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Selective Perturbation of Ligand Field Excited States in Polypyridine Ruthenium(II) Complexes

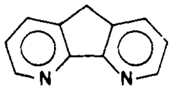
Leslie J. Henderson, Jr., Frank R. Fronczek, and William R. Cherry*

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received November 18, 1983

Abstract: A new bipyridine-type ligand which allows the selective perturbation of ligand field (LF) excited-state energies is introduced. Any metal-to-ligand charge-transfer (MLCT) excited states occur at nearly the same energy as in the bipyridine complex. The syntheses of the corresponding ruthenium(II) complexes and their photophysical properties are reported. The results clearly support a current model for the excited-state behavior of polypyridine complexes in which the lowest MLCT decays by thermal population of a higher lying LF state. This method of selective LF-state perturbation nicely complements the perturbation of MLCT states achieved by modification of the ligand's reduction potential.

The field of inorganic and organometallic photochemistry has grown explosively within the last decade.[1] Several general principles governing photophysical and photochemical behavior have begun to emerge. For example, most photoextrusion processes apparently originate from a ligand field (LF) excited state. A decisive tool that has aided in the elucidation of these principles has been the selective perturbation of metal-to-ligand charge-transfer (MLCT) excited states.[2] This approach has been especially useful in the investigation of pyridine and polypyridine metal complexes. By systematically varying the reduction potential of the pyridine ligand with para substituents, Ford and co-workers modified the identity of the lowest excited state in $Ru(NH_3)_5py^{2+}$ (py = para-substituted pyridine).[3] When the substituent was electron donating, the lowest excited states had mainly LF character and photosubstitution was efficient. On the other hand, when the substituent was an acceptor, the lowest excited state had mainly MLCT character and the photosubstitution efficiency was greatly decreased.

We now wish to report a convenient method for selectively perturbing the energy of LF states while leaving MLCT states nearly unchanged. This method is based upon the 4,5-diazafluorene ligand (**1**). The methylene bridge in **1** distorts the bipyridine portion of the molecule so as to reduce the nitrogen-metal overlap. Hence, **1** is effectively lower than bpy in the spectrochemical series which translates into an energetic lowering of any LF states. On the other hand, the reduction potentials of both **1** and bpy should be similar so that any changes in the energy of MLCT states are expected to be modest.



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The system chosen to illustrate the utility of this approach was $Ru(bpy)_n(\mathbf{1})_{3-n}$. The photophysics of the parent, $Ru(bpy)_3^{2+}$, is well-known, and the pertinent details are shown in Figure 1.[4] An initially formed singlet MLCT state undergoes very rapid intersystem crossing to the corresponding triplet state. This ^{3}MLCT state has been extensively studied and has been shown to be composed of at least three closely spaced states with widely different lifetimes.[5] However, at or above 77 K, all three states are essentially equally populated, and hence, this state may be considered an "average state".

Besides the processes of radiative and radiationless decay, a third, thermally activated process may deactivate this triplet state.[6] By evaluating either the luminescent lifetime or quantum yield as a function of temperature, the activation energy for this process was determined to be 3600 cm^{-1}.[6] The fact that this thermally populated state is nonluminescent, rapidly decays to the ground state, and results in a photosubstitution reaction indicates that its identity is most likely an LF excited state.[7] The proximity of these two excited states makes this system ideal for examining any effects induced by the substitution of **1** for bpy.

Experimental Section

General. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Elemental analyses were performed by Micro-Anal Co., Tuscson, Az. The NMR spectra were recorded on either a Bruker WP200 or Varian A-60A spectrometer. Mass spectra were obtained on a Varian GC-Mass Spec HP5985A spectrometer. The IR spectra were recorded on a Perkin-Elmer Model 7278 or 621 spectrometer. Absorption spectra were recorded on a Cary 14 spectrometer. The emission spectra were recorded with an SLM 4800S spectrometer and were corrected for photomultiplier response. All solvents were purified by standard procedures.[8]

