional group termination, a different scenario is presented, and the auxiliary ligand (an electron donor) remains constant with only the electron-accepting ability of the terminal group to influence the imidazole conduit. The effect of increasing the electron-accepting ability of the functional group draws electron density from the imidazole bridge, hence resulting in a lower vibrational frequency but greater electron density situated benzene-substituted ring. This effect is mediated as the electron-accepting ability of the functional group is changed from BPIP to NPIP.

2.2. Results: Part II—Effect of Changing the Terminal Group Position. Having fully explored the systematic variation of functional group change on the polypyridyl ligand, it was decided to examine the relationships in the more subtle structural changes of systematic regioisomerism. To this end, the *para*-, *meta*-, and *ortho*-positioned nitrile (CPIP) ligands were synthesised to create the $[Ru(phen)_2L]$ [2]+, $[Ru(bpy)_2L]^{2+}$, and $[Ru(biq)_2L]^{2+}$ variants. Figure 8 show the absorption spectra of $[Ru(phen)_2L]^{2+}$-based complexes, and it can be readily seen that the positional variation of the end group has little effect on the spectral profile albeit inducing a minor shifting of the λ_{max} from 455 nm to 458 nm to 458 nm for the *meta*, *para*, and *ortho* positions, respectively.

The luminescence spectra show little or no variation in the electronic band gap when considering positional changes with biquinoline as auxiliary ligands, and a more significant effect is observed when moving to bipyridine and phenanthroline, respectively. This variation is consistent with the redox potential of the auxiliary ligands, bipyridine −0.8 V, biquinoline −1.4 V, and phenanthroline −1.6 V and clearly shows the influence of the auxiliary ligands even when considering the direct substitution on the polypyridyl terminal ring structure.

To further explore the changes to the excited state, as the position of the terminal group is systematically varied, the luminescence yield and lifetimes were calculated and measured, respectively. These values can be found in Table 4.

Due to the minute changes in the spectral profile brought about by varying the position of the substituent from *para*, *ortho*, and *meta* position, it is difficult to correlate the Stokes shift with any electronic parameter. This should be possible as well-defined correlations were seen for the auxiliary ligand changes [7] and functional group change, so it would suggest that the relative dominance of the nonradiative rate which was seen in the earlier trend may be absent. Furthermore, no obvious correlation of Stokes shift with the luminescence yield is observed which further suggested that although the Stokes shift can be seen as a gauge of nonradiative decay, this would only present a linear relationship with yield if the radiative rate was to remain unchanged. The calculated photophysical rates can be found in Table 5.

The radiative and nonradiative rates calculated are shown in Table 5. It is evident that there is no dominant effect; the variations in both rates are small and follow no well-defined trend relative to the electronic parameters. The certainty is that in no way can the nonradiative rate be considered to be dominant, and this is to be expected as the positional change on the terminal benzene ring would not be expected to have a major effect on the vibrational coherence on the ring structure or extend to the bridging imidazole ring.

Figure 9 shows the Raman spectra of all three possible regioisomers. It can be clearly seen in the range from 1330 cm^{-1}–1400 cm^{-1} that there is a shifting of the imidazole ring stretch as the terminal group position is changed.

In the previous section, the Raman stretching frequency of the bridging imidazole was used to reconcile the opposing changes in electronic density across the imidazole ring, and by association, the effect of the functional group changes on the benzene ring. However, in the case of the terminal group change, significant electronic and vibrational effects were observed such as the correlation of stokes shift with luminescence yield which have been absent for the regioisomers.

The position of the imidazole stretch frequency was plotted as a function of luminescence yield. This was undertaken to show that the sensitivity of Raman spectroscopy to the pi conjugated backbone make it a far better tool to gauge electronic conjugation and by extension potential avenue from nonradiative decay. A well-defined relationship with the direct Raman measurement of the complex and the luminescence yield would confirm the validity of this experimental study.

