Linear Multinuclear Ru^{II} Photosensitizers

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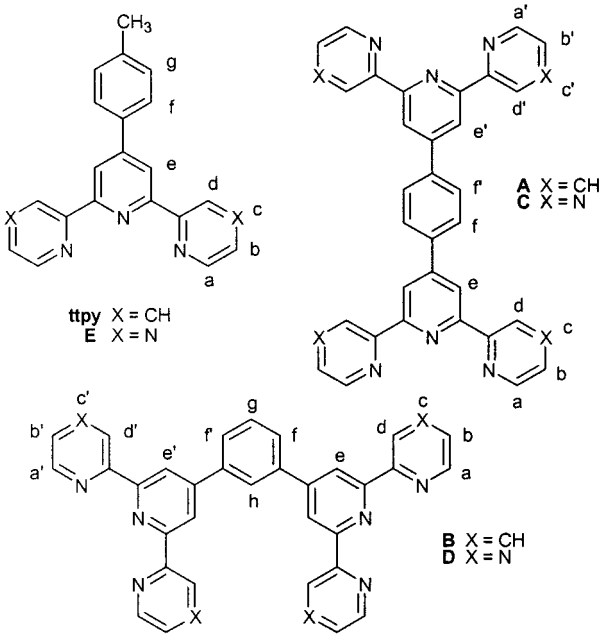
Four ditopic bridging ligands, containing 2,2′:6′,2′′-terpyridine and 2,6-dipyrazinylpyridine (dpp) metal-binding units attached through *p*- or *m*-phenylene linkages, have been incorporated into eight mono-, di- and trinuclear linear Ru^{II} complexes. These were characterized by UV/Vis spectroscopy and cyclic voltammetry, and by their ability to undergo light-induced electron transfers to methylviologen. The dpp-bearing complexes were more difficult to prepare but were superior sensitizers, a fact attributable to longer excited state lifetimes and an electrostatically favored reductive quenching pathway.

Introduction

Ruthenium(II)−polypyridine complexes act as light absorption sensitizers,[1] a characteristic that can be put to use in solar energy conversion and storage applications. A critical limitation on the photo-responsiveness is the concentration of the sensitizer's excited state that can be achieved, and this notably depends on the excited state lifetime (τ) and on the extinction coefficient (ε) for the metal-to-ligand charge transfer (MLCT) absorption that leads to the excited state. One approach to improving the photoactivity is to increase the number of metal atoms in the sensitizer and the probability of light absorption. Dendritic assemblies epitomize this idea,[2] but electrostatic considerations make them unattractive because their globular structures and high charges would impede electron transfers to positively charged acceptors, such as methylviologen (MV^{2+}), and/or, in the case of neutral or anionic acceptors, would facilitate the energy-wasting reverse electron transfer that regenerates the initial states. The effect of charge repulsion can be minimized with linear multinuclear arrays, where an end-on approach by an electron acceptor is minimally affected by repulsions from the more distal metal centers. Hence, the electrostatics can be relatively insensitive to the sensitizer chain length while the light absorption would increase with chain length.

We have recently communicated the preparation and characterization of a linear trinuclear Ru^{II} complex in which the "back-to-back" bis(terpy) ligand **A** bridges the metal centers. This material was assessed as a photosensitizer relative to the mono- and dinuclear analogues.[3] In the above-mentioned report, the assessment used measurements of the rates of formation of the methylviologen radical cation ($MV^{\cdot+}$) from methylviologen (MV^{2+}) in CH_3CN in the presence of a sacrificial reductant (triethanolamine) according to a set protocol.[4] Comparisons were also made with $[Ru(\mathbf{ttpy})_2]^{2+}$ (**ttpy** = 4′-*p*-tolyl-2,2′:6′,2′′-terpyridine), a related complex of known τ (0.95 ns in CH_3CN).[5] This paper provides full details of that work and extends it by exploring the photoactivity of several new complexes of related bridging ligands, namely the *meta* isomer of **A** (ligand **B**) and the dipyrazinylpyridine (dpp) analogues of **A** and **B** (ligands **C** and **D**). It was anticipated that the *meta* linkages



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of **B** and **D** would enable electrostatically easier access, by MV^{2+}, to the areas between metal atoms in di- and trinuclear complexes and to the central metal atoms in trinuclear cases, while the dpp ligands would be expected to promote longer τ values.[6]

Results and Discussion

Synthesis

Bis(terpyridine) **A** is known, and has been prepared by two routes.[7,8] We prepared it by the one-pot method developed for the synthesis of dpp ligands,[6] and recently applied this to other terpy-based materials.[9] In this remarkable reaction, a total of seven reactant molecules condense and expel six molecules of H_2O, then undergo two cycles of aerial dehydrogenation. The isolated yield (39%) was entirely similar to those of the previous preparations but with less effort and in less time. The linkage isomer **B** was produced under the same conditions from isophthalaldehyde and in a similar yield (37%).[10] Its X-ray crystal structure showed a lack of co-planarity consistent with the absence of a resonance pathway of communication between terpy units. Its NMR spectra showed a single set of pyridine signals, which implies free rotation about the terpy-to-linker bonds. A useful spectroscopic marker for the complexes of **A** and **B** was the most downfield ^{1}H NMR signal, i.e. the singlet from the central pyridine 3′/5′-H (at δ = 8.83 ppm in free **A**; δ = 8.84 ppm in free **B**).

By similar reactions with acetylpyrazine, the bis(dpp) ligands **C** and **D** were obtained in isolated yields of 42% and 37%, respectively. Those materials are soluble only in trifluoroacetic acid (TFA) and could not be properly recrystallized. Their NMR spectra in [D]TFA were inconclusive, but their identities were confirmed by EI-MS and, for **C**, by conversions to Ru^{II} complexes (see below).

