UNIVERSI PHOTOPHYSICAL PROPERTIES OF IDRIS POLYNUCLEAR COMPLEXES CONTAINING PHENYLPYRIDINE-IRIDIUM(III) UNITS



Noorshida Mohd Ali

A thesis submitted to The University of Sheffield in partial fulfilment of the requirements for the Degree of Doctor of Philosophy

Department of Chemistry

University of Sheffield

Sheffield S3 7HF

ABSTRACT

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^{N IDR} The content of this thesis is concerned with twofold areas of research: i) the synthesis of VERSITI F various types of bis(phenylpyridine) iridium(III) dicyanide complexes, and studies of their structural and photophysical behaviour; ii) the synthesis and studies of iridium(III) complexes, containing two fluorinated phenylpyridine-type ligands and two pyrazolyl-pyridine units, and their lanthanide complexes.

Chapter One describes the general principles of luminescent cyclometallated complexes of transition metal ions. A brief introduction about spectroscopic properties of lanthanides and sensitisation of their luminescence is provided. Examples of previous research by Ward group and from other groups into cyanide-bridged *d-f* complexes and Ir/Ln bimetallic complexes are described.

Chapter Two describes the synthesis of bis(phenylpyridine) iridium(III) dicyanide complexes and the used of these complexes as the basis of cyanide-bridged polynuclear assemblies, in both coordination networks with lanthanide(III) cations and, discrete molecular species by bridging to ${\text{Re}(\text{phen})(\text{CO})_3}^+$ units. The structural and photophysical behaviour of these complexes have been performed.

Chapter Three describes the structure of the anionic complex $[Ir(ppy)_2(CN)_2]^-$ and its solvent environment in water have been studied by DFT calculations, in order to get further information on the specific solvent-solute interaction governed by the hydrogen bond in the solvation hydration shell.

Chapter Four describes the preparation of a series of luminescent complexes based on $\{Ir(F_2ppy)_2\}$ [$F_2ppy = cyclometallating anion of 2-(2',4'-difluorophenyl)pyridine] units, with two pyrazolyl-pyridine units, separated with spacer groups butyl (CH₂)₄, methoxyphenyl and benzophenone, of which first N,N-chelating terminus was coordinated to Ir(III) and the second was bound to Ln(III). The photophysical properties of the Ir/Ln dyads have been investigated in solution.$

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1. Luminescent Cyanometallates Based on Phenylpyridine-Ir(III) Units: Solvatochromism, Metallochromism, and Energy-Transfer in Ir/Ln and Ir/Re Complexes; N. M. Ali, V. L. MacLeod, P. Jennison, I. V. Sazanovich, C. A. Hunter, J. A. Weinstein and M. D. Ward, *Dalton Trans.*, 2012, **41**, 2408-2419.



ABBREVIATIONS

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N IDRI<mark>Chemicals</mark>ersiti pendidikan sultan idris universiti pendidikan sultan idris

М	Metal
L	Ligand
рру	2-phenylpyridine
phen	1,10-phenanthroline
2,4-dfppy	2-(2',4'-difluorophenyl)pyridine
4-tfmppy	2-(4'-trifluoromethylphenyl)pyridine
3,5-dfppy	2-(3',5'-difluorophenyl)pyridine
pypz	3-(2-pyridyl)-pyrazole
PPN ⁺	Bis(triphenylphosphine)iminium cation
PPNC1	Bis(triphenylphosphine)iminium chloride
Ln	Lanthanide
Ln(hfac) ₃	hfac = 1,1,1,5,5,5-hexafluoro-pentane-2,4-dionate
KCN	Potassium cyanide
MeCN	Acetonitrile
МеОН	Methanol
EtOH	Ethanol
THF	Tetrahydrofuran
DCM	Dichloromethane
DMF	N,N'-dimethyl formamide

Other terms

Abs	Absorbance
VR	Vibrational relaxation
IC	Internal conversion
F	Fluorescence
ISC	Intersystem crossing
Р	Phosphorescence
S	Singlet state
Т	Triplet state
SOC	Spin-orbit coupling
ERSTERENDIDIKAN SULTAN IDR	Metal-to-ligand charge transfer SULTAN IDRIS UNIVERSITI PENDIDIKA
LMCT	TAN IDDIS Ligand-to-metal charge transfer