In Figure 10, it can be again seen that the luminescence yield shows a good correlation with the imidazole stretch frequency. Also evident is the positive slope linear trend as seen for the direct substitution on the terminal ring structure. From this well-defined relationship, it can be concluded that the direct measurement of the vibrational activity can provide an accurate gauge of the state of the system with regards to increasing luminescence yield. The ability of Raman spectroscopy to be extremely sensitive to delocalisation of pi electrons across the polypyridyl backbone allows it to account for subtle electronic such as positional changes of the substituent group. Although the study of the positional changes results in neither the radiative or nonradiative process being changed preferentially, the vibrational study seems to be able to account for the changes induced at both a vibrational and electronic level in the complexes.

In summary, the effect of changing the electron withdrawing effects of the functional group works, in two opposing ways, by varying the electron density at both the imidazole ring and the substituted benzene ring. This ability to reduce the electron density at the substituted benzene ring by adding a less electron-accepting functional group, such as Br, limits the contribution across the imidazole bridge. This has been shown to increase the luminescence and hence reducing the vibrational coherence on the benzene ring and thus the potential for nonradiative decay.

It is evident that the variation of the auxiliary ligand plays the major role in the maintenance of vibrational coherence and hence the nonradiative decay. Once the polypyridyl ligand is constant the effect of auxiliary ligand change is relatively easy to reconcile; however, the changing of both polypyridyl and auxiliary ligands will introduce

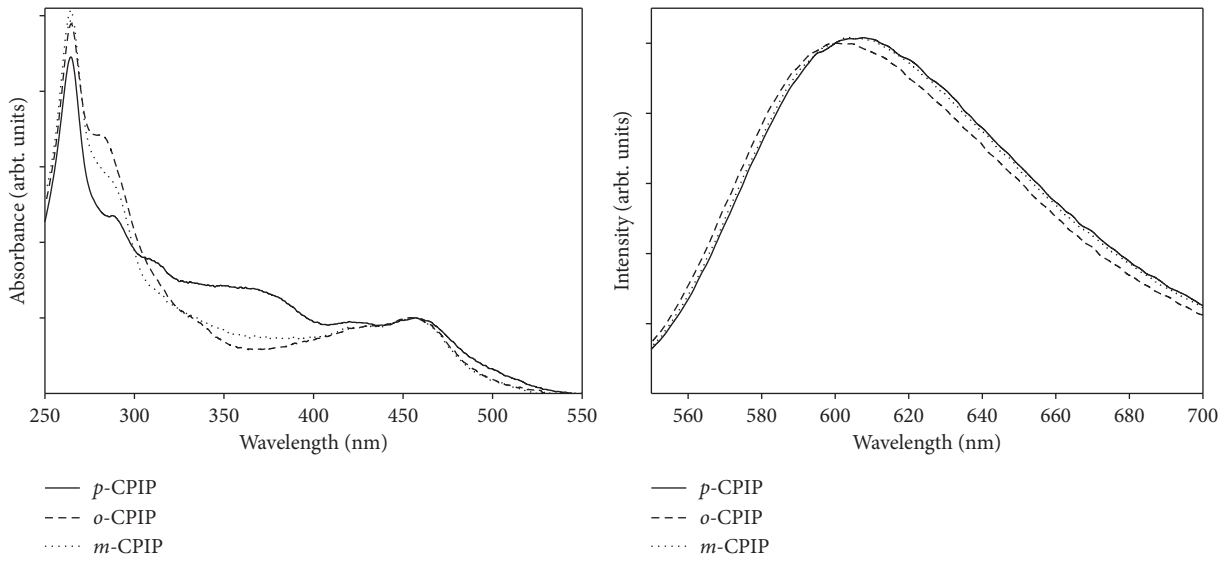

Figure 8: Normalised UV/Vis (a) and luminescence (b) spectra of $[Ru(phen)_2L]^{2+}$, where L is *m*-CPIP, *p*-CPIP, and *o*-CPIP, respectively.

Table 4: Luminescence data for ruthenium complexes aerated in acetonitrile.

