

MLCT Excited-State Behavior of Trinuclear Ruthenium(II) 2,2'-Bipyridine Complexes

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ABSTRACT. Four trinuclear ruthenium (II) polypyridyl complexes were synthesized and a detailed investigation of their excited-state properties was performed. The tritopic sexi-pyridine bridging ligands were obtained via *para* or *meta* substitution of a central 2,2'-bipyridine fragment. A *para* connection between the 2,2'-bipyridine chelating moieties of the bridging ligand led to a red-shifted MLCT absorption band in the visible part of the spectra, while *meta* connection induced a broadening of the LC transitions in the UV region. A convergent energy transfer from the two peripheral metal centers to the central Ru(II) moiety was observed for all trinuclear complexes. These complexes were in thermal equilibrium with an upper-lying $^3\text{MLCT}$ excited state over the investigated range of temperatures. For all complexes, deactivation via the ^3MC excited state was absent at room temperature. Importantly, the connection in *para* position for both central and peripheral 2,2'-bipyridine of the bridging ligand resulted in a trinuclear complex (T_{pp}) that absorbed more visible light, had a longer-lived excited state and a higher photoluminescence quantum yield than the parent $[\text{Ru}(\text{bpy})_3]^{2+}$, despite its red-shifted photoluminescence. This behavior was attributed to the presence of a highly delocalized excited state for T_{pp} .

KEYWORDS Ruthenium, Polynuclear, MLCT, Delocalization, Energy transfer

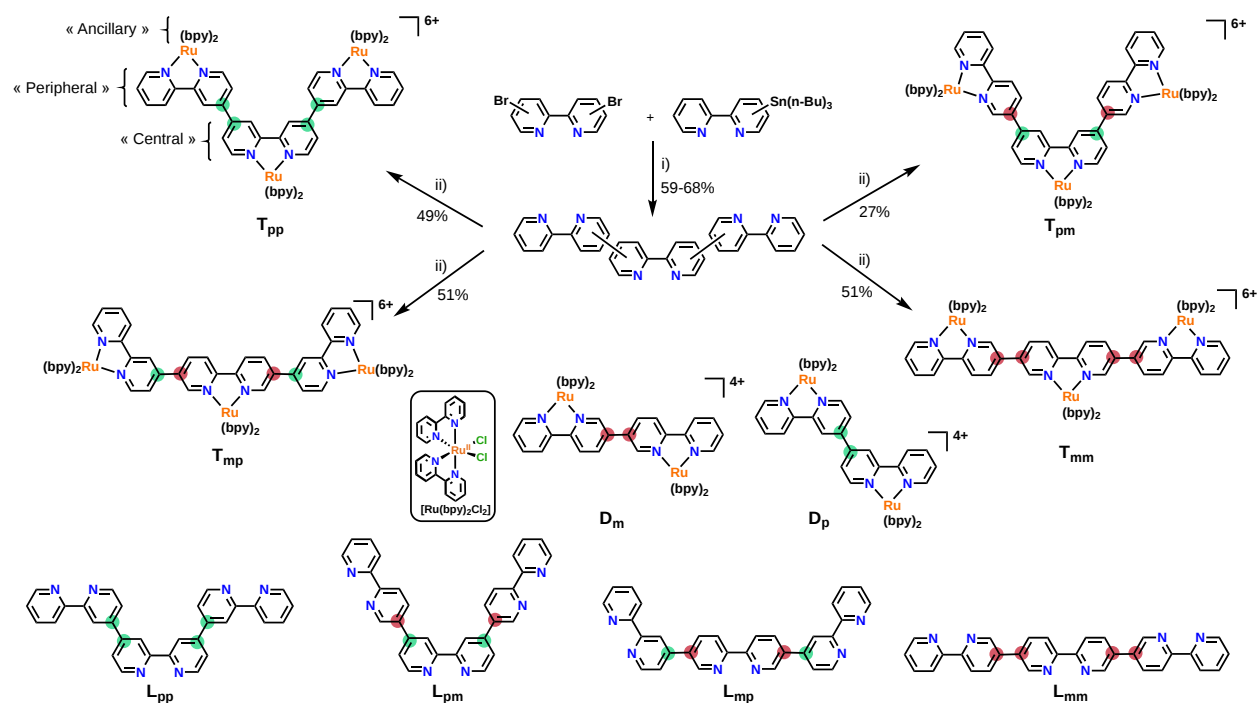
INTRODUCTION

For decades,^{1, 2} the interest in the photophysical and photochemical properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ and its derivatives has remained unaltered and $[\text{Ru}(\text{bpy})_3]^{2+}$ -type complexes have found many applications in photocatalysis, artificial photosynthesis, sensing, nanoscale machines...³⁻⁶ Light absorption by $[\text{Ru}(\text{bpy})_3]^{2+}$ predominantly occurs in the high energy portion of the solar spectrum. Increasing the light absorption at lower energy while maintaining appreciable photoluminescence (PL) and a long-lived excited state is of prime interest. A strategy to absorb light at longer

wavelengths is to decrease the HOMO-LUMO energy gap which typically results in bathochromic shifts of the absorption and photoluminescence.^{7, 8} While this strategy allows longer wavelength light to be absorbed, the molar absorption coefficient typically remains unaltered. A promising approach to increase the molar absorption coefficient is to turn to polynuclear complexes. In addition, the bridging ligand connecting the different metal centers can display lower energy π^* acceptor orbitals and hence also induce bathochromic shifts of the MLCT absorption bands and photoluminescence.^{9, 10} Therefore, polynuclear complexes are prime candidates to absorb light more efficiently at longer wavelengths than mononuclear $[\text{Ru}(\text{bpy})_3]^{2+}$ type complexes. Moreover, the red-shifted photoluminescence is accompanied by a larger non-radiative deactivation rate constant (k_{dnr}) to the ground state, as predicted by the energy gap law, and consequently yields shorter excited-state lifetimes.¹¹⁻¹⁴ This drawback can be partially prevented in polynuclear complexes by judicious bridging ligand design, in which a more delocalized excited state results in a smaller k_{dnr} .¹⁵⁻²² Dinuclear Ru(II) complexes based on a ditopic bridging ligand were far more thoroughly investigated²³ compared to trinuclear Ru(II) complexes based on a tritopic bridging ligand. Most of the tritopic ligands described in the literature are comprised of bi- or tridentate polypyridyl chelating moieties and can be separated into two categories: tritopic ligands with chemically equivalent binding sites^{9, 24-30} and tritopic ligands with at least one chemically inequivalent binding site.³¹⁻⁴⁰ In the latter case, although all Ru(II) centers have identical ancillary ligands, an efficient convergent energy transfer could be evidenced (molecular antenna).^{31, 34, 36-38,}

⁴¹ Surprisingly, in this category, most of the reported examples are based on tritopic ligands with terpyridine-type binding sites while bipyridine-based tritopic bridging ligands remain scarcely studied.⁴¹

In this study, different strategies for assembling three $[\text{Ru}(\text{bpy})_3]^{2+}$ subunits into trinuclear complexes were investigated and the photophysical properties of the resulting complexes were studied. The four trinuclear Ru(II) complexes are based on tritopic sexi-pyridine bridging ligands and six 2,2'-bipyridine (bpy) ancillary ligands (**Scheme 1**). The different bridging ligands investigated are composed of two peripheral 2,2'-bipyridine moieties connected to a central 2,2'-bipyridine moiety. Connections between the bipyridines were varied between the *meta* and *para* position for the central as well as for the peripheral bipyridine moieties resulting in four regioisomeric, tritopic ligands (**Scheme 1**). For sake of clarity, the resulting complexes are termed “T” for trinuclear, followed by “p” or “m” for *para* or *meta* substitution, respectively. The first substitution letter stands for the modification of the central 2,2'-bipyridine while the second letter corresponds to the modification of the peripheral 2,2'-bipyridine.



Scheme 1: Synthetic scheme of the desired ligands (L_{pp} , L_{pm} , L_{mp} , L_{mm}) and complexes (T_{pp} , T_{pm} , T_{mp} , T_{mm}). i) $[\text{Pd}(\text{PPh}_3)_4]$, toluene, argon, 6 days, 135 °C ii) $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, AgNO_3 , $(\text{CH}_2\text{OH})_2/\text{H}_2\text{O}$:9/1, 180 °C, MW, 1h. Structures of the related dinuclear complexes (D_{p} , D_{m}). Green and red circles indicate *para* and *meta* substitutions, respectively.

The four trinuclear complexes were characterized by UV-visible absorption spectroscopy, cyclic and differential pulsed voltammetry, as well as by steady-state and time-resolved photoluminescence over a wide range of temperatures. The experimental results reported herein indicate that the geometry of the bridging ligand and therefore the connection between the Ru(II) subunits plays a decisive role in the photophysical properties. Strikingly, the connection of three 2,2'-bipyridine fragments via the para position (4,4') resulted in a complex (**T_{pp}**) that absorbed more visible light at longer wavelengths, exhibited a longer excited-state lifetime and a higher photoluminescence quantum yield than the parent [Ru(bpy)₃]²⁺ complex. The other bridging ligands yielded trinuclear complexes (**T_{pm}**, **T_{mp}**, **T_{mm}**) that exhibited excited-state lifetimes and photoluminescence quantum yields smaller than [Ru(bpy)₃]²⁺.

