Luminescence Quenching in Supramolecular Systems: A Comparison of DNA- and SDS Micelle-Mediated Photoinduced Electron Transfer between Metal Complexes

M. R. Arkin,[†] E. D. A. Stemp,[†] C. Turro,[‡] N. J. Turro,[‡] and J. K. Barton*,[†]

Contribution from the Beckman Institute, California Institute of Technology, Pasadena, California 91125, and Department of Chemistry, Columbia University, New York, New York 10027

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Abstract: Photoinduced electron transfer reactions between photoexcited $Ru(phen)_2dppz^{2+}$ (phen = 1,10-phenanthroline, dppz = dipyridophenazine) and acceptors $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$ (phi = 9,10-phenanthrenequinone diimine, bpy = 2,2′-bipyridine) are compared in micelles and DNA. Both microheterogeneous environments contain a negatively charged surface and hydrophobic interior and the cationic complexes associate strongly with each. However, reactions between molecules bound to DNA or to micelles show striking differences which can be correlated with the unique character of the highly ordered, π-stacked basepairs in DNA compared to the disordered, aliphatic chains in the micelles. In DNA, $Rh(phi)_2bpy^{3+}$ quenches $*Ru(phen)_2dppz^{2+}$ on a fast time scale (unimolecular rate constant $\geq 10^8$ s^{-1}), whereas no detectable quenching of *Ru(II) emission by $Rh(phen)_2phi^{3+}$ is observed. In contrast, both complexes quench equally well in SDS micelles. Although static quenching on the nanosecond time scale is observed for $Rh(phi)_2bpy^{3+}$ in DNA, reactions in SDS occur dynamically by intramicellar diffusion, with a bimolecular rate constant of 1.1×10^8 M^{-1} s^{-1} for $Rh(phi)_2bpy^{3+}$ and 1.2×10^8 M^{-1} s^{-1} for $Rh(phen)_2phi^{3+}$. Reactions on DNA are also shown to be DNA-mediated in that no solvent-isotope effects are observed in the quenching. In addition, there is enantioselectivity seen in reactions on the right-handed DNA helix but not in the achiral micelle, indicating that quenching is sensitive to the geometry of intercalation. Efficient electron transfer quenching in DNA compared to SDS micelles therefore provides evidence against the cooperative association of molecules on DNA and for the importance of intercalative stacking of the donor and acceptor for fast electron transfer through the DNA π-stack.

Introduction

Recent research has focused on electron transfer reactions between molecules bound to macromolecular assemblies such as polymers, micelles, and biomolecules.[1−3] Such systems could provide one route to producing long-lived charge separation and, ultimately, artificial photosynthesis. In comparing supramolecular systems, it is important to understand how the host medium manipulates the reactivity of the guest molecules. In this report, we compare and contrast the photoinduced reactions between transition metal complexes which bind tightly both to the DNA helix and to SDS micelles. The contrasts in reactions observed in these two media point to the importance of π-stacking within the DNA double helix in mediating electron transfer chemistry.

Several groups have addressed whether the π-stacked bases of the DNA polymer provide an effective pathway for electron transfer reactions.[4−11] Studies in our laboratory have focused on reactions between transition metal complexes which bind to DNA by intercalation and/or surface interactions.[4−6] Intercalation, which for metal complexes involves the insertion of one aromatic, heterocyclic ligand between the base pairs of DNA, derives binding stabilization through π-stacking and thus may serve as a sensitive probe of the DNA π-stack. In fact, studies[5] comparing luminescence quenching of intercalated or groove bound reactants demonstrate that intercalation of both the donor and acceptor is required for rapid and efficient quenching.

[†] Beckman Institute, California Institute of Technology.
[‡] Columbia University.
* Author to whom correspondence should be addressed.
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(1) (a) Jones, W. E.; Baxter, S. M.; Strouse, G. F. Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363. (b) Fox, M. A. *Accts. Chem. Res.* **1992**, *25*, 569. (c) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (d) Bowler, B. D.; Raphael, A. L.; Gray, H. B. *Prog. Inorg. Chem.* **1990**, *38*, 259.

(2) (a) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982. (b) Turro, N. J.; Barton, J. K.; Tomalia, D. A. *Accts. Chem. Res.* **1991**, *11*, 332.

(3) (a) Onuchic, J. N.; Beratan, D. N.; Winkler, J. R.; Gray, H. B. *Ann. Rev. Biophys. Biomol. Struct.* **1992**, *21*, 349. (b) Boxer, S. G. *Ann. Rev. Biophys. and Biophys. Chem.* **1990**, *19*, 267. (c) Arkin, M. R.; Yenkins, Y. C.; Barton, J. K. *Adv. Chem. Ser.* **1995**, *246*, 449. (d) Stemp, E. D. A.; Barton, J. K. In *Metal Ions in Biology* 1995, in press. (e) Meade, T. J. In *Metal Ions in Biology* 1995, in press.

(4) (a) Barton, J. K.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 6391. (b) Purugganan, M. D.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *Science* **1988**, *241*, 1645.

(5) Murphy, C. J.; Arkin, M. R.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 5315.

(6) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. *Science* **1993**, *262*, 1025.

(7) (a) Brun, A. M.; Harriman, A. *J. Am. Chem. Soc.* **1994**, *116*, 10383. (b) Brun, A. M.; Harriman, A. *J. Am. Chem. Soc.* **1992**, *114*, 3656.

(8) (a) Meade, T. J.; Kayyem, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 352. (b) Risser, S. M.; Beratan, D. N.; Meade, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 2508.

(9) **.** (a) Snart, R. S. *Biopolymers* **1968**, *6*, 293. (b) Hoffmann, T. A.; Ladik, J. *Adv. Chem. Phys.* **1964**, *7*, 84. (c) Miller, J. H.; Swenberg, C. E. *Can. J. Phys.* **1990**, *68*, 962. (d) Dee, D.; Baur, M. E. *J. Chem. Phys.* **1974**, *60*, 541.

(10) (a) Warman, J. M.; de Haas, M. P.; Schouten, P. G. In *Radiation Research: A 20th-Century Perspective Volume II: Congress Proceedings*; Dewey, W. C., Edington, M., Fry, R. J. M., Hall, E. J., Witmore, G. F., Eds.; Academic Press: 1992; p 93. (b) Candeias, L. P.; Steenken, S. *J. Am. Chem. Soc.* **1993**, *115*, 2437.

(11) (a) Whillans, D. W. *Biochim. Biophys. Acta* **1975**, *414*, 193. (b) Fromhertz, P.; Rieger, B. *J. Am. Chem. Soc.* **1986**, *108*, 5361. (c) Atherton, S. J.; Beaumont, P. C. *J. Phys. Chem.* **1987**, *91*, 3993. (c) Baguley, B. C.; Le Bret, M. *Biochemistry* **1984**, *23*, 937. (d) Houée-Levin, C.; Gardés-Albert, M.; Rouscilles, A.; Ferradini, C.; Hickel, B. *Biochemistry* **1991**, *30*, 8216. (e) Cullis, P. M.; McClymont, J. D.; Symons, C. R. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 591.

