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Photophysical Properties of some Ruthenium (II) Homoleptic substituted terpyridine complexes.

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Abstract

Several homoleptic Ruthenium (II) substituted terpyridine are synthesized and characterized. Their photophysical properties were investigated in acetonitrile. The effect of ligand structure on the photophysical properties is to be elucidated. Steady-state absorption and luminescence emission have shown a metal to ligand charge transfer phenomena. The wavelength of maximum absorption was found to be very similar for all complexes. The wavelength of maximum emission was very variable ranging from 663 nm to 863 nm depending on the electron donating/withdrawing ability of the substituent attached to the terpyridyl ligand. It has been found that the longest wavelength of maximum luminescence was for the strong electron donating substituents such as dimethoxy, methoxy, and methyl groups on the phenyl ring. Luminescence lifetime is measured for all complexes and were found to be in the range 0.43 to 1.76 ns for all complexes except for furyl substituted complex where lifetime of 3.05 ns is obtained. Among all substituted terpyridine, furyl bipyridyl complex shows enhanced luminescence quantum yield and luminescence lifetime.

Keywords: Ruthenium (II) terpyridyl complexes; Steady state, lifetime, Metal to ligand charge transfer.

1. Introduction

Terpyridines and their derivatives, a class of nitrogen-containing aromatic compounds, were originally synthesized by Morgan and Burstall, by subjecting pyridine to prolonged heating in the presence of anhydrous ferric chloride in an autoclave [1]. The name "terpyridine" is derived from its tridentate ligand structure of connected three aromatic pyridine rings through three single carbon-carbon bridges. This unique structure facilitates the chelation with a broad spectrum of transition metal and lanthanide ions. The enhanced stability of the resultant coordination complexes arises from the σ -donor/ π -acceptor nature of the M-N bonds formed [2]. The structure of 2,2':6',2''-terpyridine ligand (tpy), is shown in scheme 1. Over the years,

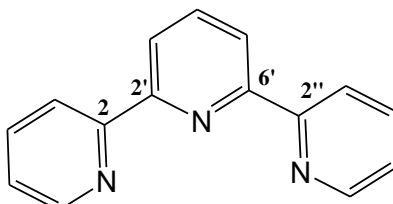
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researchers have elucidated the structural aspects of terpyridine complexes with various metal ions, establishing them as valuable tools in the design and study of coordination compounds. The straightforward functionalization of (tpy) with various organic moieties and their capacity to establish stable complexes with diverse transition metal ions have led to a countless of potential applications such as catalysis, materials science, and medicinal chemistry [3].



Scheme1: structure of 2,2':6',2''-terpyridines (tpy).

In the field of catalysis, for instance, terpyridine-based catalysts exhibited remarkable efficiency in various transformations, including C-C coupling reactions and hydrogenation processes. These findings fuelled the exploration of terpyridines as versatile tools in synthetic chemistry [4-6]. Terpyridines are also have found applications in the field of the development of luminescent materials. Their unique electronic structure imparts excellent photophysical properties, making terpyridines ideal candidates for applications in light-emitting diodes (LEDs), sensors, and imaging agents. Researchers exploited the luminescent properties of terpyridines to design novel materials for optoelectronic devices [7, 8]. Moreover, the biological activity of terpyridines has attracted attention in medicinal chemistry [9, 10]. Studies have explored their potential as anticancer agents, antimicrobial agents, and imaging probes for diagnostic purposes [11-13]. The ability of terpyridines to coordinate with metal ions has been leveraged for targeted drug delivery and imaging applications, opening new avenues in the field of theragnostic [14].

Francis Burstall [15] reported a reaction between RuCl_3 and 2,2' bipyridine (bpy) at 250 °C in the past, resulting in the formation of the red salt $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. The stability of this complex, along with its distinct electrochemical and photophysical properties, has been implemental in the development of a diverse range of octahedral ruthenium polypyridyl complexes.

The luminescence of these complexes hinges on the energy level of their triplet excited states. For instance, complexes such as $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, have very long excited state and show

strong emissions [16-19], while complexes incorporating tridentate 2,2';6',2''-terpyridine ligands, e.g. [Ru(tpy)₂]Cl₂, do not display emission at room temperature and have very short excited state [20-22]. The emission observed in [Ru(bpy)₃]Cl₂ originates from the significant energy gap between the triplet metal-centered (³MC) and triplet metal-to-ligand charge transfer (³MLCT) excited states. On the other hand, this ³MC-³MLCT energy gap decreases in the tpy-containing complexes such as [Ru(tpy)₂]Cl₂, and [Ru(tpy)(bpy)Cl]Cl which promotes non-radiative decay via the ³MC states [23, 24].

