

Luminescent Ruthenium Polypyridyl Complexes Containing Pendant Pyridinium Acceptors

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Introduction

Many molecular approaches to solar energy conversion emphasize light collection by an isolated chromophoric center, followed by charge transfer to a nearby electron acceptor.¹ Slightly more sophisticated approaches incorporate linkages between the two, with the idea of controlling the separation step as well as subsequent (unproductive) charge recombination.² Classic examples of both are based on photo-initiated reactions of tris(bipyridyl)ruthenium(II) (an excellent excited-state reductant) with methylviologen or other alkylated (bi)pyridinium ions (i.e. good to excellent acceptors). In these reactions the acceptor ion can be either freely diffusing³ or connected to the chromophore by a hydrocarbon tether.⁴ Here we describe an interesting variant in which neither a spacer nor diffusion is employed. Instead (bi)pyridinium ions are attached *directly* to Ru(bpy)₃²⁺. We reasoned that, in these assemblies, charge transfer (CT) might be exceptionally rapid because of the exceptional proximity of the donor and acceptor components. Instead we find that CT is exceptionally slow—so slow, in fact, that it is not observed during the lifetime of the photo-excited donor state. Further exploration (by electrochemistry, fluorescence spectroscopy, and X-ray crystallography) suggests that the attachment chemistry itself alters the chromophore excited-state energetics sufficiently to account for the unusual and unexpected loss of charge-transfer reactivity in this well-known system.

Our entry into the linked systems was stimulated by the observation that ruthenium phenanthroline (phen) complexes containing free (noncoordinated) pyridyl functionalities will rapidly oxidatively electropolymerize in dry solvents.⁵ (Examples of polymerizable complexes include Ru(phen)₂(4,4'-bpy)₂²⁺, Ru(phen)₂(bis(4-pyridyl)ethylene)₂²⁺, and Ru(phen)₂

(bis(4-pyridyl)ethane)₂²⁺.) Although the exact mechanism of electropolymerization has yet to be established with certainty, the available indirect evidence is consistent with nucleophilic attack by one of the available remote bipyridyl nitrogens at one of the phenanthroline carbons, after activation of the phen ligand by coordinated metal (Ru) oxidation.^{5c} Subsequent elimination of a phen H atom is apparently accomplished by spontaneous reduction of the metal center—leaving behind, therefore, a positively charged pyridyl nitrogen and a nitrogen(bipyridyl)–carbon(phen) bond. The availability of two phen and two bipyridyl ligands per metal complex leads to multiple linkages per complex and, therefore, cross-linked metallopolymer formation.

Experimental Section

Synthesis of [RuL₂L'-L](PF₆)₃. The hexafluorophosphate salt of RuL₃²⁺ (L = bpy or phen)⁶ was converted to the 3+ form by electrochemical oxidation at +1.4 V in dry acetonitrile containing tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. The oxidized (green) solution was added to an excess of L' (=4-phenylpyridine, *tert*-butyl-4-pyridine or 4,4'-bpy) in CH₃CN. The mixture rapidly turned orange, indicating formation of Ru(II). After 1 h of stirring, the solvent was removed. The residue was extracted with boiling chloroform to remove excess electrolyte. The crude product was purified by repetitive (3×) column chromatography on activated alumina with 1:1 acetonitrile/toluene as eluent; the second of two orange components was collected in each case. Generally satisfactory elemental analyses (C, H, N, P) were obtained for each of four new compounds prepared in this way.⁷ In part because of inefficiencies in the chromatography, yields for purified compounds were only a few percent.

Measurements. Cyclic voltammetry experiments (200 mV s⁻¹, except as indicated) were run in 0.1 M TBAH in deoxygenated acetonitrile by using a single-compartment cell. The cell contained either a platinum disk or wire working electrode, a platinum counter electrode, and a saturated (NaCl) calomel electrode (SSCE) with control provided by a PAR 273 or Pine RDE4 potentiostat. Voltammograms were recorded on a Houston Instruments Model 2000 X-Y recorder.