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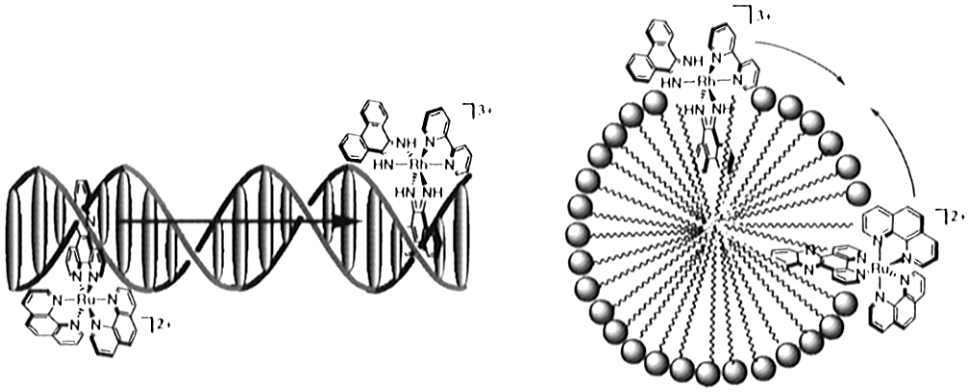
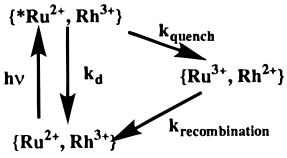


Figure 1. Supramolecular assemblies: schematic pictures of $Ru(phen)_2dppz^{2+}$ and $Rh(phi)_2bpy^{3+}$ bound to DNA by intercalation (left) and to SDS micelles in the Stern layer (right). Both environments provide binding energy by electrostatic attractions and hydrophobic interactions. The hydrophobic interaction varies, however, in that B-form DNA contains a highly ordered stack of aromatic heterocycles, while SDS micelles form a disordered array of aliphatic chains. Arrows indicate that electron transfer proceeds through the DNA π-stack between spatially fixed reactants, whereas electron transfer in micelles requires diffusion of reactants.

Our recent investigations of DNA-mediated electron transfer have taken advantage of derivatives of $Ru(phen)_2dppz^{2+}$, shown in Figure 1, as a photoexcited donor. Two-dimensional NMR studies[12] of Δ-$Ru(phen)_2dppz^{2+}$ bound to a hexamer duplex have shown that the dppz ligand intercalates into B-form DNA from the major groove, and emission titrations[13] have indicated a DNA binding affinity of 6×10^7 M^{-1}. In aqueous solutions, the excited state of $Ru(phen)_2dppz^{2+}$ is highly quenched due to proton transfer from the solvent to the dipyridophenazine ligand ($\tau = 250$ ps[14]).[15−20] When the ligand is protected from water, as by intercalation into DNA[15−19] or binding to anionic micelles,[20] luminescence is observed on the nanosecond time scale. Emission for the metal complex bound to DNA is characterized by a biexponential decay which is sensitive to the sequence of the DNA and to the structure of the ligand environment.[15−19]

The DNA-bound acceptor $Rh(phi)_2bpy^{3+}$ is also shown in Figure 1. For several phi complexes of Rh(III), two-dimensional NMR studies have indicated that the phi ligand intercalates into B-form DNA from the major groove.[21−23] The depth of intercalation has been shown to depend upon the shape of the ancillary ligands. Rh(III) complexes containing the phi ligand are useful probes of DNA structure, since irradiation with ultraviolet light leads to cleavage of the DNA strand at the site of complex binding.[24−29] For example, $Rh(phen)_2phi^{3+}$ binds preferentially to sites on the DNA which are opened in the major groove ($K_b \approx 10^6$ M^{-1}), owing to steric clashes between the nonintercalated phen ligands and major-groove substituents.[24,25,28,29] $Rh(phi)_2bpy^{3+}$, on the other hand, binds to DNA with low sequence-selectivity,[24,25,27] with an average association constant of 10^7 M^{-1}.

The reaction cycle of interest is depicted below. In the presence of B-form DNA, complexes of the formula $Rh(phi)_2L^{3+}$, where L = bpy or phen, quench the emission of dppz complexes of Ru(II) and Os(II) on a subnanosecond time scale.[5,30] Experiments utilizing intercalated complexes covalently tethered to a 15-mer oligonucleotide have established that these quenching reactions can occur efficiently over long distances (>40 Å).[6] For the photoexcited donors $Ru(DMP)_2dppz^{2+}$ (DMP = 4,7-dimethyl-1,10-phenanthroline) and $Os(phen)_2dppz^{2+}$ quenched by $Rh(phi)_2bpy^{3+}$, electron transfer intermediates have been observed by transient absorption spectroscopy.[30,31] Finally, recent work on picosecond time scales has yielded rate constants of recombination on the order of 10^{10} s^{-1} for DNA-mediated reactions between a variety of noncovalently bound metallointercalators.[14] What are the characteristics of the DNA duplex that serve to mediate fast, efficient, long-range reactions?



In this report, we compare the quenching of photoexcited $Ru(phen)_2dppz^{2+}$ [*Ru(II)] by two intercalators, $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$, mediated through binding to DNA or to sodium dodecyl sulfate (SDS) micelles (Figure 1). SDS micelles provide a particularly useful environment to compare the quenching of *Ru(II) by tris chelate complexes of Rh(III). Like DNA, SDS brings the molecules together in a supramolecular system which is both hydrophobic and negatively charged.

(12) (a) Dupureur, C. M.; Barton, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 10286. (b) Dupureur, C. M.; Barton, J. K. Submitted for publication.
(13) Hiort, C.; Lincoln, P.; Norden, B. *J. Am. Chem. Soc.* **1993**, *115*, 3448.
(14) Arkin, M. R.; Stemp, E. D. A.; Holmlin, R. E.; Barton, J. K.; Hoermann, A.; Olson, E.; Barbara, P. Submitted for publication.
(15) Friedman, A. E.; Chambron, J.-C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960.
(16) Friedman, A. E.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *Nucleic Acids Res.* **1991**, *19*, 2595.
(17) Jenkins, Y.; Friedman, A. E.; Turro, N. J.; Barton, J. K. *Biochemistry* **1992**, *31*, 10809.
(18) Hartshorn, R. M.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 5919.
(19) Turro, C.; Bossmann, S. H.; Jenkins, Y.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 9026.
(20) Chambron, J.-C.; Sauvage, J.-P. *Chem. Phys. Lett.* **1991**, *182*, 603.
(21) David, S. S.; Barton, J. K. *J. Am. Chem. Soc.* **1993**, *115*, 2984.
(22) (a) Collins, J. G.; Shields, T. P.; Barton, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 9840. (b) Shields, T. P.; Barton, J. K. *Biochemistry* **1995**, *34*, 15049.
(23) Hudson, B.; Dupureur, C. M.; Barton, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 9379.
(24) (a) Pyle, A. M.; Long, E. C.; Barton, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4520. (b) Pyle, A. M.; Morii, T.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 9432.
(25) Sitlani, A.; Long, E. C.; Pyle, A. M.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 2302.
(26) Sitlani, A.; Barton, J. K. *Biochemistry* **1994**, *33*, 12100.
(27) Uchida, K.; Pyle, A. M.; Morii, T.; Barton, J. K. *Nucleic Acids Res.* **1989**, *17*, 10259.
(28) Chow, C. S.; Behlen, L. S.; Uhlenbeck, O. C.; Barton, J. K. *Biochemistry* **1992**, *31*, 972.
(29) Campisi, D.; Morii, T.; Barton, J. K. *Biochemistry* **1994**, *33*, 4130.
(30) (a) Holmlin, R. E.; Barton, J. K. *Inorg. Chem.* **1995**, *34*, 7. (b) Holmlin, R. E.; Stemp, E. D. A.; Barton, J. K. Submitted for publication.
(31) Stemp, E. D. A.; Arkin, M. R.; Barton, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 2375.