The monotopic **ttpy** was used as a terminal ligand. It could also be prepared by the one-pot method from acetylpyridine and *p*-tolualdehyde in 46% yield after recrystallization, while a 70% yield was obtained by our earlier, two-step method.[11]

[Ru(**ttpy**)Cl_3][12] was activated with $AgBF_4$,[13] then treated with 1 equiv. of **A** to form [(**ttpy**)Ru(**A**)]$(PF_6)_2$ in 70% yield, after chromatography and anion exchange. In contrast, [Ru(**A**)$_2$]$(PF_6)_2$ was obtained in only 40% yield, by treatment of $RuCl_3$ with 2 equiv. of **A**; 2 equiv. of [(**ttpy**)Ru(**A**)]$(PF_6)_2$ and 1 equiv. of $RuCl_3$ were heated in 1,2-ethanediol to form the trinuclear complex [(**ttpy**)Ru(**A**)Ru(**A**)-Ru(**ttpy**)]$(PF_6)_6$ in 87% yield, after anion exchange and recrystallization. The dinuclear analogue [(**ttpy**)Ru(**A**)-Ru(**ttpy**)]$(PF_6)_4$ was needed for comparative purposes. It is a known species[14] which we prepared from 2 equiv. of $AgBF_4$-activated [(**ttpy**)$RuCl_3$] and **A** in a yield of 19% (not optimized), after anion exchange, chromatography and a second cycle of anion exchange.

^{1}H and COSY NMR spectroscopy were used to confirm the structures. Complexation was indicated by a strong upfield migration of the doublets from 6-H, which juts out above the plane of the perpendicular ligand and experiences the effect of its ring current. Two sets of terpy signals were obtained with [Ru(**A**)$_2$]$(PF_6)_2$, including singlets for 3′/5′-H at δ = 9.14 ppm and 8.98 ppm for the complexed and free terpy units, respectively, and the phenylene singlet of **A** was replaced by a pair of doublets in this less symmetrical species. Though [(**ttpy**)Ru(**A**)]$(PF_6)_2$ has been previously reported,[15] it was characterized only by NMR spectroscopy. Here, three sets of partially overlapping terpy signals were evident, including three distinct 3′/5′-H singlets at δ = 9.12, 9.02 and 8.97 ppm for bound **A**, **ttpy** and free **A** terpyridine units, respectively, as well as phenylene doublets. With the trinuclear complex [(**ttpy**)Ru(**A**)Ru(**A**)Ru(**ttpy**)]$(PF_6)_6$, three sets of terpy ^{1}H NMR signals were expected but the majority overlapped considerably, reflecting the similarities in the three ligand environments, including those from the phenylene spacer, which appeared together as one large singlet. However, the three distinct central pyridine 3′/5′-H singlets at lowfield positions (δ = 9.23, 9.21 and 9.06 ppm) confirmed the lack of symmetry and metal coordination. [(**ttpy**)Ru(**A**)Ru(**ttpy**)]$(PF_6)_4$ showed only two sets of terpy signals reflecting the higher symmetry, including a phenylene singlet and 3′/5′-H singlets at δ = 9.19 and 9.05 ppm for metal-bound terpy units of **A** and **ttpy**, respectively.

An entirely analogous sequence from the *m*-linked ligand **B** led to PF_6^- salts of [(**ttpy**)Ru(**B**)]$^{2+}$, [(**ttpy**)Ru(**B**)Ru(**B**)-Ru(**ttpy**)]$^{6+}$ and [(**ttpy**)Ru(**B**)Ru(**ttpy**)]$^{4+}$. The yields were slightly lower than in the *p*-linked cases (65%, 70% and 17%, respectively). In the latter preparation, we found that [Ru(**ttpy**)$_2$]$^{2+}$ was a contaminant, presumably arising from a ligand exchange process. This contaminant and the reduced yields imply some resistance to coordinate to **B**, in comparison with **A**, perhaps due to steric encumbrance or increased repulsions between metal centers. The dinuclear [(**ttpy**)Ru(**B**)Ru(**ttpy**)]$^{4+}$ also appeared as a side-product in the preparation of [(**ttpy**)Ru(**B**)]$^{2+}$ and necessitated chromatographic purification. The ^{1}H NMR spectra of the **B** complexes were very similar to those of the **A** series, except for the singlet-doublet-triplet pattern from the *m*-phenylene linkage, and showed only one set of pyridine signals per distinct terpy unit, again consistent with free rotation of the terpy units about the linkage.

The reactions with the pyrazine-containing ligands were less straightforward. Attempted preparation of [(**ttpy**)Ru(**C**)]$^{2+}$ from (**ttpy**)$RuCl_3$ and **C** in ethane-1,2-diol produced only the ligand-exchange product [Ru(**ttpy**)$_2$]$^{2+}$, owing to the poor solubility of **C**. Using TFA as a co-solvent was helpful, and the best solvent found was a TFA/ethane-1,2-diol (5:1) mixture that led to a 70% yield of [(**ttpy**)Ru(**C**)]$(PF_6)_2$ after anion exchange and chromatography. The ^{1}H NMR spectra differ from those of the all-terpy series in that the lowest field signals are now due to the pyrazinyl 3/3′′-H instead of the pyridine 3′/5′-H. The pyrazinyl 5-H and 6-H are weakly coupled but COSY spectroscopy revealed a long-range W-coupling between 3-H and 5-H. The dinuclear species [(**ttpy**)Ru(**C**)Ru(**ttpy**)]$(PF_6)_4$ was obtained in 20% yield from Ag^+-activated [(**ttpy**)$RuCl_3$]

and **C** in a mixture of TFA and ethane-1,2-diol. Chromatography was required to separate the desired material from the now abundant $[Ru(\mathbf{ttpy})_2]^{2+}$ impurity. The ^1H NMR spectrum was similar to that of the mononuclear analogue, simplified by symmetry, and COSY spectroscopy was used to identify one pyrazinyl 3-H singlet, two pyridine 3′/5′-H singlets and one phenylene singlet, all consistent with the structure. Unfortunately, all attempts at preparing the trinuclear analogue failed, producing only a brown-black, paramagnetic material. Similarly, all complexation reactions with ligand **D** failed as well. Treatment of $[(\mathbf{ttpy})RuCl_3]$ with 1 equiv. of **D** also produced a paramagnetic product. With 0.5 equiv., $[Ru(\mathbf{ttpy})_2]^{2+}$ was the major product and the desired dinuclear species was only a minor constituent detectable by NMR spectroscopy and ESI-MS. It became obvious that the *m*-phenylene linkage and the lower basicity of dpp units, relative to terpy, decreased the reactivity of the ligand. An alternate route was attempted to circumvent the latter problem. Treatment of $RuCl_3$ with 0.5 equiv. of **D** in EtOH provided a brown-black precipitate, putatively $[Cl_3Ru(\mathbf{D})RuCl_3]$, but treatment of this with **ttpy** in ethane-1,2-diol to produce the dinuclear compound led to $[Ru(\mathbf{ttpy})_2]^{2+}$ as the only detectable product.