RESULT AND DISCUSSION

Synthesis and characterization: The four tritopic sexi-pyridine ligands, **L_{pp}**, **L_{pm}**, **L_{mp}** and **L_{mm}**, were synthesized through a Stille coupling between 4 or 5-(tributylstannyl)-2,2'-bipyridine and 4,4'- or 5,5'-dibromo-2,2'-bipyridine in the presence of [Pd(PPh₃)₄] (**Scheme 1**). The corresponding complexes, **T_{pp}**, **T_{pm}**, **T_{mp}** and **T_{mm}**, were synthesized by heating the corresponding tritopic ligand with an excess of [Ru(bpy)₂Cl₂] in the presence of silver nitrate in an ethylene glycol/water mixture for one hour at 180 °C under microwave irradiation. The complexes were purified by column chromatography on silica gel and isolated as hexafluorophosphate salts after ion metathesis. The four complexes were present as a mixture of stereoisomers, complicating ¹H NMR characterization. The chemical composition of the trinuclear complexes was confirmed by high resolution mass spectrometry (HRMS) using electrospray ionization (ESI). The recorded mass spectra featured a series of well-defined peaks corresponding to adducts of the trinuclear complexes with PF₆⁻ counterions with charged states ranging from 2+ to 6+ (**Figure 1A and**

Figures S19-S34). Since the four trinuclear complexes are regioisomers, they have the same chemical composition and m/z ratios, resulting in identical mass distributions. In order to ensure the regioisomeric purity of each compound, ESI-MS was associated with traveling wave ion mobility spectrometry (TWIMS).^{42, 43} TWIMS is an experimental technique that allows for separation of ions based on their mobility in a cell filled with a buffer gas (He or N₂) under an applied electric field. The drift time spent in such a mobility cell is directly proportional to the ion collisional cross section (CCS), which is associated to the 3D structure of the complex. The four trinuclear complexes were characterized by ESI-TWIMS-MS in their 2+ charged state (*i.e.* with four PF₆⁻ counter-ions). All four trinuclear complexes exhibited narrow and unimodal arrival time distribution (ATD). However, the four regioisomeric complexes displayed distinct time distribution (**Figure 1**) arising from the different 3D structures in the gas phase, which points to the regioisomeric purity of the four complexes. In order to gain more insights into the spatial structure of each complex, molecular dynamics (MD) simulations were performed to generate candidate structures for each system. The theoretical average values of the associated collisional cross sections were in good agreement with the experimental values (less than 3% difference, **Table 1**). The corresponding ion structures are reported in **Figure S35**.

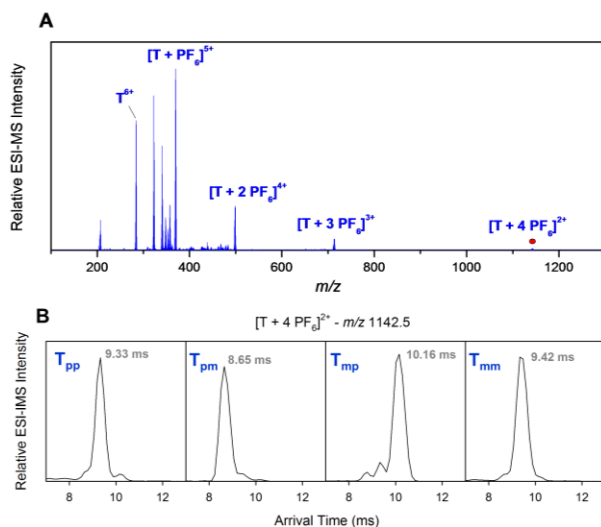


Figure 1: (A) Representative ESI-MS spectrum of a trinuclear complex. Adducts of T with PF_6^- counterions are highlighted. (B) Arrival time distributions recorded for m/z 1142.5, corresponding to $[\text{T} + 4 \text{PF}_6]^{2+}$ (red dot) for each trinuclear complex.

Table 1. Experimental and theoretical collisional cross sections derived from TWIMS-MS experiments and molecular dynamics simulations, respectively. Experimental values are averaged over three separate experiments while theoretical values are averaged over 250 candidate structures extracted from MD simulations. Errors correspond to standard deviations.

Complex	Experimental CCS ($\text{\AA}^2$)	Theoretical CCS ($\text{\AA}^2$)
T_{pp}	370.2 ± 1.3	374.4 ± 3.4
T_{pm}	353.4 ± 0.6	361.8 ± 3.0
T_{mp}	391.1 ± 0.7	395.8 ± 2.8
T_{mm}	372.6 ± 1.1	379.2 ± 3.0

Ground state properties: The electrochemical properties of the complexes were investigated by cyclic and differential pulse voltammetry (**Figure S36-S37**) and the corresponding data are gathered in **Table 2**. The observation of a single three-electron oxidation wave at an identical potential for the four complexes indicated that the peripheral and central Ru(II) centers underwent simultaneous oxidation and hence were behaving as independent centers.⁴⁴ For Ru(II)

polypyridyl complexes, it is usually accepted that the reduction processes are ligand centered.⁴⁵ The first two one-electron reduction event were attributed to reductions of the bridging ligand, upon comparison with the parent complex $[\text{Ru}(\text{bpy})_3]^{2+}$. The geometry of the bridging ligand strongly influenced the reduction patterns of the trinuclear complexes. The first reduction occurred at more positive potentials when the central bipyridine of the bridging ligand was connected via the meta (5,5') position (T_{mp} , T_{mm}) compared to a connection via the para (4,4') position (T_{pp} , T_{pm}). Hence, this first reduction was attributed to a central 2,2'-bipyridine-based reduction.^{46, 47} Both T_{pp} and T_{pm} exhibited similar potentials for the first ligand-centered reduction. For complexes with a central bipyridine substituted in meta position, a *para*-substitution of the peripheral bipyridines (T_{mp}) resulted in a complex that was more easily reduced than the meta-substituted ones (T_{mm}). The second reduction wave appeared to be controlled by the substitution of the peripheral bipyridine of the bridging ligand. Indeed, in the complexes where these peripheral bipyridines were connected via the meta position to the central one (T_{pm} , T_{mm}), a smaller difference in redox potential between the first and the second reduction wave (90-100 mV) was observed in comparison to the complexes where the peripheral bipyridines were connected to the central one via their para position (T_{pp} , T_{mp} , 160 mV).¹⁶ The second reduction process was therefore attributed to the reduction of one peripheral bipyridine of the bridging ligand.

Table 2. Oxidation and reduction potentials (V vs Ag/AgCl). Redox potentials can be estimated vs NHE by adding 0.2 V.

Complex	$E_{1/2}(\text{Ru}^{\text{III/II}})^{[\text{a}]}$		$E_{1/2}(\text{L}^{n/n-1})^{[\text{b}]}$		
	(V vs Ag/AgCl)		(V vs Ag/AgCl)		
T_{pp}	+1.38	−0.93	−1.09	−1.45	−1.59
T_{pm}	+1.38	−0.93	−1.02	−1.25	−1.44
T_{mp}	+1.38	−0.78	−0.94	−1.43	−1.59
T_{mm}	+1.38	−0.86	−0.96	−1.44	−1.54
$[\text{Ru}(\text{bpy})_3]^{2+}$	+1.30	−1.31	−1.50	−1.75	

[a] Cyclic voltammetry in acetonitrile. [b] Differential pulse voltammetry in DMF.

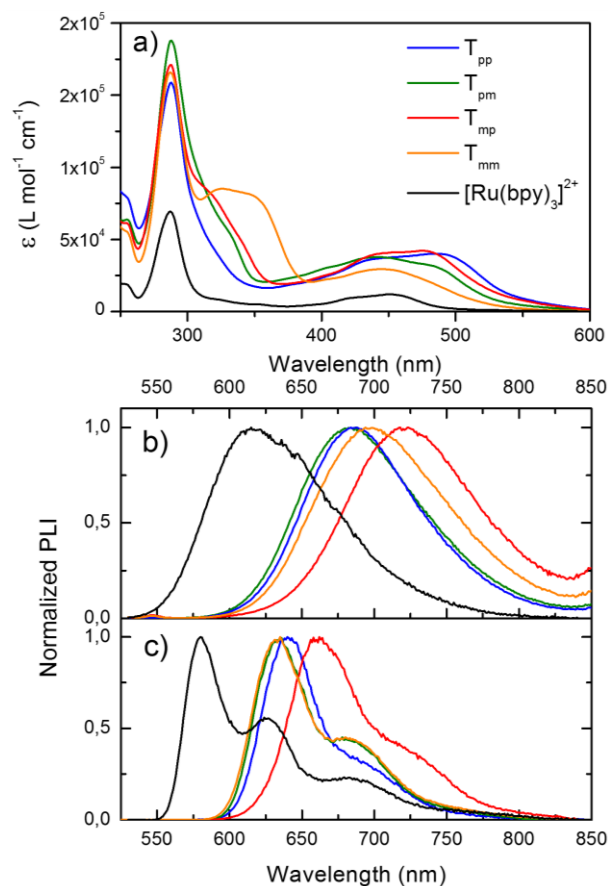


Figure 2. UV-Visible absorption spectra for the complexes in acetonitrile at 293 K (a), normalized steady-state photoluminescence spectra of the complexes in acetonitrile solution at 293 K (b) and in butyronitrile rigid matrix at 77 K (c).