Unlike DNA, however, SDS contains no highly organized pathway, such as the DNA π-stack, which might mediate reactions over a long distance. Thus, micelle-mediated reactions are expected to rely on molecular collisions.

Many analogous studies of electron transfer reactions have utilized $Ru(bpy)_3^{2+}$ as a photoexcited donor bound to SDS micelles.[32−38] Several groups have shown that cationic complexes containing hydrophobic ligands, such as RuL_3^{2+} [35,36,39−41] and $Co(phen)_3^{3+}$, [42] bind to micelles in the Stern layer. This mode of interaction is similar to intercalation in that it maximizes electrostatic interactions with the charged head groups and nestles the hydrophobic portions of the molecules in the organic portion of the supramolecular structure. The kinetics of quenching of $*Ru(bpy)_3^{2+}$ emission in SDS micelles have been shown to vary dramatically, depending on the location of the bound quencher. Therefore, dynamic quenching is observed when both donor and acceptor are able to diffuse within the micelle[37] or when the acceptor is dissolved in aqueous solution.[36] In contrast, static quenching, which occurs on a time scale that is fast relative to the excited-state lifetime, has been seen when a hydrophobic quencher is bound deeply within the micellar interior.[32]

In the nanosecond flash photolysis experiments reported here, $Rh(phi)_2bpy^{3+}$ is found to quench Ru(II) emission statically in DNA but in a dynamic fashion in anionic micelles. Furthermore, $Rh(phen)_2phi^{3+}$ is seen to quench the emission of $*Ru(phen)_2dppz^{2+}$ in micelles, but no quenching is evident in DNA. We propose that the differences observed depend on the unique features of the DNA π-stack which facilitate electron transfer between intercalators. Differences observed in quenching between $Rh(phen)_2phi^{3+}$ and $Rh(phi)_2bpy^{3+}$ must be related to differences in the intercalation of these two quenchers. Therefore, DNA-mediated electron transfer reactions between metallointercalators are found to be sensitive not only to the mode of binding but also to the nature of the intercalator/DNA stacking interaction.

Experimental Section

Materials. $[Ru(phen)_2dppz]Cl_2$ and $[Rh(phi)_2bpy]Cl_3$ were prepared according to literature procedures[43,44] and further purified by high performance liquid chromatography. Enantiomers were resolved using standard protocols[12,21,45] and analyzed by circular dichroism spectroscopy. $[Rh(phen)_2phi]Cl_3$ was prepared as described earlier.[44] Sodium dodecyl sulfate (Pierce) was used as received. Sonicated calf thymus DNA was purchased from Sigma and exchanged into 5 mM tris, 50 mM NaCl, pH 8.5 by ultrafiltration (Amicon). For titrations in deuterated solvent, stock solutions were prepared by repeatedly dissolving the complex in D_2O and drying. Deuterated buffer was prepared from 1 M tris-d_{11} in D_2O (Cambridge Isotope Labs).

Instrumentation. Steady-state emission experiments were performed with an SLM 8000 fluorimeter using a xenon arc lamp as the light source. Time-resolved measurements utilized the laser facilities in the Beckman Institute Laser Resource Center, as has been described.[16] Experiments with DNA were accomplished using an excimer-pumped dye laser containing Coumarin 480 (Exciton). Laser powers were 1.0−1.5 mJ at 10 Hz and the pulse width was ca. 20 ns. For SDS systems, excitation at 532 nm was provided by a Nd:YAG laser; the power at the sample was 10−15 mJ at 10 Hz and the laser pulse width was 8 ns.

Methods. All experiments were performed in aerated solution. For titrations with sonicated calf thymus DNA, concentrated stock solutions of metal complexes were added to DNA solutions, followed by extensive shaking. The ratio of base pairs/Ru(II) was 50. When micelles were used, samples were prepared by adding concentrated solutions of detergent to dilute metal complexes to avoid precipitation. The concentration of micelles was determined by the equation $[mic] = ([SDS] - cmc)/\tilde{n}$, where cmc is the critical micelle concentration and $\tilde{n}$ is the aggregation number (62 in water).[32,46,47] The cmc is not expected to change dramatically upon addition of metal complex and has been reported to drop from 8 to 7 mM when 200 μM $Ru(bpy)_3^{2+}$ is added.[38a]

Reasonable fits to time-resolved measurements on micelle samples were obtained by defining single-exponential decays without deconvolution or by assuming biexponential fits with deconvolution. For the latter algorithm, one decay rate was always faster than the pulse width and was not considered to be important in describing the actual emission lifetime of the *Ru(II) complex. Both fitting procedures give similar results. Steady-state intensities were measured by integrating time-resolved decay traces. Stern−Volmer plots were used to extract bimolecular quenching rate constants (k_{obs}) according to the equation

$$I_o/I = \tau_o/\tau = 1 + K_{SV}[Q]; \quad K_{SV} = k_{obs}/k_o$$

where I_o = emission intensity in the absence of quencher (Q), I = emission intensity at quencher concentration [Q], τ_o = intrinsic emission lifetime, τ = emission lifetime at [Q], k_o = the intrinsic decay constant of the unquenched donor. Quenching is considered to be dynamic when $I_o/I = \tau_o/\tau$, while static quenching is characterized by large discrepancies between intensity (I_o/I) and lifetime (τ_o/τ) quenching.

Electrochemistry. Reduction potentials for $Ru(phen)_2dppz^{2+}$ and Rh(III) complexes were measured using instrumentation described previously[5] at a scan rate of 100 mV/s. Complexes were dissolved in dry DMF (Fluka) with 100 mM tetrabutylammonium hexafluorophosphate as supporting electrolyte. $Ru(phen)_2dppz^{2+}$ and $Rh(phi)_2bpy^{3+}$ gave reversible and quasi-reversible voltammagrams, respectively. $Rh(phen)_2phi^{3+}$ showed complex and irreversible electrochemistry, and, therefore, reduction potentials are not reported.