Steady-state emission spectra were collected on a Perkin-Elmer MPF-44A spectrofluorometer and were subsequently corrected for instrument response. Time-resolved measurements were made in deoxygenated acetonitrile by using a nitrogen-pumped dye laser (PRA LN1000 and LN102; 300–700 ps pulse width at ~5 Hz) as a tunable excitation source. Emitted light was collected at 90°, passed through a cutoff filter, focused onto a Jarell Ash monochromator, and detected with a Hamamatsu R928 photomultiplier tube that had been modified for fast response. Data collection was triggered with a photodiode. The PMT response was digitized and averaged (typically 200 shots) with a LeCroy 9400 digital oscilloscope (125 MHz bandwidth). Several sets were then further averaged and fit to a single exponential decay function.

X-ray Crystallography. Crystals of [Ru(bpy)₂(bpy-4,4'-bpy)](PF₆)₃ (1) suitable for X-ray crystallographic measurements were grown at ambient temperature from a mixture of acetonitrile and toluene. A ruby plate having the dimensions 0.28 × 0.23 × 0.12 mm was mounted on a glass fiber. Measurements were made on an Enraf Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 centered reflections in the range 15.20 < 2θ < 20.7°. On the basis of packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be P1̄ (No. 2). The data were collected at a temperature of -120 ± 1 °C using the ω-θ scan technique to a maximum 2θ value of 47°. Of the 8664 reflections which were collected, 8210 were unique. The intensities of three representative reflections, which were measured after

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(7) A slightly low analysis for phosphorous was obtained, however, for [Ru(phen)₂(phen-*tert*-butylpyridinium)](PF₆)₃ (calc, 7.67%; found, 6.39%). In all other respects this compound behaved normally.

Chart 1

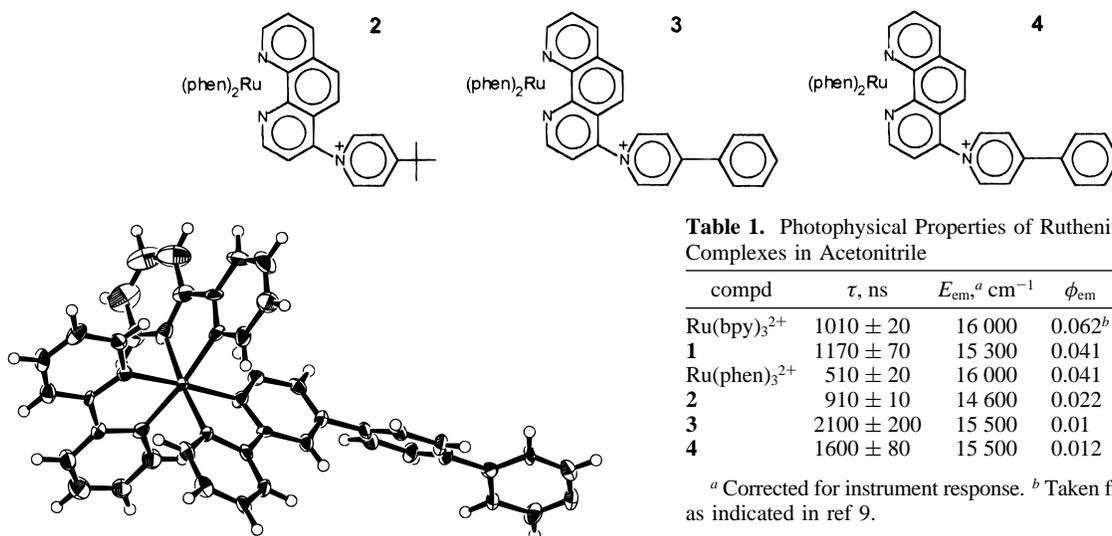


Figure 1. ORTEP drawing of $\text{Ru}(\text{bpy})_2(\text{bpy-4,4}'\text{-bpy})^{2+}$.

every 90 min of X-ray exposure time, remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo $K\alpha$ is 32.0 cm^{-1} . An analytical absorption correction was applied which resulted in transmission factors ranging from 0.86 to 0.95. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4815 reflections with $I > 3\sigma(I)$ and 640 variable parameters and gave $R(F) = 0.067$ and $R_w(F) = 0.73$. TEXSAN crystallographic software (Molecular Structure Corp., College Station, TX) was used for all calculations.