U	MMCT NIVERSITI PENDIDIKAN SULTAN LC	Metal-to-metal charge-transfer IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIV Ligand-centred	ERSITI PENDID
N IDF	AIS UNIVERSITI PENDIDIKAN MC	SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS Metal-centred	UNIVERSITI F
	LUMO	Lowest unoccupied molecular orbital	
	НОМО	Highest occupied molecular orbital	
	OLED	Organic light emitting diode	
	NIR	Near-infrared	
	UV	Ultra violet	
	AETE	Absorption-energy transfer-emission	
	fac	Facial	
	BET	Back electron-transfer	
	PEnT	Photoinduced energy transfer	
	PET	Photoinduced electron transfer	
	Q	Quenching	
	FTIR		
	S	Strong intensity signal	
		Medium intensity signal	
	ATR	Attenuated total reflectance	
	NMR		
	CDCl ₃	Deuterated chloroform	
	CD ₃ CN	Deuterated acetonitrile	
	δ	Chemical shift	
	ppm	Parts per million	
	S	Singlet	
	đ	Doublet	
	t	Triplet	
	m	Multiplet	
	COSY	Correlation spectroscopy	
	Hz	Hertz	

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	Experimental techniques an	id terms
	NIVERSITI PENDIDIKAN SULIAN FTIR	Fourier transform infrared spectroscopy
N IDF	NMR	Nuclear Magnetic Resonance
	ESMS	Electrospray ionization mass spectrometry
	UV/Vis	Ultraviolet/visible
	λ_{exc}	λ excitation
	λ_{em}	λ emission
	Φ	Quantum yield
	τ	Luminescence lifetime
	ES	Electrospray
	m/z	Mass to charge ratio
	V	Unit cell volume
	Z	Formula units per unit cell
	F _o , F _c	Observed and calculated structure factors
	R_1, wR_2	R-indices (based on F and F ² respectively)
	μ	Linear absorption coefficient
	ŕÅ	Angstrom (10^{-10} m)
	a, b, c	Unit cell dimensions
	α, β, γ	Unit cell angles
	<i>F</i> (000)	No. electrons per unit cell
	Theoretical study	
	DFT	Density functional theory
	РСМ	Polarisable continuum model
	FWHM	Full Width Half Maximum
	B3LYP	Becke's three parameter functional and the Lee-Yang-Parr
		functional

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CHAPTER 1

Introduction

1.1 Luminescence, Fluorescence and Phosphorescence

Luminescence is the emission of light from any substance and occurs from an electronically excited state. Generally, luminescence processes begin by the absorption of a photon by the molecule which results in the formation of an excited state by promotion of an electron to a higher energy unfilled orbital. This excited state is then deactivated, and decay to the ground state may take place by one of the three ways: (i) decomposition of the original molecule (photochemistry), (ii) radiative decay which means the emission of photon (luminescence), and (iii) non-radiative decay, in which thermal energy is lost. Photoluminescence is one of the forms of luminescence, and is the process of absorption of a photon followed by emission of a photon which can either be equivalent or not depending on the amount of internal energy lost by non-radiative transitions.

Additionally, luminescence is formally divided into two categories: fluorescence and phosphorescence, which depend on the nature of the excited state. In excited singlet states, the electron in the excited orbital is paired (by opposite spin) to the second electron in the ground state orbital. Consequently, return to the ground state is a spin allowed transition and occurs rapidly by emission of a photon, which is known as fluorescence. The emission rates

of fluorescence are normally 10^8 s⁻¹ or faster and thus a typical fluorescence lifetime is 10 ns or less.¹ Phosphorescence also involves the emission of a photon but from triplet excited states, in which the electron in the excited orbital has the same spin orientation as the ground state electron. Transitions to the ground state are spin-forbidden and the emission rates are slow (10^3 to 10^0 s⁻¹), and hence phosphorescence lifetimes are usually milliseconds to seconds.¹ According to selection rules, emission without a change in multiplicity is called fluorescence (typically $S_1 \rightarrow S_0$ transition), while the term phosphorescence refers to an emission in which the spin multiplicity changes (typically $T_1 \rightarrow S_0$ transition).²⁻⁶

