

Synthesis and Characterization of a Novel Linear Trinuclear Ruthenium(II) Complex: Variation of Photosensitization Ability with Chain Length in a Homologous Series

Simona Vaduvescu and Pierre G. Potvin*

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario M3J 1P3, Canada

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A new, one-step preparation of 1,4-di(2,2':6',2''-terpyridin-4'-yl)-benzene was employed in the synthesis of a linear trinuclear Ru(II) complex, which was compared to mononuclear and dinuclear analogues using UV–vis spectrometry, cyclic voltammetry, and ability to sensitize the photogeneration of methyl viologen radical cation. The chain length-dependent increase in sensitization ability was consistent with an increasing molar absorbance and with an end-on approach of the photoreactants mitigating the increasing charge.

Ruthenium(II)–polypyridine complexes have been found to exhibit excellent properties as light absorption sensitizers and light emission sensitizers.¹ These could be used for a variety of applications, including the splitting of water by solar radiation. Linear multinuclear Ru(II) complexes are rarer, but photophysical properties have been measured for several whose metal binding sites are linked by ethynyl and ethynylaryl spacers.² As with simple aryl spacers, these acetylenic linkages do not promote strong metal–metal communication, but they do lead to longer excited-state (triplet) lifetimes, owing to extended π -system delocalization. However, this benefit is generally purchased at the expense of the triplet energy while, at the same time, the key metal-to-ligand charge transfer (MLCT) absorption shifts to lower energy, the first (ligand-centered) reduction potential becomes less negative, and the metal oxidation potential, although less affected, becomes less positive. These trends are departures from the desirable features of the parent mononuclear complexes and can ultimately impair the sensitizer utility. An alternative way to increase the concentration of the photoexcited state is to increase the number of

metals and the probability of light absorption. Dendritic assemblies epitomize this idea,³ but their high charge would impede electron transfers to positively charged acceptors, such as methyl viologen (MV^{2+}), and/or would favor the reverse transfer with neutral or anionic acceptors. If the metals are instead in a linear array, then an end-on approach by the acceptor should be less sensitive to increases in charge upon chain elongation.

To probe these ideas, we studied a short series of complexes incorporating the “back-to-back” bis-terpyridine bridging ligand 1,4-di(2,2':6',2''-terpyridin-4'-yl)benzene (**L**). We report a new, one-pot synthesis of **L**, the elaboration of mono-, di-, and trinuclear complexes, and an evaluation of their photosensitization ability as a function of chain length.

There are relatively few literature methods for terpyridine synthesis,^{4–6} and **L** has previously been prepared by two of them.^{4,5} We employed the one-pot method developed by Liegghio et al. for dipyrzinylpyridines.⁷ In this instance, seven molecules are condensed at once to provide **L** in 39% yield, after recrystallization ($CHCl_3/CH_3OH$), a yield entirely comparable to those previously reported for longer routes.^{4,5} We have successfully applied this method to prepare the *m*-phenylene analogue of **L**, as well as the dipyrzinylpyridine analogues. NMR analysis (¹H, ¹³C, COSY), EI-MS, and elemental analysis confirmed the structure of **L**.

The mononuclear precursor has been prepared from Ag^+ -activated⁸ (ttpy)RuCl₃ (ttpy is 4'-*p*-tolyl-2,2':6',2''-terpyridine)⁹ but only characterized by NMR.¹⁰ Column chromatography (alumina, 31:2:1 CH_3CN /saturated KNO_3/H_2O) and

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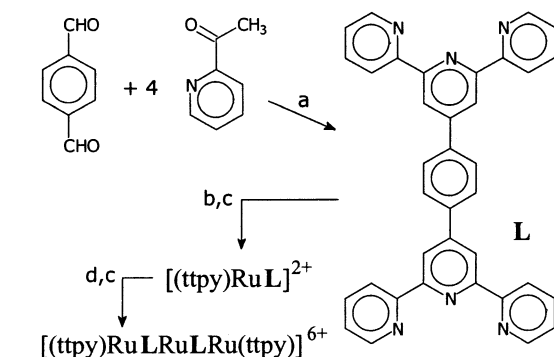
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* To whom correspondence should be addressed. E-mail: pgpotvin@yorku.ca.