The ground state absorption spectra of the complexes are shown in **Figure 2a** and the absorption band maxima are gathered in **Table 3**. The absorption spectra are typical of Ru(II) polypyridyl complexes.⁴⁵ The intense absorption bands in the UV region were attributed to ligand-centered transitions and those recorded between 400 and 550 nm were due to spin-allowed metal-to-ligand charge transfer (¹MLCT) transitions. The absorption spectra of the four trinuclear complexes did not simply represent a three-fold increase of the [Ru(bpy)₃]²⁺ absorption spectra (**Figure S38**), as would be expected for three non-interacting [Ru(bpy)₃]²⁺ fragments, but rather, displayed new optical transitions. In the UV region, a broadening of the $\pi \rightarrow \pi^*$ ligand-centered transition around 290 nm was observed and became more pronounced as the number of linearly arranged pyridine

moieties increased ($T_{mm} > T_{mp} > T_{pm} > T_{pp}$). In the case of T_{mm} , where six pyridine moieties are arranged in a linear orientation, a new distinct transition appeared at 336 nm. For the $^1\text{MLCT}$ transitions, T_{pp} , T_{pm} and T_{mp} exhibited two distinct transition bands, one centered at a similar energy as for $[\text{Ru}(\text{bpy})_3]^{2+}$ (~ 450 nm) and a second at lower energy (~ 480 nm). T_{mm} on the other hand only displayed one transition band at higher energy. The transitions at 450 nm were attributed to $^1\text{MLCT}$ transitions from the Ru(II) centers to orbitals localized on the external 2,2'-bipyridine (bpy) ancillary ligands, as well as orbitals localized on the bridging ligands. The $^1\text{MLCT}$ transition at 480 nm only involved the bridging ligands.⁴⁸ The molar absorption coefficients associated with the transitions at 480 nm increased as the number of para-connected 2,2'-bipyridines on the bridging ligand increased, such that $T_{pp} > T_{mp} > T_{pm}$. This agreed with previous observations of complexes with 2,2'-bipyridine ligands substituted in the 4,4' positions that exhibited more intense $^1\text{MLCT}$ transitions than their corresponding complexes substituted in the 5,5' positions.^{46, 49} All trinuclear complexes reported herein exhibited molar absorption coefficients for the $^1\text{MLCT}$ transitions appreciably larger than $[\text{Ru}(\text{bpy})_3]^{2+}$ (**Figure 2 and S38**).

A correlation between the energy of the more bathochromic distinct $^1\text{MLCT}$ transition and the redox energy ($\Delta E_{1/2} = E_{\text{Ru(III/II)}} - E_{\text{L(n/n-1)}}$), also known as spectroelectrochemical correlation,^{8, 50} was observed for the *para*-substituted derivatives, T_{pp} and T_{pm} , (**Figure S40**) indicating that the same orbitals were involved in both the electrochemical and photophysical processes. For the *meta*-substituted derivatives, *i.e.* T_{mp} and T_{mm} , the absence of correlation most probably originates from the fact that the first ligand-centered reduction process occurs on the central 2,2'-bipyridine moiety of the bridging ligand and its *meta* substitution results in $^1\text{MLCT}$ transition with moderate oscillator strength. As a result, the intensity of the $^1\text{MLCT}$ transition correlated to the first

reduction and oxidation processes could be too weak to appear as a distinct feature or could even be hidden in the tail of the transitions occurring at higher energy.

Table 3. Photophysical properties of the trinuclear complexes and $[\text{Ru}(\text{bpy})_3]^{2+}$.

Complex	Absorption	Luminescence						
	293 K ^[a]	293 K ^[a]					77 K ^[g]	
	$\lambda_{\text{max}}(\text{nm}); \epsilon (\text{M}^{-1}\text{cm}^{-1})$	λ_{max} (nm) ^[b]	τ (ns) ^[c]	Φ_{PL} ^[c,d]	k_r ^[c,e] (10^4 s^{-1})	k_{nr} ^[c,f] (10^6 s^{-1})	λ_{max} (nm) ^b	τ (μs)
T_{pp}	484 (40100), 440 (36600), 288 (158800)	684	1815 (345)	0.121 (0.022)	6.7	0.5	641	6.2
T_{pm}	485 (31200), 442 (37800), 288 (188000)	683	623 (224)	0.048 (0.017)	7.7	1.5	635	4.6
T_{mp}	475 (42200), 450 (40800), 287 (171100)	721	298 (117)	0.0095 (0.0028)	3.2	3.3	662	2.6
T_{mm}	445 (29500), 326 (85200), 287 (166100)	698	312 (175)	0.014 (0.0089)	4.5	3.2	633	3.4
$[\text{Ru}(\text{bpy})_3]^{2+}$ ^[h]	450 (12000), 287 (69400)	615	890 (170)	0.094 (0.018)	11.0	1.0	579	4.8

[a] acetonitrile solution. [b] excitation at 450 nm. [c] in argon purged acetonitrile solution with values for air-equilibrated solution in parentheses, uncertainties are estimated to be 5%. [d] $[\text{Ru}(\text{bpy})_3]^{2+}$ in air-equilibrated acetonitrile used as reference ($\Phi_{\text{PL}}=0.018$),⁵¹ uncertainties are estimated to be 10%. [e] $k_r = \Phi_{\text{em}}/\tau$. [f] $\tau = 1/(k_r+k_{nr})$. [g] Butyronitrile rigid matrix. [h] from reference¹⁰.

Excited-state properties. At 77 K, in a rigid matrix, as well as at 293 K in fluid solution, all trinuclear complexes exhibited photoluminescence with a single exponential excited-state lifetime. The trinuclear complexes are composed of two types of Ru(II) centers, *i.e.* two peripheral and one central. The experimental observation of one single exponential luminescent lifetime indicated that the photoluminescence arose from only one type of Ru(II) center. This was made possible by an energy transfer between the two types of Ru(II) centers, and supported by the close match between the absorption and excitation spectra (**Figure S41-S44**). The photoluminescence of related dinuclear complexes **D_p** and **D_m**¹⁰ (**Scheme 1**) was recorded at higher energy than for the corresponding trinuclear complexes, both at 77 K and 293 K. The red-shifted photoluminescence

of the trinuclear complexes compared to the dinuclear analogue strongly suggested that, in the trinuclear complexes, a convergent energy transfer is taking place from the peripheral Ru(II) to the central Ru(II) subunits. Hence, it was proposed that the ³MLCT excited-state responsible for the photoluminescence corresponded to a charge transfer between the central bipyridine moiety and the central Ru center. Franck-Condon line-shape analysis of the photoluminescence recorded at 77 K (**Figures S45-S48**) yielded better insight into the excited-state properties. The photoluminescence spectra were fit according to **equation 1** where E_0 corresponds to the energy difference between the ground- and excited-state potential energy surfaces in their 0th vibrational level, S_M is the Huang-Rhys factor, also known as the coupling factor that gauges the geometric distortion between the ground and excited state, $\hbar\omega_m$ corresponds to the vibrational energy spacing in the ground-state potential energy surface for the mode contributing the most to the geometric distortion and $\Delta\nu_{1/2}$ is the full-width at half-maximum of the transition (fwhm).^{52, 53} The extracted data are gathered in **Table 4**.

$$I(\tilde{\nu}) = \sum_{v_m=0}^{\infty} \left[\left(\frac{E_0 - v_m \hbar \omega_m}{E_0} \right)^3 * \frac{S_M^{v_m}}{v_m!} * \exp \left\{ -4 \ln 2 \left[\frac{\tilde{\nu} - E_0 + v_m \hbar \omega_m}{\Delta\nu_{1/2}} \right]^2 \right\} \right] \text{ Eq.1}$$

Table 4. Fitting Parameters Obtained from the Franck-Condon Line-Shape Analysis^[a]

Complex	E_0 (cm ⁻¹)	$\hbar\omega_M$ (cm ⁻¹)	S_M	Fwhm (cm ⁻¹)
T_{pp}	15650	1170	0.33	1010
T_{pm}	15790	1190	0.46	990
T_{mp}	15140	1220	0.39	1160
T_{mm}	15820	1220	0.47	1020

[a] At 77 K in butyronitrile rigid matrix, no parameters were constrained for the fitting calculations.

The vibrational modes ($\hbar\omega_M$) were found to be of similar magnitude for all complexes, *i.e.* 1170-1220 cm⁻¹. These values were in good agreement with that of an average acceptor vibrational mode of C–C and C–N stretches in polypyridine type ligands, as already stated in literature.^{54, 55, 53, 56} In

spite of small differences in E_0 (~ 15600 - 15800 cm^{-1}), $\mathbf{T}_{pp}$ exhibited a significantly smaller Huang-Rhys factor (S_M) than $\mathbf{T}_{pm}$ and $\mathbf{T}_{mm}$, indicating a more delocalized excited state in $\mathbf{T}_{pp}$.¹⁶⁻¹⁹ A delocalized excited state suggested that the excited electron was delocalized over a large molecular framework, which decreases the amplitude of geometric distortions of the C–C and C–N bonds.¹⁵ Consequently, the excited state was less distorted in comparison to the ground state, resulting in a decrease in the vibrational overlap between these two states.¹⁸ The small S_M for $\mathbf{T}_{mp}$ could be explained by its smaller E_0 , as a decrease in E_0 is usually accompanied by a concomitant decrease in the Huang-Rhys factor.^{12, 53, 57-59} At 77 K, deactivation of the $^3\text{MLCT}$ excited-state via the activated pathways to the upper lying $^3\text{MLCT}$ and ^3MC excited states were negligible (vide infra) and hence the excited-state lifetimes were determined by the activationless direct radiative (k_{dr}) and non-radiative (k_{dnr}) deactivation rate constants. The trend in excited-state lifetimes at 77 K ($\tau_{\mathbf{T}_{pp}} > \tau_{\mathbf{T}_{pm}} > \tau_{\mathbf{T}_{mm}}$) for the three complexes with similar E_0 was attributed mainly to the variation in Huang-Rhys factors ($S_M(\mathbf{T}_{pp}) < S_M(\mathbf{T}_{pm}) < S_M(\mathbf{T}_{mm})$), as k_{dnr} increases when S_M increases.¹⁸ The excited-state lifetime of $\mathbf{T}_{mp}$ was the shortest of all trinuclear complexes, which was linked to its 600 cm^{-1} smaller E_0 value compared to the other complexes. The Englman-Jortner energy gap law¹¹ states that when the energy gap decreases (E_0), k_{dnr} increases and hence the excited-state lifetime is shortened.^{14, 58}