As is common with aromatic materials and Ru complexes, elemental analyses often return correct H compositions but low C and/or N compositions, even in the presence of extra oxidation catalyst, presumably due to incomplete combustion and/or the formation of stable carbides and nitrides. Mass and isotopic distribution analyses (ESI, MALDI or high resolution MALDI) were used to confirm the structural assignments. Fortunately, the precipitation of PF_6^- salts enabled purification, which was made evident by chromatographic homogeneity and the absence of extraneous NMR peaks.

UV/Vis Spectroscopy

The electronic spectra of all complexes in CH_3CN showed intense π-π* bands below 350 nm and MLCT bands ($\lambda_{max.}$) at 490−500 nm, reported in Table 1, in complete analogy with $[Ru(\mathbf{ttpy})_2]^{2+}$.[16] In addition, the complexes of **C** showed shoulders near 450 nm. With the *p*-linked ligands **A** and **C**, the position of $\lambda_{max.}$ drifted slightly toward the red with an increasing number of metal centers, while $\lambda_{max.}$ remained constant with the *m*-linked ligand **B**. Relative to $[Ru(\mathbf{ttpy})_2]^{2+}$, each added dpp or terpy unit and each added metal center constitutes an electron-withdrawing group. The drift with a *p*-linkage is likely a result of electron withdrawal on the ligands' π systems and stabilization of the ligand π* orbitals, relative to the metal-centered orbitals. The lack of such a drift with the *m*-linkage is probably owing to the absence of a resonance path for electronic transmission, and the 2 nm shift in $\lambda_{max.}$ with $[(\mathbf{ttpy})Ru(\mathbf{B})]^{2+}$ then represents the inductive contribution of an added terpy unit. At the same time, the ε values grew upon increasing the number of metal atoms, as expected. It is interesting to note that the ε values of all the mononuclear complexes $[(\mathbf{ttpy})RuL]^{2+}$ (L = **A**−C) are larger than for the homoleptic case, where L = **ttpy**. This is even more pronounced with the homoleptic $[Ru(\mathbf{A})_2]^{2+}$ ($\lambda_{max.}$ = 496 nm, ε = 42700 $M^{-1}\cdot cm^{-1}$). Because the MLCT $\lambda_{max.}$ values are all of lower energies than with $[Ru(\mathbf{ttpy})_2]^{2+}$, it is reasonable to conclude that the bridging ligands have lower π* orbital energies than does the terminal ligand **ttpy**, and are therefore the repositories of the excited electron density.

Electrochemistry

The results of cyclic voltammetry are also reported in Table 1. As is typical for complexes of this nature,[14,17] the new complexes show single reversible oxidation waves at potentials that are practically insensitive to chain length and at least two reduction waves that are somewhat less constant. Owing to their additional nitrogen atoms, the two complexes of **C** show particularly positive $E(Ru^{III/II})$ potentials, lying between the value for the homoleptic dpp complex $[Ru(\mathbf{E})_2]^{2+}$ (+1.62 V)[6] and that for the bis(terpy) complex $[Ru(\mathbf{ttpy})_2]^{2+}$ (+1.25 V).[18] The first reduction potentials of the new complexes are all positive compared with that of $[Ru(\mathbf{ttpy})_2]^{2+}$. Along with the spectroscopic evidence, this suggests that reduction adds an electron to the bridging ligands, rather than to the terminal **ttpy** whose π* orbital is evidently at a higher energy.

In accordance with the more negative reductions of the terpy-based ligands, we can assign the first and second reduction waves shown by the complexes of **C** to reductions

Table 1. Key spectroscopic, electrochemical and photochemical data

Compound[a]	$\lambda_{max.}$ [nm]	ε [104 $M^{-1}\cdot cm^{-1}$]	E_{ox} [V vs. SCE]	E_{red} [V vs. SCE]	k_f [10^{-5} s^{-1}]	k_q [10^{-3} s^{-1}]	χ [mM]	$\Delta G^{\ddagger}_{FET}$ [eV]	$\Delta G^{\ddagger}_{RET}$ [eV]
$[(\mathbf{ttpy})_2Ru]^{2+}$	490[b]	1.55[b]	1.25[c]	−1.24,[c] −1.42[d]	1.12(1)[e]	8.8(6)[e]	11(4)[e]	0.24	0.22
$[(\mathbf{ttpy})Ru(\mathbf{A})]^{2+}$ [f]	496	3.27	1.27	−1.18, −1.42	1.93(18)	7.4(9)	26(4)	0.25	0.23
$[\{(\mathbf{ttpy})Ru\}_2\mathbf{A}]^{4+}$ [f]	502	5.98	1.27[g]	−1.18, −1.45[g]	1.086(2)	2.40(16)	45(3)	0.29	0.25
$[\{(\mathbf{ttpy})Ru(\mathbf{A})\}_2Ru]^{6+}$ [f]	504	7.33	1.27	−1.03, −1.23	1.339(5)	3.67(1)	36.3(2)	0.32	0.26
$[(\mathbf{ttpy})Ru(\mathbf{B})]^{2+}$	492	2.61	1.28	−1.22, −1.44	1.01(5)	2.5(3)	40(5)	0.25	0.23
$[\{(\mathbf{ttpy})Ru\}_2\mathbf{B}]^{4+}$	492	3.70	1.28	−1.18, −1.45	1.98(4)	4.2(3)	47(3)	0.30	0.25
$[\{(\mathbf{ttpy})Ru(\mathbf{B})\}_2Ru]^{6+}$	492	6.96	1.28	−1.18, −1.37	0.95(3)	3.79(11)	25(1)	0.33	0.27
$[(\mathbf{ttpy})Ru(\mathbf{C})]^{2+}$	456, 504	1.48, 2.01	1.48	−0.86, −1.25, −1.65	3.48(2)	7.0(3)	50(2)	0.38	0.32
$[\{(\mathbf{ttpy})Ru\}_2\mathbf{C}]^{4+}$	454, 506	2.54, 3.33	1.49	−0.85, −1.25, −1.65	2.31(13)	4.7(13)	49(13)	0.42	0.34

[a] Uncertainties in least significant digits appear in brackets. [b] From Mikel and Potvin.[16] [c] From Kalyanasundaram et al.[18] [d] In DMSO, from Constable et al.[31] [e] From Potvin et al.[4] [f] From Vaduvescu and Potvin.[3] [g] From Collin et al.[14]

of the relatively electron-poor bridging and electron-rich terminal ligands, respectively. Since $E(Ru^{III/II}) - E(L^{0/-})$ is known to correlate with the MLCT energy,[19] the higher-energy MLCT bands of the **C** complexes can then be assigned to Ru→**ttpy** transitions, and the lower-energy bands to Ru → **C** transitions. With these pairings, the correlation is fairly good ($r^2 > 0.92$).