Results

Quenching in the Presence of DNA. Variations in Acceptor. Figure 2a indicates the quenching of $*Ru(phen)_2dppz^{2+}$ by three Rh(III) complexes bound to DNA. As has been reported previously,[5] $Rh(phi)_2bpy^{3+}$ serves as a remarkably efficient quencher of Ru(II) emission, yielding Stern−Volmer quenching curves which are upward-curving and indicative of quenching by a primarily static mechanism. Figure 3a presents the time-resolved decays of *Ru(II) in the presence of increasing concentration of $Rh(phi)_2bpy^{3+}$; the large static component to

(32) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.
(33) Turro, N. J.; Khudyakov, I. V.; Gopidas, K. R. *Chem. Phys.* **1992**, *162*, 131.
(34) Gopidas, K. R.; Leheny, A. R.; Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 7335.
(35) Kunjappu, J. T.; Somasundaran, P.; Turro, N. J. *J. Phys. Chem.* **1990**, *94*, 8464.
(36) Dressick, W. J.; Hauenstein, B. L., Jr.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1984**, *23*, 1107.
(37) Kuzmin, M. G.; Soboleva, I. V. *J. Photochem. Photobiol. A: Chemistry* **1995**, *87*, 43.
(38) (a) Meisel, D.; Matheson, M. S.; Rabini, J. *J. Am. Chem. Soc.* **1978**, *100*, 117. (b) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1989**, *93*, 1426. (c) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1983**, *87*, 4529. (d) Wolszczak, M.; Thomas, J. K. *Radiat. Phys. Chem.* **1991**, *38*, 155. (e) el Torki, F. M.; Schmehl, R. H.; Reed, W. F. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 349.
(39) Ottaviani, M. F.; Ghatlia, N. D.; Turro, N. J. *J. Phys. Chem.* **1992**, *96*, 6075.
(40) Snyder, S. W.; Buell, S. L.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1989**, *93*, 5265.
(41) Hauenstein, B. L. Jr.; Dressick, W. J.; Buell, S. L.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 4251.
(42) (a) Davies, K.; Hussam, A. *Langmuir* **1993**, *9*, 3270. (b) Davies, K. M.; Hussam, A.; Rector, B. R. Jr.; Owen, I. M.; King, P. *Inorg. Chem.* **1994**, *33*, 1741.
(43) Amouyal, E.; Homsi, A.; Chambron, J.-C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1990**, *6*, 1841.
(44) Pyle, A. M.; Chiang, M. Y.; Barton, J. K. *Inorg. Chem.* **1990**, *29*, 4487.
(45) Yoshikawa, Y.; Yamasaki, K. *Coord. Chem. Rev.* **1979**, *28*, 205.
(46) Granath, K. *Acta Chem. Scand.* **1953**, *7*, 297.
(47) Coll, H. *J. Phys. Chem.* **1970**, *74*, 520.

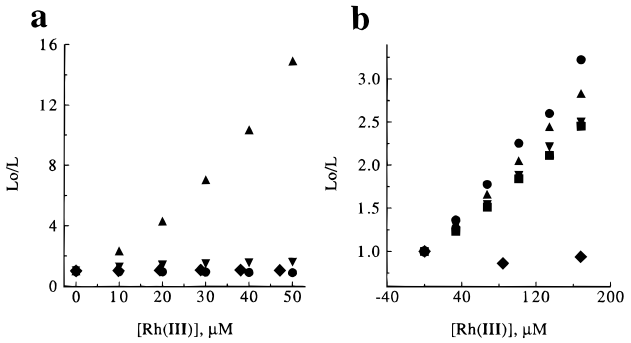


Figure 2. Stern−Volmer plots describing luminescence quenching of $Ru(phen)_2dppz^{2+}$ by complexes of Rh(III). a: Quenching of lifetimes and emission intensity of 10 μM $Ru(phen)_2dppz^{2+}$ by $Rh(phi)_2bpy^{3+}$ (intensity, ▲; lifetimes, ▼), $Rh(phen)_2phi^{3+}$ (intensity, ●), and $Rh(phen)_3^{3+}$ (intensity, ◆) in the presence of 1 mM nucleotides of sonicated calf thymus DNA in 5 mM tris, 50 mM NaCl, pH 8.5. b: Quenching of photoexcited $Ru(phen)_2dppz^{2+}$ (84 μM) by $Rh(phi)_2bpy^{3+}$ (intensity, ▲; lifetimes, ▼), $Rh(phen)_2phi^{3+}$ (intensity, ●; lifetimes, ■), and $Rh(phen)_3^{3+}$ (intensity, ◆). [SDS] = 13 mM monomer in water. In contrast to quenching in DNA, both $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$ cause a similar reduction in $*Ru(phen)_2dppz^{2+}$ emission lifetime. Additionally, quenching is primarily dynamic in nature, compared to the large static component observed for $Ru(phen)_2dppz^{2+}$ and $Rh(phi)_2bpy^{3+}$ bound to DNA.

quenching is manifested by a large loss in initial intensity with only a small change in curve shape. As is also shown in Figure 2a, and contrasting the titration with $Rh(phi)_2bpy^{3+}$, no luminescence quenching is observed in the presence of $Rh(phen)_2phi^{3+}$, and the emission lifetimes actually increase slightly, from 160 ns/860 ns to 170 ns/915 ns at 5 equiv of Rh(III). Similar behavior has been seen when a variety of intercalators which cannot quench $*Ru(phen)_2dppz^{2+}$ are added to $Ru(phen)_2dppz^{2+}$ bound to DNA.[48] In addition, no reaction is observed between $*Ru(phen)_2dppz^{2+}$ and $Rh(phen)_3^{3+}$. This lack of reactivity is expected, due to the weaker binding of $Rh(phen)_3^{3+}$ to DNA and its lower reduction potential.[49] The driving force for electron transfer between *Ru(II) + $Rh(phen)_3^{3+}$ is close to 0 mV, compared to 560 mV[50] for the reaction of $*Ru(phen)_2dppz^{2+}$ and $Rh(phi)_2bpy^{3+}$.

Effects of Solvent Deuteration. Table 1 describes the effect of deuterated solvent on reactions between intercalated donor and acceptor. Experiments on fast time scales have shown that the lifetime of the excited state of $Ru(phen)_2dppz^{2+}$ is 250 ps in water and 550 ps in D_2O, giving an isotope effect of 2.3.[14] Similar solvent-isotope effects are seen in the emission lifetimes of $Ru(phen)_2dppz^{2+}$ bound to DNA. Table 1 presents the lifetimes of Δ- and Λ-$Ru(phen)_2dppz^{2+}$ in calf thymus DNA, where the two intercalative binding geometries of Δ-Ru(II) show k_H/k_D ratios of 2.6 for the short lifetime and 1.5 for the long; similar isotope effects are evident with the Λ-isomer bound to DNA. The emission lifetimes in the absence of quencher show large isotope effects because proton transfer from solvent provides a major pathway for excited-state decay.[19]

In contrast to quenching by solvent, no strong isotope effects are observed in the fraction of quenching of $*Ru(phen)_2dppz^{2+}$ by $Rh(phi)_2bpy^{3+}$ in DNA (Table 1). Picosecond transient absorption measurements also show a $k_H/k_D \approx 1$ for the rate of ground-state recovery of Ru(II).[14] The absence of a solvent-isotope effect indicates that quenching of *Ru(II) by $Rh(phi)_2bpy^{3+}$ in the presence of DNA is not mediated by water but rather involves metallointercalators bound to the DNA polymer. Furthermore, the slow dissociation of intercalators from DNA[12,21,22] ensures that the metal complexes are fixed during the time scale of the reaction.