Preparation of 4,5-Diazafluoren-9-one[9] Phenanthroline (0.12 mol, 23.55 g) and KOH (0.22 mol, 12.22g) were added to 1000 mL of water and brought to reflux. Potassium permanganate (0.38 mol, 60.78 g) in 500 mL of water was added dropwise to the refluxing mixture. After addition, the solution was refluxed for 0.5 h and filtered to remove MnO_2. When the solution was cooled, crude 4,5-diazafluoren-9-one precipitated as yellow needles. Recrystallization from water yielded 5.42 g (25%) of the desired ketone: mp 212-213 °C (lit.[9] mp 211, 218, and 215-216 °C); mass spectrum, *m/e* (rel intensity) 182; IR $\nu_{C=O}$ 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.81 (d, 2 H, J = 5.1 Hz), 7.99 (d, 2 H, J = 7.5 Hz), 7.35 (dd, 2 H, J = 5.1 and 7.5 Hz).

Preparation of 4,5-Diazafluorene (1).[10] Hydrazine hydrate (85%, 14 mL) and 4,5-diazafluoren-9-one (0.025 mol, 4.6 g) were placed in a steel bomb and heated to 165 °C for 18 h. When the solution was cooled, a white solid was filtered from the dark red liquid. Extraction of the red liquid with $CHCl_3$ yielded additional solid. The combined solid portions were added to benzene in order to separate the soluble diazafluorene from its insoluble dimer. After filtration, addition of hexane to the benzene fraction yielded white needles. Final purification was accomplished by column chromatography (silica gel, EtAc/cyclohexane 1:1): mp 171-173 °C (lit.[10] mp 172 °C); mass spectrum, *m/e* (rel intensity) 168; NMR

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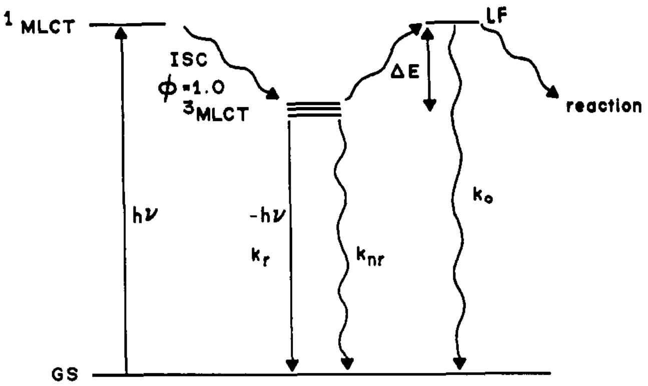

Figure 1. Photophysics of polypyridine ruthenium complexes.

Table I. Absorption Spectra for Nickel(II) Complexes[a]

complex	$^3A_2 \rightarrow {}^3T_2$, cm^{-1}	$^3A_2 \rightarrow {}^3T_1$, cm^{-1}
$Ni(H_2O)_6^{2+}$	8850	14900
$Ni(\mathbf{1})_3^{2+}$	10250	16950
$Ni(bpy)_3^{2+}$	12660	20830

[a] Water:acetone solvent (2:1) at 25 °C.

(CD_3CN) δ 8.71 (d, 2 H, J = 4.4 Hz), 7.85 (d, 2 H, J. = 7.8 Hz), 7.26 (dd, 2 H, J = 4.4 and 7.8 Hz), 3.83 (s, 2 H).

Preparation of *cis*-Dichlorobis(bipyridine)ruthenium. The procedure suggested by Whitten and co-workers[11] was followed without change. Absorption spectrum (ethanol): 515 and 375 nm.