Photochemistry

Under visible light irradiation and in the presence of triethanolamine (TEOA) as a sacrificial reductant, Ru^{II} complexes are able to generate the methylviologen radical cation ($MV^{\cdot+}$) from methylviologen (MV^{2+}) to different degrees. In real-life photoredox applications, there would be no sacrificial donor present, but the excited state could be reductively quenched at an electrode surface or by a reversibly reduced electron relay molecule such as MV^{2+} at an illuminated organic-aqueous interface. Comparisons between sensitizers in terms of the kinetic parameters governing this process have previously enabled us to probe steric, electrostatic and solvent effects on activity,[16,20,21] and we wished, in the present work, to probe the effect of increasing the Ru chain length *N*. Using our standard protocol,[4] we measured the time courses of $MV^{\cdot+}$ development at room temperature in CH_3CN at 600 nm with a sensitizer concentration of 4×10^{-5} M. The key results presented in Table 1 are the first-order rate constants k_f and k_q for $MV^{\cdot+}$ formation and anaerobic quenching, respectively, and the anaerobic yields χ, given by $k_f[MV^{2+}]_0/(k_f + k_q)$. The usual mechanism is oxidative quenching of the excited state of the sensitizer ($Ru^{II*} + MV^{2+} \rightarrow Ru^{III} + MV^{\cdot+}$) followed by reverse electron transfer to (quenching of) $MV^{\cdot+}$ ($Ru^{III} + MV^{\cdot+} \rightarrow Ru^{II} + MV^{2+}$), or competitive trapping ($Ru^{III} + TEOA \rightarrow Ru^{II} + TEOA^{\cdot+}$) which allows $MV^{\cdot+}$ to accumulate. Additionally, Table 1 reports estimates of $\Delta G^{\ddagger}_{FET}$ and $\Delta G^{\ddagger}_{RET}$, the Marcus activation energies for the forward and reverse electron transfers, respectively, for end-on approaches by $MV^{2+/\cdot+}$ to the terminal metals. Their computations and the values for electrostatically less favorable approaches are detailed in the Supporting Information (see also the footnote on the first page of this article).

All of the new complexes are better sensitizers than $[Ru(\mathbf{ttpy})_2]^{2+}$,[4] with higher k_f and χ values. This may reflect generally longer τ values owing to a greater π-delocalization and π^* stabilization in the bridging ligands which, as discussed earlier, are the preferred sites for the excited electrons. Clearly, there is variation between the **A** and **B** series, in spite of similarities in structures, properties (E_{ox}, E_{red}, λ, ε/N) and even $\Delta G^{\ddagger}$ values. Part of the success of $[\{(\mathbf{ttpy})Ru\}_2\mathbf{B}]^{4+}$ relative to the **A** analogue may be due to easier access to the areas between the metal atoms, but this advantage does not appear to carry forward to the trinuclear case.

Because of similar properties *within* a ligand series and virtually identical structures at the metal termini, we can make the a priori assumption that the differences in sensitizer activities within a series should be largely electrostatic and not photophysical in origin, an assumption which our results should confirm or deny. The constant k_f incorporates the concentration of excited state species (Ru^{II*}) and will depend on $\Delta G^{\ddagger}_{FET}$, which contains the electrostatic barrier to the forward electron transfer which increases with increasing *N*, while k_q incorporates the concentration of the Ru^{III} photoproduct and depends on $\Delta G^{\ddagger}_{RET}$, which contains the corresponding electrostatic barrier. The constants k_q and k_f, however, are linked because a higher k_f leads to a higher concentration of Ru^{III} and therefore a higher k_q. Both, then, also depend on the photophysical properties that govern the production of Ru^{II*}, including ε and τ. However, the ratio k_q/k_f ($= [MV^{2+}]_0/\chi - 1$) was previously shown to equal $k_r[MV^{2+}]_0/k_t[TEOA]_0$,[4] where k_r and k_t are the second-order rate constants for the reactions of the Ru^{III} photoproduct with the $MV^{\cdot+}$ co-product (reverse electron transfer) and with TEOA (trapping), respectively. This ratio is therefore a measure of the competition between the non-productive and productive fates of the Ru^{III} form of the sensitizer. The first constant, k_r, will vary within a series according to $\exp(-\Delta G^{\ddagger}_{RET})$, while k_t involves encounters with the neutral TEOA and should remain constant within a series. Hence, if the sensitizers within a series only differed in electrostatic terms, k_q/k_f should steadily decrease as $\Delta G^{\ddagger}_{RET}$ steadily increases with *N*. The values in Table 1 reveal that this is not so, with $[\{(\mathbf{ttpy})Ru\}_2\mathbf{A}]^{4+}$ and $[\{(\mathbf{ttpy})Ru(\mathbf{B})\}_2Ru]^{6+}$ being particularly outstanding. Moreover, k_f should vary with $\varepsilon \exp(-\Delta G^{\ddagger}_{FET})$, but $\ln(k_f/\varepsilon)$ does not uniformly decrease as $\Delta G^{\ddagger}_{FET}$ increases. These findings imply that the sensitizers within a series also differ in their photophysical characteristics, such as τ, orbital overlap, approach geometry or approach distance, which this study cannot probe. Nevertheless, Table 1 identifies the most effective sensitizers $[\{(\mathbf{ttpy})Ru(\mathbf{A})\}_2Ru]^{6+}$, $[\{(\mathbf{ttpy})Ru\}_2\mathbf{B}]^{4+}$, and especially the two complexes of **C**, as meriting further study.