The [Ru(tpy)₂]²⁺ complexes possess a geometry that allows for the design of triads where the two additional components are positioned in opposing directions relative to the photosensitizer. Moreover, these complexes exhibit chirality with two symmetry planes and a C₂ axis. As a result, the addition of a substituent at the 4' position of each tpy ligand does not result in isomeric mixtures. Despite having a shorter excited-state lifetime and weaker luminescence in fluid solution at room temperature, these complexes offer this geometric advantage [4, 25-28]. The purpose of this sentence is to explain why these triads are the subject of extensive research. This type of complexes is highly effective at photosensitizing systems that undergo fast photo-induced electron transfer, such as dye-sensitized solar cells [29, 30]. Multiple efforts have been made to adjust the redox and photophysical characteristics of homoleptic transition metal complexes by introducing electron-donating or electron-withdrawing groups onto the 2,2':6',2''-terpyridine ligand [31-33].

In addition, it was essential to optimize the properties of the excited state of the [Ru(tpy)₂]²⁺ complexes in order to utilize them as triplet sensitizers [34]. A significant amount of effort has been devoted to increase their excited state lifetimes by modifying the structure of terpyridine to enhance its ligand field and elevate the energy level of ³MC [35, 36] or by lowering the ³MLCT state through incorporating electron-withdrawing/donating substituents on tpy ligand. These treatment lead to enlarge the energy gap between the ³MLCT state and the ³MC states, and the lifetimes could be extended to several hundreds of nanosecond [37]. Additionally, the incorporation of organic chromophores, such as anthracene [38], terthiophene [39], and ferrocene [40], onto a tpy ligand has the potential to substantially prolong luminescence lifetimes, reaching durations as extensive as 1.8 μs [25, 41, 42]. However, the current luminescence lifetime attained in terpyridine complexes is still insufficient [43-51].

We have previously synthesized, characterized and investigated their photophysical properties in a series of papers for different series of luminescent metal complexes [52-59]. In this work several homoleptic terpyridine ruthenium complexes are prepared with various substituted terpyridine ligands in an attempt to extend the excited-state lifetimes of these complexes. We aimed to lower the ³MLCT energy and /or increase the ligand field strength by the use of strong σ -donor ligands. The photophysical properties and the excited state lifetime of the prepared complexes were extensively studied. We believe that unveiling new properties and applications will position terpyridines to play an increasingly important role in addressing the challenges of the modern scientific landscape.

2. Experimental

2.1. Materials and reagents

Ruthenium chloride ($\text{RuCl}_3 \cdot \text{XH}_2\text{O}$), 2-Acetylpyridine, 4-methoxy benzaldehyde, methyl benzaldehyde, 4-chloro benzaldehyde, 4-bromo benzaldehyde, 4-nitro benzaldehyde, benzaldehyde and furfural aldehyde, acetonitrile (ACN), dimethyl formamide (DMF) and ethanol (EtOH) were purchased from sigma Aldrich. Potassium hydroxide pellets, ammonia solution, ammonium thiocyanate, ammonium hexafluorophosphate NH_4PF_6 (Acros organic), and diethyl ether were all analytical grade quality.

2.2. Instruments and measurements

Thermo-Scientific (Nicolet 6700) Fourier transform infrared (FT-IR) spectrometer was used to measure the IR spectra of KBr pellets. The Shimadzu 6000 Spectrofluorophotometer was used to measure the luminescence emission spectra, and the Shimadzu UV-1900 UV-VIS Spectrophotometer was used to gather the steady state absorption spectra in acetonitrile. Fluorescence lifetime decays were assessed using EasyLife of Optical Building Blocks, Canada (OBB) by means of a 432 nm LED as the excitation light source.