Results and Discussion

X-ray crystallographic measurements definitively establish the structure of **1** as a tris(bipyridyl)ruthenium dication (excited-state electron donor) with a 4,4'-bipyridinium ion (putative electron acceptor) attached at the 4 site of a single 2,2'-bpy ligand via a nitrogen-carbon bond. From the structure (ORTEP drawing, Figure 1) the interplanar angle between the unique 2,2'-bipyridine and the closer of the two 4,4'-bpy rings is 28° , while the interplanar angle between the pair of 4,4'-bpy rings is 24° . That the compound forms at all is interesting in that related bpy-containing compounds designed for electropolymerization via similar nitrogen-carbon bond formation are either unreactive or only marginally reactive in terms of metallopolymer film formation.⁵ (Phen-containing compounds, however, are reactive.) In any case, by analogy to **1** the structures of **2–4** can be represented schematically as shown in Chart 1. It should be mentioned that the single-crystal X-ray structure of **4** has also recently been established.^{5c}

All four compounds exhibit the intense orange color and allowed metal-to-ligand charge-transfer (MLCT) transitions that are characteristic of ruthenium(II) bipyridine and phenanthroline complexes.⁸ Excitation in the MLCT region reveals that all of the new compounds luminesce with quantum efficiencies (Table 1) similar to those for $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$, despite the presence of pyridinium ions. Time-resolved emission studies confirm that the appended pyridinium species are ineffective as quenchers; rather than attenuating luminescence lifetimes, attached "quenchers" induce modest increases. Further analysis (Table 1) shows that the lifetime increases are associated

Table 1. Photophysical Properties of Ruthenium Polypyridyl Complexes in Acetonitrile

compd	τ , ns	E_{em} , ^a cm^{-1}	ϕ_{em}	k_r , ^c s^{-1}	k_{nr} , ^c s^{-1}
$\text{Ru}(\text{bpy})_3^{2+}$	1010 ± 20	16 000	0.062 ^b	6.1×10^4	9.3×10^5
1	1170 ± 70	15 300	0.041	3.5×10^4	8×10^5
$\text{Ru}(\text{phen})_3^{2+}$	510 ± 20	16 000	0.041	8.2×10^4	1.9×10^6
2	910 ± 10	14 600	0.022	2.4×10^4	1.1×10^6
3	2100 ± 200	15 500	0.01	5×10^3	4.7×10^5
4	1600 ± 80	15 500	0.012	8×10^3	6×10^5

^a Corrected for instrument response. ^b Taken from ref 10. ^c Calculated as indicated in ref 9.

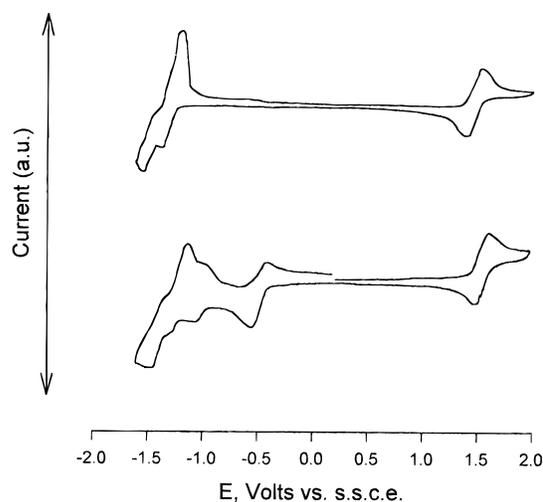


Figure 2. Cyclic voltammetric responses for $\text{Ru}(\text{phen})_3^{2+}$ (top) and $\text{Ru}(\text{phen})_2(\text{phen-4,4}'\text{-bpy})^{3+}$ (bottom) in deoxygenated acetonitrile.

primarily with decreases in rate constants for nonradiative decay (k_{nr}), although small changes in rate constants for radiative decay are also evident.^{9,10} Finally, Table 1 also shows that pyridinium ion attachment leads to small, but easily observable, red shifts in corrected luminescence energy maxima (E_{em}).