	Luminescence lifetimes (ns)			Relative luminescence yield*		
	p-CPIP	*o*-CPIP	*m*-CPIP	*p*-CPIP	*o*-CPIP	*m*-CPIP
Bpy	128	135	130	0.032	0.034	0.029
Phen	107	107	102	0.039	0.039	0.043
Biq	4	4	4	0.018	0.015	0.019

*Relative to 0.095 as measured for $[Ru(bpy)_3]^{2+}$.

Table 5: Aerated photophysical rates for ruthenium polypyridyl complexes.

	k_{rad} ($s \times 10^5$)			k_{nrad} ($s \times 10^6$)		
	p-CPIP	*o*-CPIP	*m*-CPIP	*p*-CPIP	*o*-CPIP	*m*-CPIP
Bpy	2.5	2.52	2.23	7.56	7.16	7.47
Phen	3.64	3.64	4.22	8.98	9.98	9.938
Biq	4.5	3.75	4.75	245.5	246.3	245.2

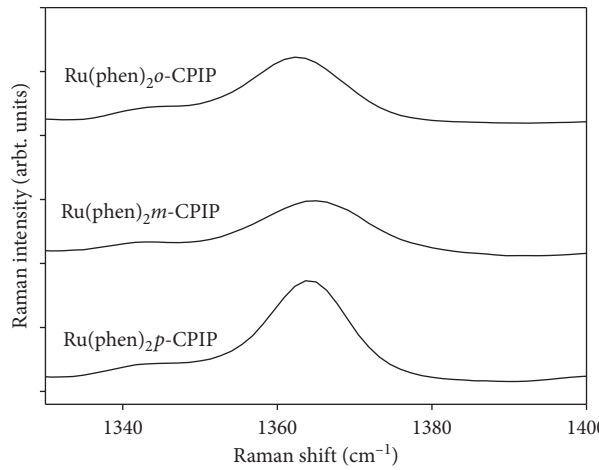

Figure 9: Raman spectra of imidazole ring stretch for the positionally substituted CN.

competing effects. These effects make a unified expression of the effect of the auxiliary/polypyridyl ligand change difficult to quantify, but it is apparent that there are both vibrational and electronic components to this effect. Analysis of the variation of Raman bands has shown to be effective in reconciling the changes induced in vibrational and electronic structures. The one drawback being the inability to monitor the terminal benzene substituted ring directly is influential in the excited state characteristics. The indirect measurements using the bridging imidazole ring are effective albeit requiring a great deal of more understanding of the relative variation of the electronic density across the complex.

3. Conclusions

This study focuses on the effect of terminal group change of the main polypyridyl ligand and the manifestation of these structural changes in both the electronic and vibrational spectra of a series of systematically varied ruthenium complexes. It establishes structure-property relationships for the series presented through investigation of the electronic absorption and emission characteristics. A well-defined relationship is found to exist between the absorption and emission wavelengths and the electronic nature of polypyridyl end-group ligand as measured by the electron affinity for the end group.

The relative electron withdrawing effects of the polypyridyl ligands are shown to manifest themselves in a complex push-pull nature due to the electronically dominant auxiliary ligand attached. In tailoring the electronic characteristics of the complexes, it is shown that the effect of systematically changing the terminal group works mediate the effective electron delocalisation originated for the auxiliary ligand on the ruthenium centre. This effect is not linear in nature but rather consisting of two plateaus

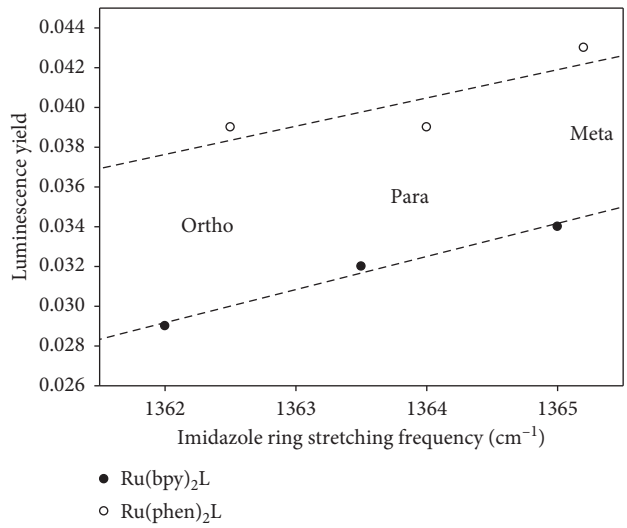

Figure 10: Luminescence yield against imidazole ring stretch for the positionally substituted CN.

representing a fully delocalised regime and a fully localised density of electronic states.