The change from rigid matrix to room temperature fluid solution was accompanied by an expected bathochromic shift of the photoluminescence maxima due to enhanced solvation effects in the fluid medium (**Figure 2**).¹⁴ At 293 K, the trinuclear complexes possessing a bridging ligand with a *para*-substituted central bipyridine ($\mathbf{T}_{pp}$, $\mathbf{T}_{pm}$) exhibited photoluminescence maxima at similar wavelengths. When the central bipyridine was meta-substituted ($\mathbf{T}_{mp}$, $\mathbf{T}_{mm}$), red-shifted photoluminescence occurred (**Figure 2**). The corresponding photoluminescence lifetimes and

quantum yields followed the same trend ($T_{pp} > T_{pm} > T_{mm} > T_{mp}$) as observed at 77 K. T_{pp} and T_{pm} possessed larger global radiative rates constants (k_r) than T_{mp} and T_{mm} , yet these variations remained moderate. The non-radiative deactivation rate constants (k_{nr}), gathering the direct and activated deactivation pathways (k_{dnr} , k_{3MLCT} , k_{3MC}), exhibited a more contrasting behavior among the complexes.

For all trinuclear complexes, a correlation between the photoluminescence maxima at 293K and the $\Delta E_{1/2}$ ($\Delta E_{1/2} = E_{Ru(III/II)} - E_{L(n/n-1)}$) was noted (**Figure S39**), indicating that orbitals of similar nature were involved in both the electrochemical and photoluminescence processes. This agreed with a lowest energy excited state, corresponding to a charge transfer between the central Ru and the central bipyridine part of the bridging ligand.^{7, 8, 50}

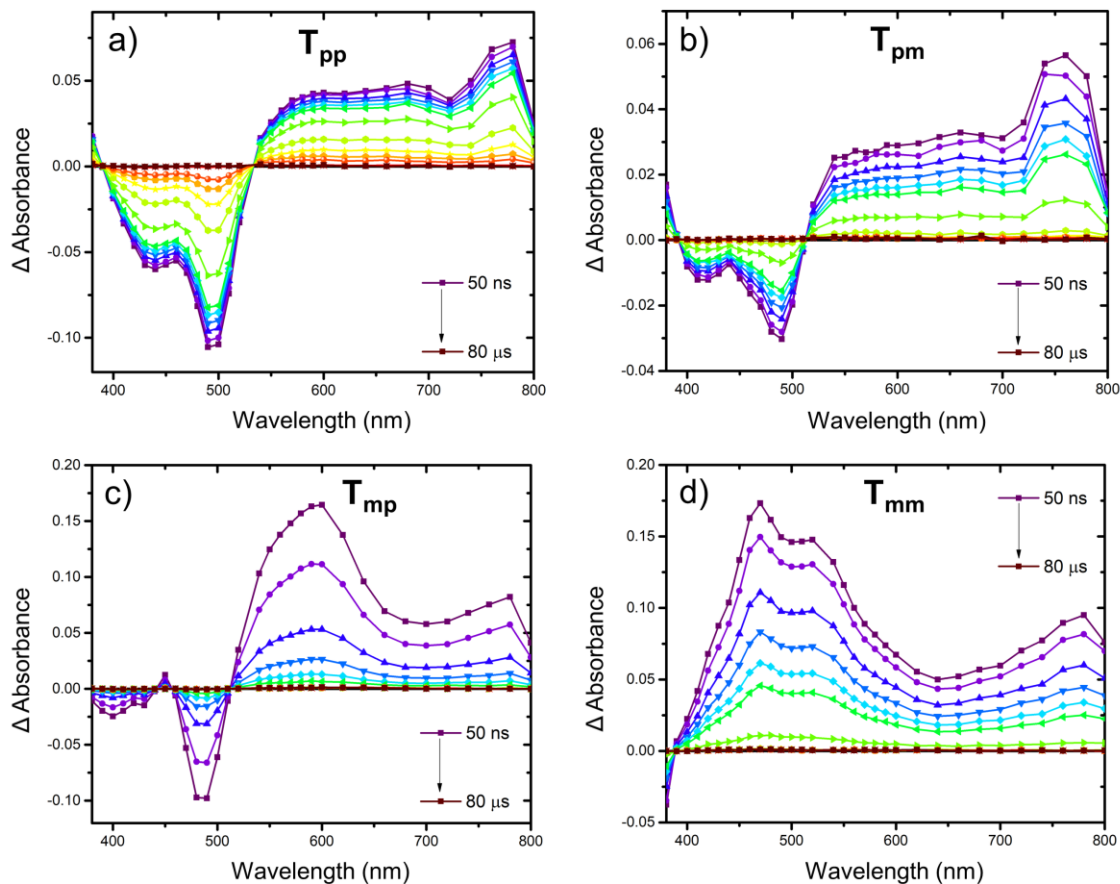


Figure 3: Transient absorption spectra at 293 K of T_{pp} (a), T_{pm} (b), T_{mp} (c), and T_{mm} (d) after pulsed 532 nm excitation in argon purged butyronitrile.

Nanosecond transient absorption spectra of the trinuclear complexes in butyronitrile at 293 K are presented in **Figure 3**. For all complexes, the transient absorption changes decayed according to a unimolecular process over the whole spectral range on a timescale consistent with photoluminescence lifetime measurements, attributed to deactivation of the lowest $^3\text{MLCT}$ excited-state. Energy transfer between metal centers in polynuclear polypyridine complexes usually takes place on the femto- to picosecond timescale.⁶⁰⁻⁶² Hence, the energy transfer had already occurred within the timescale of the transient spectra measurements and the observed excited-state corresponds therefore to the lowest $^3\text{MLCT}$. The transient absorption spectra of T_{pp} was most similar to the one of $[\text{Ru}(\text{bpy})_3]^{2+}$,⁶³ where the bleaching between 400 and 520 nm was attributed to the formal oxidation of Ru(II) to Ru(III) and the positive features between 520 and 800 nm were attributed to intra-ligand transitions of the formally monoreduced bridging ligand ($\text{L}_{\text{pp}}^{\bullet-}$).^{22, 64, 65} The transient absorption spectra of the three other complexes exhibited more unusual behaviors. In comparison to T_{pp} , a moderate decrease in the 450 nm bleaching was observed for T_{pm} . In the case of T_{mp} , this bleach was of smaller intensity and it was completely absent for T_{mm} where, instead, a strong positive transient absorption was observed between 390 and 800 nm, with a maximum localized at 470 nm. This feature at 470 nm increased with the number of pyridine moieties arranged in a linear fashion within the bridging ligand ($\text{T}_{\text{mm}} > \text{T}_{\text{mp}} > \text{T}_{\text{pm}} > \text{T}_{\text{pp}}$). As in the ground state UV-visible spectra, an increase in the number of linearly arranged pyridines induced a broadening of the $\pi \rightarrow \pi^*$ transitions localized on the bridging ligand. Therefore, it was proposed that the transient absorption centered at 470 nm was due to transitions mainly localized on the mono-reduced bridging ligand ($\text{L}^{\bullet-}$), as shown experimentally and theoretically in related dinuclear complexes.¹⁰

Variable temperature photoluminescence. Steady-state and time-resolved photoluminescence measurements in butyronitrile at variable temperatures were performed in order to gain better insight into the excited-state deactivation pathways of trinuclear complexes. First, temperature dependent time-resolved photoluminescence measurements allowed to identify the different deactivation pathways from the lowest $^3\text{MLCT}$ excited-state and the corresponding deactivation kinetic rate constants. Second, temperature dependent steady-state photoluminescence measurements, and more precisely photoluminescence quantum yields, allowed to identify the pathways exhibiting radiative deactivation.^{66, 67} The observed changes in the photoluminescence lifetimes and quantum yields for each trinuclear complex are shown in **Figure 4** and 5.