2.3.1. Synthesis of the terpyridine ligands

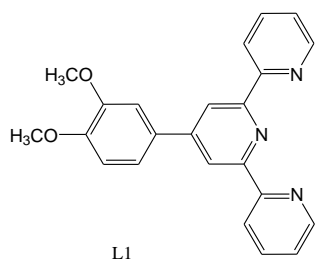
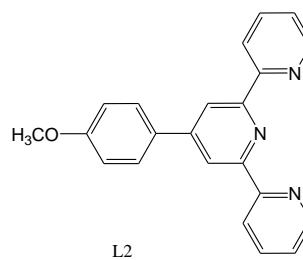
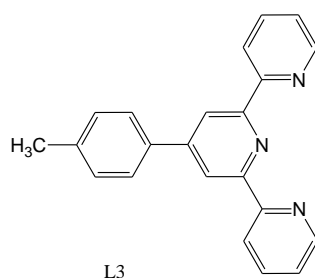
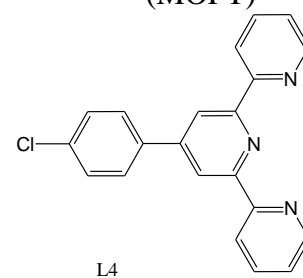
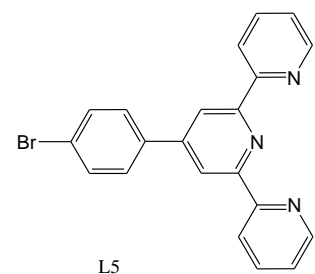
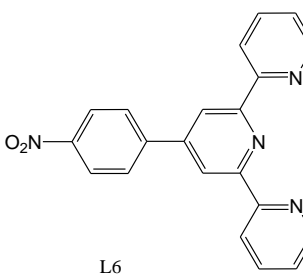
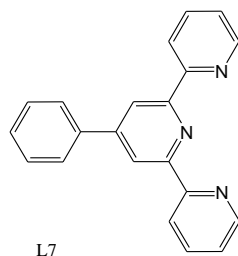
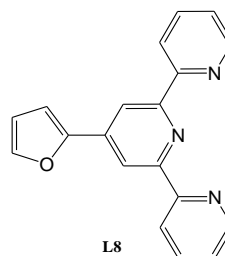
In this work eight different ligands were prepared according to the method described previously [60], by adding 2-Acetylpyridine to aryl aldehyde (X-CHO, (where X groups are one of the following: 3,4-dimethoxyphenyl (DMOP), 4-methoxyphenyl (MOP), 4-methylphenyl (MP), 4-chlorophenyl (CIP), 4-bromophenyl (BrP), 4-nitrophenyl (NP), phenyl (P), and furyl (F))) and KOH, in a 2:1:2 molar ratio, respectively in round bottomed flask. Then this mixture is stirred with 20 ml of NH_4OH and 50 ml of EtOH overnight at 110°C. Thereafter,

the precipitated solid is collected by filtration and washed with cold EtOH at least three times, then dried at 40-50°C overnight. The structures of the prepared ligands are as shown in Scheme 2.

2.3.2. Synthesis of Homoleptic ruthenium terpyridine complexes $[\text{Ru}(\text{Xtpy})_2](\text{PF}_6)_2$

The homoleptic set of ruthenium terpyridines complexes under investigations are synthesized and characterized as described previously in literature [61, 62] The complexes were prepared as follows:

The appropriate ligand (L1-L8) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ are mixed in (2:1) molar ratio and heated to 150° C overnight in a solution of ethanol/Di ionized water in (3: 1) volume ratio. Thereafter, the solvent's volume is reduced by evaporation, subsequently, a saturated solution of NH_4PF_6 was added to the reaction mixture until the produced complex is precipitated, then filtrated, and washed by diethyl ether (Et_2O) until the filtrate becomes colorless. The product is isolated and dried.

4'-(3,4 - Methoxy phenyl)-2,2',6',2''
terpyridine (DMOPT)4'-(4 - Methoxy phenyl)-2,2',6',2''
terpyridine
(MOPT)4'-(3,4 - Methyl phenyl)-2,2',6',2''
terpyridine
(MPT)4'-(4 - chloro phenyl)-2,2',6',2''
terpyridine
(CIPT)4'-(4 - bromo phenyl)-2,2',6',2''
terpyridine
(BrPT)4'-(4- Nitro phenyl)-2,2',6',2'' terpyridine
(NPT)4' - phenyl -2,2',6',2'' terpyridine
(PT)4' - (furfural)-2,2',6',2'' terpyridine
(FT)**Scheme 2.** Structure of the different prepared terpyridine ligands.

3. Results and discussion

3.1. FTIR spectroscopy study:

The Ru(II) complexes of the parent ligands and their FTIR spectra were recorded in the 4000-400 cm^{-1} range on a KBr disc. Fig. 1, and some selected characteristic frequencies such as $\nu(\text{C-H})$, $\nu(\text{C=C})$, $\nu(\text{Ru-N})$ and $\nu(\text{PF}_6^-)$ anion are specified in Table 1. The obtained values of the absorption peaks for both ligands and their related complexes confirm the existence of coordination between these ligands and the Ruthenium metal center.

Table (1) : FTIR data of Homoleptic ruthenium (II) substituted terpyridine complexes of the form $[\text{Ru}(\text{XTPY})_2]\text{PF}_6$.