The two **C**-containing complexes show higher activities in spite of having the highest barriers $\Delta G^{\ddagger}_{FET}$. They probably benefit from longer τ values than the all-terpy complexes of **A** and **B** because the first dpp complex, $[Ru(\mathbf{E})_2]^{2+}$, showed a longer τ (18 ns at 667 nm)[6] than its terpy analogue $[Ru(\mathbf{ttpy})_2]^{2+}$ (0.95 ns at 640 nm).[22] In addition, the redox potentials for the **C**-containing complexes lie about 0.2 V more positive of those of the other complexes and this is probably sufficient to enable reductive quenching (formally $Ru^{II*} + TEOA \rightarrow Ru^{I} + TEOA^{\cdot+}$), as was the case in other complexes with high E_{ox} values.[23–25] Reductive quenching has an electrostatic advantage over oxidative quenching because it involves initial encounters with neutral TEOA instead of cationic MV^{2+}, and because the wasteful reverse electron transfer (formally $Ru^{I} + TEOA^{\cdot+} \rightarrow Ru^{II} + TEOA$) is electrostatically disfavored relative to the forward reaction, whereas the opposite is true in oxidative quenching ($Ru^{III} + MV^{\cdot+} \rightarrow Ru^{II} + MV^{2+}$). Moreover, the $TEOA^{\cdot+}$ by-product can be deprotonated in an alkaline medium ($TEOA^{\cdot+} \rightarrow H^+ + H_{-1}TEOA^{\cdot}$) to generate a reducing species[26] that is depleted by O_2.[4] This consumption of $TEOA^{\cdot+}$ further reduces the probability of reverse electron transfer, thereby leaving more of the re-

duced form of the sensitizer able to produce $MV^{\cdot+}$ (Ru^{I} + $MV^{2+} \rightarrow Ru^{II}$ + $MV^{\cdot+}$) in electrostatically more favorable encounters than is the case in oxidative quenching. These combined electrostatic advantages would contribute to a faster net accumulation of the ultimate photoproduct, $MV^{\cdot+}$, as witnessed with ligand **C**.

Conclusion

Ditopic bridging ligands can be assembled in a one-pot reaction and incorporated into short, linear multinuclear assemblies that act as photosensitizers in spite of electrostatic repulsions. The photochemical experiments have identified $[\{(\mathbf{ttpy})Ru(\mathbf{A})\}_2Ru]^{6+}$, $[\{(\mathbf{ttpy})Ru\}_2\mathbf{B}]^{4+}$ and both complexes of **C** as candidates for photophysical studies, in order to elucidate the origins of the difference in behavior between the **A** series and the **B** series and the origin of the better activity for the **C** series. However, the dpp-containing ligands **C** and **D** were fraught with solubility and reactivity problems that need to be addressed. An obvious improvement to the general design is to add negatively charged groups to the peripheries which can constitute binding sites for positively charged electron acceptors such as MV^{2+} since this has proven to be of great benefit in mononuclear species.[21] However, the ideal linear multinuclear sensitizer will absorb light anywhere along the chain and relay the excited electron to the ends (the so-called antenna effect), where electrostatic repulsions with acceptors can be minimized. Another improvement would therefore be to use the most electron-poor ligands at the termini.

Experimental Section

General Remarks: NMR spectroscopic data were obtained with a Bruker AMX 400 MHz spectrometer in CD_3CN (unless indicated otherwise) at 25 °C and are reported relative to $SiMe_4$. The signal assignments were made on the basis of COSY spectra and use the position letters appearing in the structural diagrams. A Kratos Profile mass spectrometer was used for EI-MS acquisitions. MALDI-MS data were acquired with a Voyager-DE STR MALDI/TOF instrument and ESI-MS data with a Sciex Targa 6000E MS/MS system. High resolution MALDI-MS (HR-MALDI-MS) was performed by the McMaster Regional Center for Mass Spectrometry, Hamilton, ON, Canada with a Micromass TofSpec 2E instrument. UV/Vis spectra were obtained at room temperature with a Hewlett−Packard 8452A diode array spectrophotometer, with 10^{-5} M solutions in spectroscopic-grade solvents. Cyclic voltammetry was performed with a Cypress System three-electrode configuration consisting of a reference Ag/AgCl wire electrode and platinum wire working and auxiliary electrodes, using CH_3CN distilled from P_2O_5 and stored over 4-Å molecular sieves, in solutions containing 0.1 M n-Bu_4NPF_6. Half-wave potentials were calculated as the average of the cathodic and anodic peak potentials.[27] The current-scan rate dependence was evaluated for each sample to check the reversibility, and ferrocene was added at the end of each run as an internal reference (+0.425 V vs. SCE in CH_3CN).[28] Photochemical data were obtained using the apparatus and data treatment described earlier,[4] with stirred CH_3CN solutions containing the sensitizer (4×10^{-5} M), $MV(PF_6)_2$ (0.01 M) and triethanolamine (0.05 M). Reagents and spectroscopic-grade solvents (Sigma−Aldrich) were used directly. Anhydrous solvents were purchased in Sigma−Aldrich Sure-seal bottles. All other solvents were reagent-grade quality (Caledon Chemical Ltd.) and used directly. $[Ru(\mathbf{ttpy})Cl_3]$ was prepared in 71% yield by a literature method[12], with its identity verified by ESI-MS [m/z (%) = 531 (100)]. Thin-layer chromatography was used to monitor reactions and chromatography and was carried out on Macherey−Nagel Polygram Sil G/UV silica gel plates and Alox N/UV alumina plates. Column chromatography was performed employing silica gel (ca. 200−400 mesh, 60 Å) or neutral alumina (ca. 150 mesh, 58 Å), both from Sigma−Aldrich. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, ON, Canada.

4′-*p*-Tolyl-2,2′:6′,2"-terpyridine (ttpy): 2-Acetylpyridine (1.00 g, 8.3 mmol) was added to a solution of *p*-tolualdehyde (0.50 g, 4.2 mmol) in CH_3OH (32 mL). 15% aq. KOH (2.9 mL) and conc. NH_4OH (29 mL) were then added to the solution and vigorous stirring was maintained for 3 d. The yellow precipitate that formed was removed by vacuum filtration, washed with water to neutral pH and dissolved in $CHCl_3$ (40 mL). The solution obtained was washed with H_2O (3 × 30 mL). The organic fraction was dried with $MgSO_4$ and freed of solvent in vacuo. The residue was recrystallized from $CHCl_3/Et_2O$ to yield 0.61 g (46%) of **ttpy**, m.p. 168 °C. ^1H NMR ($CDCl_3$): δ = 8.77 (2 s, 4 H, *a* + *e*), 8.71 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *d*), 7.92 (dd, 2 H, *c*), 7.87 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *f*), 7.39 (dd, $^3J_{H,H}$ = 5 Hz, 2 H, *b*), 7.35 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *g*), 2.46 (s, 3 H, CH_3) ppm. EI-MS: m/z (%) = 324 (100) [$M^{\cdot+}$], in agreement with the literature data.[11,29,30]

