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, whereas the 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 3MLCT 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 the para position for both central and peripheral 2,2′-bipyridines of the bridging ligand resulted in a trinuclear complex (T_{PP}) that absorbed more visible light, had a longer-lived excited state, and had a higher photoluminescence quantum yield than the parent [Ru(bpy)]_{2+}, despite its red-shifted photoluminescence. This behavior was attributed to the presence of a highly delocalized excited state for absorption by [Ru(bpy)_{3}]^{2+} predominantly occurs in the high thermal equilibrium with an upper-lying 3MLCT 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 the para position for both central and peripheral 2,2′-bipyridines of the bridging ligand resulted in a trinuclear complex (T_{PP}) that absorbed more visible light, had a longer-lived excited state, and had a higher photoluminescence quantum yield than the parent [Ru(bpy)]_{2+}, despite its red-shifted photoluminescence. This behavior was attributed to the presence of a highly delocalized excited state for absorption by [Ru(bpy)_{3}]^{2+}.

INTRODUCTION

For decades, the interest in the photophysical and photochemical properties of [Ru(bpy)]_{2+} and its derivatives has remained unaltered, and [Ru(bpy)]_{2+}-type complexes have found many applications in photocatalysis, artificial photosynthesis, sensing, nanoscale machines, etc. Light absorption by [Ru(bpy)]_{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. 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. Therefore, polynuclear complexes are prime candidates to absorb light more efficiently at longer wavelengths than mononuclear [Ru(bpy)]_{2+}-type complexes. Moreover, the red-shifted photoluminescence is accompanied by a larger direct 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. 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}. Dinuclear Ru(II) complexes based on a ditopic bridging ligand were far more thoroughly investigated compared to trinuclear Ru(II) complexes based on a tritopic bridging ligand. Most of the trinuclear 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 and tritopic ligands with at least one chemically inequivalent binding site. In the latter case, although all Ru(II) centers have identical ancillary ligands, an efficient convergent energy transfer could be evidenced (molecular antenna). Surprisingly, in this category, most of the reported examples are based on tritopic ligands with terpyridine-type binding sites, whereas bipyridine-based tritopic bridging ligands remain scarcely studied.
In this study, different strategies for assembling three [Ru(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 positions for the central as well as for the peripheral bipyridine moieties, resulting in four regioisomeric, tritopic ligands (Scheme 1). For the 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.

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 play 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 and 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(PPh$_3$)$_4$] (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 positions for the central as well as for the peripheral bipyridine moieties, resulting in four regioisomeric, tritopic ligands (Scheme 1). For the 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.

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and central Ru(II) centers underwent simultaneous oxidation of a single three-electron oxidation wave at an identical potential for all 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 events were attributed to reductions of the bridging ligand, upon comparison with the parent complex [Ru(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 to a connection via the para ($4,4'$) position. 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 the 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 ($T_{mm}$), a smaller difference in redox potential between the first and the second reduction waves (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.

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.46 The intense absorption bands in the UV region were attributed to ligand-centered transitions,44 whereas the theoretical values were averaged over 250 candidate structures extracted from MD simulations. Errors correspond to standard deviations.

Table 2. Oxidation and Reduction Potentials (V vs Ag/AgCl)$^b$

<table>
<thead>
<tr>
<th>complex</th>
<th>$E_{1/2}^{(Ru(II)/II)} (V vs Ag/AgCl)$</th>
<th>$E_{1/2}^{(L^{(n-1)-})} (V vs Ag/AgCl)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{pp}$</td>
<td>+1.38</td>
<td>−0.93</td>
</tr>
<tr>
<td>$T_{pm}$</td>
<td>+1.38</td>
<td>−0.93</td>
</tr>
<tr>
<td>$T_{mp}$</td>
<td>+1.38</td>
<td>−0.78</td>
</tr>
<tr>
<td>$T_{mm}$</td>
<td>+1.38</td>
<td>−0.86</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$_2^+$</td>
<td>+1.30</td>
<td>−1.31</td>
</tr>
</tbody>
</table>

$^b$Cyclic voltammetry in acetonitrile. $^b$Differential pulse voltammetry in DMF. Redox potentials can be estimated vs NHE by adding 0.2 V.