Electrochemical measurements offer some insight into both the energetic and kinetic effects. Figure 2 compares cyclic voltammetric responses for $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{phen})_2(\text{phen-4,4}'\text{-bpy})^{3+}$. Particularly noteworthy are (a) the appearance of a nearly reversible wave at -0.54 V , assigned as the attached 4,4'-bipyridinium⁺⁰ couple and (b) a small positive shift (0.1 V) in the $\text{Ru}(\text{III/II})$ formal potential (E_f) following bipyridinium ion attachment. The latter effect can be understood in terms of conventional substituent inductive effects upon coordinated

(9) Radiative (k_r) and nonradiative (k_{nr}) decay rate constants were calculated from $\phi_r = k_r \tau$ and $\tau = (k_r + k_{nr})^{-1}$, where ϕ_r is the radiative quantum yield. (We assume, in the absence of any direct information to the contrary, that ¹MLCT to ³MLCT conversion occurs with unit efficiency.) Absolute ϕ_r values for **1–4** were determined in deoxygenated solutions by measuring yields relative to $\text{Ru}(\text{bpy})_3^{2+}$ and assuming $\phi_r(\text{Ru}(\text{bpy})_3^{2+}) = 0.062$.^{13c} When defined in this way, k_{nr} includes contributions from both conventional nonradiative decay and intersystem crossing (d-d state) decay pathways.

(10) A reviewer has pointed out the apparent decreases in radiative decay rate constant following chromophore derivatization (see Table 2) might instead be indicative of inefficient "singlet" to "triplet" excited-state interconversion.

Table 2. Ground- and Photo-Excited-State Redox Properties of Polypyridyl Complexes in Acetonitrile

compd	$E_f(\text{RuL}_3^{3+/2+})$ or $E_f(\text{RuL}_2\text{L-L}^{4+/3+})$, V	$E_f(\text{py}^{+/0})$, V	$E_f(\text{RuL}_3^{3+/2+*})$ or $E_f(\text{RuL}_2\text{L-L}^{4+/3+*})$, ^b V
Ru(bpy) ₃ ²⁺	1.29		-0.82
1	1.37	-0.53 ^c	-0.66
Ru(phen) ₃ ²⁺	1.29		-0.82
2	1.31	-0.88	-0.63
3	1.42	-0.65 ^d	-0.63
4	1.38	-0.54	-0.66

^a Determined from eq 1a. ^b Determined from eq 1b. ^c Measured at 400 mV s⁻¹. ^d Measured at 1000 mV s⁻¹.

metal potentials. The positively charged (bi)pyridinium species should exert a substantial electron-withdrawing effect, making electron removal from Ru(II) more difficult and thereby shifting $E_f(\text{Ru}^{\text{III/II}})$ in the positive direction. As indicated in Table 2, similar effects exist for **1–3**.

The combination of ground-state electrochemical data and excited-state emission energies in principle permits potentials for excited-state oxidation to be calculated. As suggested by both eqs 1a (applicable to RuL_3^{n+}) and 1b (applicable to $\text{RuL}_2\text{L-}$

$$E_f(\text{RuL}_3^{3+/2+*}) = E_f(\text{RuL}_3^{3+/2+}) - E(0-0) \quad (1a)$$

$$E_f(\text{RuL}_2\text{L-L}^{4+/3+*}) = E_f(\text{RuL}_2\text{L-L}^{4+/3+}) - E(0-0) \quad (1b)$$

L^{m+}), the most appropriate approach to calculating these is to use 0–0 emission energies, $E(0-0)$. These energies clearly will exceed E_{em} . For Ru(bpy)₃^{2+*} in acetonitrile, the difference between $E(0-0)$ and E_{em} can be estimated as 1040 cm⁻¹.¹¹ If a similar difference is assumed to apply to Ru(phen)₃²⁺ and **1–4**, then the excited-state potentials shown in Table 2 are obtained. Notably, the potentials for the pyridinium-derivatized species are appreciably positive of those for the parent complexes, presumably now because of pendant cation stabilization of the coordinated bpy (or phen) anion.