Preparation of Bis(bipyridine)(4,5-diazafluorene)ruthenium(II). cis-Dichlorobis(bipyridine)ruthenium (1.3 mmol, 0.664 g) and 4,5-diazafluorene (1.3 mmol, 0.2145 g) were refluxed in 30 mL of ethanol for 4 h. The solution was filtered hot and ammonium hexafluorophosphate (1 g) was added. After the solution stood overnight, crystals of $[Ru(bpy)_2(\mathbf{1})^{2+}][PF_6^-]_2$ precipitated. These were repeatedly recrystallized from acetone/water and ethanol/water. Single crystals suitable for X-ray diffraction were obtained by slow liquid-liquid diffusion: NMR (CD_3CN) δ 8.50 (d, 4 H, J = 7.8 Hz), 8.05 (m, 8 H), 7.88 (d, 2 H, J = 4.8 Hz), 7.47 (m, 8 H), 4.39 (s, 2 H). Anal. Calcd for $C_{31}H_{24}N_6P_2F_{12}Ru$: C, 42.39; H, 2.78; N, 9.64. Found: C, 43.09; H, 2.89; N, 9.59.

Preparation of Tris(4,5-diazafluorene)ruthenium(II). 4,5-Diazafluorene (2.3 mmol, 0.388 g) was added to 30 mL of propanol and brought to reflux. A previously prepared ruthenium blue solution[12] (10 mL) was added dropwise. The solution was refluxed 3 h and filtered hot, and ammonium hexafluorophosphate was added to the red filtrate. The resulting solution was kept overnight at 0 °C. The yellow/orange crystals were filtered and purified by repeated recrystallizations from acetone/water: NMR (CD_3CN) δ 8.11 (d, 6 H, J = 7.7 Hz), 7.81 (d, 6 H, J = 5.4 Hz), 7.45 (dd, 6 H, J = 7.7 and 5.4 Hz), 4.41 (s, 6 H). Anal. Calcd for $C_{33}H_{24}N_6P_2F_{12}Ru$: C, 44.26; H, 2.70; N, 9.38. Found: C, 44.82; H, 2.76; N, 9.28.

Quantum Yield Determinations. All quantum yields were determined with $Ru(bpy)_3^{2+}$ in water as a standard (φ = 0.042[6]). The spectra were corrected for variations in lamp intensity and photomultiplier response. The spectra were integrated in wavenumbers.

Emission Lifetimes. All lifetimes were determined by the single-photon counting method.[13]

Results and Discussion

The physical and spectroscopic properties of **1** agreed with those in the literature.[9] In order to verify that **1** is indeed a weaker ligand than bpy, complexes of Ni(II) were prepared. The selection of Ni(II) was based upon the readily identifiable LF states for amine complexes.[14] As seen in Table I, the LF transitions were found to undergo a bathochromic shift as the ligand was varied from bpy to **1** to water. Clearly, **1** is a weaker σ-bonding ligand than bpy.[15]

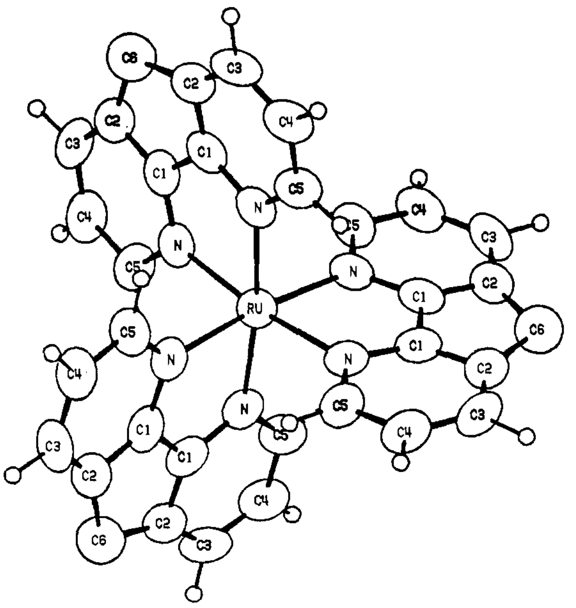

Figure 2. Structure for $Ru(bpy)_2(\mathbf{1})^{2+}$ as determined by X-ray diffraction. Note that **1** is disordered into three positions with a population of 1/3.