Table 1. Emission Lifetimes of $Ru(phen)_2dppz^{2+}$ in Supramolecular Environments

sample	medium	H_2O τ (ns)	H_2O %	D_2O τ (ns)	D_2O %	quenching H_2O vs D_2O
Δ-$Ru(phen)_2dppz^{2+}$	DNA[a]	150	80	385	75	0.95[c]
		850	20	1260	25	
Λ-$Ru(phen)_2dppz^{2+}$	DNA[a]	40	80	74	70	
		150	20	290	30	
$Ru(phen)_2dppz^{2+}$	SDS[b]	80	−	220	−	1.12[d]

[a] 10 μM Ru(II), 1 mM sonicated calf thymus DNA, 5 mM tris (or tris-d_{11}), 50 mM NaCl, pH 8.5. [b] 40 μM Ru(II), 13 mM SDS monomers. [c] Ratio of I_o/I in H_2O and D_2O at 3 equiv of $Rh(phi)_2bpy^{3+}$. [d] Ratio of k_{obs} in H_2O and D_2O.

Table 2. Intensity Quenching of the Enantiomers of $Ru(phen)_2dppz^{2+}$ by the Enantiomers of $Rh(phi)_2bpy^{3+}$

Ru/Rh	I_o/I, SDS[a]	I_o/I, DNA[b]
Δ/Δ	1.52	3.90
Λ/Δ	1.56	1.50
Λ/Λ	1.50	1.27

[a] 84 μM Ru(II), 168 μM Rh(III), 13 mM SDS in water. [b] 10 μM Ru(II), 20 μM Rh(III), 1 mM nucleotides DNA in 5 mM tris, 50 mM NaCl, pH 8.5.

Effects of a Change in Donor Chirality. Since both the donor and acceptor are chiral, their enantiomers might be expected to behave differently in the environment of right-handed DNA. Indeed, the photophysical properties of $Ru(phen)_2dppz^{2+}$ and its derivatives are sensitive to the twist of the double-helix; the left-handed Λ isomer has shorter luminescence lifetimes (Table 1) and, therefore, greater accessibility to water[12,13] than does the right-handed Δ enantiomer. Table 2 shows that the reaction between these metallointercalators bound to DNA is also affected by their chirality.[14] The most efficient quenching occurs between Δ-$Ru(phen)_2dppz^{2+}$ and Δ-$Rh(phi)_2bpy^{3+}$, with 75% being quenched at 2 equiv of Rh(III). However, the other pairs of enantiomers do react, and quenching in each case is primarily static (Table 2).

Quenching in the Presence of SDS Micelles. Association of Metal Complexes with Micelles. Many earlier studies have established that cationic metal complexes containing hydrophobic ligands bind to anionic micelles in the Stern layer, and binding affinities near 10^5 M^{-1} have been suggested.[40,42] Binding of the Rh(III) acceptors is established by UV−visible spectroscopy. In the presence of DNA, the ultraviolet spectra of phi complexes of Rh(III) are known to undergo hypochromic, red shifts in the phi transitions centered near 360 nm ($\Delta\lambda_{max} \approx$ 13 nm).[25] Upon the addition of SDS above the cmc, both $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$ show 10 nm shifts in these bands to lower energies but without significant hypochromicity (Figure 1, Supporting Information). Binding of $Ru(phen)_2dppz^{2+}$ to SDS micelles is indicated by the onset of emission above the cmc.[20] These complexes are expected to remain bound to the micelle during the lifetime of the experiment, with a lower limit for the residence time of $Ru(phen)_2dppz^{2+}$ being provided by the excited-state lifetime in D_2O/SDS (ca. 220 ns).

The emission of $Ru(phen)_2dppz^{2+}$ is sensitive to the micellar environment. The decrease in lifetime relative to $Ru(phen)_2dppz^{2+}$ bound to DNA indicates a greater water accessibility in the micelle. As in DNA, emission in micelles also

(48) One interpretation of this effect is that binding of intercalators rigidifies the DNA helix, which, secondarily, serves to increase the luminescence of DNA-bound $Ru(phen)_2dppz^{2+}$.

(49) $E^{1/2}$ (Rh^{III}/Rh^{II}) ≈ −0.67 V vs NHE. Chan, S. F.; Chow, M.; Creutz, C.; Matsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369.

(50) $E^{1/2}(Ru^{III}/*Ru^{II}) = -0.61$ V vs NHE; $E^{1/2}(Rh^{III}/Rh^{II}) = -0.05$ V vs NHE.

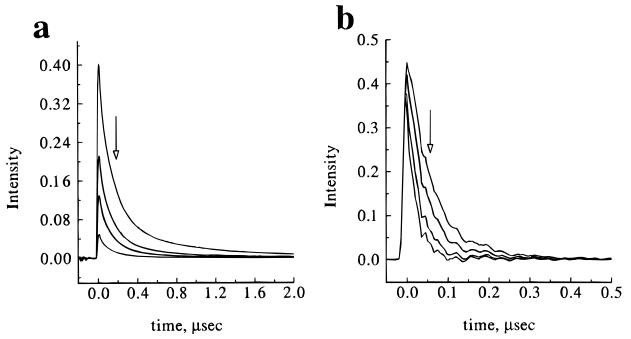


Figure 3. Time-resolved emission decays of *Ru(phen)$_2$dppz^{2+} in DNA (a) and SDS micelles (b) as a function of added quencher. a: 10 μM Ru(phen)$_2$dppz^{2+}, 0, 10, 20, 50 μM Rh(phi)$_2$bpy^{3+}, 1 mM DNA nucleotides, 5 mM tris, 50 mM NaCl, pH 8.5. b: 84 μM Ru(phen)$_2$-dppz^{2+}, 0, 40, 80, 160 μM Rh(phi)$_2$bpy^{3+}, 13 mM SDS monomers.

shows a large solvent isotope effect (Table 1, $k_H/k_D = 2.8$). The time-resolved luminescence decay can reasonably be fit to a single exponential in SDS/water. The rate of emission decay decreases slightly as the ratio of Ru/SDS increases, from 1.3×10^7 s^{-1} at 0.1 Ru/micelle to 1.7×10^7 s^{-1} at 1.0 Ru/micelle. This dynamic quenching of *Ru(phen)$_2$dppz^{2+} could arise from binding competition as well as self-quenching.[51]

Effects of Variation in Acceptor. In contrast to the *static* quenching of *Ru(phen)$_2$dppz^{2+} by Rh(phi)$_2$bpy^{3+} in DNA, Rh(phi)$_2$bpy^{3+} quenches *Ru(II) emission in SDS by a primarily *dynamic* mechanism, as indicated by the similarity in Stern−Volmer plots of I_o/I and τ_o/τ vs [Q] in Figure 2b. The emission decay, presented in Figure 3b, emphasizes the change in the shape of the decay curve with little loss in initial intensity.