Ground-State Properties. The electrochemical properties of the complexes were investigated by cyclic and differential pulse voltammetry (Figures S36 and 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 events were attributed to reductions of the bridging ligand, upon comparison with the parent complex [Ru(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 the 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 ($T_{mm}$), a smaller difference in redox potential between the first and the second reduction waves (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.

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.46 The intense absorption bands in the UV region were attributed to ligand-centered transitions,44 whereas the theoretical values were averaged over 250 candidate structures extracted from MD simulations. Errors correspond to standard deviations.

Table 1. Experimental and Theoretical Collisional Cross Sections Derived from TWIMS-MS Experiments and Molecular Dynamics Simulations, Respectively$^a$

<table>
<thead>
<tr>
<th>complex</th>
<th>experimental CCS ($\AA^2$)</th>
<th>theoretical CCS ($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{pp}$</td>
<td>370.2 ± 1.3</td>
<td>374.4 ± 3.4</td>
</tr>
<tr>
<td>$T_{pm}$</td>
<td>353.4 ± 0.6</td>
<td>361.8 ± 3.0</td>
</tr>
<tr>
<td>$T_{mp}$</td>
<td>391.1 ± 0.7</td>
<td>395.8 ± 2.8</td>
</tr>
<tr>
<td>$T_{mm}$</td>
<td>372.6 ± 1.1</td>
<td>379.2 ± 3.0</td>
</tr>
</tbody>
</table>

$^a$Experimental values are averaged over three separate experiments, whereas theoretical values are averaged over 250 candidate structures extracted from MD simulations. Errors correspond to standard deviations.
transitions at 450 nm were attributed to $^1$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 $^1$MLCT transition at 480 nm only involved the bridging ligands. A correlation between the energy of the most bathochromic distinct $^1$MLCT transition and the energy associated with the redox process ($\Delta E_{1/2} = E_{1/2}(\text{Ru}^{III/II}) - E_{1/2}(L/n)\lambda$), also known as spectroelectrochemical correlation, was observed for the $'$-substituted derivatives, $T_{pp}$ and $T_{nn}$ (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 $T_{mn}$, 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 a $^1$MLCT transition with moderate oscillator strength. As a result, the intensity of the $^1$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.

**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 (Figures 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 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 $^3$MLCT 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

### Table 3. Photophysical Properties of the Trinuclear Complexes and [Ru(bpy)$_3$]$^{2+}$

<table>
<thead>
<tr>
<th>complex</th>
<th>absorption $\lambda_{max}$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>luminescence</th>
<th>293 K$^a$</th>
<th>293 K$^b$</th>
<th>77 K$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{pp}$</td>
<td>459 (10100), 440 (36600), 288 (158800)</td>
<td>684</td>
<td>1815 (345)</td>
<td>0.121 (0.022)</td>
<td>6.7</td>
<td>0.5</td>
</tr>
<tr>
<td>$T_{nn}$</td>
<td>485 (31200), 442 (37800), 288 (188800)</td>
<td>684</td>
<td>623 (224)</td>
<td>0.048 (0.017)</td>
<td>7.7</td>
<td>1.5</td>
</tr>
<tr>
<td>$T_{mp}$</td>
<td>475 (42200), 450 (40800), 287 (171100)</td>
<td>721</td>
<td>298 (117)</td>
<td>0.0095 (0.0028)</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>$T_{mn}$</td>
<td>445 (29500), 326 (85200), 287 (166100)</td>
<td>698</td>
<td>312 (175)</td>
<td>0.014 (0.0089)</td>
<td>4.5</td>
<td>3.2</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>450 (12000), 287 (69400)</td>
<td>615</td>
<td>890 (170)</td>
<td>0.094 (0.018)</td>
<td>11.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$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%. $^d$[Ru(bpy)$_3$]$^{2+}$ in air-equilibrated acetonitrile used as reference ($\Phi_{PL} = 0.018$); uncertainties are estimated to be 10%. $^e$From ref 10.