Figure 1.1.1 shows the excitation and decay processes by using a Jablonski diagram. The first transition is the absorbance of a photon of a particular energy by the molecule. This is the method by which an electron is excited from a lower energy level to a higher energy level. The energy of the photon is then transferred to the particular electron. However, once an electron is excited, there are many ways that energy may be dissipated. The first is through vibrational relaxation, a non-radiative process. This relaxation occurs between vibrational levels, so generally electrons will not change from one electronic level to another through this method. However, if vibrational energy levels strongly overlap with electronic energy levels, the excited electron can possibly move from a vibrational level in one electronic state to a higher vibrational level in a lower electronic state. This process is called internal conversion (IC). Usually, due to a lack of overlap between vibrational and electronic excited states, and a large energy difference between the ground state and first excited state, internal conversion is very slow for an electron to return to the ground state. Therefore, decay of the first excited state by fluorescence (radiative process) can effectively compete with internal conversion. Molecules in the excited state (S_1) , can also undergo a spin conversion to the first triplet state (T_1) by intersystem crossing (ISC), a non-radiative process. This process involves transition between energy states of different spin states. Emission from T₁ is termed phosphorescence (radiative process), and is generally shifted to longer wavelength relative to the fluorescence because the T_1 state is lower in energy than the S_1 state.

Chapter 1 : Introduction



Figure 1.1.1 Jablonski diagram of excitation and decay processes in which, the radiative transitions are represented by straight arrows and non-radiative transitions by dashed arrows.

1.2 Luminescent Cyclometallated Complexes of Transition Metal Ions

Recently, luminescent cyclometallated complexes of transition metal ions with d^6 electronic configuration such Ru(II), Os(II), Ir(III) and Re(I) and d^8 electronic configuration like Pt(II), Pd(II) and Au(III) have attracted much interest due to their rich photophysical and photochemical properties. In contrast to conventional organic fluorophores, which are singlet emitters, cyclometallated complexes of transition metal ions, which contain a metal and one or more organic ligands, display mixed singlet-triplet states. In metal complexes there are three types of excited states: (a) metal-centred (MC) excited states, from the promotion of an electron from t_{2g} to e_g orbitals; (b) ligand-centred (LC) states that are $\pi - \pi^*$ transitions; (c) metal-to-ligand charge transfer states (MLCT), which can be understood with the aid of an energy level diagram shown in Figure 1.2.1. Singlet – singlet absorptions are an electronic transition from metal t_{2g} orbitals to empty ligand orbitals or centred on the ligand, that is from π orbitals to empty π^* orbitals, without spin change, which are allowed and are identified by

large extinction coefficients.⁷ On the contrary, singlet – triplet absorptions are transitions with spin change and are forbidden, therefore associated with small extinction coefficients. For example, a typical compound [Ru(bipy)₃]²⁺, energy is absorbed in the visible region of the spectrum, populating a metal-to-ligand charge transfer (¹MLCT) state that corresponds to the transfer of one electron from the metal-centred HOMO to the ligand-centred LUMO. Intersystem crossing then quantitatively populates the ³MLCT state, which is generally deactivated through the emission of a photon or non-radiative decay (loss of heat).⁸



Figure 1.2.1 Schematic and simplified molecular orbital diagram for an octahedral d^6 metal complex involving 2-phenylpyridine-type ligands in which various possible transitions are indicated. Reproduced from reference 7.

Therefore, the photophysical properties of the cyclometallated complexes are remarkably different from organic fluorophores because those complexes have long lifetimes due to the triplet excited state whose collapse is spin-forbidden. For instance, the emission decay lifetime of the ³MLCT state in [Ru(bipy)₃]²⁺ is of the order of 500 ns,⁹ much longer than typical emission lifetimes of fluorescent organic molecules, which are usually of the order of 1-10 ns.¹ One of the consequences of introducing a heavy metal ion onto an organic ligand is to promote an efficient ISC of the singlet to the triplet excited state, which can lead to a high quantum yield of emission from the triplet state at room temperature.¹⁰ Interestingly, the phosphorescence behaviour of transition metal complexes has found potential for the construction of organic light-emitting diodes (OLEDs) for display or lighting applications.¹¹ In addition, those complexes are attractive for applications in photochemistry,¹² organic optoelectronics,¹³ luminescent sensors^{7,14-16} and biological probes.⁹