1,4-Bis(2,2′:6′,2"-terpyridin-4′-yl)benzene (A): The same procedure as for **ttpy** was applied, using 2-acetylpyridine (1.00 g, 8.3 mmol) and terephthalaldehyde (0.2764 g, 2.1 mmol) at reflux for 48 h. Recrystallization from $CHCl_3$ and CH_3OH yielded 0.4427 g of **A** (39%), m.p. > 300 °C. ^1H NMR ($CDCl_3$): δ = 8.83 (s, 4 H, *e*), 8.79 (d, $^3J_{H,H}$ = 4.2 Hz, 4 H, *a*), 8.74 (d, $^3J_{H,H}$ = 7.0 Hz, 4 H, *d*), 8.09 (s, 4 H, *f*), 7.92 (dd, $^3J_{H,H}$ = 7.0 Hz, 4 H, *c*), 7.39 (dd, $^3J_{H,H}$ = 4.2 Hz, 4 H, *b*) ppm. MALDI-MS: m/z (%) = 541 (100) [M^+]. $C_{36}H_{24}N_6$ (540.6): calcd. C 79.98, H 4.47, N 15.54; found C 79.57, H 4.73, N 12.31.

1,4-Bis(2,6-dipyrazinylpyridin-4-yl)benzene (C): A mixture of acetylpyrazine (500 mg, 4.1 mmol) and terephthalaldehyde (135 mg, 1.0 mmol) in CH_3OH (50 mL) containing 15% aq. KOH (1.2 mL) and conc. NH_4OH (11.5 mL) was vigorously stirred while heating to reflux for 48 h. The precipitate formed was removed by vacuum filtration and washed with water to neutral pH. The compound proved to be soluble only in TFA and insoluble in all common organic solvents. It was dried under vacuum and a yield of 42% (0.2285 g) was obtained, m.p. > 300 °C. EI-MS: m/z (%) = 545 (100) [M^+]. $C_{32}H_{20}N_{10}$ (544.6): calcd. C 70.58, H 3.70, N 25.72; found C 69.90, H 3.80, N 25.10.

1,3-Bis(2,6-dipyrazinylpyridin-4-yl)benzene (D): The same procedure as for **C** with isophthalaldehyde produced 0.2013 g (37% yield) of **D**, which was similarly insoluble, m.p. > 300°C. EI-MS: m/z (%) = 545 (100) [M^+]. $C_{32}H_{20}N_{10}$ (544.6): calcd. C 70.58, H 3.70, N 25.72; found C 69.93, H 3.81, N 25.13.

$[Ru(A)_2](PF_6)_2$: A solution of **A** (80.0 mg, 0.15 mmol) in DMF (10 mL) was added to a solution of $RuCl_3 \cdot 3H_2O$ (19.4 g, 0.07 mmol) in DMF (10 mL) and the mixture was heated to reflux under Ar for 24 h. Addition of the cooled red solution to a saturated aqueous solution of NH_4PF_6 precipitated the product as a red solid. Purification by column chromatography (alumina; CH_3CN/satd. KNO_3/H_2O, 7:1:0.5, containing 1% $N(C_2H_5)_3$] pro-

duced 41.2 mg (40%). ^{1}H NMR: δ = 9.14 (s, 4 H, *e*), 8.98 (s, 4 H, *e′*), 8.82 (m, 8 H, *a′*, *d′*), 8.74 (d, $^3J_{H,H}$ = 8 Hz, 4 H, *d*), 8.45 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, *f*), 8.36 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, *f′*), 8.10 (t, $^3J_{H,H}$ = 7 Hz, 4 H, *c′*), 8.01 (t, $^3J_{H,H}$ = 7 Hz, 4 H, *c*), 7.57 (m, 8 H, *b′*, *a*), 7.24 (t, $^3J_{H,H}$ = 7 Hz, 4 H, *b*) ppm. MALDI-MS: *m*/*z* (%) = 593 (100) [M^{2+}]. $C_{72}H_{48}F_{12}N_{12}P_2Ru$ (1472.3): calcd. C 58.74, H 3.29, N 11.42; found C 59.15, H 3.49, N 10.89.

[(ttpy)Ru(A)](PF$_6$)$_2$: A mixture of [Ru(**ttpy**)Cl$_3$] (55.0 mg, 0.1 mmol) and $AgBF_4$ (62.5 mg, 0.3 mmol) was heated to reflux in acetone (25 mL) for 3 h. The AgCl precipitate was filtered off and the volume of the resultant violet solution was halved under reduced pressure. DMF (15 mL) was added and the remaining acetone removed. The resultant solution was added to a pre-heated (80 °C) solution of **A** (84.0 mg, 0.15 mmol) in DMF (25 mL) and the mixture was heated to reflux under Ar for 2 h. The cooled red solution was added to a saturated aqueous solution of NH_4PF_6. The red precipitate was collected by vacuum filtration, washed with water (3 × 30 mL) and Et_2O (3 × 30 mL), and freed of solvent under vacuum. Column chromatography (alumina; CH_3CN/satd. KNO_3/H_2O, 31:2:1, containing 0.66% $N(C_2H_5)_3$] and re-precipitation (NH_4PF_6) afforded 87.8 mg (70% yield) of [(**ttpy**)Ru(**A**)](PF$_6$)$_2$. The ^{1}H NMR spectroscopic data are in agreement with literature data.[15] ESI-MS: *m*/*z* (%) = 483 (100) [M^{2+}]. $C_{58}H_{41}F_{12}N_9P_2Ru$ (1255.0): calcd. C 55.51, H 3.29, N 10.04; found C 55.86, H 3.50, N 9.77.