**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 photoluminescence recorded at 77 K (Figures S45–S48) yielded better insight into the excited-state properties. The photoluminescence spectra were fit according to eq 1, where \( E_0 \) corresponds to the energy difference between the ground- and excited-state potential energy surfaces in their zeroth 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 states, \( \hbar \omega_M \) 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.

\[
I(\nu) = \sum_{i=0}^{\infty} \left( \frac{E_i - \nu_i \hbar \omega_M}{E_0} \right)^3 \frac{S_M}{4 \pi} \exp \left\{ -4 \ln 2 \left( \frac{\nu - E_0 + \nu_i \hbar \omega_M}{\Delta \nu_{1/2}^i} \right) \right\}
\]

(1)

Table 4. Fitting Parameters Obtained from the Franck–Condon Line-Shape Analysis

<table>
<thead>
<tr>
<th>complex</th>
<th>( E_0 ) (cm(^{-1}))</th>
<th>( \hbar \omega_M ) (cm(^{-1}))</th>
<th>( S_M )</th>
<th>fwhm (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{pp} )</td>
<td>15650</td>
<td>1170</td>
<td>0.33</td>
<td>1010</td>
</tr>
<tr>
<td>( T_{pm} )</td>
<td>15790</td>
<td>1190</td>
<td>0.46</td>
<td>990</td>
</tr>
<tr>
<td>( T_{mp} )</td>
<td>15140</td>
<td>1220</td>
<td>0.39</td>
<td>1160</td>
</tr>
<tr>
<td>( T_{mm} )</td>
<td>15820</td>
<td>1220</td>
<td>0.47</td>
<td>1020</td>
</tr>
</tbody>
</table>

\(^a\)At 77 K in butyronitrile rigid matrix; no parameters were constrained for the fitting calculations.

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.

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 the literature.54,55,53,56 Despite small differences in \( E_0 \) (\( \sim 15600–15800 \) cm\(^{-1}\)), \( T_{pp} \) exhibited a significantly smaller Huang–Rhys factor \( (S_M) \) than \( T_{pm} \) and \( T_{mm} \), indicating a more delocalized excited state in \( T_{pp} \).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. 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 \( T_{mp} \) 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. At 77 K, deactivation of the \(^3\)MLCT excited state via the activated pathways to the upper-lying \(^3\)MLCT and \(^3\)MC excited states was 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 \( (\tau_{pp} > \tau_{pm} > \tau_{mm}) \) for the three complexes with similar \( E_0 \) was attributed mainly to the variation in Huang–Rhys factors \( (S_M(T_{pp}) < S_M(T_{pm}) < S_M(T_{mm})) \), as \( k_{dnr} \) increases when \( S_M \) increases.18 The excited-state lifetime of \( T_{mp} \) was the shortest of all the trinuclear complexes, which was linked to its smaller \( E_0 \) value compared to the other complexes. The Englman–Jortner
energy-gap law\textsuperscript{11} states that, when the energy gap decreases ($E_0$), $k_{dnr}$ increases and hence the excited-state lifetime is shortened.\textsuperscript{14,58}

The change from a rigid matrix to a 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).\textsuperscript{14} At 293 K, the trinuclear complexes possessing a bridging ligand with a para-substituted central bipyridine ($T_{pp}$, $T_{pm}$) exhibited photoluminescence maxima at similar wavelengths. When the central bipyridine was meta-substituted ($T_{mp}$, $T_{mm}$), 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 rate constants ($k_r$) than $T_{mp}$ and $T_{mm}$, yet these variations remained moderate. The non-radiative deactivation rate constants ($k_{dnr}$), grouping the direct and activated deactivation pathways ($k_{dnr}$, $k_{MLCT}$, $k_{MC}$), exhibited a more contrasting behavior among the complexes.