1.2.1 Iridium(III) Polypyridyl Complexes

Octahedral iridium(III) complexes with cyclometallating phenylpyridine ligands have been the subject of intensive studies due to their high emission quantum efficiencies ($\Phi_p = 0.1 - 0.9$) and long-lived excited states, generally in the μ s region.^{17,18} In most cases, the emission lifetimes of iridium(III) complexes are longer than those of Ru(II), Os(II) and Re(I) complexes. These complexes also exhibit intense phosphorescence at room temperature that is consistent with strong spin-orbit coupling (SOC) of the d^6 central atom. In fact, there are several factors that contribute to cyclometallated iridium(III) complexes having high triplet quantum yields including:¹¹ i) the strong ligand field strength of the phenyl anion increases the energy between t_{2g} and e_g orbitals leading to an enhanced gap between the e_g and LUMO of the ligand; and ii) the close lying (LC) $\pi - \pi^*$ and MLCT states together with the heavy atom effect enhance the spin-orbit coupling.

In addition, the natures of the emissive states of iridium(III) polypyridyl complexes are quite diverse, resulting in very rich photophysical properties which are distinctly different from those of common Ru(II), Os(II) and Re(I) polypyridyl complexes.^{19,20} Hence, IVERSITI PENDIDIKAN SULTAN IDRIS investigations into luminescent iridium(III) complexes have blossomed over the past few SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS years. For example, in 2-phenylpyridine (ppy)-based iridium(III) complexes, the excited triplet state, which is responsible for phosphorescence, is a combination of the LC and the MLCT triplet excited state, that is a mixed (triplet) excited state. While the coordination complexes $[Ir(bipy)_3]^{3+}$ (bipy=2,2'-bipyridine), $[Ir(phen)_3]^{3+}$ (phen=1,10-phenanthroline) and $[Ir(tpy)_2]^{3+}$ (tpy=2,2':6',2"-terpyridine) are typical ³LC emitters.^{21,22} These different excited states allow iridium(III) polypyridyl complexes to show remarkable emission that is tuneable over the whole of the visible region. For instance, whilst common Ru(II) and Os(II) polypyridines emit in the red or near-infrared (NIR) region and Re(I) polypyridines from green to red, the emission of Ir(III) complexes can occur from the blue to the red region of the spectrum, depending on the nature of the ligands.²³

Furthermore, Iridium(III) is capable of forming a large range of complexes, including mono-, bis- and tris-cyclometallated complexes. For example, the complex $[Ir(ppy)_3]$ (Figure 1.2.1.1a) has been at the centre of OLED studies for being an efficient triplet green emitter, and was first reported by Watts and co-workers in 1985.²⁴ An alternative to neutral *tris*-orthometallated complexes is represented by mixed ligand cationic iridium complexes $[Ir(ppy)_2(bipy)]^+$ (Figure 1.2.1.1b) which was also reported by Watts.²⁵



Figure 1.2.1.1 Two tris-bidentate iridium(III) complexes: (a) fac-[Ir(N^C-ppy)₃] (b) [Ir(N^C-ppy)₂(N^N-bpy)]⁺. Reproduced from reference 26.

Chapter 1 : Introduction

Presently, there are only a few reports of materials showing pure blue emission at room temperature. Thus, the design and development of blue-light-emitting iridium(III)¹ PENDID complexes is highly desirable and has become an area of significant interest.^{27,28} Since the ^{VERSITEF} lowest excited state is ³LC-dominant, employing different cyclometallating ligands enables the excited-state energy of Ir(III) complexes to be varied over a wide spectral range.²⁹ Up to now, most strategies to tune the photophysical properties of the phenylpyridine-based iridium(III) complexes have been substitution of donor and/or acceptor moieties on the pyridine and/or the phenyl groups.³⁰ In principle, the emission colour of iridium(III) complexes is particularly sensitive to the substituents on the ligand attached to the central metal. Therefore, appropriate substituents on the 2-phenylpyridine ligands or on the bipyridine (or phenanthroline), cause shifting of the light emission from the red to the almost blue region of the visible spectrum (Figure 1.2.1.2).³¹



Figure 1.2.1.2 Photoluminescence spectra of iridium phosphors (room temperature, 2 MeTHF solutions). Reproduced from reference 32.

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From the view point of ligand chromophores, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels are mainly located on the pyridyl portion and phenyl segment of the phenylpyridine ligand, respectively, and so are affected by the presence of ligand substituents. In principle, in order to blue-shift the emission wavelength in iridium(III) complexes, the HOMO-LUMO energy gap should be increased by stabilising the HOMO and/or destabilising the LUMO energy levels. The addition of electron withdrawing groups to the phenyl ring has been used as one way to achieve this goal. The most common electron withdrawing group used for this purpose is fluorine, and a typical example of this blue shifting is seen for fac-Ir(F₂ppy)₃ in Figure 1.2.1.2.