The relationship between the luminescence yield and lifetime establishes that the dominant effect of the of end-group variation on the polypyridyl ligands is a manipulation in the nonradiative decay rate. However, the positional change shows a negligible change in both photophysical rates.

The inability of the Stokes shift to accurately account for the variation in luminescence yield led to the examination of the vibrational spectrum in an effort to reconcile both Stokes and the energy gap law as a measure of the luminescence yield for low band gap material and proxyoligomeric structures.

Raman spectroscopy of the complexes leads to the assignment of a vibrational mode unique to the polypyridyl ligand, the frequency of which is shown to vary in a well-defined manner with the luminescence yield, indicating it can be used as an empirical guide to the push-pull effect of polypyridyl ligand change for both positional and end-group changes. This empirical relationship was also shown to be evident in regioisomeric changes where no significant changes in absorption or emission were evidenced. This study highlights how the polypyridal ligand and the molecule inherent vibrational coherence can be examined via Raman spectroscopy. This method can be used a direct measurement of both the electronic and vibrational changes and steric effects caused by end-group variation, where absorption, emission, and photophysical rates proved nonconclusive.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The FOCAS Institute is funded under the National Development Plan 2000–2006 with assistance from the European Regional Development Fund. L. Perdisatt acknowledges the Abbest Scholarship support.

References

[1] A. M. Florea and D. Büsselberg, "Cisplatin as an anti-tumor drug: cellular mechanisms of activity, drug resistance and induced side effects," *Cancer*, vol. 3, no. 1, pp. 1351–1371, 2011.

[2] M. S. Novak, G. E. Buchel, B. K. Keppler, and M. A. Jacupec, "Biological properties of novel ruthenium- and osmium-nitrosyl complexes with azole heterocycles," *Journal of Biological Inorganic Chemistry*, vol. 21, no. 3, pp. 347–356, 2016.

[3] S. T. Haque and E. H. Chowdhury, "Recent progress in delivery of therapeutic and imaging agents utilizing organic-inorganic hybrid nanoparticles," *Current Drug Delivery*, vol. 15, no. 4, pp. 485–496, 2018.

[4] S. Page, "Ruthenium compounds as anticancer agents," *Education in Chemistry*, vol. 26–29, 2012.

[5] E. S. Antonarakis and A. Emadi, "Ruthenium-based chemotherapeutics: are they ready for prime time?," *Cancer Chemotherapy and Pharmacology*, vol. 66, no. 1, pp. 1–9, 2010.

[6] M. P. M. Marques, "Platinum and palladium polyamine complexes as anticancer agents: the structural factor," *ISRN Spectroscopy*, vol. 2013, Article ID 287353, 29 pages, 2013.

[7] G. Mestroni, E. Alessio, G. Sava, S. Pacor, and M. Coluccia, *Metal Complexes in Cancer Chemotherapy*, B. K. Keppler, Ed., Vol. 157, VCH, Weinheim, Germany, 1993.

[8] G. K. Gransbury, P. Kappen, C. J. Glover et al., "Comparison of KP1019 and NAMI-A in tumour-mimetic environments," *Metallomics*, vol. 8, no. 8, pp. 762–773, 2016.

[9] T. Gianferrara, I. Bratsos, and E. Alessio, "A categorization of metal anticancer compounds based on their mode of action," *Dalton Transactions*, vol. 37, pp. 7588–7598, 2009.