For all trinuclear complexes, a correlation between the photoluminescence maxima at 293 K and the $\Delta E_{1/2} = \Delta E_{1/2} = E_{1/2} (\text{Ru}^{3+}/\text{II}) - E_{1/2} (\text{L}^{n+}/n-1)$ 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 the lowest energy-gap law\textsuperscript{11} states that, when the energy gap decreases ($E_0$), $k_{dnr}$ increases and hence the excited-state lifetime is shortened.\textsuperscript{14,58}

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.

Nanosecond transient absorption spectra of the trinuclear complexes 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 steady-state photoluminescence measurements allowed identifying the different deactivation pathways from the lowest $3^1\text{MLCT}$ excited state and the corresponding deactivation kinetic rate constants. Second, temperature dependent steady-state photoluminescence measurements, and more precisely...
photoluminescence quantum yields, allowed identifying the pathways exhibiting radiative deactivation. The observed changes in the photoluminescence lifetimes and quantum yields for each trinuclear complex are shown in Figures 4 and 5.

The photophysical scheme of the parent mononuclear complex [Ru(bpy)₃]²⁺ is well established and was useful in interpreting the changes in excited-state lifetimes of the trinuclear complexes (Scheme 2).

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. This lowest 3MLCT is deactivated by a 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). The observed changes in photoluminescence lifetimes (τ) for the trinuclear complexes were fit according to eq 2 or 3, depending on whether deactivation through the 3MC was observed, in addition to the deactivation via the upper-lying 3MLCT.

\[
\frac{1}{\tau} = k_{dr} + k_{3MLCT} = k_{dr} + k_{3MC} e^{E_{3MC}/RT}
\]

(2)

\[
\frac{1}{\tau} = k_{dr} + k_{3MLCT} + k_{3MC}
\]

(3)

In these equations, \(k_{dr}\) and \(k_{3MC}\) 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. The three lowest 1MLCT excited states were in thermal equilibrium with the 4th upper-lying 3MLCT excited state (1MLCT\textsubscript{lowest} \rightarrow 3MLCT\textsubscript{upper}). Deactivation through the reversible thermal population of the 4th upper-lying 1MLCT is associated with the rate constant \(k_{3MLCT}\), with a small activation energy (\(E_{3MLCT} \approx 300-1000 \text{ cm}^{-1}\)) and small pre-exponential factor (\(A_{3MLCT} \sim 10^5-10^7 \text{ s}^{-1}\)). 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. In eq 3, deactivation through the 3MC has been considered, which comes from the reversible or irreversible thermal population of the 3MC excited state. This population was associated with the rate constant \(k_{3MC}\) and exhibited a large activation energy (\(E_{3MC} > 3000 \text{ cm}^{-1}\)) and pre-exponential factor (\(A_{3MC} \sim 10^{12-10^{14}} \text{ s}^{-1}\)). For this pathway, the pre-exponential factor \(A_{3MC}\) was associated with high frequency vibrations whose activation led to the
Table 5. Kinetic Parameters for the Excited-State Decay in Argon Purged Butyronitrile

<table>
<thead>
<tr>
<th>complex</th>
<th>$k_{dr} + k_{dnr}$ (s$^{-1}$)</th>
<th>$\Phi_{\text{MLCT}}$ (s$^{-1}$)</th>
<th>$E_{\text{MLCT}}$ (cm$^{-1}$)</th>
<th>$A_{\text{MC}}$ (s$^{-1}$)</th>
<th>$E_{\text{MC}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{pp}$</td>
<td>$3.5 \times 10^{4}$</td>
<td>$5.1 \times 10^{6}$</td>
<td>750</td>
<td>$1.2 \times 10^{13}$</td>
<td>4720</td>
</tr>
<tr>
<td>$T_{pm}$</td>
<td>$6.3 \times 10^{4}$</td>
<td>$4.7 \times 10^{6}$</td>
<td>390</td>
<td>$1.5 \times 10^{13}$</td>
<td>4540</td>
</tr>
<tr>
<td>$T_{mp}$</td>
<td>$5.5 \times 10^{6}$</td>
<td>$8.4 \times 10^{7}$</td>
<td>960</td>
<td>$d$</td>
<td>$d$</td>
</tr>
<tr>
<td>$T_{mm}$</td>
<td>$1.8 \times 10^{6}$</td>
<td>$1.2 \times 10^{7}$</td>
<td>510</td>
<td>$d$</td>
<td>$d$</td>
</tr>
<tr>
<td>$[\text{Ru(bpy)}_{3}]^{2+}$</td>
<td>$4.1 \times 10^{5}$</td>
<td>$2.6 \times 10^{6}$</td>
<td>500</td>
<td>$1.1 \times 10^{13}$</td>
<td>3460</td>
</tr>
</tbody>
</table>