Compound	$\nu(\text{C-H})$	$\nu(\text{PF}_6^-)$ anion	$\nu(\text{Ru-N})$	$\nu(\text{C=C})$
L1: DMOPT	3073	-	-	1601
$[\text{Ru}(\text{DMOPT})_2](\text{PF}_6)_2$	3089	844-555	446	1601
L2: MOPT	2995	-	-	1605
$\text{Ru}(\text{MOPT})_2(\text{PF}_6)_2$	3089	841-558	444	1601
L3: MPT	3010	-	-	1601
$[\text{Ru}(\text{MPT})_2](\text{PF}_6)_2$	3083	839-556	451	1605
L4: CIPT	3063	-	-	1604
$[\text{Ru}(\text{CIPT})_2](\text{PF}_6)_2$	3057	846-556	486	1609
L5: BrPT	3057	-	-	1606
$[\text{Ru}(\text{BrPT})_2](\text{PF}_6)_2$	3076	840-557	452	1611
L6: NPT	3060	-	-	1671
$[\text{Ru}(\text{NPT})_2](\text{PF}_6)_2$	-	836-555	436	1600
L7: PT	3049	-	-	1610
$[\text{Ru}(\text{PT})_2](\text{PF}_6)_2$	3060	537-558	448	1607
L8: FT	3133	-	-	1609
$[\text{Ru}(\text{FT})_2](\text{PF}_6)_2$	3080	832-558	445	1614

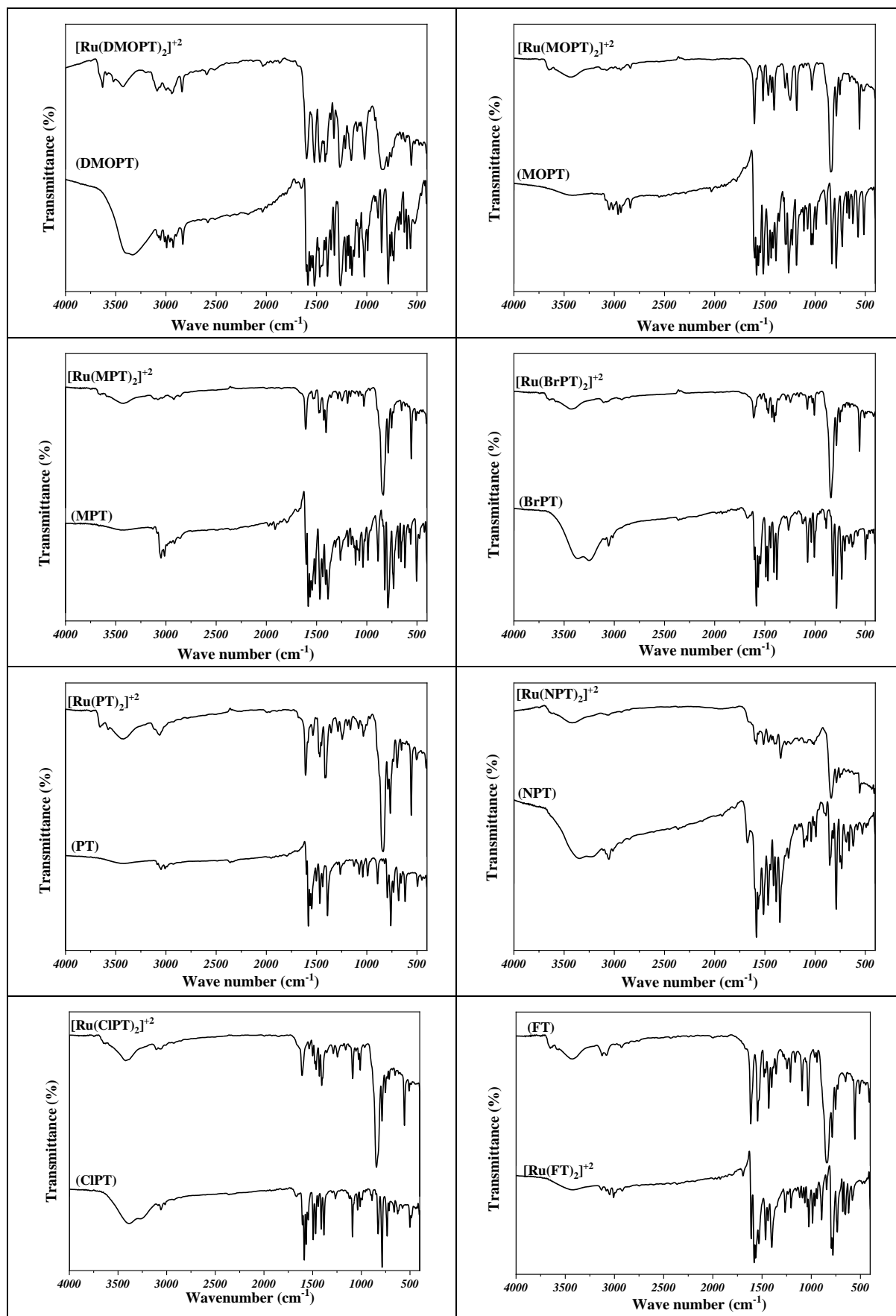


Fig.1: FT-IR of $[\text{Ru}(\text{Xtpy})_2]^{+2}$ complexes and their corresponding ligands, Xtpy is a substituted terpyridine.