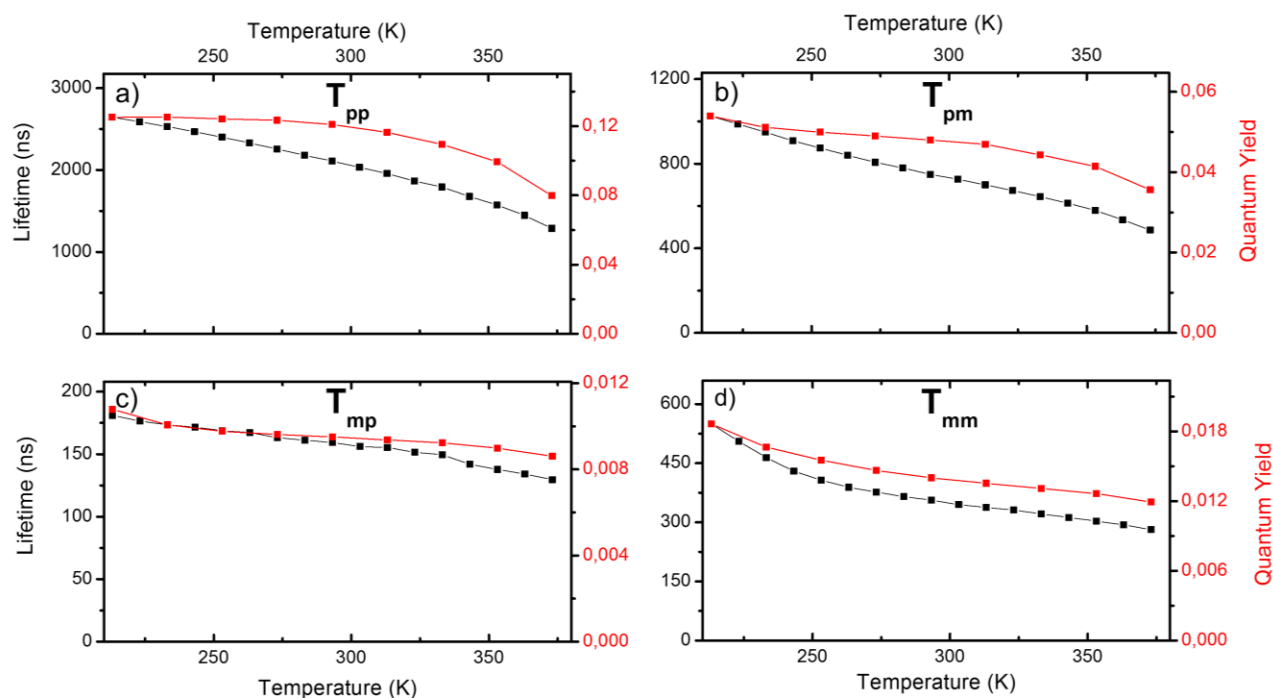


Figure 4: Photoluminescence lifetimes (black squares) and quantum yields (red squares) as a function of temperature for T_{pp} (a), T_{pm} (b), T_{mp} (c) and T_{mm} (d) in argon purged butyronitrile.

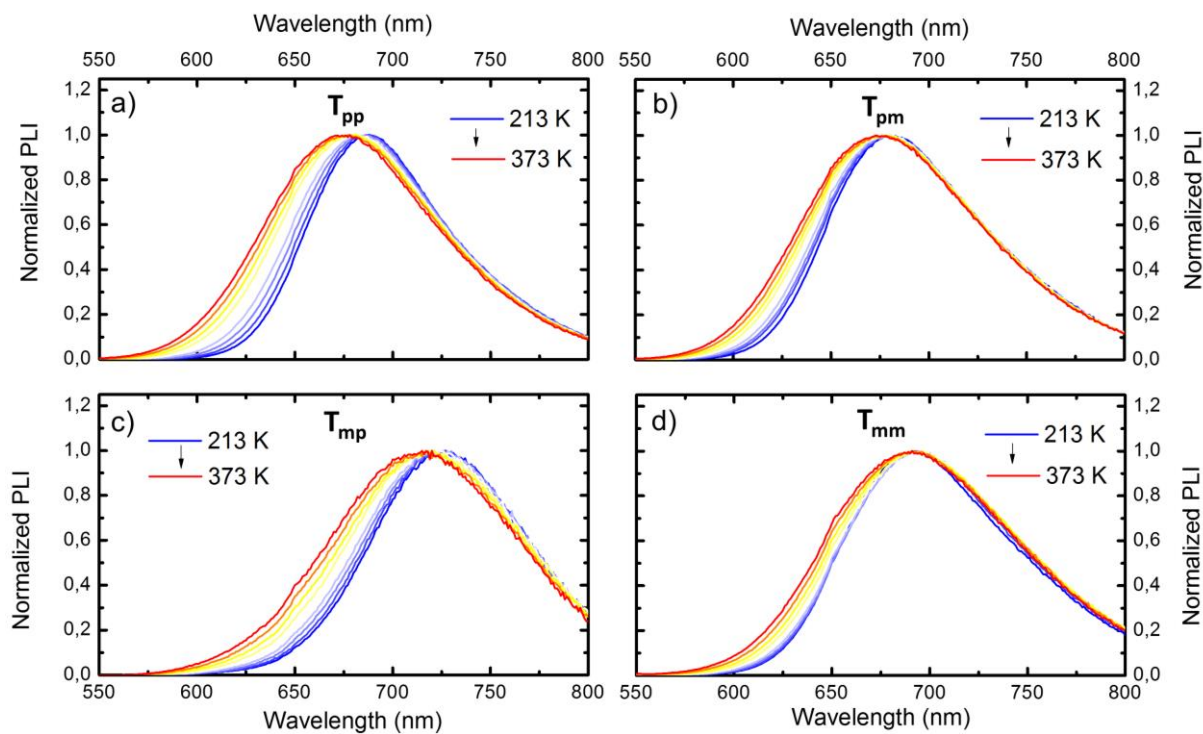
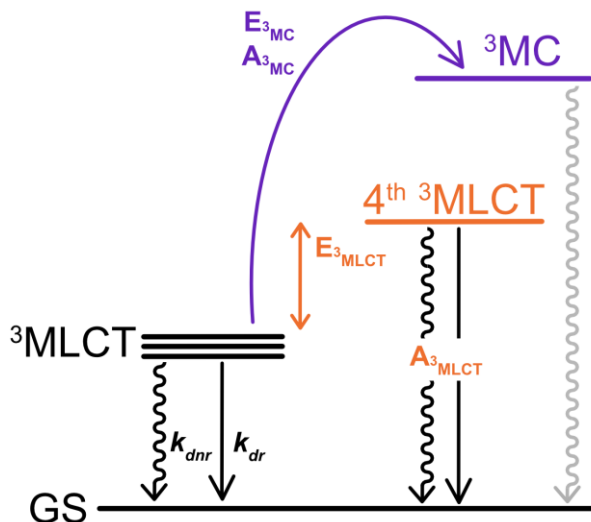


Figure 5: Normalized photoluminescence as a function of temperature for T_{pp} (a), T_{pm} (b), T_{mp} (c) and T_{mm} (d) in argon purged butyronitrile.

The photophysical scheme of the parent mononuclear complex $[\text{Ru}(\text{bpy})_3]^{2+}$ is well established and was useful in interpreting the changes in excited-state lifetimes of the trinuclear complexes (**Scheme 2**).

[Ru(bpy)₃]²⁺-type complexes

$$\begin{array}{ll} E_{3MC} > 3000 \text{ cm}^{-1} & E_{3MLCT} = 300\text{-}1000 \text{ cm}^{-1} \\ A_{3MC} = 10^{12}\text{-}10^{14} \text{ s}^{-1} & A_{3MLCT} = 10^5\text{-}10^7 \text{ s}^{-1} \end{array}$$



Scheme 2: Photophysical scheme of [Ru(bpy)₃]²⁺-type complexes with a range of typical activation energies and pre-exponential factors.

The lowest ³MLCT excited-state of [Ru(bpy)₃]²⁺ consists of three closely lying ³MLCT states in thermal equilibrium which, at temperatures greater than 77 K, behave as a single state.^{66, 67} This lowest ³MLCT is deactivated by direct radiative and non-radiative process to the ground-state, as well as by thermally activated processes, such as the population of an upper lying (4th) ³MLCT and/or an upper lying metal-centered state (³MC).⁶⁸⁻⁷⁰ The observed changes in photoluminescence lifetimes (τ) for the trinuclear complexes were fit according to **equations 2** or **3**, depending on whether deactivation through the ³MC was observed, in addition to the deactivation via the upper lying ³MLCT.^{68, 71-73}

$$1/\tau = k_{dr} + k_{dnr} + k_{3MLCT} = k_{dr} + k_{dnr} + A_{3MLCT} e^{-E_{3MLCT}/RT} \quad \text{Eq. 2}$$

$$1/\tau = k_{dr} + k_{dnr} + k_{3MLCT} + k_{3MC} = k_{dr} + k_{dnr} + A_{3MLCT} e^{-E_{3MLCT}/RT} + A_{3MC} e^{-E_{3MC}/RT} \quad \text{Eq. 3}$$

In these equations, k_{dr} and k_{dnr} are the activationless direct radiative and non-radiative decay rate constants from the three closely lying ³MLCT excited states to the ground state,

considered to remain constant over the range of temperatures studied.⁶⁸ The three lowest ³MLCT excited states were in thermal equilibrium with the 4th upper lying ³MLCT excited state (³MLCT_{lowest} ↔ ³MLCT_{upper}). Deactivation through the reversible thermal population of the 4th upper lying ³MLCT is associated to the rate constant k_{3MLCT} , with a small activation energy ($E_{3MLCT} \sim 300\text{-}1000\text{ cm}^{-1}$) and small pre-exponential factor ($A_{3MLCT} \sim 10^5\text{-}10^7\text{ s}^{-1}$).^{68, 74} The energy of activation E_{3MLCT} corresponded to the energy gap between these states (**Scheme 2**) and the pre-exponential factor A_{3MLCT} , corresponded to the sum of the radiative and non-radiative decay rate constants from the upper-lying ³MLCT excited-state to the ground state.^{9, 75, 68} In **equation 3**, deactivation through the ³MC has been considered, which comes from the reversible or irreversible⁷⁵ thermal population of the ³MC excited state. This population was associated to the rate constant k_{3MC} , and exhibited a large activation energy ($E_{3MC} > 3000\text{ cm}^{-1}$) and pre-exponential factor ($A_{3MC} \sim 10^{12}\text{-}10^{14}\text{ s}^{-1}$).^{7, 72} For this pathway, the pre-exponential factor A_{3MC} was associated with high frequency vibrations whose activation led to the ³MLCT-³MC surface crossing and E_{3MC} represents therefore the activation energy to reach the surface crossing point. The parameters extracted from **equations 2** and **3** are gathered in **Table 5** and the corresponding excited-state deactivation rate constants for each trinuclear complex are shown in **Figure 6**, as a function of temperature.