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Scheme 1^a

^a Conditions: (a) 10:1 NH_4OH –15% aq KOH , MeOH , reflux, 48 h. (b) $(\text{tpy})\text{RuCl}_3$, 3 equiv AgBF_4 , acetone, reflux, 3 h; then **L**, DMF , reflux, Ar, 2 h. (c) Excess aq NH_4PF_6 . (d) 0.5 equiv $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, ethane-1,2-diol, cat. *N*-methyl morpholine, Ar, reflux, 24 h.

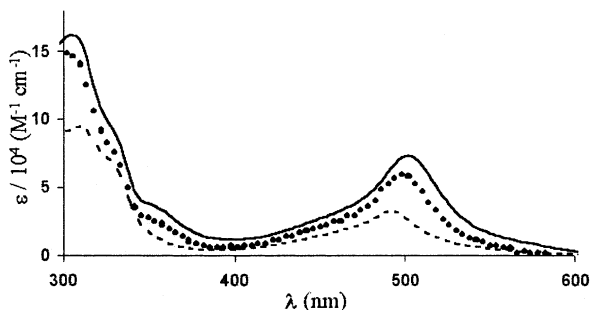


Figure 1. UV-vis spectra of mono- (---), di- (···), and trinuclear complexes (—).

reprecipitation (NH_4PF_6) afforded a comparable yield (70%) of $[(\text{tpy})\text{RuL}](\text{PF}_6)_2$, further characterized by ESI-MS and elemental analysis.

The trinuclear complex was prepared in a straightforward fashion by coupling 2 equiv of $[(\text{tpy})\text{RuL}]^{2+}$ with RuCl_3 , followed by precipitation (NH_4PF_6) and recrystallization ($\text{CH}_3\text{CN}/\text{Et}_2\text{O}$), to afford $[(\text{tpy})\text{RuL}_2\text{RuL}_2\text{Ru}(\text{tpy})](\text{PF}_6)_6$ in 87% yield (Scheme 1). Its structure was confirmed by NMR (^1H , COSY) and ESI-MS analysis, though elemental analysis of pure material returned low carbon and nitrogen contents, presumably owing to incomplete combustion. The dinuclear analogue $[(\text{tpy})\text{RuL}_2\text{Ru}(\text{tpy})](\text{PF}_6)_4$ was prepared according to the published method.¹¹

The electronic spectra (Figure 1) of the complexes in CH_3CN showed $\pi-\pi^*$ transitions near 300 nm and MLCT envelopes peaking near 500 nm (Table 1). As the chain length increased, there was a slight red shift in λ_{max} but a pronounced increase in the molar extinction coefficients (ϵ), entirely in accord with the findings of Janini et al.¹² As was found for the dinuclear complex, cyclic voltammetry of the trinuclear species (in 0.1 M nBu_4PF_6 in CH_3CN) showed little evidence of metal–metal communication, with a single Ru–

Table 1. Variations in Spectral, Electrochemical, and Photochemical Properties with the Number of Metals (N)^a

N	1	2	3
MLCT λ_{max} (nm)	496	502	504
$\epsilon_{\text{MLCT}}/10^4$ ($\text{M}^{-1} \text{cm}^{-1}$)	3.27	5.98	7.33
E_{ox} (V vs SCE)	1.27	1.27 ^b	1.27
E_{red} (V vs SCE)	−1.18	−1.18 ^b	−1.03
$k_{\text{f}} \times 10^5$ (s^{-1})	1.93(18)	1.086(2)	1.339(5)
$k_{\text{q}} \times 10^3$ (s^{-1})	7.4(9)	2.40(16)	3.67(1)
χ (mM)	26(4)	45(3)	36.3(2)

^a Numbers in parentheses are the uncertainties in the least significant digits. ^b Reference 11.