[10] J. Liu, W. J. Mei, L. J. Lin et al., "Electronic effects on the interactions of complexes $[Ru(phen)_2(p\text{-}L)]^{2+}$ (L=MOPIP, HPIP, and NPIP) with DNA," *Inorganica Chimica Acta*, vol. 357, no. 1, pp. 285–293, 2004.

[11] H. M. Nguyen, D. N. Nguyen, and N. Kim, "Improved performance of dye-sensitized solar cells by tuning the properties of ruthenium complexes containing conjugated bipyridine ligands," *Advances in Natural Sciences: Nanoscience and Nanotechnology*, vol. 1, article 025001, 2010.

[12] S. J. Payne, G. L. Fiore, C. L. Fraser, and J. N. Demas, "Luminescence oxygen sensor based on a ruthenium(II) star polymer complex," *Analytical Chemistry*, vol. 82, no. 3, pp. 917–921, 2010.

[13] M. J. Rose and P. K. Mascharak, "Photoactive ruthenium nitrosyls: effects of light and potential application as NO donors," *Coordination Chemistry Reviews*, vol. 252, no. 18–20, pp. 2093–2114, 2008.

[14] L. O'Neill, L. Perdisatt, and C. O'Connor, "Correction to: "The influence of auxiliary ligands on the photophysical characteristics of a series of ruthenium (II) polypyridyl complexes"," *Journal of Physical Chemistry A*, vol. 116, no. 48, p. 11987, 2012.

[15] L. O'Neill, P. Lynch, M. McNamara, and H. J. Byrne, "Correlation of vibrational intensity with fluorescence lifetimes in π conjugated polymers," *Polymer*, vol. 49, no. 19, pp. 4109–4114, 2008.

[16] L. Luke O'Neill, *Photophysics of organic conjugated systems*, Ph.D. dissertation, Dublin Institute of Technology, Dublin, Ireland, 2006.

[17] L. O'Neill and H. J. Byrne, "Structure–property relationships for electron–vibrational coupling in conjugated organic

oligomeric systems," *Journal of Physical Chemistry B*, vol. 109, no. 26, pp. 12685–12690, 2005.

[18] L. O'Neill, P. Lynch, M. McNamara, and H. J. Byrne, "Vibrational characterization and fluorescence optimization of polycyclic polymers," *Journal of Physical Chemistry B*, vol. 111, no. 28, pp. 7999–8005, 2007.

[19] L. Perdisatt, S. Moqadasi, L. O'Neill et al., "Synthesis characterisation and DNA intercalation studies of regioisomers of ruthenium (II) polypyridyl complexes," *Journal of Inorganic Biochemistry*, vol. 182, pp. 71–82, 2018.

[20] H. Chao, R.-H. Li, C. W. Jiang, H. Li, L.-N. Ji, and X.-Y. Li, "Mono-, di- and tetra-nuclear ruthenium(II) complexes containing 2,2′-*p*-phenylenebis(imidazo[4,5-*f*]phenanthroline): synthesis, characterization and third-order non-linear optical properties," *Journal of the Chemical Society, Dalton Transactions*, no. 12, pp. 1920–1926, 2001.

[21] G. Whittaker, A. R. Mount, and M. R. Heal, *Physical Chemistry*, BIOS, Oxford, UK, 2000.

[22] L. Messori, F. Abbate, G. Marcon et al., "Gold(III) complexes as potential antitumor agents: solution chemistry and cytotoxic properties of some selected gold(III) compounds," *Journal of Medicinal Chemistry*, vol. 43, no. 19, pp. 3541–3548, 2000.

[23] A. A. Adeniyi and P. A. Ajibade, "The spectroscopic and conductive properties of Ru(II) complexes with potential anticancer properties," *Journal of Spectroscopy*, vol. 2014, Article ID 656830, 14 pages, 2014.

[24] S. Chowdhury, H. Kishi, G. W. Dillow, and P. Kebarle, "Electron affinities of substituted nitrobenzenes," *Canadian Journal of Chemistry*, vol. 67, no. 4, pp. 603–610, 1989.