3.2. Photophysical properties of $[\text{Ru}(\text{Xtpy})_2](\text{PF}_6)_2$ complexes:

3.2.1. Steady-state measurements:

The photophysical properties of the studied homoleptic ruthenium (II) complexes of the form $[\text{Ru}(\text{Xtpy})_2](\text{PF}_6)_2$ where Xtpy is a substituted terpyridine (X = hydrogen, 1,2-dimethoxybenzene, anisole, toluene, 1-chlorobenzene, 1-bromobenzene, 1-nitrobenzene and furane are studied in acetonitrile. The absorption spectra for the homoleptic complexes are shown in Fig. 2 and their normalized spectra in Fig.3. The corresponding luminescence emission spectra are presented in Fig. 4 and their normalized analogue in Fig. 5. The luminescence quantum yield of the studied complexes in acetonitrile, the absorption and luminescence emission maxima are collected in Table 2.

Investigating the absorption spectra of the studied complexes reveals electronic multiple transitions in the UV region and one transition in the visible region of the spectrum. The electronic transitions in the UV region are attributed to the ligand centered $\pi-\pi^*$ and $n-\pi^*$ transitions. The strong absorption bands in the visible region are attributed to the spin allowed singlet metal to ligand charge transfer ($^1\text{MLCT}$) transition. Fig. 2 clearly shows the shift in the LC and $^1\text{MLCT}$ bands with the type of ligand. The wavelength of maximum absorption of the substituted phenyl ring was found to be red shifted relative to the parent complex by about 3-4 nm.

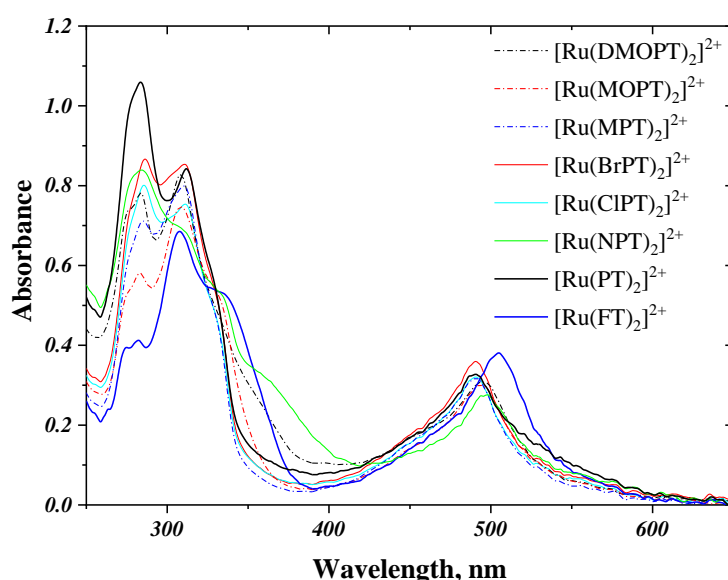


Fig. 2: The absorption spectra of homoleptic ruthenium (II) substituted terpyridine complexes.

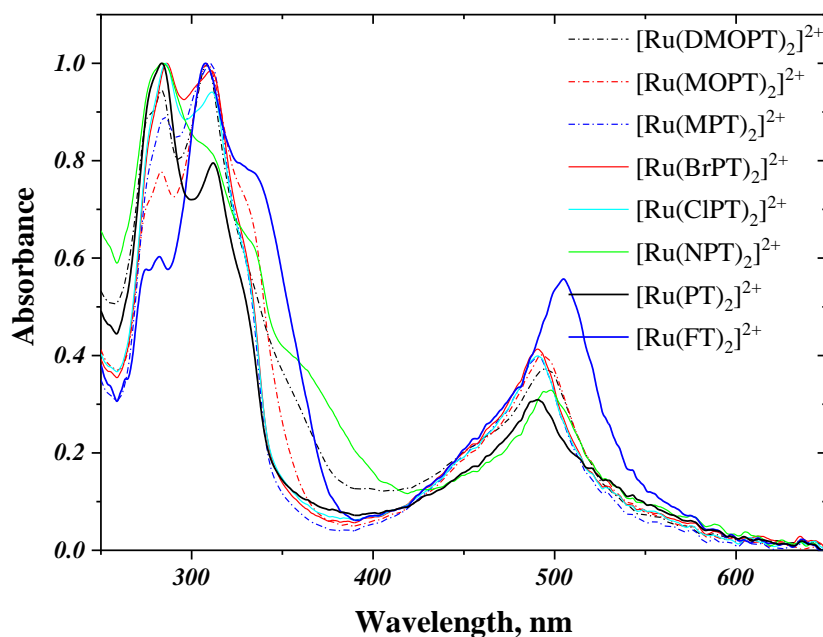


Fig. 3: Normalized absorption spectra of homoleptic ruthenium (II) substituted terpyridine complexes normalized to the intense uv peaks.