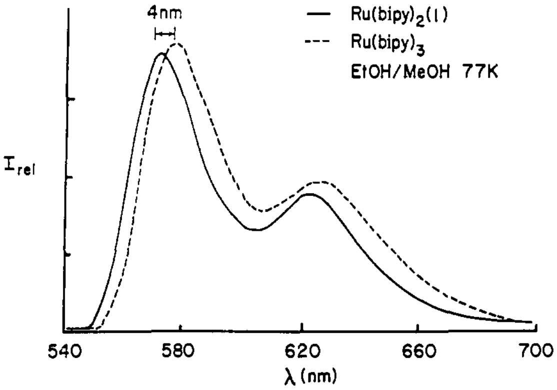

Figure 3. Emission spectra for **2** and **3** at 77 K in EtOH/MeOH (4:1). The emission intensity of **2** has been decreased (~40%) to facilitate comparison.

Table II. Emission Parameters for Ruthenium(II) Complexes

complex	λ_{max},[a] nm	φ(77)[b]	τ(77),[c] μs	φ(298)[d]	τ(298),[e] ns
$Ru(bpy)_3^{2+}$	578	0.33	5.2	4.2×10^{-2}	630
$Ru(bpy)_2(\mathbf{1})^{2+}$	574	0.56	5.9	8×10^{-4}	f
$Ru(bpy)_2(\mathbf{4})^{2+}$	609	0.23	4.3	5.6×10^{-3}	137
$Ru(\mathbf{1})_3^{2+}$	~585[g]	low			

[a] Corrected emission maximum at 77 K in EtOH/MeOH (4:1). [b] Emission quantum yield at 77 K in EtOH/MeOH (4:1); ±20%. [c] Emission lifetime at 77 K in EtOH/MeoH (4:1); ±10%. [d] Emission quantum yield at 298 K in water; ±5%. [e] Emission lifetime at 298 K in water; ±10%. [f] Too weak to measure. [g] Very weak emission.

The preparation of $Ru(bpy)_2(\mathbf{1})^{2+}$ (**2**) followed literature precedence.[11] The spectral properties were entirely consistent with the proposed structure. Furthermore, X-ray diffraction revealed that the PF_6^- salt crystallized in trigonal space group $P3_{c1}$ with a = 11.002 (2) Å, c = 16.350 (6) Å, Z = 2, and d = 1.689 g/cm^3 and is isomorphous with $[Ru(bpy)_3][PF_3]_2$. Refinemeent using 480 observations measured with Mo Kα radiation to θ = 23° on an Enraf Nonius CAD4 diffractometer led to R = 0.063. The

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(15) Further evidence is provided by the structure of $Ni(\mathbf{1})_3^{2+}$, where the average Ni–N bond length was determined to be 2.149 Å. The corresponding bond length in $Ni(bpy)_3^{2+}$ has been reported to be 2.089 (1) Å.[16]

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Table III. Radiative and Radiationless Decay Rate Constants for Polypyridine Ruthenium Complexes at 77 K

	$10^4 k_r{}^{a,b}$	$10^5 k_{nr}{}^{a,c}$
$Ru(bpy)_3{}^{2+}$	6.3	1.3
$Ru(bpy)_2(\mathbf{1})^{2+}$	9.5	0.8
$Ru(bpy)_2(\mathbf{4})^{2+}$	5.4	1.8

[a] EtOH/MeOH, 77 K (4:1). [b] Evaluated from $\phi(77)/\tau(77)$. [c] Evaluated from $1/\tau(77) - k_r$.

cation, shown in Figure 2, has crystallographic symmetry D_3, requiring the diazafluorene methylene group to be disordered into three positions with a population of 1/3. The average structure exhibits a Ru–N distance of 2.074 (6) Å and a N–Ru–N bite angle of 80.1 (4)°. The bidentate ligand is slightly nonplanar, having a N–C1–C1′–N′ torsional angle of −7.1°, and the octahedral twist angle is 51.3°. The PF_6^- anion has crystallographic C_3 symmetry with an average P–F distance of 1.49 (1) Å and is affected by high thermal motion.