Table 5. Kinetic parameters for the excited-state decay in argon purged butyronitrile.

Complex	$k_{dr} + k_{dnr}\text{ (s}^{-1}\text{)}$	$A_{3MLCT}\text{ (s}^{-1}\text{)}$	$E_{3MLCT}\text{ (cm}^{-1}\text{)}$	$A_{3MC}\text{ (s}^{-1}\text{)}$	$E_{3MC}\text{ (cm}^{-1}\text{)}$
T_{pp} ^[a]	$3.5 \cdot 10^5$	$5.1 \cdot 10^6$	750	$1.2 \cdot 10^{13}$	4720
T_{pm} ^[a]	$6.3 \cdot 10^5$	$4.7 \cdot 10^6$	390	$1.5 \cdot 10^{13}$	4540
T_{mp} ^[a]	$5.5 \cdot 10^6$	$8.4 \cdot 10^7$	960	[d]	[d]
T_{nm} ^[b]	$1.8 \cdot 10^6$	$1.2 \cdot 10^7$	510	[d]	[d]
[Ru(bpy) ₃] ²⁺ ^[c]	$4.1 \cdot 10^5$	$2.6 \cdot 10^6$	500	$1.1 \cdot 10^{13}$	3460

[a] Temperature range for the fitting was 213-373 K. [b] Temperature range for the fitting was 253-373 K. [c] from reference ¹⁰. [d] Not observed.

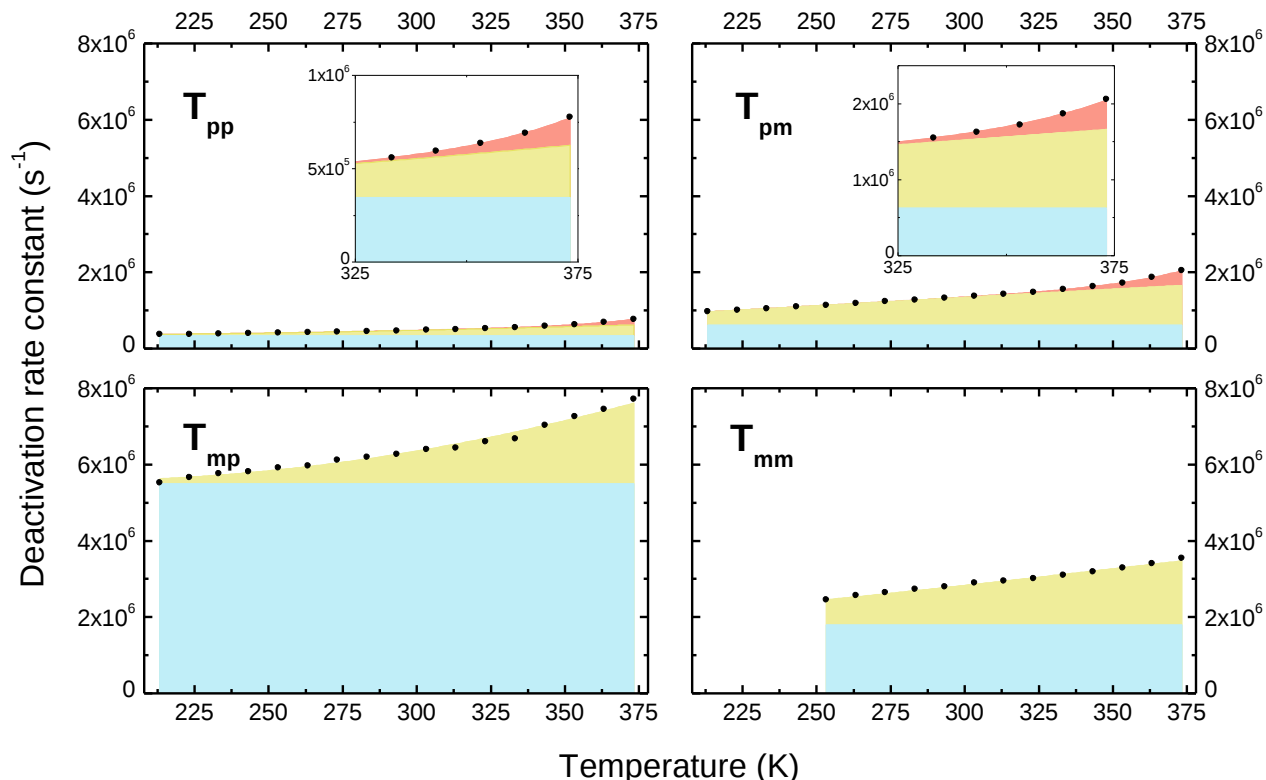


Figure 6: Excited-state deactivation rate constants for the trinuclear complexes: (blue) direct radiative and non-radiative rate constants ($k_{dr} + k_{dnr}$), (yellow) thermally activated deactivation via the upper lying ³MLCT (k_{3MLCT}), (red) thermally activated deactivation pathway via the upper lying ³MC (k_{3MC}) and (dot) experimental data.

Within the trinuclear complexes, an energy transfer occurred from the peripheral ruthenium subunits to the central ruthenium subunits, which was followed by photoluminescence from a ³MLCT excited-state centered on the central ruthenium and the central bipyridine part of the bridging ligand.

Deactivation via an upper lying ³MLCT excited state (k_{3MLCT}) was observed for all trinuclear complexes over the whole range of temperatures investigated. The deactivation rate constant A_{3MLCT} from the upper-lying ³MLCT was one order of magnitude faster than from the lowest ³MLCT ($k_{dr} + k_{dnr}$) as is usually observed for this class of compounds ($A_{3MLCT}/k_{dr} + k_{dnr} \approx 10$).⁶⁸ The upper-lying ³MLCT excited state exhibited smaller deactivation rate constant for T_{pp} and T_{pm} than for T_{mp} and T_{mm} (Table 5). Surprisingly, the energy gap between the two ³MLCT excited states was more influenced by the substitution of the *peripheral* bipyridines of the bridging ligand.

When the latter were *para*-substituted (**T_{pp}** and **T_{mp}**), the energy gap (E_{3MLCT}) was approximately twice as large as for *meta*-substitution (**T_{pm}** and **T_{mm}**). Therefore, complexes with *para*-substituted peripheral bipyridines (**T_{pp}**, **T_{mp}**) underwent proportionally less deactivation through the upper 3MLCT than **T_{pm}**, **T_{mm}**. Both effects combined, resulted in a significantly lower k_{3MLCT} for **T_{pp}** in comparison to the other trinuclear complexes (**Figure 6**).

For the complexes with the *central* bipyridine substituted in the *para* position (**T_{pp}**, **T_{pm}**) an additional deactivation pathway via the 3MC excited state was observed, but it was only significant at temperatures larger than 350 K (**Figure 6**).⁷⁵ The pre-exponential factor was similar ($A_{3MC} \approx 10^{13} \text{ s}^{-1}$) for the two complexes and the activation energy (E_{3MC}) for **T_{pm}** was around 200 cm^{-1} smaller than that of **T_{pp}**. It is well-known that a stabilization of the lowest 3MLCT excited-state usually results in an increase of the energy gap (E_{3MC}).^{9, 76, 77} This explained our inability to observe deactivation through the 3MC excited-state for **T_{mp}** and **T_{mm}** as their lowest 3MLCT excited states were more stabilized. Thermal population of the 3MC excited-state usually leads to non-radiative deactivation to the ground state, as well as ligand loss.⁷⁸⁻⁸² For all the trinuclear complexes, the absence of deactivation through the 3MC excited state at room temperature induced a much higher photostability in comparison to $[\text{Ru}(\text{bpy})_3]^{2+}$.^{20, 71, 76, 83} For all trinuclear complexes, the activationless k_{dr} and k_{dnr} accounted for at least half of the excited-state decay at 293 K (**Figure 6**). The trinuclear complexes were only moderately or weakly photoluminescent at room temperature, such that $k_{dr} + k_{dnr} \approx k_{dnr}$. Therefore, k_{dnr} controls the excited-state lifetimes as confirmed by the determined value of k_{dnr} (*vide infra*, **Table 6 and S5**). The values of k_{dnr} were investigated by the energy-gap law in its simplest form (**equation 4**).^{15, 17, 18, 53, 84-86}

$$\ln(k_{dnr}) = c - \frac{\gamma E_0}{\hbar \omega_M} \quad \text{Eq. 4}$$

$$\gamma = \ln\left(\frac{E_0}{S_M \hbar \omega_M}\right) - 1 \quad \text{Eq. 5}$$

Table 6. Luminescence quantum yield for the different $^3\text{MLCT}$ excited states of each trinuclear complexes.