[25] Q. X. Zhen, Q.-L. Zhang, J.-G. Liu, B.-H. Ye, L.-N. Ji, and L. Wang, "Synthesis, characterization and DNA binding of ruthenim(II) complexes containing the atatp ligand," *Journal of Inorganic Biochemistry*, vol. 78, no. 4, pp. 293–298, 2000.

[26] L. Zang, Y. Che, and J. S. Moore, "One-dimensional self-assembly of planar pi-conjugated molecules: adaptable building blocks for organic nanodevices," *Accounts of Chemical Research*, vol. 41, no. 12, pp. 1596–1608, 2008.

[27] H. Deng, H. Xu, Y. Yang et al., "Synthesis, characterization, DNA-binding and cleavage studies of [Ru(bpy)2(actatp)]2+ and [Ru(phen)2(actatp)]2+ (actatp=acenaphthereno[1,2-b]-1,4,8,9-tetraazariphenylence)," *Journal of Inorganic Biochemistry*, vol. 97, no. 2, pp. 207–214, 2003.

[28] S. Shi, J. Liu, J. Li et al., "Electronic effect of different positions of the $-NO_2$ group on the DNA-intercalator of chiral complexes $[Ru(bpy)_2L]^{2+}$ (L = *o*-npip, *m*-npip and *p*-npip)," *Dalton Transactions*, no. 11, p. 2038, 2005.

[29] C. Sauteret, J. P. Hermann, R. Frey et al., "Optical nonlinearities in one-dimensional-conjugated polymer crystals," *Physical Review Letters*, vol. 36, no. 16, pp. 956–959, 1976.

[30] J. B. Birks, *Organic Molecular Photophysics*, John Wiley & Sons, Hoboken, NJ, USA, 1973.

[31] J. F. Endicott, B. Schlegel, M. D. J. Uddin, and D. Seniveratne, "MLCT excited states and charge delocalization in some ruthenium/ammine/polypyridyl complexes," *Coordination Chemistry Reviews*, vol. 229, no. 1-2, pp. 95–106, 2002.

[32] O. Bräm, F. Messina, A. M. El-Zohry, A. Cannizzo, and M. Chergui, "Polychromatic femtosecond fluorescence studies of metal–polypyridine complexes in solution," *Chemical Physics*, vol. 393, no. 1, pp. 51–57, 2012.

[33] E. Kleinpeter, "Push-pull alkenes: structure and -electron distribution," *Journal of the Serbian Chemical Society*, vol. 71, no. 1, pp. 1–17, 2006.

[34] H. Meier, "Conjugated oligomers with terminal donor–acceptor substitution," *Angewandte Chemie International Edition*, vol. 44, no. 17, pp. 2482–2506, 2005.

[35] J. R. Lakowicz, *Principles of Flourescence Spectroscopy*, Vol. 1, Springer Science &Business Media, Berlin, Germany, 2006.

[36] M. Arias, J. Concepcion, I. Crivelli et al., "Influence of ligand structure and molecular geometry on the properties of d6 polypyridinic transition metal complexes," *Chemical Physics*, vol. 326, no. 1, pp. 54–70, 2006.

[37] C. Doffek, J. Wahsner, E. Kreidt, and M. Seitz, "Breakdown of the energy gap law in molecular lanthanoid luminescence: the smallest energy gap is not universally relevant for non-radiative deactivation," *Inorganic Chemistry*, vol. 53, no. 7, pp. 3263–3265, 2014.

[38] H. L. Chen, Y. F. Huang, C. P. Hsu et al., "Direct measurements of intersystem crossing rates and triplet decays of luminescent conjugated oligomers in solutions," *Journal of Physical Chemistry A*, vol. 111, no. 38, pp. 9424–9430, 2007.

[39] C. Latouche, P.-H. Lanoë, J. A. Gareth Williams, V. Guerchais, A. Boucekkine, and J. L. Fillaut, "Switching of excited states in cyclometalated platinum complexes incorporating pyridylacetylide ligands (Pt–C≡C–py): a combined experimental and theoretical study," *New Journal of Chemistry*, vol. 35, no. 10, p. 2196, 2011.