$^a$Temperature range for the fitting was 213–373 K. $^b$Temperature range for the fitting was 253–373 K. $^c$From ref 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 $3\text{MLCT}$ excited state centered on the central ruthenium subunits, which was followed by photoluminescence from a $3\text{MC}$ excited state, (red) thermally activated deactivation pathway via the upper-lying $3\text{MC}$ ($k_{\text{MC}}$) and (dot) experimental data.

Table 6. Luminescence Quantum Yield for the Different $3\text{MLCT}$ Excited States of Each Trinuclear Complex

<table>
<thead>
<tr>
<th>complex</th>
<th>$\Phi$ $3\text{MLCT}$ ($k_{dr}/k_{dr} + k_{dnr}$)</th>
<th>$k_{dr}$ (s$^{-1}$)</th>
<th>$k_{dnr}$ (s$^{-1}$)</th>
<th>$\Phi$ $3\text{MC}$ thermally activated ($A_{3\text{MC}}/A_{3\text{MC}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{pp}$</td>
<td>0.13 $\pm$ 0.01</td>
<td>$4.6 \times 10^{4}$</td>
<td>$3.0 \times 10^{5}$</td>
<td>0.07 $\pm$ 0.01</td>
</tr>
<tr>
<td>$T_{pm}$</td>
<td>0.065 $\pm$ 0.005</td>
<td>$4.1 \times 10^{4}$</td>
<td>$5.9 \times 10^{5}$</td>
<td>0.030 $\pm$ 0.005</td>
</tr>
<tr>
<td>$T_{mp}$</td>
<td>0.010 $\pm$ 0.001</td>
<td>$5.6 \times 10^{4}$</td>
<td>$5.4 \times 10^{6}$</td>
<td>0.004 $\pm$ 0.002</td>
</tr>
<tr>
<td>$T_{mm}$</td>
<td>0.020 $\pm$ 0.002</td>
<td>$3.6 \times 10^{4}$</td>
<td>$1.8 \times 10^{6}$</td>
<td>0.004 $\pm$ 0.002</td>
</tr>
</tbody>
</table>

$3\text{MLCT}-3\text{MC}$ surface crossing and $E_{3\text{MC}}$ represents therefore the activation energy to reach the surface crossing point. The parameters extracted from eqs 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.

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 $3\text{MLCT}$ excited state centered on the central ruthenium and the central bipyridine part of the bridging ligand.