There is additionally a dramatic difference in the quenching behavior of Rh(phen)$_2$phi^{3+} in the two systems. When bound to SDS micelles in water, both Rh(phi)$_2$bpy^{3+} and Rh(phen)$_2$-phi^{3+} quench Ru(phen)$_2$dppz^{2+} emission to similar extents (Figure 2b), whereas Rh(phen)$_2$phi^{3+} does not serve as a quencher of *Ru(phen)$_2$dppz^{2+} emission when bound to DNA (Figure 2a). This interesting result suggests that there are important differences between how the DNA polymer and the SDS micelles participate in this chemisty. As in DNA, Rh-(phen)$_3^{3+}$ does not quench the excited state of Ru(phen)$_2$dppz^{2+}, presumably as a result of the low driving force for electron transfer.[49,50]

Variation in Micellar Concentration. For a range of Ru/SDS ratios, quenching by both Rh(phi)$_2$bpy^{3+}and Rh(phen)$_2$phi^{3+} yields linear Stern−Volmer plots (Figure 2b). Application of the Stern−Volmer equation yields Stern−Volmer constants (K_{SV}) of 8700 and 9000 M^{-1} for Rh(phi)$_2$bpy^{3+}and Rh-(phen)$_2$phi^{3+}, respectively, at 84 μM Ru, 13 mM SDS monomers. Between Ru/micelle ratios of 0.1−1.0, plots of τ_o/τ vs Rh/SDS yield similar values for K_{SV} (Figure 4), indicating that quenching is determined by the distribution of donors and acceptors among micelles[52] and not by their absolute concentration.

If quenching of a molecule of *Ru(phen)$_2$dppz^{2+} by a Rh-(III) complex involves diffusion within a micelle (as opposed to diffusion of an unbound quencher through the solvent[36]), then increasing the number of micelles should reduce the amount of quenching by sequestering acceptors in donorless micelles. The following kinetic model has been derived by Berezin and co-workers[53] in describing reactions which follow Stern−Volmer kinetics and in which the reactants are bound tightly to the micelle:

$$k_{obs} = (k_m/V)K_aK_b/[(K_a + K_b) + K_aK_bC]$$

where k_m is the micellar quenching rate, V is the partial molar volume of SDS in the micelle, C = [SDS] − cmc, and K_a and K_b are the equilibrium dissociation constants for reactants a and b, respectively. This model predicts that the inverse of the observed quenching rate k_{obs} will be proportional to C. Figure 5 shows such a plot for quenching of *Ru(phen)$_2$dppz^{2+} by Rh(phen)$_2$phi^{3+} and by Rh(phi)$_2$bpy^{3+} as the concentration of detergent varies from 10−30 mM. The plot of $1/k_{obs}$ vs C is linear over a 10-fold range of micelle concentration, from approximately 32−350 μM, supporting the notion that quenching occurs by diffusion within a micelle. From the slope (V/k_m) the true bimolecular rate constant (k_m) can be determined, assuming a value for the partial volume V. V is 0.25 M^{-1} for donor/acceptor residing in the volume of the micelle and 0.14 M^{-1} for complexes restricted to the Stern layer.[42] Given a value for V of 0.14 M^{-1}, true bimolecular rate constants are found from the slope to be 1.1×10^8 and 1.2×10^8 M^{-1} s^{-1} for Rh(phi)$_2$bpy^{3+}and Rh(phen)$_2$phi^{3+}, respectively.[54] Additionally, the slope/intercept ratio suggests association constants for donor and acceptor on the order of 5×10^4 M^{-1}, assuming $K_a = K_b$ and cmc = 8 mM[55] (values for the intercept are negative for cmc < 7.8 mM). Although the small value for the intercept (10^{-13} Ms) implies a large uncertainty in the binding constants, this value is similar to earlier estimates of binding constants for less hydrophobic tris chelate complexes of Ru(II),[40] Co-(II),[42] and Co(III).

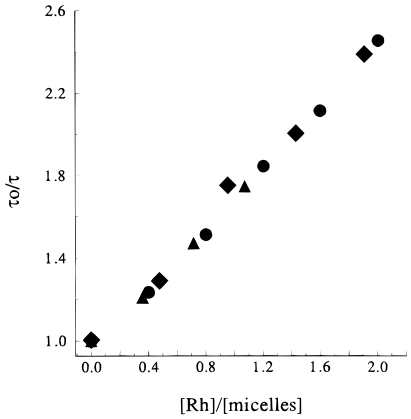


Figure 4. Stern−Volmer analysis of quenching of Ru(phen)$_2$dppz^{2+} by Rh(phen)$_2$phi^{3+} at three ratios of Ru/SDS. Slopes of quenching plots are the same for Ru:SDS ratios of 0.1 (▲), 0.5 (◆), and 1.0 (●). Quenching therefore depends on the distribution of acceptors among micelles, rather than the absolute concentration of donors and acceptors.

Mechanism of Quenching in the Micelle. Photoinduced electron transfer is the most likely mechanism of quenching of *Ru(phen)$_2$dppz^{2+} by Rh(phi)$_2$bpy^{3+} and Rh(phen)$_2$phi^{3+} in SDS micelles. Evidence for electron transfer is provided by transient absorption spectroscopy with a related donor, Ru(DMP)$_2$dppz^{2+} (DMP = 4,7-dimethyl-1,10-phenanthroline). Previously we observed a long-lived Ru(III) species generated by reaction of *Ru(DMP)$_2$dppz^{2+} and Rh(phi)$_2$bpy^{3+} bound to DNA.[31] Compared to Ru(phen)$_2$dppz^{n+} ($E^{3+/2+}$ = 1.61 V), Ru(DMP)$_2$dppz^{n+}

(51) Triplet−triplet annihilation has been invoked previously to describe the ground-state recovery of Ru(bpy)$_3^{2+}$ bound to SDS micelles. See: Lachish, U.; Ottolenghi, M.; Rabani, J. *J. Am. Chem. Soc.* **1977**, *99*, 8062.

(52) Gehlen, M. H.; De Schryver, F. C. *Chem. Rev.* **1993**, *93*, 199.

(53) Berezin, I. V.; Martinek, K.; Yatsimirskii, A. K. *Russian Chem. Rev.* **1973**, *42*, 787.

(54) Multiplying by the volume of the micelle gives unimolecular rate constants of 7.8×10^8 s^{-1} and 8.6×10^8 s^{-1} for Rh(phi)$_2$bpy^{3+} and Rh(phen)$_2$phi^{3+} respectively.

(55) Mukerjee, P.; Mysels, K. J. "Critical Micelle Concentration of Aqueous Surfactant Systems", NSRDS-NBS 36, U.S. Government Printing Office, Washington, D.C., 1971.

Table 3. Parameters for quenching of $Ru(phen)_2dppz^{2+}$ by phi complexes of Rh(III)

quencher[a]	solvent	pK_a	K_{SV} (M^{-1})[b]	4 equiv quencher I_o/I	4 equiv quencher τ_o/τ
$Rh(phi)_2bpy^{3+}$	water	6.7	7300		
$Rh(phi)_2bpy^{3+}$	pH 8.5 tris		upward-curving	2.13	1.8
$Rh(phen)_2phi^{3+}$	water	6.3	8700	2.48	2.4
$Rh(phen)_2phi^{3+}$	pH 8.5 tris		2750	1.5	1.4
$Rh([12]S_4ane)phi^{3+}$ [c]	water	2.3	upward-curving	2.0	1.8
$Rh(NH_3)_4phi^{3+}$	water	9.5		0.93	

[a] 40 μM Ru, 13 mM SDS. [b] From $\tau_o/\tau = 1 + K_{SV}[Q]$. [c] $[12]S_4$ane = 1,4,7,10-tetrathiacyclododecane.