Complex	$\Phi ^3\text{MLCT}$ ($k_{dr}/k_{dr} + k_{dnr}$)	k_{dr} (s^{-1})	k_{dnr} (s^{-1})	$\Phi ^3\text{MLCT}$ Thermally activated ($A_{^3\text{MLCT radiative}} / A_{^3\text{MLCT}}$)
T_{pp}	0.13 ± 0.01	$4.6 \cdot 10^4$	$3.0 \cdot 10^5$	0.07 ± 0.01
T_{pm}	0.065 ± 0.005	$4.1 \cdot 10^4$	$5.9 \cdot 10^5$	0.030 ± 0.005
T_{mp}	0.010 ± 0.001	$5.6 \cdot 10^4$	$5.4 \cdot 10^6$	0.004 ± 0.002
T_{mm}	0.020 ± 0.002	$3.6 \cdot 10^4$	$1.8 \cdot 10^6$	0.004 ± 0.002

The variations of $\ln(k_{dnr})$ with the photoluminescence maxima in butyronitrile solution at 213 K are presented in **Figure 7** for each trinuclear complexes and the two related dinuclear complexes. Here, the PL_{max} at 213 K was used to estimate the energy gap in solution and to minimize contributions from population and photoluminescence of the upper-lying $^3\text{MLCT}$ occurring at higher temperatures.⁸⁴ A linear correlation between $\ln(k_{dnr})$ and PL_{max} was obtained for **T_{pm}**, **T_{mp}**, **T_{mm}** and **D_m**, as suggested by **equation 4**. This agreed well with previous studies of series of Ru(II) and Os(II) complexes, where the energy gap was varied by changing the non-chromophoric ligand (not implicated in emission process).^{14, 53, 58, 84, 87} In this study, the chromophoric ligand was instead varied and such a correlation was therefore interesting, as it suggested that for the four complexes, the Huang-Rhys factor (S_M) decreased linearly with the energy gap. As a consequence, γ remained constant (**Equation 5**), and $\hbar\omega_M$ as well as the vibronically induced electronic coupling were essentially invariant.^{14, 53, 84, 86, 87}

T_{pp} and **D_p** did not show any correlation with the other complexes. Franck-Condon line-shape analysis of the photoluminescence spectra at 77 K revealed that both **T_{pp}** and **D_p** possessed significantly more delocalized excited states than the related dinuclear and trinuclear complexes, as was underlined by their low Huang-Rhys factors (S_M).¹⁰ In fluid solution, at higher temperatures, the same observation was expected to hold and lower S_M values would result in

smaller k_{dnr} , as revealed by **equations 4** and **5**. This was previously reported in mononuclear^{15, 18} and polynuclear^{17, 19, 22} complexes.

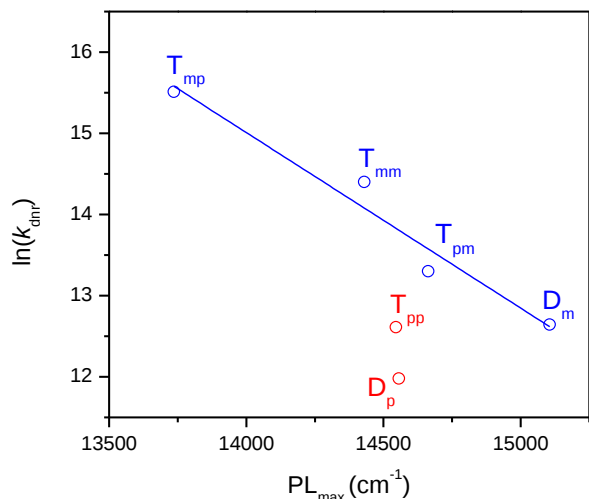


Figure 7: Energy-gap law plot of $\ln(k_{dnr})$ versus PL_{max} measured at 213 K in butyronitrile solution. The blue line represents the linear fit for T_{pm} , T_{mp} , T_{mm} and D_m according to **equation 4** with a slope of (-500 cm^{-1}) .

To sum up, the careful study of the different deactivation pathways from the lowest ³MLCT excited-states for the series of trinuclear complexes highlighted specific observations. For T_{pm} , T_{mp} and T_{mm} , k_{dnr} was governed, as expected, by the energy-gap law where a decrease in photoluminescence energy was accompanied by an increase in k_{dnr} . We propose that the excited state of T_{pp} is further delocalized on the bridging ligand, compared to the three other trinuclear complexes, as evidenced by its lowest S_M value. This further significantly decreased γ (**Equation 5**) and consequently k_{dnr} (**Equation 4**). The *para*-substitution of the *peripheral* bipyridines of the bridging ligand (T_{pp} , T_{mp}) resulted in a larger energy gap between the lower and upper ³MLCT, which in turn decreased the relative kinetic rate of deactivation via the upper ³MLCT compared to the corresponding *meta*-substituted complexes (T_{pm} , T_{mm}). The stabilization of the lowest ³MLCT increased the activation energy to the ³MC which made population of that state virtually absent at 293 K for all complexes (**Figure 8**).

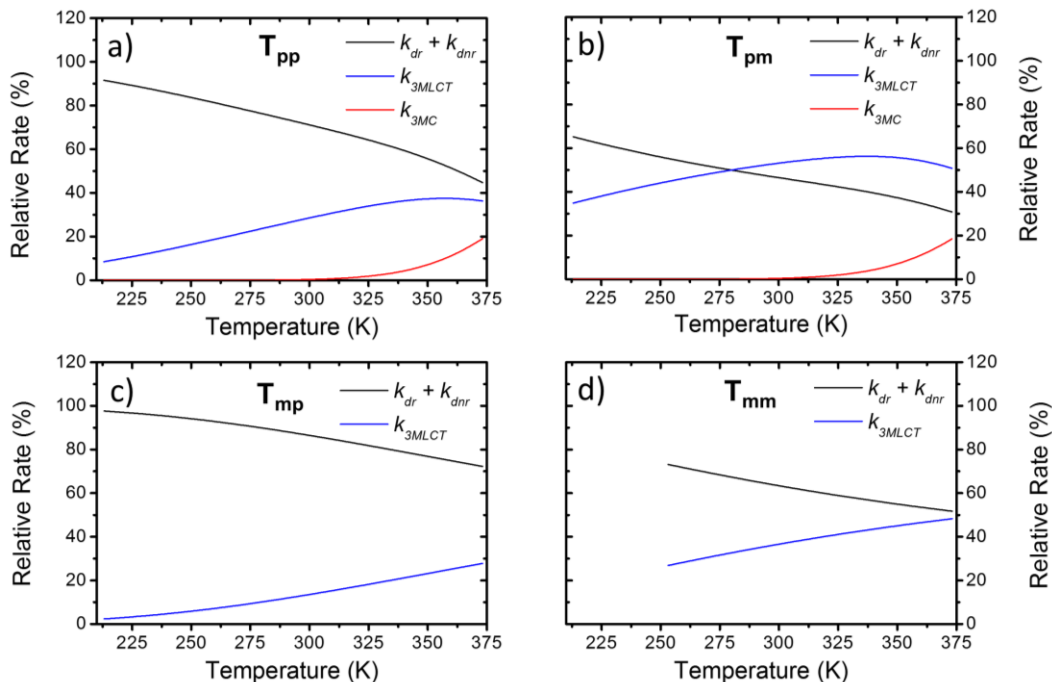


Figure 8: Relative rates of deactivation of the lowest $^3\text{MLCT}$ excited state of T_{pp} (a), T_{pm} (b), T_{mp} (c) and T_{mm} (d) via different pathways. (Black) direct radiative and nonradiative deactivation to the ground state, (blue) thermally activated deactivation through the upper lying $^3\text{MLCT}$ excited state and (red) thermally activated deactivation through the ^3MC excited state.

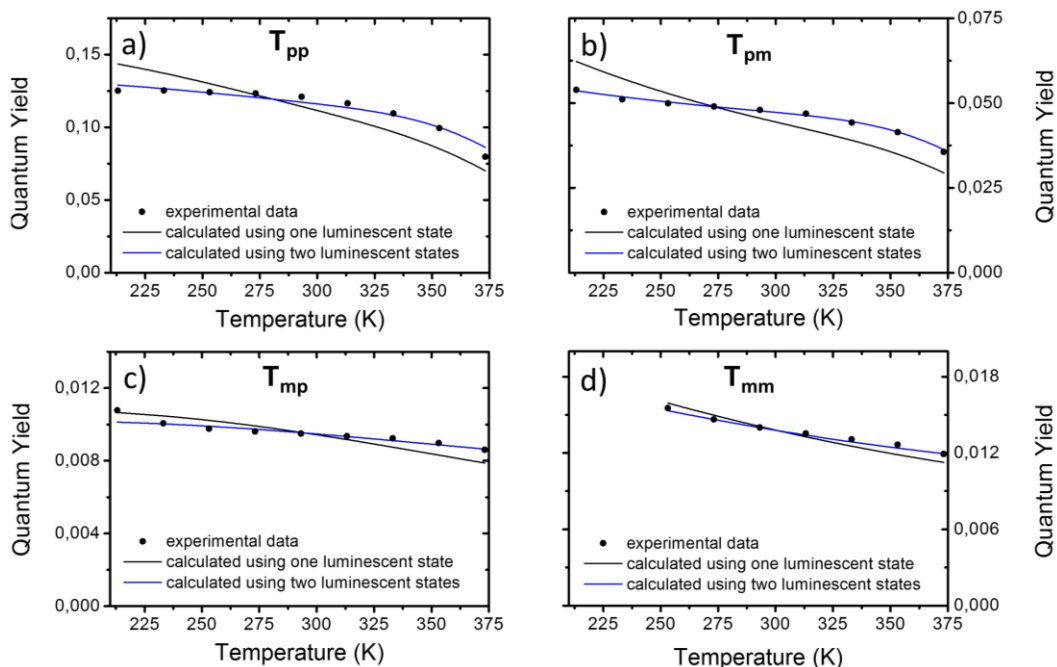


Figure 9: Measured and calculated quantum yields of T_{pp} (a), T_{pm} (b), T_{mp} (c) and T_{mm} (d) as a function of temperature. The black dots represent the experimentally determined photoluminescence quantum yields at various temperatures. The black line represents the calculated photoluminescence quantum yields only if the lowest $^3\text{MLCT}$ excited-state were luminescent. The blue line represents the calculated quantum yields if the lowest and the thermally activated $^3\text{MLCT}$ excited state were luminescent.