On the other hand, the effect of substituents on the corresponding luminescence emission spectra was much more pronounced than the corresponding absorption spectra. For example, replacement of the phenyl ring at the 4'-tpy with furyl ring results in blue shift of about 28 nm. In addition, the substitution on the phenyl group shows a dramatic shift in the position of the luminescence maximum. The presence of the electron donating dimethoxy group shows a huge red shift in the luminescence maximum which decreases with the substitution with methoxy group and methyl group. The presence of electron withdrawing substituents on the phenyl ring shows a blue shift in the luminescence emission maximum relative to the parent phenyl substituent.

The luminescence emission quantum yield of the sample, F_s was obtained using the following Eq. using $[\text{Os}(\text{bpy})_3]^{2+}$ as a reference [63]:

$$\Phi_s = \left(\frac{\text{Area}_s}{\text{Area}_r} \right) \left(\frac{\text{Abs}_r}{\text{Abs}_s} \right) \left(\frac{n_s^2}{n_r^2} \right) \Phi_r \quad (1)$$

Where Area_s and Area_r are the luminescence emission area of the sample and the reference, respectively. Abs_r and Abs_s are the absorbance at the wavelength of excitation of the reference and sample, respectively. The refractive index, n , is the same as the solvent for the sample and the reference is the same. The luminescence quantum yields collected in Table 2 was found to

be in the range $0.9 - 4.6 \times 10^{-4}$ and reveal that any substitution on the phenyl ring results in diminishing the quantum yield with the highest quantum yield is for furyl substituted terpyridyl complex.

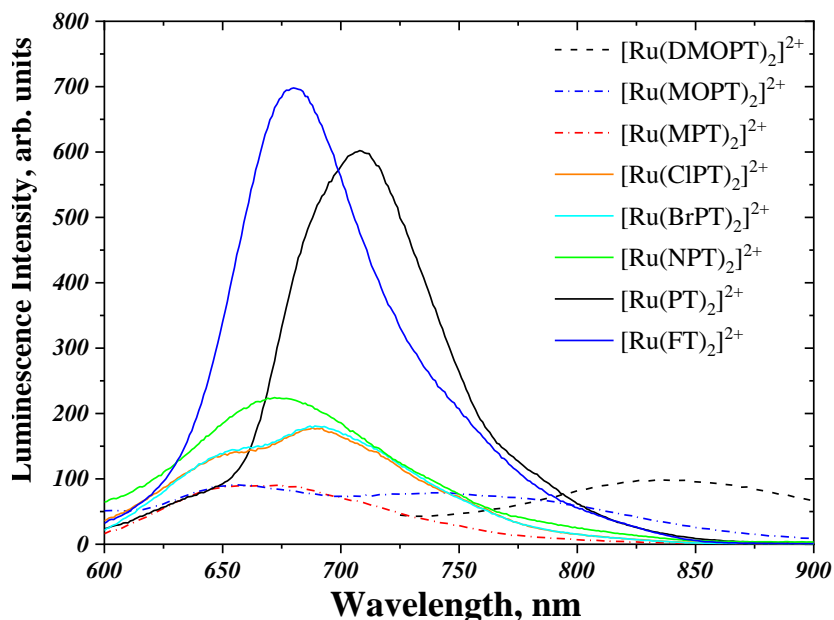


Fig. 4: The Luminescence emission spectra of homoleptic ruthenium (II) substituted terpyridine complexes.