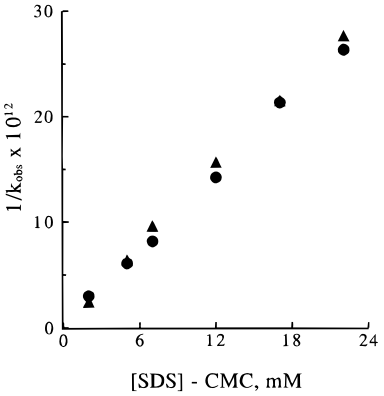


Figure 5. Plots of $1/k_{obs}$ vs concentration of detergent-cmc for the quenching of $Ru(phen)_2dppz^{2+}$ by $Rh(phen)_2phi^{3+}$ (●) and $Rh(phi)_2bpy^{3+}$ (▲).

($E^{3+/2+}$ = 1.54 V) is less unstable in the 3+ oxidation state and has a shorter excited state lifetime; both properties improve detection of the transient intermediate. The intrinsic lifetime of $*Ru(DMP)_2dppz^{2+}$ in SDS is too short to be determined accurately with the time resolution of our instrument. However, quenching of the emission intensity occurs upon addition of Rh(III), with the concomitant increase of a transient signal which decays with a rate constant of 3.7×10^6 s^{-1} (Figure 6).[56] This rate constant is significantly longer than the excited-state decay of the $*Ru(DMP)_2dppz^{2+}$ complex, and is consistent with transient formation of Ru(III). It is noteworthy that electron transfer intermediates are sometimes not seen for reactions in micelles, presumably due to reduced cage-escape yield.[33,36,38a,d]

Other plausible mechanisms for quenching, including energy transfer and excited-state proton transfer, do not account for the dynamic quenching observed. Energy transfer is unlikely, due to the very small amount of spectral overlap between the absorption spectra of the acceptors and the emission profile of the donor. Excited-state proton transfer[19] has been ruled out by the experiments summarized in Table 3 (see also Figure 2, Supporting Information). Four phi complexes of Rh(III), spanning a broad range of pK_a, were tested for reaction with $*Ru(phen)_2dppz^{2+}$; no correlation between pK_a and quenching was found. Additionally, the presence of 10 mM tris buffer at pH 8.5 did not eliminate quenching of $*Ru(phen)_2dppz^{2+}$ by either $Rh(phi)_2bpy^{3+}$ (pK_a = 6.7) or $Rh(phen)_2phi^{3+}$ (pK_a = 6.3).

A few interesting differences are noteworthy, however, in comparing protonated and deprotonated quenchers. First, the amount of luminescence quenching is less in pH 8.5 buffer than in water. Second, Stern−Volmer plots are now upward-curving and, in the case of $Rh(phi)_2bpy^{3+}$, show a greater proportion of static quenching. These changes are not due to the addition of 10 mM salt, since 10 mM tris buffered to pH 5.7 did not affect the quenching (data not shown). It is also noteworthy that no significant pH effects are seen in the quenching of $Ru(phen)_2dppz^{2+}$ by $Rh(phi)_2bpy^{3+}$ bound to DNA.

Effects with Enantiomers. In order to compare the effects of enantiomers in the chiral environment of DNA and the achiral medium of SDS micelles, quenching of the pure enantiomers of $*Ru(phen)_2dppz^{2+}$ was also considered. Table 2 shows that, unlike the large effects in quenching efficiency between diasteriomeric pairs bound to DNA, differences in quenching in micelles were within the experimental error of the measurements.

Discussion

Quenching in the Presence of DNA. Reaction Environment. Reactions between *Ru(II) and Rh(III) bound to DNA are best described as occurring in a DNA medium. There are no solvent-isotope effects in electron transfer efficiencies or rates, indicating that the solvent does not play a role in the quenching reaction (Table 1). One would expect a correlation between quenching in DNA and changes in the DNA medium and the binding of the donor/acceptor to the double helix. In fact, we have shown here that the binding of $Ru(phen)_2dppz^{2+}$ to DNA strongly influences quenching, since there is a relationship between the chirality of the metal complex and its reaction with intercalated $Rh(phi)_2bpy^{3+}$. Importantly, Figure 2 shows that the medium itself plays a critical role in the rates of quenching of $*Ru(phen)_2dppz^{2+}$ by $Rh(phi)_2bpy^{3+}$. In the disordered environment of the micelle, quenching occurs with diffusion-controlled rates. In contrast, unimolecular, subnanosecond quenching is observed when these metallointercalators are bound in the highly ordered medium of the DNA helix. Quenching depends on the supramolecular environment.

Effect of Acceptor. Quenching of *Ru(II) bound to DNA is highly sensitive to the choice of DNA-bound electron acceptor. $Rh(phi)_2bpy^{3+}$ quenches the emission of *Ru(II) by a static mechanism, as shown by large changes in emission intensity and small changes in lifetime (Figures 2a and 3a). By contrast, the seemingly similar $Rh(phen)_2phi^{3+}$ does not quench *Ru(II) emission at all, despite a comparably high binding constant for intercalation to B-form DNA. This interesting result is compared to quenching in SDS micelles below.

DNA as a Mediator for Long-Range Reaction. Although experiments between randomly bound intercalators do not directly address the distance-dependence of electron transfer, reactions between $*Ru(phen)_2dppz^{2+}$ and $Rh(phi)_2bpy^{3+}$ noncovalently bound to DNA appear to occur over a long distance. Assuming random binding, at 1 eq Δ-$Rh(phi)_2bpy^{3+}$, donor/acceptor pairs are an average of 25 base pairs apart, and 4% of pairs are in closest contact. However, at this concentration, we observe that 30% of Δ-$*Ru(phen)_2dppz^{2+}$ is quenched and thus propose that reactions occur at long range. This analysis is consistent with experiments between metallointercalators covalently bound to an oligonucleotide, where quenching was found to occur rapidly over 40 Å.[6]

Diastereomeric Effects on Quenching. Varying the chirality of both donor and acceptor dramatically effects the quenching of *Ru(II) bound to DNA (Table 2), and the effects are correlated with the stacking of the complex into the DNA helix. In the case of the donor, 30% of the Δ enantiomer is quenched at 1 eq. Δ-$Rh(phi)_2bpy^{3+}$, compared to only 15% quenching

(56) *Rh(III) is generated by laser excitation at 532 nm (ϵ_{532} = 1230 M^{-1} cm^{-1}), and the transient signals for the *Rh(III)−Rh(III) difference spectrum are, in general, large. Therefore, full spectral characterization of transient absorption spectra is not possible, and transient intermediates have been identified primarily at the 422 nm isosbestic point in the *Rh(III)−Rh(III) difference spectrum.

of the Λ-isomer. The excited-state lifetimes in the absence of quencher are longer for the right-handed isomer (150/850 ns) than for the left-handed one (40/150 ns). Since water quenches the excited state ($k_H/k_D \approx 2.3$), longer emission lifetimes imply decreased solvent accessibility and increased stacking with the DNA bases. Thus, deeper intercalation results in better quenching. These results can be contrasted to reactions between isomers in SDS micelles, where no significant differences between diastereomeric pairs are observed.[57] The correlation between excited-state lifetime and quenching efficiency points to the importance of stacking interactions in mediating electron transfer between DNA-bound molecules.