The absorption spectra of **2** and $Ru(bpy)_3{}^{2+}$ (**3**) were found to be nearly superimposable. The low-temperature (77 K) emission spectra for **2** and **3** are shown in Figure 3. The intensities and lifetimes were comparable (Table II), and the radiative and radiationless decay rate constants were found to be similar for both complexes (Table III). Furthermore, very few differences in the band shapes of these spectra were apparent. The small 4-nm bathochromic shift noted for **3** supports the contention that any MLCT's are only slightly affected by substitution of **1** for bpy. As the temperature is raised to 298 K, both spectra underwent a substantial bathochromic shift and a loss of fine structure. However, the most spectacular change was noted in their relative emission intensities (Table II). At this temperature, the emission intensity for **3** was almost 50-fold larger than that for **2**. In fact, the emission intensity from **2** was so low that the lifetime could not be evaluated.

The above results can be readily rationalized within the context of the previously proposed model for the photophysics of **3**.[6,7] As mentioned earlier, the lowest excited MLCT state is deactivated by three processes: radiative decay (k_r), radiationless decay (k_{nr}), and thermal population of a higher excited LF state ($k_0 \exp(-\Delta E/RT)$). This LF state undergoes very efficient radiationless decay to the ground state. At 77 K, just the first two processes are operational and both **2** and **3** have similar emission lifetimes and intensities. Only when the temperature is raised does thermal population of the LF state become important. Since this LF state is energetically lower in **2** than in **3**, population is much more efficient for **2** at 298 K. This results in the drastic reduction of the emission intensity noted for **2** relative to **3**.

Furthermore, the emission intensities for **2**, **3** and $Ru(bpy)_2(py)_2{}^{2+}$ (py = pyridine) were determined as a function of temperature, and the results are shown in Figure 4. For **3**, there is little change in the emission intensity until around 270 K, after which the intensity rapidly decreases. This behavior has been previously observed, and the results in Figure 4 agree with these earlier reports.[6,7,17] Generally, the variation of the emission intensity (or lifetime) of **3** as a function of temperature can be accounted for with only a single activated process. However, Allsopp et al.[17] have suggested a function with two exponential terms; the second term has a very small activation energy (200 cm^{-1}) and is required only to accurately describe the low-temperature region.

In contrast, a dramatic decrease in the emission intensity of **2** occurs at a much lower temperature, clearly indicating a lower LF state than that in **3**. However, a second activated process is also observed, and it occurs in the same temperature region as in the case of **3**. Why two activated processes are apparent rather than just one is at present unclear. However, the behavior of **2** is very similar to that observed for $Ru(bpy)_2(py)_2{}^{2+}$ (see Figure 4) which supports the contention that **1** is weaker than bpy in the spectrochemical series.

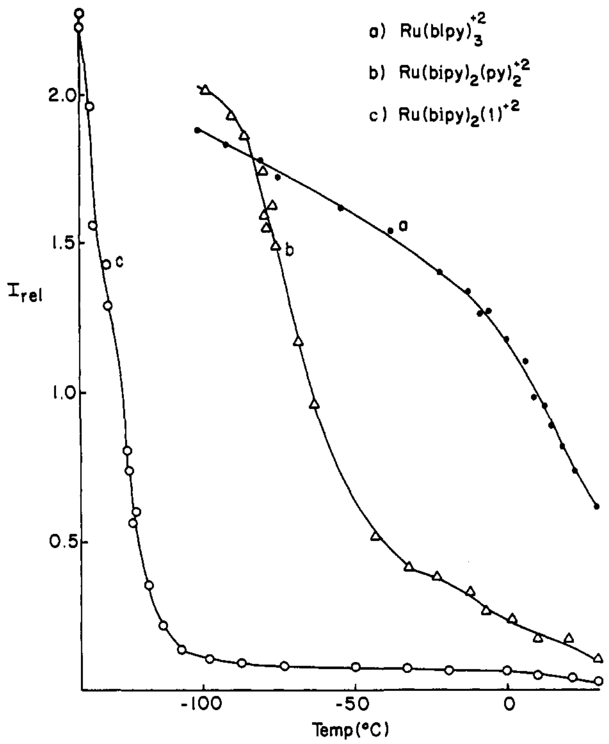


Figure 4. Relative emission intensity as a function of temperature for $Ru(bpy)_3{}^{2+}$, $Ru(bpy)_2(\mathbf{1})^{2+}$, and $Ru(bpy)_2(py)_2{}^{2+}$.