Forrest and co-workers³³ demonstrated that bis[2-(2,4difuorophenyl)pyridine]picolinate iridium(III) (Figure 1.2.1.3a) could be used as a blue emission phosphor in an electroluminescent device with 2-(2,4-difuorophenyl)pyridine ligands being responsible for the colour of the emission. The introduction of fluorine atoms results in an increase of the triplet excitation energy and hence, a blue-shift of the phosphorescence compared with that of *fac*-[Ir(ppy)₃].

In addition, De Angelis and Nazeeruddin³⁴ have recently reported a cationic Ir(III) complex, $[Ir(2,4-difluorophenyl)pyridine)_2(4,4'-dimethylamino-2,2'-bipyridine)](PF_6)$ (Figure 1.2.1.3b) which exhibits very strong blue-green emission at 463 nm with a high quantum yield of 85% in acetonitrile solution at room temperature. For this cationic Ir(III) complex, the fluorine atoms introduced onto the phenyl ring of ppy stabilise the HOMO energy level, and the electron releasing substituent (dimethylamino) on the bipy (N^N) ligand, destabilises of the (N^N) ligand-based LUMO. This increases the HOMO-LUMO gap and hence the emission energies.

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Figure 1.2.1.3 Structures of (a) Ir(2,4-difluorophenylpyridine)₂(picolinate). Reproduced from reference 33. (b) [Ir(2,4-difluorophenylpyridine)₂(4,4'-dimethylamino-2,2'-bipyridine)](PF₆). Reproduced from reference 34.

An alternative approach was used by Thompson and Forrest in 2005,³² who tried to stabilise the HOMO of iridium cationic complexes using a 1-phenylpyrazole ligand (ppz). It was reported that replacing the pyridyl ring with either an *N*-pyrazolyl or *N*-heterocyclic carbene-based group leads to a significant increase in the LUMO energy and, consequently, increases the emission energy of complexes coordinated to these ligands. Therefore, it becomes possible to observe efficient blue or near-UV phosphorescence at room temperature from iridium(III) complexes (Figure 1.2.1.4) that have cyclometallated *N*-pyrazolyl- or carbene-based ligands.



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Figure 1.2.1.4 Molecular structures of fac-Ir(flz)<sub>3</sub> (flz = 1-[(9,9-dimethyl-2-
INIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN
fluorenyl)]pyrazolyl), an analogue of fac- Ir(ppz)<sub>3</sub>. Reproduced from reference 32.
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Recently, Hu et al. reported a novel blue-green-emitting cationic iridium complex, $[Ir(ppz)_2(pzpy)]PF_6$ (complex 1), with phenylpyrazole (ppz) as the cyclometallated ligands and 2-(1-phenyl-1H-pyrazol-3-yl)pyridine (pzpy) as the ancillary ligand. Because of the phenylpyrazole cyclometallated ligands, complex 1 exhibited enlarged energy gap and blueshifted 77 K emission spectrum at compared to а reference complex $[Ir(ppy)_2(pzpy)]PF_6$ (complex 2), with phenylpyridine (ppy) as the cyclometallated ligands (Figure 1.2.1.5).³⁵



Figure 1.2.1.5 Molecular structures of [Ir(ppz)₂pzpy]PF₆ (complex 1) and [Ir(ppy)₂pzpy]PF₆ (complex 2). Reproduced from reference 35.

1.2.2 Luminescent Cyanometallate Complexes

The coordination chemistry of cyanide is a matter of widespread interest in various fields of chemistry and biochemistry, since about three centuries ago when the iron(III) hexacyanoferrate(II) (better known as Prussian Blue) was discovered.³⁶⁻³⁸ The area of cyanide bridged networks has recently expanded to cover a wide variety of applications based on luminescence including optical amplification in luminescent sensors and OLED displays.³⁹⁻⁴¹ Luminescent cyanometallates, for example [Ru(diimine)(CN)₄]²⁻ which have a fascinating combination of self-assembly abilities and photophysical properties were first reported by UNIVE Scandola Di and Nco-workers isin 1986.⁴² refore instance, the acyanoruthenate is complex NDIDIKAN SULTAN IDRIS UNIVERSITI PENDIDIKAN SULTAN IDRIS