[(ttpy)Ru(B)](PF$_6$)$_2$: This complex was prepared by the same procedure as with **A**, using [Ru(**ttpy**)Cl$_3$] (55.0 mg, 0.1 mmol), $AgBF_4$ (62.5 mg, 0.3 mmol), DMF (10 mL), ligand **B**[10] (84.0 mg, 0.15 mmol) in DMF (15 mL), previously heated to 80 °C, and heating at reflux under Ar for 2 h. Workup, chromatography and re-precipitation (NH_4PF_6) as before afforded a yield of 65% (0.0816 g) of [(**ttpy**)Ru(**B**)](PF$_6$)$_2$. ^{1}H NMR: δ = 9.13 (s, 2 H, **B**-*e*), 9.00 (s, 4 H, **B**-*e′*, **ttpy**-*e*), 8.78 (m, 4 H, **B**-*a′*, **B**-*d′*), 8.70 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, **B**-*d*), 8.65 (d, $^3J_{H,H}$ = 8 Hz, 2 H, **ttpy**-*d*), 8.33 (m, 2 H, **B**-*f*/*f′*), 8.21 (m, 2 H, **B**-*g*, **B**-*h*), 8.12 (m, 4 H, **ttpy**-*f*, **B**-*c′*), 7.97 (m, 4 H, **B**-*c*, **ttpy**-*c*), 7.60 (m, 4 H, **ttpy**-*g*, **B**-*b′*), 7.45 (m, 4 H, **B**-*a*, **ttpy**-*a*), 7.21 (2 t, 4 H, **B**-*b*, **ttpy**-*b*), 2.54 (s, 3 H, CH_3) ppm. ESI-MS: *m*/*z* (%) = 482 (75) [M^{2+}]. $C_{58}H_{41}F_{12}N_9P_2Ru$ (1255.0): calcd. C 55.51, H 3.29, N 10.04; found C 55.86, H 3.49, N 9.68.

[(ttpy)Ru(C)](PF$_6$)$_2$: This complex was prepared by the same procedure as for **A**, using [Ru(**ttpy**)Cl$_3$] (112.0 mg, 0.2 mmol) and $AgBF_4$ (125.0 mg, 0.6 mmol) in acetone (40 mL), complete removal of the acetone, 1,2-ethanediol (15 mL) instead of DMF, **C** (170.0 mg, 0.3 mmol) in TFA (25 mL) and heating to reflux under Ar for 3 h. Workup, chromatography (CH_3CN/satd. KNO_3/H_2O, 50:2:1) and re-precipitation (NH_4PF_6) as before afforded a yield of 70% (0.1763 g) of [(**ttpy**)Ru(**C**)](PF$_6$)$_2$. ^{1}H NMR: δ = 9.99 (s, 2 H, **C**-*d′*), 9.91 (s, 2 H, **C**-*d*), 9.31 (s, 2 H, **C**-*e*), 9.03 (s, 2 H, **C**-*e′*), 8.97 (s, 2 H, **ttpy**-*e*), 8.79 (m, 4 H, **C**-*b′*, **C**-*a′*), 8.69 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, **ttpy**-*d*), 8.49 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, **C**-*f*), 8.39 (m, 4 H, **C**-*a*, **C**-*f′*), 8.16 (d, $^3J_{H,H}$ = 7 Hz, 2 H, **ttpy**-*f*), 8.02 (t, 2 H, **ttpy**-*c*), 7.62 (m, 4 H, **ttpy**-*g*, **C**-*b*), 7.41 (d, $^3J_{H,H}$ = 5 Hz, 2 H, **ttpy**-*a*), 7.23 (t, 2 H, **ttpy**-*b*), 2.58 (s, 3 H, CH_3) ppm. HR-MALDI-MS: *m*/*z* (%) = 969.237 (100); $[RuC_{54}H_{37}N_{13}]^{2+}$ requires 969.044. $C_{54}H_{37}F_{12}N_{13}P_2Ru$ (1259.0): calcd. C 51.52, H 2.96, N 14.46; found C 52.20, H 3.56, N 13.94.

[(ttpy)Ru(A)Ru(ttpy)](PF$_6$)$_4$: This complex was prepared by the same procedure as for [(**ttpy**)Ru(**A**)](PF$_6$)$_2$, using [Ru(**ttpy**)Cl$_3$] (53.0 mg, 0.1 mmol), $AgBF_4$ (77.5 mg, 0.3 mmol) in acetone (25 mL), DMF (10 mL), **A** (27.0 mg, 0.05 mmol) in DMF (10 mL), and heating at reflux under Ar for 3 h. Workup as before afforded a yield of 19% (18.7 mg) of [(**ttpy**)Ru**A**Ru(**ttpy**)](PF$_6$)$_4$. ^{1}H NMR: δ = 9.19 (s, 4 H, **A**-*e*), 9.05 (s, 4 H, **ttpy**-*e*), 8.78 (d, $^3J_{H,H}$ = 8 Hz, 4 H, **A**-*d*), 8.71 (d, $^3J_{H,H}$ = 8 Hz, 4 H, **ttpy**-*d*), 8.62 (s, 4 H, **A**-*f*), 8.17 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, **ttpy**-*f*), 8.03 (m, 8 H, **A**-*c*, **ttpy**-*c*), 7.64 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, **ttpy**-*g*), 7.51 (m, 8 H, **A**-*a*, **ttpy**-*a*), 7.26 (m, 8 H, **A**-*b*, **ttpy**-*b*), 2.58 (s, 6 H, CH_3) ppm. ESI-MS: *m*/*z* (%) = 348 (75) [M^{4+}].

[(ttpy)Ru(B)Ru(ttpy)](PF$_6$)$_4$: This complex was prepared by exactly the same procedure as for [(**ttpy**)Ru(**A**)Ru(**ttpy**)](PF$_6$)$_4$, using [Ru(**ttpy**)Cl$_3$] (52.6 mg, 0.1 mmol), $AgBF_4$ (79.3 mg, 0.3 mmol) and **B**[10] (28.0 mg, 0.05 mmol), affording a yield of 17% (16.7 mg) of [(**ttpy**)Ru(**B**)Ru(**ttpy**)](PF$_6$)$_4$. ^{1}H NMR: δ = 9.27 (s, 4 H, **B**-*e*), 9.02 (s, 4 H, **ttpy**-*e*), 8.80 (d, $^3J_{H,H}$ = 7.3 Hz, 4 H, **B**-*d*), 8.68 (d, $^3J_{H,H}$ = 8.3 Hz, 4 H, **ttpy**-*d*), 8.47 (m, 4 H, **B**-*f*, **B**-*g*, **B**-*h*), 8.13 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, **ttpy**-*f*), 7.99 (m, 8 H, **B**-*c*, **ttpy**-*c*), 7.60 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, **ttpy**-*g*), 7.48 (m, 8 H, **B**-*a*, **ttpy**-*a*), 7.23 (m, 8 H, **B**-*b*, **ttpy**-*d*), 2.55 (s, 6 H, CH_3) ppm. ESI-MS: *m*/*z* (%) = 347 (100) [M^{4+}]. $C_{80}H_{58}F_{24}N_{12}P_4Ru_2$ (1969.4): calcd. C 48.79, H 2.97, N 8.53; found C 48.24, H 3.45, N 8.45.