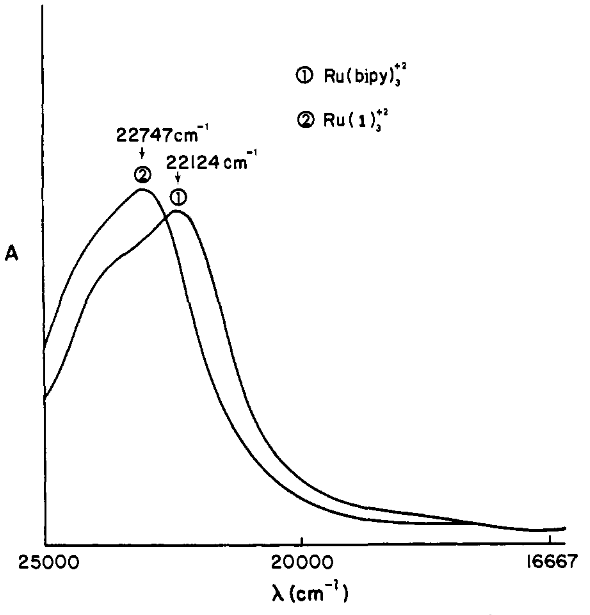
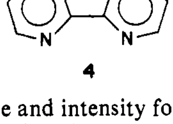


Figure 5. Absorption spectra for $Ru(bpy)_3{}^{2+}$ and $Ru(\mathbf{1})_3{}^{2+}$ in water at 298 K. The intensities are arbitrary and are not intended to imply relative extinction coefficients.

In order to further substantiate these conclusions, several other complexes have been investigated. First, $Ru(bpy)_2(\mathbf{4})^{2+}$ has been prepared and its emission properties examined. As seen in Table II, the emission lifetime and intensity for this complex at 298 K were found to be intermediate between **2** and **3**. This results from the fact that **4** is more easily reduced than **1** which necessitates a lower MLCT state. This conclusion is confirmed by the sub-



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stantial bathochromic shift in the emission maximum. Consequently, *both* the LF and MLCT states have been energetically lowered with the result that their energy difference is not varied dramatically by the substitution of **4** for bpy.

Additionally, $\mathrm{Ru}(\mathbf{1})_3^{2+}$ has been prepared, and, again, its spectroscopic properties have been investigated. The absorption spectra for both $\mathrm{Ru(bpy)}_3^{2+}$ and $\mathrm{Ru(I)}_3^{2+}$ are shown in Figure 5. There is a small bathochromic shift (~600 cm^{-1}) in the absorption band assigned to the MLCT transition. Again, this indicates that MLCT states are not substantially affected by substitution of **1** for bpy. In contrast to the previous complexes, this complex did not emit at 298 K. In fact, only a very weak emission was observed even at 77 K. This weak emission displayed none of the fine structure apparent in **2** and **3**. Consequently, we suggest that this polypyridine ruthenium(II) complex has the lowest excited state characterized by mainly a LF configuration. Taking into account the small bathochromic shift in the MLCT state, these results suggest that the LF state's energy has been reduced by approximately 3000 cm^{-1}. On the basis of the results for the Ni(II) complexes, this seems a very reasonable estimate.

In summary, the 4,5-diazafluorene ligand permits the selective perturbation of LF states. The application of this approach to polypyridine ruthenium complexes leads to the conclusion that the MLCT and LF states are in thermal equilibrium. This approach will surely assist in the assignment and "fine tuning" of the excited states in other polypyridine complexes.

Acknowledgment. This material is based upon work supported by NSF (CHE-8205698) and the LSU Center for Energy Studies, under U.S. Department of Energy Grant No. DE-FG-0580ER1019F. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE or of the LSU Center for Energy Studies. We thank R. A. Auerbach, W. Wacholtz, and R. H. Schmehl of Tulane University for measuring some low-temperature lifetimes and for some very helpful discussions.