The normalized steady-state photoluminescence spectra of all trinuclear complexes exhibited a broadening of the photoluminescence band toward higher energy upon increased temperature. This broadening was accompanied by a blue shift of the photoluminescence maxima for **T_{pp}** and **T_{mp}** (**Figure 5a-d**). Usually, for Ru(II) polypyridyl complexes, neither significant shift of the photoluminescence maxima or photoluminescence band broadening are observed over the whole range of temperatures studied.^{75, 88, 89} For all the complexes, a decrease in the excited-state lifetimes and photoluminescence quantum yields was observed when the temperature increased. However, this decrease was less pronounced for the photoluminescence quantum yield (**Figure 4a-d**). This can originate from an activated deactivation pathway possessing significant contribution of radiative deactivation. The upper-lying ³MLCT excited state is a prime candidate for displaying radiative deactivation to the ground state, as previously described.^{10, 69, 89-93} Fitting the measured photoluminescence quantum yield at various temperatures ($\phi(T)$) to **Equations 6** or **7** allowed to determine the deactivation radiative rate constants either for the lowest ³MLCT excited state or for the lowest and the upper ³MLCT excited-states.^{10, 66}

$$\phi(T) = \frac{k_{dr}}{k_{dr} + k_{dnr} + A_{3MLCT}e^{-E_{3MLCT}/RT} + A_{3MC}e^{-E_{3MC}/RT}} \quad \text{Eq. 6}$$

$$\phi(T) = \frac{k_{dr} + A_{3MLCT \text{ radiative}}e^{-E_{3MLCT}/RT}}{k_{dr} + k_{dnr} + A_{3MLCT}e^{-E_{3MLCT}/RT} + A_{3MC}e^{-E_{3MC}/RT}} \quad \text{Eq. 7}$$

The parameters required for the fitting ($k_{dr} + k_{dnr}$, A_{3MLCT} , E_{3MLCT} , A_{3MC} and E_{3MC}) are gathered in **Table 5**. In the case where only the lowest ³MLCT exhibited significant radiative deactivation, the photoluminescence quantum yield was fit using **Equation 6** which allowed to determine k_{dr} . **Equation 7** was used to determine k_{dr} and $A_{3MLCT \text{ radiative}}$, when both the lower- and upper-lying ³MLCT excited state exhibited significant radiative deactivation. In this equation, $A_{3MLCT \text{ radiative}}$ corresponds to the radiative deactivation rate constant of the upper lying ³MLCT excited state to the ground state. For all trinuclear complexes, the fitting of ϕ_{PL} as function of temperature was

significantly improved when radiative deactivation from both the upper and lower $^3\text{MLCT}$ excited states were considered (**Figure 9a-d**). Photoluminescence originating from the upper $^3\text{MLCT}$ occurred at higher energy than from the lowest $^3\text{MLCT}$, inducing a photoluminescence band broadening for all complexes when the temperature was increased (**Figures 4-5**).^{89, 90, 93} The significant blue shift of the photoluminescence maxima of **T_{pp}** and **T_{mp}** originated from the larger energy gap between the lower and upper lying $^3\text{MLCT}$ excited states ($> 700\text{ cm}^{-1}$) (**Table 5**). The photoluminescence quantum yields of the lowest $^3\text{MLCT}$ ($k_{dr}/(k_{dr} + k_{dnr})$) and upper-lying $^3\text{MLCT}$ ($A_{3\text{MLCT radiative}}/A_{3\text{MLCT}}$) were determined and the results are gathered in **Table 6**. For all complexes, the photoluminescence quantum yield of the upper-lying $^3\text{MLCT}$ excited state was smaller than the lower-lying $^3\text{MLCT}$, in agreement with the observed decrease in photoluminescence quantum yield upon temperature increased (**Figure 4a-d**). An approximation of the energy difference between the photoluminescence maxima of the upper and lower $^3\text{MLCT}$ was determined by deconvolution of the photoluminescence spectra of **T_{pp}** and **T_{mp}** at 213K and 373 K (**Figure S57-S58**). The energy differences were respectively 1000 cm^{-1} for **T_{pp}** and 990 cm^{-1} for **T_{mp}**, in reasonable agreement with the energy gap obtained from the analysis of the kinetic data ($E_{3\text{MLCT}} = 750\text{ cm}^{-1}$ for **T_{pp}** and $E_{3\text{MLCT}} = 960\text{ cm}^{-1}$ for **T_{mp}**).^{69, 91, 92}

CONCLUSIONS

The use of sexi-pyridine bridging ligands with non-equivalent chelating moieties induced, for all trinuclear complexes, convergent energy transfers from the two peripheral Ru(II) centers to the central Ru(II) moieties. The structures of the bridging ligands substantially influenced the photophysical properties of the resulting complexes. For the ground-state absorption properties, a *para* connection between the 2,2'-bipyridine chelating moieties of the bridging ligand yielded a bathochromic shift of the MLCT absorption bands in the visible part of the spectrum, while a *meta*

connection induced a broadening of the LC transitions in the UV region. The excited-state properties were also strongly influenced by the bridging ligand structures, with important changes in the excited-state lifetimes. An in-depth study of the deactivation pathways as a function of temperature yielded better insight into the excited-state behavior deactivation pathways for each trinuclear complex. It was evidenced that k_{dnr} exhibited the strongest changes among the series and dominated the other deactivation pathways. For **T_{pm}**, **T_{mm}** and **T_{mp}**, k_{dnr} increased as the energy gap between the lowest ³MLCT excited state and the ground state decreased. We propose that the smaller k_{dnr} value for **T_{pp}** (smaller than expected from the energy gap law) originated from a more delocalized excited state over the whole bridging ligand, decreasing the displacement change and vibrational overlap, and consequently k_{dnr} .¹⁷ The direct radiative rate constant (k_{dr}) remained similar for the trinuclear series. The excited states of the four trinuclear complexes were in thermal equilibrium with an upper-lying ³MLCT excited state over the range of temperature studied. *Para*-substitution of the peripheral 2,2'-bipyridines (**T_{pp}**, **T_{mp}**) increased E_{3MLCT} between the lower and upper ³MLCT compared to the *meta*-substituted complexes (**T_{pm}**, **T_{mm}**), resulting in a decrease of the relative rate of deactivation via the upper ³MLCT ($k_{3MLCT} / \sum_i k_i$). For all complexes, deactivation via the ³MC excited-state was absent at room temperature. Indeed, stabilization of the lowest ³MLCT among the series resulted in the expected increase of the activation energy (E_{3MC}) for the ³MLCT-³MC surface crossing. Unexpected radiative deactivation from the upper lying ³MLCT excited state occurred in all trinuclear complexes reported herein. The larger energy gap between the lower and upper ³MLCT (E_{3MLCT}) for **T_{pp}** and **T_{mp}** induced a significant blue shift of the photoluminescence maxima upon temperature increase. It should be mentioned that photoluminescence arising from more than one ³MLCT excited-state is likely more present in the

literature than actually reported,^{10, 66, 69, 89-92} as time-resolved photoluminescence experiments have not always been accompanied by steady-state photoluminescence experiments.

All in all, this study underlines the striking influence of the bridging ligand geometry in polynuclear complexes. The connection in *para* position for both central and peripheral 2,2'-bipyridine of the bridging ligand, resulted in a complex, **T_{pp}**, that absorbs more visible light, has a longer-lived excited state and a higher photoluminescence quantum yield than the parent [Ru(bpy)₃]²⁺, despite having a red-shifted photoluminescence. The strategy of developing polynuclear complexes with a significantly delocalized excited state represents thus a promising strategy to obtain low energy absorber with long-lived excited states able to perform subsequent photo-triggered chemical reactions.

ASSOCIATED CONTENT

Supporting Information. Experimental section, ¹H NMR, ¹³C NMR, Mass spectrometry, Electrochemistry, Franck-Condon lineshape analysis, Variable temperature experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Any funds used to support the research of the manuscript should be placed here (per journal style).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

L. T.-G. is a postdoctoral researcher of the Fonds de la Recherche Scientifique – FNRS. S.C. and B.E. gratefully acknowledge the UCLouvain for financial support. The authors acknowledge Gerald J. Meyer for the scientific generosity and providing access to his equipment. Steady-State and time-resolved absorption and photoluminescence experiments were performed using instrumentation in the CHASE Instrumentation Facility established by the Center for Hybrid Approaches in Solar Energy to Liquid Fuels, CHASE, an Energy Innovation Hub funded by the US Department of Energy, Office of Basic Energy Sciences, Office of Science, under award number DE-SC0021173. The UMONS lab is grateful to the F.R.S.-FNRS for financial support in the acquisition of the Waters Synapt G2-Si mass spectrometer. QD is a FNRS research fellow.

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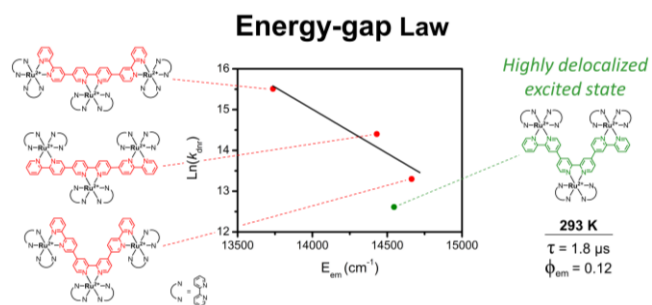
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Synopsis: A detailed photophysical study of trinuclear complexes was performed using steady-state and time-resolved photoluminescence measurements at variable temperature as well as nanosecond transient absorption spectroscopy. The results were compared with the prototypical $[\text{Ru}(\text{bpy})_3]^{2+}$.