Deactivation via an upper-lying $3\text{MLCT}$ excited state ($k_{3\text{MLCT}}$) was observed for all trinuclear complexes over the whole range of temperatures investigated. The deactivation rate constant $A_{3\text{MLCT}}$ from the upper-lying $3\text{MLCT}$ was 1 order of magnitude faster than that from the lowest $3\text{MLCT}$ ($k_{dr} + k_{dnr}$) as is usually observed for this class of compounds ($A_{3\text{MLCT}}/k_{dr} + k_{dnr} \approx 10$). The upper-lying $3\text{MLCT}$ excited state exhibited a 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 $3\text{MLCT}$ 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 ($E_{3\text{MC}}$) was approximately twice as large as that for meta substitution ($T_{pm}$ and $T_{mm}$). Therefore, complexes with para-substituted peripheral bipyridines ($T_{pp}$ and $T_{mp}$) underwent proportionally less deactivation through the upper $3\text{MC}$ than $T_{pm}$ and $T_{mm}$. Both effects combined resulted in a significantly lower $k_{3\text{MC}}$ 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 $3\text{MC}$ excited state was observed, but it was only significant at temperatures higher than 350 K (Figure 6). The pre-exponential factor was similar ($A_{3\text{MC}} \approx 10^{13}$ s$^{-1}$) for the two complexes, and the activation energy ($E_{3\text{MC}}$) for $T_{pm}$ was around 200 cm$^{-1}$ smaller than that of $T_{pp}$. It is well-known that a stabilization of the lowest $3\text{MC}$ excited state usually results in an increase of the energy gap ($E_{3\text{MC}}$). This explained our inability to observe deactivation through
the $^{3}$MC excited state for $T_{pp}$ and $T_{mm}$ as their lowest $^{3}$MLCT excited states were more stabilized. Thermal population of the $^{3}$MC 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 $^{3}$MC excited state at room temperature induced a much higher photostability in comparison to [Ru(bpy)$_3$]$^{2+}$.$^{20,71,76,83}$ For all trinuclear complexes, the activationless $k_{dr}$ and $k_{d_{nr}}$ 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 $k_{dr} + k_{d_{nr}} \approx k_{d_{nr}}$. Therefore, $k_{d_{nr}}$ controls the excited-state lifetimes as confirmed by the determined value of $k_{d_{nr}}$ (vide infra, Tables 6 and S5). The values of $k_{d_{nr}}$ were investigated by the energy-gap law in its simplest form (eq 4).$^{15,17,18,53,84} - \gamma \frac{E_0}{\hbar \omega_{M}}$ \begin{equation} \ln(k_{d_{nr}}) = c - \gamma \frac{E_0}{\hbar \omega_{M}} \end{equation} \begin{equation} \gamma = \ln \left( \frac{E_0}{S_M \hbar \omega_{M}} \right) - 1 \end{equation} The variations of $\ln(k_{d_{nr}})$ with the photoluminescence maxima in butyronitrile solution at 213 K are presented in Figure 7 for each trinuclear complex and the two related dinuclear complexes. Here, the $P_{\max}$ at 213 K was used to estimate the energy gap in solution and to minimize contributions from population and photoluminescence of the ground state, as well as ligand loss. $^{78}$ A linear correlation between $\ln(k_{d_{nr}})$ and $P_{\max}$ was obtained for $T_{pm}$, $T_{mm}$, and $D_{mm}$ according to eq 4 with a slope of $(-500 \text{ cm}^{-1})$. $^{15}$ Figure 7. Energy-gap law plot of $\ln(k_{d_{nr}})$ versus $P_{\max}$ measured at 213 K in butyronitrile solution. The blue line represents the linear fit for $T_{pp}$, $T_{mp}$, $T_{mm}$, and $D_{mm}$ according to eq 4 with a slope of $(-500 \text{ cm}^{-1})$. $^{15}$

The upper-lying $^{3}$MLCT excited state usually leads to non-radiative deactivation to the upper $^{3}$MLCT compared to the corresponding $meta$-substituted complexes ($T_{pm}$, $T_{mm}$). The stabilization of the lowest $^{3}$MLCT increased the activation energy to the $^{3}$MC which made population of that state virtually absent at 293 K for all complexes (Figure 8).