Registry No. 1, 245-37-4; **2**, 91606-23-4; **3**, 15158-62-0; **4**, 50890-67-0; $\mathrm{Ru(bpy)_2(\mathbf{4})}^{2+}$, 91606-24-5; $\mathrm{Ru}(\mathbf{1})_3^{2+}(\mathrm{PF_6}^-)_2$, 91606-26-7; $\mathrm{Ni}(\mathbf{1})_3^{2+}$, 91606-27-8; *cis*-dichlorobis(bipyridine)ruthenium, 19542-80-4; ruthenium dichloride, 13465-51-5; phenanthroline, 12678-01-2.

Supplementary Material Available: Table of coordinate and isotropic thermal parameters for $[\mathrm{Ru(bpy)_2(\mathbf{1})}][\mathrm{PF_6}]_2$ (1 page). Ordering information is given on any current masthead page.

Novel Rose Bengal Derivatives: Synthesis and Quantum Yield Studies

Joseph J. M. Lamberts, Douglas R. Schumacher, and D. C. Neckers*

Contribution from the Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403. *Received January 31, 1984*

Abstract: The synthesis of several rose bengal derivatives soluble in nonpolar solvents is described. The bis(triethylammonium salt) of rose bengal, **2**, and the triethylammonium salt of the benzyl and ethyl esters of rose bengal, **10** and **11**, are soluble in methylene chloride and chloroform (Scheme I). The tributylammonium salt of the octyl ester of rose bengal, **12**, is also soluble in toluene. The quantum yields of singlet oxygen formation in methanol are equal to, or approaching, that of the disodium salt of rose bengal, **1** (Table VI). The derivatives also show good quantum yields in nonpolar solvents although they are somewhat lower in these solvents than they are in methanol. Electronic absorption spectroscopy points to dye association and equilibration between the quinoid and the lactonic forms or between solvent separated and tight ion pair of the dyes as possible reasons for the lower quantum yields in nonpolar solvents.

Rose bengal (3′,4′,5′,6′-tetrachloro-2′-(2,4,5,7-tetraiodo-6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoic acid, bis(sodium salt)) is one of the most efficient and most used singlet oxygen sensitizers (Table I). Though this sensitizer is very useful in polar solvents, it is essentially insoluble in typical organic solvents such as pentane and methylene chloride, and in these solvents effectively no singlet oxygen is formed. Rose bengal, commercially available as the disodium salt, has a major disadvantage in applications in which either the polar solvent reacts with the products of singlet oxygenation or the reagent reacts with or is insoluble in the polar medium. One solution to the problem was that reported "by our group and Schaap's" over 10 years ago; in that instance we immobilized rose bengal via the C-2′ carboxylate center to lightly cross-linked polystyrene beads.[1-3] This polymer-based rose bengal system is made compatible with most nonpolar solvents by virtue of the nonpolar polystyrene backbone, and the polymer serves as a vehicle to carry the polar sensitizer into the proximity of reagents dissolved in a nonpolar solvent. There are several limitations of polymer rose bengal, however. One of the more important is that its quantum yield of singlet oxygen formation is about one-half that of rose bengal "dissolved in poor solvents". Rose bengal may also be solubilized in nonpolar solvents by the addition of crown ethers,[4-7] but under these conditions one still faces the several problems indigenous to rose bengal itself.[2,3] Among the most important and major disadvantages of commercial rose bengal is impurity. Samples obtained from commercial manufacturers are rarely more than 90% rose bengal. The samples always contain inorganic impurities, and sometimes other polyhalogenated uranine salts contaminate the samples (see Experimental Section). Chromatographic purification of the sensitizer is largely ineffective, and the rose bengal samples obtained after even the most elaborate of these purification schemes[8,9] are generally no more pure than was the original commercial sample. Also the quantities of purified material obtained chromatographically are very minimal. Thus, physical measurements made with and synthetic processes carried

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