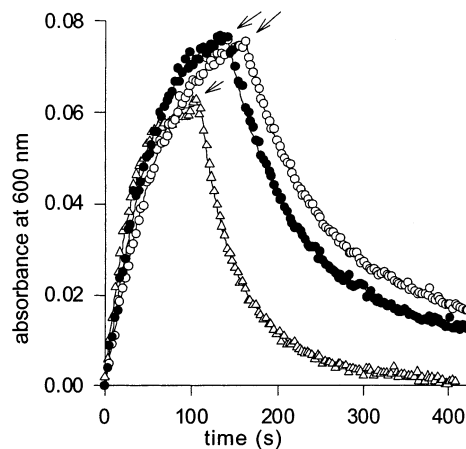


Figure 2. Typical plots of photogeneration of MV^{+} with mononuclear (Δ), dinuclear (\circ), and trinuclear complexes (\bullet). For clarity, only every third data point is plotted. The arrows indicate the time at which the light was turned off. The solid lines are the least-squares fitted lines.

(III/II) couple at the same potential throughout the series, essentially the same as with the parent complex $[\text{Ru}(\text{tpy})_2]^{2+}$ (1.25 V).¹¹ The reduction waves were not well defined in all cases, but the first reduction values were all less negative than with $[\text{Ru}(\text{tpy})_2]^{2+}$ (−1.24 V),¹³ suggesting the involvement of the bridging ligand. As was the case with $[\text{Ru}(\text{tpy})_2]^{2+}$ ($\tau = 0.95$ ns in CH_3CN),¹⁴ the complexes explored here apparently do not emit at room temperature.

Using the published procedure to test the relative sensitizer ability, the rate of generation of MV^{+} from 0.01 M MV^{2+} in stirred CH_3CN under continuous irradiation at 400–600 nm was monitored in the presence of 40 μM sensitizer and 0.05 M triethanolamine as sacrificial reductant. Typical time courses are presented in Figure 2, and Table 1 reports the pseudo-first-order rate constants for the formation (k_{f}) and quenching (k_{q}) of MV^{+} fitting the kinetic model¹⁵

$$\frac{d[\text{MV}^{+}]}{dt} = k_{\text{f}}[\text{MV}^{2+}]_0 - (k_{\text{f}} + k_{\text{q}} + k_{\text{d1}})[\text{MV}^{+}]_t - k_{\text{d2}}[\text{MV}^{+}]_t^2$$

where k_{d1} and k_{d2} were given by the aerobic decay in the dark ($k_{\text{f}} = k_{\text{q}} = 0$). The yields of MV^{+} varied from sample to sample, according to their O_2 contents, but Table 1 reports

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the yields χ expected under anaerobic conditions ($k_{d1} = k_{d2} = 0$). No MV^{*+} was detected in the absence of sensitizer.

All three complexes tested here were better than $[Ru-(tpy)_2]^{2+}$, which was a relatively poor sensitizer.¹⁵ Overall, the di- and trinuclear species are better sensitizers than the mononuclear precursor, as measured by χ , apparently because k_f does not decrease with an increasing number of metal centers (N) as fast as k_q does. Both k_f and k_q decreased as N increased from 1 to 2, despite a near doubling of ϵ . However, they rebounded as N increased to 3, and the 50% increase in charge was apparently mitigated to a degree beyond that provided by the smaller increase in ϵ . Though we cannot exclude the possibility of a change in τ with N , the difference in the sensitizers' activity levels should be largely electrostatic in origin because of the similarities in their constitution and properties. Indeed, the observations are consistent with an end-on approach of the excited state by MV^{*+} , whence the effect of increasing charge as N increases fades with the increasing distance from the end of the chain. The activation

energies for electron transfer (ΔG^*) predicted by classical Marcus theory¹⁶ (Supporting Information) corroborate the intuitive preference for end-on approaches.

These results are promising for the deployment of such arrays in multiphase assemblies, but further improvements in activity are being sought with π -poorer dipyrzinyipyridine analogues to **L**, which should favor longer τ values, and with carboxylated capping ligands, to ameliorate the electrostatic situation and to anchor the sensitizers to organic–aqueous interfaces.

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Supporting Information Available: Characterization data for all compounds and table of computed ΔG^* values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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