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 8a–d). Usually, for Ru(II) polypyridyl complexes, neither a significant shift of the photoluminescence maxima or a photoluminescence band broadening is observed over the whole range of temperatures studied.$^{75,86,89}$ 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 8a–d). This can originate from an activated deactivation pathway possessing a significant contribution of radiative deactivation. The upper-lying $^{3}$MLCT excited state is a prime candidate for displaying radiative deactivation to the ground state, as previously described.$^{10,69,89-91}$ Fitting the measured photoluminescence quantum yield at various temperatures ($\phi(T)$) to eq 6 or 7 allowed to determine the deactivation radiative rate constants either for the lowest $^{3}$MLCT excited state or for the lowest and the upper $^{3}$MLCT excited states. $^{10,66}$ \begin{equation} \phi(T) = \frac{k_{dr}}{k_{dr} + k_{d_{nr}} + A_{\text{MLCT}} e^{-E_{\text{MC}}/RT} + A_{\text{MC}} e^{-E_{\text{MC}}/RT}} \end{equation} \begin{equation} \phi(T) = \frac{k_{dr}}{k_{dr} + A_{\text{MLCT}} e^{-E_{\text{MC}}/RT} + A_{\text{MC}} e^{-E_{\text{MC}}/RT}} \end{equation} The parameters required for the fitting ($k_{dr}$, $k_{d_{nr}}$, $A_{\text{MLCT}}$, $E_{\text{MLCT}}$, $A_{\text{MC}}$, and $E_{\text{MC}}$) are gathered in Table 5. In the case where only the lowest $^{3}$MLCT exhibited significant radiative
deactivation, the photoluminescence quantum yield was fit using eq 6 which allowed to determine $k_{dr}$. Equation 7 was used to determine $k_g$ and $A_{\text{MLCT radiative}}$ when both the lower- and upper-lying $^3\text{MLCT}$ excited state exhibited significant radiative deactivation. In this equation, $A_{\text{MLCT radiative}}$ corresponds to the radiative deactivation rate constant of the upper-lying $^3\text{MLCT}$ excited state to the ground state. For all trinuclear complexes, the fitting of $\phi_{PL}$ as a function of temperature was significantly improved when radiative deactivation from both the upper and lower $^3\text{MLCT}$ excited states was 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 

![Figure 8](image1.png)

**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 non-radiative 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 $^3\text{MC}$ excited state.

![Figure 9](image2.png)

**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 states were luminescent. The blue line represents the calculated quantum yields if the lowest and the thermally activated $^3\text{MLCT}$ excited states were luminescent.
increased (Figures 4 and 5). 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 3MLCT excited states (>700 cm^{-1}) (Table S). The photoluminescence quantum yields of the lowest 3MLCT (k_{dp}/(k_{dp}+ k_{dir})) and upper-lying 3MLCT (A_{3MLCT radiative}/A_{3MLCT}) were determined, and the results are gathered in Table 6. For all complexes, the photoluminescence quantum yield of the upper-lying 3MLCT excited state was smaller than that of the lower-lying 3MLCT, in agreement with the observed decrease in photoluminescence yield upon temperature increase (Figure 4a–d). An approximation of the energy difference between the photoluminescence maxima of the upper and lower 3MLCT was determined by deconvolution of the photoluminescence spectra of T_{pp} and T_{mp} at 213 and 373 K (Figures S57 and 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_{3MLCT} = 750 cm^{-1} for T_{pp} and E_{3MLCT} = 960 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, whereas 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_{dir} exhibited the strongest changes among the series and dominated the other deactivation pathways. For T_{mp}, T_{mm}, and T_{mp}, k_{dir} increased as the energy gap between the lowest 3MLCT excited state and the ground state decreased. We propose that the smaller k_{dir} 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_{dir}. The direct radiative rate constant (k_{dp}) 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_{mp}, T_{mm}), resulting in a decrease of the relative rate of deactivation via the upper 3MLCT (k_{3MLCT}/\sum k). 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_A) 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 a 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, and 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 the para position for both central and peripheral 2,2’-bipyridines of the bridging ligand resulted in a complex, T_{pp}, that absorbs more visible light, has a longer-lived excited state, and has 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 a low energy absorber with long-lived excited states able to perform subsequent photo-triggered chemical reactions.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03004.

Experimental section, 1H NMR, 13C NMR, mass spectrometry, electrochemistry, Franck–Condon line shape analysis, and variable temperature experiments (PDF)

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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.

Notes
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