An obvious corollary to (or restatement of) the shift in excited-state potentials is a diminution in excited-state reductant strength. A comparison of Tables 1 and 2 suggests that the diminution is sufficiently large that at least one of the expected quenching reactions (photogenerated phen anion to *tert*-butylpyridinium cation electron transfer (compound **2**)) is endergonic and, therefore, ineffective. A further consideration of the energetics suggests that the relevant quencher reduction potentials may be even more negative (i.e. less favorable for ET) than indicated in Table 1. We note that ground-state electrochemical measurements of $E_f(\text{py}^{+/0})$ are made in the presence of neutral bpy or phen. In the MLCT excited state, however, the pyridinium cation is linked to an anionic ligand (and therefore stabilized). The precise magnitude of the effect of neighboring bpy (phen) anion generation upon $E_f(\text{py}^{+/0})$ is difficult to establish experimentally. A reasonable guess, however, is that it is equal (but opposite in sign) to the inductive effect exerted by the pendant pyridinium cation upon the potential for the oxidation of the photo excited state (Table 2). Thus $E_f(\text{py}^{+/0})$, under these conditions, would be ca. 0.16–0.20 V more negative than indicated in Table 1. Of course, if the electron for pyridinium reduction comes from bpy or phen, then the inductive effect upon $E_f(\text{py}^{+/0})$ will be overestimated (since

(11) The estimate comes from a reported¹⁶ 400 cm⁻¹ vibrational reorganizational contribution to the $E(0-0)$ vs E_{em} difference for Ru(4,4'-CH₃-2,2'-bpy)₃^{2+*} at 298 K, together with a 640 cm⁻¹ solvent reorganizational energy contribution for Ru(bpy)₃^{2+*} in acetonitrile (Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098).

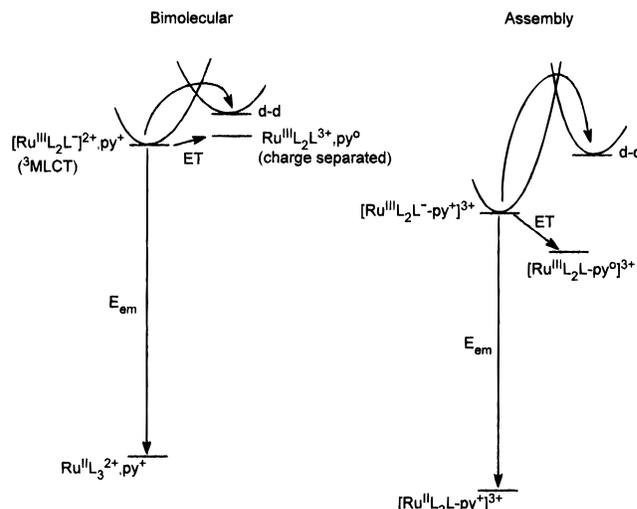


Figure 3. Qualitative energy diagrams for excited-state electron transfer, intersystem crossing, and radiative decay for a $\text{RuL}_3^{2+}/\text{py}^+$ pair ($\text{L} = \text{bpy}$ or phen) and for a $\text{RuL}_2\text{L-py}^{3+}$ assembly. In comparison to the bimolecular pair, the emissive MLCT state of the assembly is lowered in energy with respect to the d–d state resulting in an increased barrier to intersystem crossing and a red shift in luminescence energy.

py^0 will no longer experience the destabilizing electron-donating influence of a neighboring bpy or phen anion). Similarly, if the (hypothetical) fate of an electron transferred from photoexcited **1–4** is capture by (neutralization of) a pendant pyridinium ion, then the relevant shift in excited-state potentials for these species in comparison to the parent complexes (Table 2) will be overestimated.¹²