 $[Ru(bipy)(CN)_4]^2$, like its better-known cousin $[Ru(bipy)_3]^2$, has a luminescent $Ru[d(\pi)] \rightarrow$ bipy(π^*) ³MLCT excited state, which is relatively long-lived ($\approx 100 \text{ ns}$) in protic solvents.⁴³⁻⁴⁵

 $[Ru(bipy)_3]^{2+}$, whose photophysical properties have been studied for decades due to its high luminescence efficiency,⁴⁶ is relatively difficult to combine with other components as it has no externally-directed vacant coordination sites. In contrast, the presence of the four cyanide ligands in [Ru(bipy)(CN)₄]²⁻ (Figure 1.2.2.1) with their externally-directed lone pairs of electrons on the N atoms, results in additional binding sites which make [Ru(bipy)(CN)4]²⁻ far more advantageous and useful as a component of supramolecular assemblies than $[Ru(bipy)_3]^{2+}$. In particular, the lone pairs can coordinate to additional metal cations, allowing formation of polynuclear complexes via Ru-CN-M linkages. Thus, such cyanoruthenate complexes are ideal from both structural and photophysical point of view to prepare d-fcoordination networks⁴³⁻⁴⁵ as the metal chromophore can connect to lanthanides via CN bridges and also has a long-lived excited state to act as energy donor.



Figure 1.2.2.1 Structure of cvanoruthenate complexe, [Ru(bipy)(CN)4]²⁻.

[Ru(bipy)(CN₄)]²⁻ is exceptionally easy to incorporate into supramolecular assemblies because the cyanide groups are effective ligands for other metal ions, principally metal ions of groups 1, 2 and the lanthanides, enabling heteronuclear assemblies based on cyanidebridged coordination networks to be formed. The cyanide ion, which is known to form stable complexes with metal ions in both high and low oxidation states acts as a good bridging ligand.47 For example, Ward and co-workers have reported the mixed metal complex of mononuclear KLi[Ru(bipy)(CN)₄], in which the structure displays for two types of cyanide linkages: "end-on" to the hard Li⁺ cations and "side-on" to the soft K⁺ cations which are lie in the middle of a circular assembly of cyanide ligands (Figure 1.2.2.2).^{48,49}



Figure 1.2.2.2 Part of the asymmetric unit of KLi[Ru(bipy)(CN)₄]·(H₂O)₄ showing the combination of cyanide linkages. Reproduced from reference 48, 49.

Bernhardt and Martínez reported variety of dinuclear cyano-bridged $\text{Co}^{III}/\text{M}^{II}$ (M = Ru or Fe) mixed-valent complexes and one of them, [*trans*-L₁₄Co^{III}(µ-NC)Ru^{II}(CN)₃-(bpy)]⁺ cation (L₁₄ represents a pentaamine macrocycle) is shown in Figure 1.2.2.3. The structure shows the cyanide bridging is being exhibited with an "end on" interaction between the Co and Ru centres. They have also explored a new metal-to-metal charge-transfer (MMCT) energy tuning strategy by replacing the hexacyanometalate(II) unit by various combinations of *cis*-[M(CN)₄(bpy)]²⁻ and *cis*-[M(CN)₂(bpy)₂] (bipy = 2,2'-bipyridyl).⁵⁰



Figure 1.2.2.3 Crystal structure of the [trans-L14Co^{III}(μ-NC)Ru^{II}(CN)3-(bpy)]⁺ cationINIVERSITI PENDIDIKAN SULTAN IDRISUNIVERSITI PENDIDIKAN SULTAN IDRIS(L14 represents a pentaamine macrocycle). Reproduced from reference 50.RISUNIVERSITI PENDIDIKAN SULTAN IDRIS