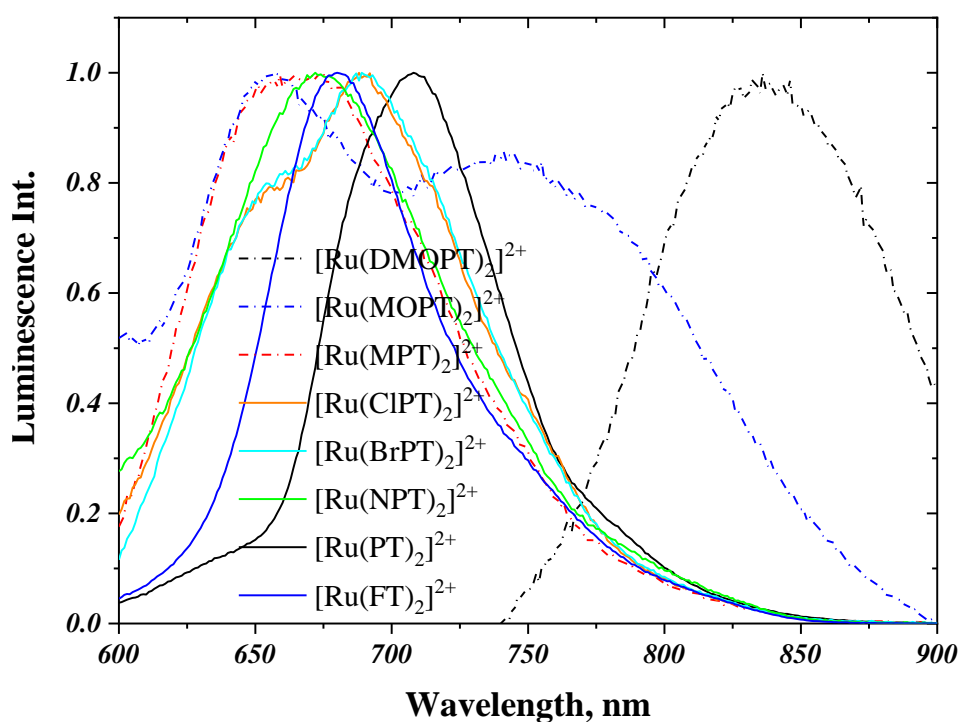


Fig. 5: Normalized Luminescence emission spectra of homoleptic ruthenium (II) substituted terpyridine complexes.

Table 2: The photophysical properties of the homoleptic ruthenium (II) complexes in acetonitrile.

	Compound	λ_{abs} , nm	λ_{em} , nm	τ_1 , ns	$\Phi_L/10^{-4}$
1	[Ru(DMOPT) ₂](PF ₆) ₂	493	863	0.43	1.74
2	[Ru(MOPT) ₂](PF ₆) ₂	492	743	1.34	1.38
3	[Ru(MPT) ₂](PF ₆) ₂	492	663	0.46	0.89
4	[Ru(CIPT) ₂](PF ₆) ₂	492	688	1.76	1.70
5	[Ru(BrPT) ₂](PF ₆) ₂	492	689	1.56	1.53
6	[Ru(NPT) ₂](PF ₆) ₂	493	672	0.46	2.39
7	[Ru(PT) ₂](PF ₆) ₂	489	708	0.48	3.96
8	[Ru(FT) ₂](PF ₆) ₂	505	680	3.05	4.64

3.2.2. Luminescence lifetime of [Ru(Xtpy)₂](PF₆)₂ complexes:

The luminescence lifetime of the homoleptic complexes were insensitive to the substituents on the phenyl terpyridine while the furyl terpyridine lifetime is relatively longer than all the complexes. Fig. 6 show the luminescence decay of the studied homoleptic complexes in acetonitrile, and their calculated lifetime (τ , ns) are listed in Table 2.

The luminescence decay was measured over the entire emission spectra. The luminescence decay was found to fit with mono-exponential function according to the following Eq.:

$$I(t) = a \exp\left(\frac{-t}{\tau}\right) \quad (2)$$

The luminescence lifetime was found to be in the range 0.43 to 1.76 ns for all phenyl and substituted phenyl terpyridyl complexes, however, the furyl terpyridyl complex shows the longest luminescence lifetime of 3.05ns.