Despite the uncertainties, direct quencher attachment clearly (a) influences the oxidizing strength of the quencher¹³ and (b) diminishes the reducing strength of the photoexcited chromophore. The cumulative energetic effects evidently are great enough (as sketched in Figure 3) to render the quenching reactions either endergonic or sufficiently weakly exergonic that intramolecular ET is unable to compete kinetically with other nonradiative decay processes (however, see below). The available emission energies also suggest a qualitative explanation for the unusual lifetime lengthening effects accompanying “quencher” attachment. In the parent complex, Ru(bpy)₃²⁺, one component of nonradiative decay from the MLCT excited state is a thermally activated intersystem crossing to a d–d state which then relaxes rapidly to the ground electronic state (Figure 3).¹⁴ Prior studies as a function of solvent^{14d} or with derivatives^{14e} have shown that as the MLCT/d–d energy gap diminishes, the activation barrier increases and the intersystem crossing kinetics

(12) An equivalent alternative view would emphasize electrostatic stabilization of the bpy (phen) anion/pyridinium cation reactant pair versus the corresponding neutral bpy (phen)/neutral pyridine radical product pair.

(13) The oxidizing strength is diminished in the sense that the cationic quencher (Q) is stabilized by the coordinated anionic ligand donor, as discussed above. From the potentials in Table 2, on the other hand, the attached quenchers are *better* oxidants (when bound to *ground-state* RuL_3^{2+}) than are the analogous free *N*-methylated pyridinium ions. For example, the reduction potential for free *N*-methyl-*N'*-bipyridinium cation (“monquat”) is -0.96 V.¹⁶ Note that this is more negative than the excited-state oxidation potential for either of the free chromophores, implying that bimolecular quenching is unlikely to occur. Replacement of methyl by benzyl, however, should shift the quencher potential in the positive direction by ca. 0.1 V (see: Loug; et al. *J. Am. Chem. Soc.* **1978**, *100*, 5790) and render the ET reactants and products approximately isoenergetic. The degree of thermodynamic accessibility (or inaccessibility) of the bimolecular analog of the intramolecular quenching reaction depends, therefore, on the choice of model compound for Q. Given the ambiguity, we have represented the bimolecular reaction as a slightly endergonic process in Figure 3.

become much less important in controlling the overall decay kinetics (i.e. the observable excited-state lifetime). Quencher attachment clearly lowers the emissive MLCT "triplet" state energy (Table 2) but presumably does not affect the energy of the metal-localized d-d state with respect to the ground state. Consequently, the barrier to intersystem crossing should increase, the crossing rate should exponentially decrease, and the overall excited-state decay rate should be determined primarily by conventional radiative and nonradiative decay mechanisms rather than d-d state accessibility. The longer lifetimes for the quencher modified complexes presumably reflect the removal (or partial removal) of the d-d pathway.

An alternative or additional explanation focuses on the approximate energetic degeneracy of the triplet MLCT state and the proposed fully charge separated state (reduced quencher state; see Figure 3). Under these conditions it is conceivable that rapid forward electron transfer (bpy or phen anion to pyridinium) is followed by back ET to repopulate the emissive MLCT state. The resulting dual excited-state equilibration could lengthen the effective emission decay time if the nonradiative decay rate for the charge separated state were slower than the corresponding decay rate for the MLCT state. Thus, under these conditions, the k_{nr} values in Table 1 would represent weighted average values of k_{nr} for two excited states.

A second alternative is that the MLCT and charge-separated states are sufficiently strongly mixed that the electron becomes delocalized over the entire phen(bpy)/pyridinium superligand. Given the nominal geometric orthogonality of the pyridine functionality and coordinated phen or bpy (28° interplanar angle; see Figure 1), delocalization would likely be achieved only after rotation about the C4-N(py) linkage.¹⁵ The resulting coplanar superligand, however, would presumably suffer less net vibrational rearrangement upon return to the electronic ground state than would either of the parent complexes. Decreased displacement implies smaller Franck-Condon factors, a diminished rate for nonradiative decay from the "super MLCT" versus MLCT excited state, and an overall increase in lifetime. It should be noted that Meyer and co-workers have recently reported several examples of such behavior for systems containing large *rigid* chromophoric ligands.^{16,17}

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Supporting Information Available: A table of elemental analyses for 1-4 (1 page). Ordering information is given on any current masthead page.

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