The Ward group has also prepared polynuclear complexes which contain two or three $[\operatorname{Ru}(\operatorname{diimine})(\operatorname{CN})_4]^{2^-}$ units connected by a single bridging ligand. The first example was dinuclear $[\{\operatorname{Ru}(\operatorname{CN})_4\}_2(\mu\text{-bpym})]^{4^-}$, which is based on the bridging ligand 2,2'-bipyrimidine.⁵¹ Additionally, the tritopic bridging ligand hexaazatriphenylene (HAT) was used to prepare the mono-, di- and trinuclear cyanoruthenate complexes $[\operatorname{Ru}(\operatorname{CN})_4(\operatorname{HAT})]^{2^-}$, $[\{\operatorname{Ru}(\operatorname{CN})_4\}_2(\mu_2-\operatorname{HAT})]^{4^-}$ and $[\{\operatorname{Ru}(\operatorname{CN})_4\}_3(\mu_3-\operatorname{HAT})]^{6^-}$ (Figure 1.2.2.4) in which one, two or three $\{\operatorname{Ru}(\operatorname{CN})_4\}^{2^-}$ units are coordinated to the bidentate sites of the ligand.^{52,53} These complexes displayed some very interesting properties, both photophysical and the ability to act as sensitisers. The presence of up to 12 cyanide groups, in particular for $[\{\operatorname{Ru}(\operatorname{CN})_4\}_3(\mu_3-\operatorname{HAT})]^{6^-}$, which can interact with solvent molecules, results in strong solvatochromism, with broad and intense MLCT absorption manifolds arising from the presence of low-lying π^* orbitals on the HAT ligand.



Figure 1.2.2.4 Structural formulae of {Ru(CN)₄}²⁻ complexes with hexaazatriphenylene. Reproduced from reference 43-45.

In order to increase the connectivity of $[{Ru(CN)_4}_3(\mu_3-HAT)]^6$, the heterometallic clusters of $[{M^{II}(tren)(\mu-CN)}_{11}{Ru_3(HAT)(CN)}]^{16+}$ (Figure 1.2.2.5) were successfully obtained by Ward and Herrera, in which the anionic cyanometallate chromophore $[{Ru(CN)_4}_3(\mu_3-HAT)]^{6-}$ is linked through cyanide bridging groups to eleven $[M^{II}(tren)]^{2+}$ units $[M = Zn^{II}, Cu^{II}; tren = tris(2-aminoethyl)amine]$. These compounds demonstrate the highest connectivity so far reported for cyanide-bridged polynuclear complexes^{52,53} after Julve and Verdaguer reported that eight cyanides of the diamagnetic octacyanometalate $[W(CN)_8]^{4-}$ units can be coordinated to paramagnetic Co(II) ions.⁵⁴



Figure 1.2.2.5 Crystal structure of the 14-nuclear cation of the [{Zn^{II}(tren)(μ-CN)}₁₁{Ru₃(HAT)(CN)}](ClO₄)₁₆ (C = grey, N = light blue, Zn = dark blue, Ru = yellow). Reproduced from reference 52,53.

In addition, there has been extensive research done by Kovacs *et al.* in this area, particularly on the study of electron transfer and photophysical behaviour of $[Ru(LL)(CN)_4]^{2-}$ where LL = 2,2'-bipyridine, 1,10-phenanthroline and their substituted derivatives. It has been demonstrated that substitution of the 2,2'-bipyridine and 1,10-phenanthroline using electron withdrawing and electron donating groups proved to be useful for fine tuning of the ³MLCT excited state.⁵⁵

However, there are several examples of cyanometallate complexes with related photophysical properties to $[Ru(bipy)(CN)_4]^{2^-}$ that have been explored. One example is $[Os(bipy)(CN)_4]^{2^-.56}$ Studies of the spectroscopic and photophysical properties of $[Os(diimine)(CN)_4]^{2^-}$ shows that, these complexes behave in the same way as their Ru(II) analogues but with lower ¹MLCT and ³MLCT energies associated with the higher-energy $d(\pi)$ orbitals of Os(II) compared to Ru(II). In particular, $[Os(diimine)(CN)_4]^{2^-}$ show very weak, short lived and low-energy luminescence in comparison to the ruthenium analogue. However, the relatively unpromising photophysical properties can be improved by the metallochromic effect, in which titration of $[Os('Bu_2bipy)(CN)_4]^{2^-}$ with Zn(II) salt in MeCN (Figure 1.2.2.6), results in the ³MLCT luminescence moving to higher energy and becoming longer lived.



Figure 1.2.2.6 Changes in (a) the UV/Vis absorption spectrum and (b) luminescence spectrum of (PPN)₂[Os(^tBu₂bipy)(CN)₄] in MeCN, on titration with Zn(ClO₄)₂·6H₂O. Reproduced from reference 56.

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