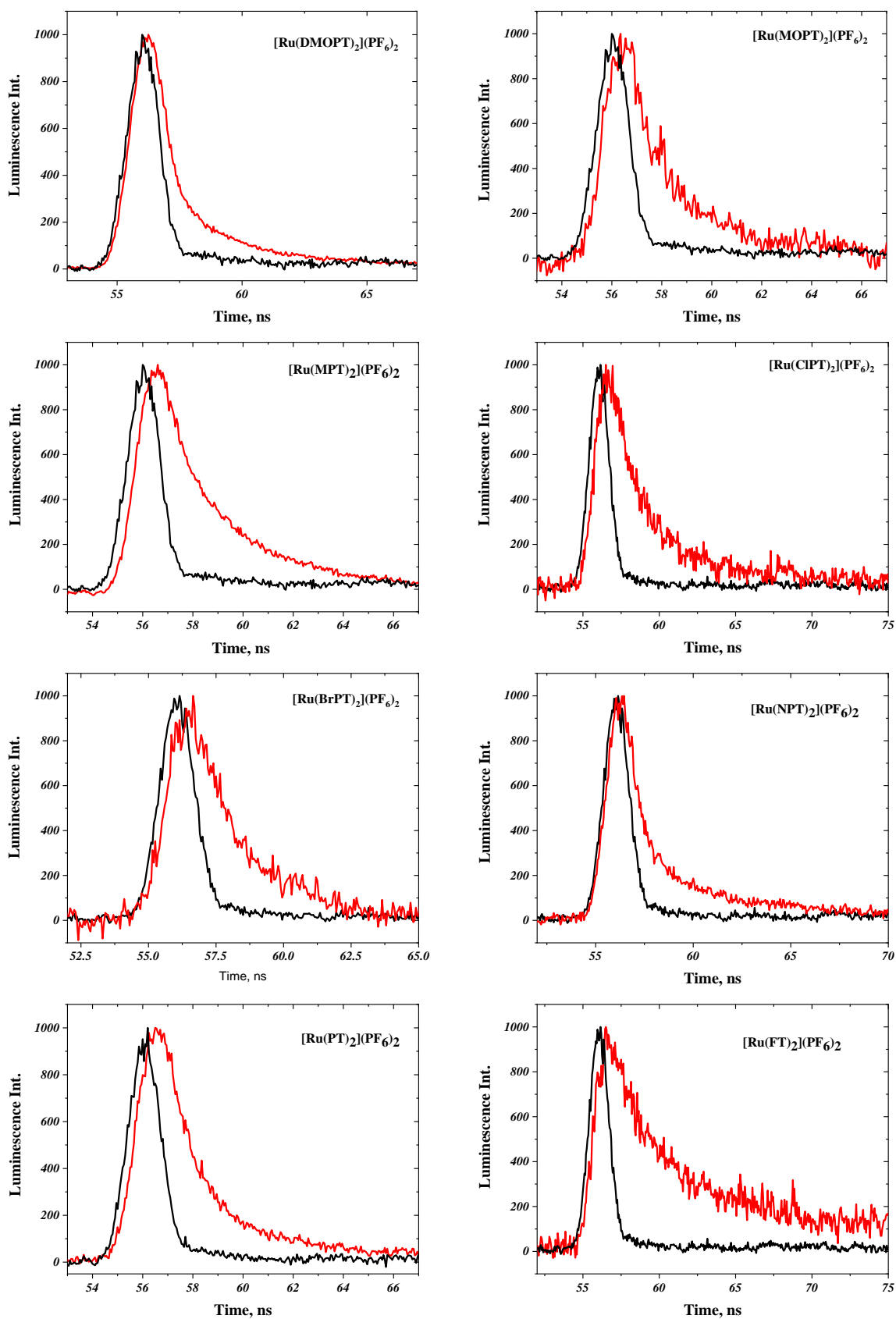


Fig. 6: The luminescence decay of $[\text{Ru}(\text{Xtpy})_2](\text{PF}_6)_2$ complexes in acetonitrile, (instrument response file (black), decay traces (red))

4. Conclusion

Number of homoleptic bis(tridentate) ruthenium(II) complexes, with a substituted phenyl 2,2':6',2''-terpyridine (tpy) ligand, were synthesized and characterized. Their photophysical properties were investigated in acetonitrile. Steady state absorption and luminescence emission was reported and demonstrated that substituents have little effect on the absorption spectra and pronounced effect on the corresponding luminescence emission spectra. It has also been found that, the nature of substituent on the phenyl ring has affected the luminescence lifetime and largely by the substitution of phenyl ring with a furyl ring which shows the longest lifetime.

5. Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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الملخص العربي

الخواص الضوء طبيعية لبعض متراكبات التربيديين المستبدلة بالروثينيوم (II)

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الملخص العربي:

تم تحضير وتوصيف العديد من التربيديين المستبدل بالروثينيوم (II) و تم دراسة خواصها الضوء طبيعية في الأسيونيتريل. وتم توضيح تأثير بنية المركب على الخواص الضوء طبيعية. أظهر امتصاص الحالة المستقرة وانبعث التلألؤ ظواهر نقل الشحنة من الفلز إلى الليجند. وقد وجد أن الطول الموجي للامتصاص الأقصى متشابه جدًا لجميع المعقدات. كان الطول الموجي للحد الأقصى للانبعاث متغيرًا جدًا ويتراوح من ٦٦٣ نانومتر إلى ٨٦٣ نانومتر اعتمادًا على قدرة العطاء / السحب الإلكتروني للبدل المرتبط بروابط تبييريديل. لقد وجد أن أطول طول موجي لأقصى قدر من التلألؤ كان للمستبدلات القوية المعطية للإلكترونات مثل مجموعات ثنائي ميثوكسي والميثيل الموجودة على حلقة الفينيل. تم قياس عمر التلألؤ لجميع المعقدات ووجد أنه في المدى من ٠,٤٣ إلى ١,٧٦ لجميع المعقدات باستثناء المركب المستبدل بالفوريل حيث تم الحصول على عمر ٣,٠٥ نانوثانية. من بين جميع التبييريديين المستبدل، يُظهر مركب فيوريل تبييريديل حصة كم الانبعاث الضوئي وعمر الانبعاث الضوئي أكبر من باقي المتراكبات.