[(ttpy)Ru(C)Ru(ttpy)](PF$_6$)$_4$: This was prepared by the same procedure as for [(**ttpy**)Ru(**C**)](PF$_6$)$_2$, using [Ru(**ttpy**)Cl$_3$] (96.0 mg, 0.2 mmol) and $AgBF_4$ (130.0 mg, 0.6 mmol) in acetone (25 mL), ethane-1,2-diol (10 mL), and a solution of **C** (50.0 mg, 0.1 mmol) in TFA (5 mL) and ethane-1,2-diol (10 mL), with heating to reflux under Ar for 24 h in the presence of *N*-methylmorpholine (2 drops). Workup, chromatography (CH_3CN/satd. KNO_3/H_2O, 7:1:0.5), to remove the minor impurity of [Ru(**ttpy**)$_2$](PF$_6$)$_2$, and re-precipitation (NH_4PF_6) as before afforded a yield of 20% (39.5 mg) of [(**ttpy**)Ru(**C**)Ru(**ttpy**)](PF$_6$)$_4$. ^{1}H NMR: δ = 9.84 (s, 4 H, **C**-*d*), 9.34 (s, 4 H, **C**-*e*), 9.04 (s, 4 H, **ttpy**-*e*), 8.70 (d, $^3J_{H,H}$ = 8 Hz, 4 H, **ttpy**-*d*), 8.64 (s, 4 H, **C**-*f*), 8.41 (d, 4 H, **C**-*a*), 8.16 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, **ttpy**-*f*), 8.03 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, **ttpy**-*c*), 7.64 (m, 8 H, **C**-*b*, **ttpy**-*g*), 7.42 (d, $^3J_{H,H}$ = 5 Hz, 4 H, **ttpy**-*a*), 7.23 (t, $^3J_{H,H}$ = 6 Hz, 4 H, **ttpy**-*b*), 2.57 (s, 6 H, CH_3) ppm. HR-MALDI-MS: *m*/*z* (%) = 1393.297 (60), $[Ru_2C_{76}H_{54}N_{16}]^{4+}$ requires 1393.509. $C_{76}H_{54}F_{24}N_{16}P_4Ru_2$ (1973.4): calcd. C 46.26, H 2.76, N 11.36; found C 46.75, H 3.07, N 11.55.

[(ttpy)Ru(A)Ru(A)Ru(ttpy)](PF$_6$)$_6$: To a solution of $RuCl_3 \cdot 3H_2O$ (9.0 mg, 0.03 mmol) in ethane-1,2-diol (30 mL) was added [(**ttpy**)-Ru(**A**)](PF$_6$)$_2$ (90.0 mg, 0.07 mmol) and *N*-methylmorpholine (9 drops). Ths solution was heated to reflux under Ar for 24 h. The addition of the cooled red solution to a saturated aqueous solution of NH_4PF_6 precipitated the product as a red solid. Recrystallization using CH_3CN/Et_2O of the red solid yielded the desired pure product in 87% yield (75.8 mg). ^{1}H NMR: δ = 9.23 (s, 4 H, **A**-*e*), 9.21 (s, 4 H, **A**-*e′*), 9.06 (s, 4 H, **ttpy**-*e*), 8.79 (2 t, 8 H, **A**-*d*, **A**-*d′*), 8.71 (d, $^3J_{H,H}$ = 7.9 Hz, 4 H, **ttpy**-*d*), 8.64 (s, 8 H, **A**-*f*, **A**-*f′*), 8.17 (d, $^3J_{H,H}$ = 7.4 Hz, 4 H, **ttpy**-*f*), 8.03 (m, 12 H, **A**-*c*, **A**-*c′*, **ttpy**-*c*), 7.64 (d, $^3J_{H,H}$ = 7.4 Hz, 4 H, **ttpy**-*g*), 7.58 (d, $^3J_{H,H}$ = 5.3 Hz, 4 H, **A**-*a*), 7.52 (m, 8 H, **A**-*a′*, **ttpy**-*a*), 7.28 (m, 12 H, **A**-*b*, **A**-*b′*, **ttpy**-*b*), 2.58 (s, 6 H, CH_3) ppm. ESI-MS: *m*/*z* (%) = 339.2 (70) [M^{6+}]. $C_{116}H_{82}F_{36}N_{18}P_6Ru_3$ (2901.0): calcd. C 48.03, H 2.85, N 8.69; found C 47.52, H 2.89, N 7.89.

[(ttpy)Ru(B)Ru(B)Ru(ttpy)](PF$_6$)$_6$: The same procedure used for [(**ttpy**)Ru(**A**)Ru(**A**)Ru(**ttpy**)](PF$_6$)$_6$ was applied using [(**ttpy**)-Ru(**B**)](PF$_6$)$_2$ (100 mg, 0.07 mmol) and $RuCl_3 \cdot 3H_2O$ (11 mg, 0.03 mmol), to produce the desired pure product in 70% yield (61 mg). ^{1}H NMR: δ = 9.29 (s, 4 H, **B**-*e*), 9.27 (s, 4 H, **B**-*e′*), 9.05 (s, 4 H, **ttpy**-*e*), 8.81 (2 t, $^3J_{H,H}$ = 9.3 Hz, 8 H, **B**-*d*, **B**-*d′*), 8.71 (d, $^3J_{H,H}$ = 8 Hz, 4 H, **ttpy**-*d*), 8.54 (m, 4 H, **B**-*f*, **B**-*f′*), 8.16 (d, $^3J_{H,H}$ = 8 Hz, 4 H, **ttpy**-*f*), 8.02 (m, 16 H, **B**-*c*, **B**-*c′*, **ttpy**-*c*, **B**-*g*, **B**-*h*), 7.63

(d, $^3J_{H,H}$ = 8 Hz, 4 H, **ttpy**-*g*), 7.58 (d, $^3J_{H,H}$ = 5 Hz, 4 H, **B**-*a*), 7.52 (m, 8 H, **B**-*a′*, **ttpy**-*a*), 7.30 (m, 12 H, **B**-*b*, **B**-*b′*, **ttpy**-*b*), 2.58 (s, 6 H, CH_3) ppm. ESI-MS: *m*/*z* (%) = 338.5 (70) [M^{6+}]. $C_{116}H_{82}F_{36}N_{18}P_6Ru_3{\cdot}2H_2O$ (2937.1): calcd. C 47.44, H 2.95, N 8.58; found C 47.60, H 2.94, N 8.25.

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