Quenching in SDS Micelles. Reaction Environment. Both donor and acceptor are tightly bound to SDS micelles, and thus electron transfer reactions between them occur within the restricted space of the micelle. Emission and absorption spectroscopies provide information on micellar binding of donor and acceptor. The donor $Ru(phen)_2dppz^{2+}$ displays an emission lifetime of ~80 ns in SDS micelles compared to a lifetime of 250 ps in aqueous solution.[14] This 320-fold increase in excited-state lifetime is indicative of removal of the dppz ligand from water. The absorption spectra of the acceptor complexes are red-shifted by 10 nm in the presence of SDS, similar to changes seen for phi complexes of Rh(III) when the solvent hydrophobicity is increased.[44]

Effects of Acceptors. Both $Rh(phen)_2phi^{3+}$ and $Rh(phi)_2bpy^{3+}$ quench the emission of $*Ru(phen)_2dppz^{2+}$ when the complexes are bound to SDS micelles. Quenching is not observed when *Ru(II) is titrated with $Rh(phen)_3^{3+}$. The lack of reactivity of $Rh(phen)_3^{3+}$ is not surprising, based on the absence of thermodynamic driving force, but it is an important control since the size and shape of micelles are known to be sensitive to the addition of ions. $Rh(phen)_3^{3+}$ is similar to $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$ in terms of charge and shape and would therefore have a similar effect on micellar structure. The quenching of $*Ru(L)_2dppz^{2+}$ by Rh(III) complexes is not due to a perturbation of the environment around the lumophore.

Kinetic Description of Quenching in SDS. For both $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$, Stern−Volmer plots based on intensity and lifetime quenching are linear and have comparable slopes; thus, quenching is dynamic for both acceptors. Berezin plots of $1/k_{obs}$ vs C are linear (Figure 5), indicating that the quenching reaction is intramicellar. The micellar quenching rate constant, extracted from the slope of the Berezin plot, is 1.1×10^8 M^{-1} s^{-1} for quenching by $Rh(phi)_2bpy^{3+}$ and 1.2×10^8 M^{-1} s^{-1} for $Rh(phen)_2phi^{3+}$. Intramicellar quenching occurs with rates close to the rate of diffusion within a micelle,[37,38b] and rates are similar for quenching by both phi complexes.

Effect of pH. Table 3 indicates that the quenching of $*Ru(phen)_2dppz^{2+}$ by Rh(III) complexes decreases when the pH is raised above the pK_a of the phi ligand;[58] furthermore, $Rh(phi)_2bpy^{3+}$ is a more efficient quencher than $Rh(phen)_2phi^{3+}$ and yields nonlinear Stern−Volmer plots. The differences between quenching by the protonated and deprotonated forms of the acceptors may be explained by both binding and electronic factors. For $Co(phen)_3^{3+/2+}$, Davies *et al.*[42] find that the binding constant for Co(III) is lower than for Co(II) and suggest that divalent metal complexes bound to SDS micelles are stabilized by hydrophobic interactions, whereas electrostatic attraction accounts for ca. 50% of binding stabilization for 3+ ions. Thus,

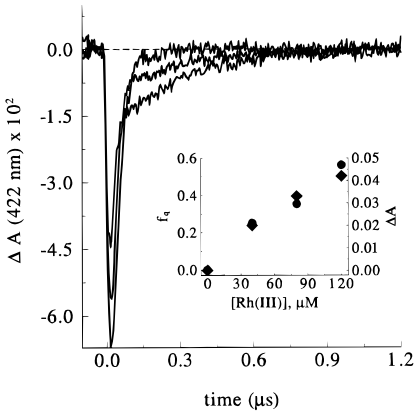


Figure 6. Transients observed at 422 nm formed by 532 nm excitation of $Ru(DMP)_2dppz^{2+}$ during titration with $Rh(phi)_2bpy^{3+}$ in SDS micelles. Addition of $Rh(phi)_2bpy^{3+}$ produces a long-lived signal which decays with a rate constant of 3.7×10^6 s^{-1}. Conditions are 10 μM Ru(II), 13 mM SDS, 0, 30, 90 μM Rh(III). Data are uncorrected for inner filter effects due to Rh(III) absorption. Inset: comparison of emission quenching (●) and yield of transient intermediate at 422 nm (◆). 40 μM Ru(II), 13 mM SDS, $\lambda_{exc} = 480$ nm. $f_q = 1 - I/I_o$.

the protonation state of phi complexes could be important in determining the nature of their binding and diffusion in SDS micelles. Additionally, the stronger binding of deprotonated $Rh(phi)_2bpy^+$ to the micelle could result in greater competition, resulting in the ejection of some $Ru(phen)_2dppz^{2+}$ from the micelle. Lastly, preliminary results suggest that the protonated and deprotonated forms of $Rh^{III}(phi)_2bpy^{3+/+}$ have different electron-transfer reactivities, and so the reduction potential might change with pH.[59]

Comparison of Quenching in DNA and SDS. We have shown that $Ru(phen)_2dppz^{2+}$, $Rh(phen)_2phi^{3+}$, and $Rh(phi)_2bpy^{3+}$ bind strongly both to DNA and to SDS micelles and that quenching of *Ru(II) can occur in both environments. However, electron transfer reactions between *Ru(II) and Rh(III) complexes display some striking differences depending on the nature of the medium. The quenching of $*Ru(phen)_2dppz^{2+}$ by $Rh(phi)_2bpy^{3+}$ is static in DNA but dynamic in SDS micelles. This interesting result demonstrates that *the structure of DNA plays a central role in mediating the electron transfer reaction*. Furthermore, the two quenchers $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$ behave differently in DNA; $Rh(phi)_2bpy^{3+}$ is a highly efficient quencher of *Ru(II) emission, while $Rh(phen)_2phi^{3+}$ does not react. In SDS micelles, by contrast, emission is quenched by a dynamic mechanism by both phi complexes with similar efficiencies.

There are several possible explanations for the differences between $Rh(phi)_2bpy^{3+}$ and $Rh(phen)_2phi^{3+}$ bound to DNA, including (i) insufficient thermodynamic driving force for $Rh(phen)_2phi^{3+}$ to oxidize *Ru(II), (ii) cooperative binding in the $Rh(phi)_2bpy^{3+}$/Ru(II) pair that is missing with $Rh(phen)_2phi^{3+}$/Ru(II), (iii) long Rh/Ru distances generated by the greater sequence-selectivity of $Rh(phen)_2phi^{3+}$, and (iv) differential binding of the acceptors to the helix, causing $Rh(phi)_2bpy^{3+}$ to be reactive while $Rh(phen)_2phi^{3+}$ is not. The experiments described here suggest that differences in stacking of the Rh(III) complexes with the DNA bases account for the quenching effects observed.

The similarity of quenching rates for the two acceptors in SDS micelles is incompatible with the first two propositions listed above. If $Rh(phen)_2phi^{3+}$ lacked the thermodynamic driving force for electron transfer, then no quenching would

(57) Diastereomeric effects in electron transfer between tris chelate complexes of Co(III/II) in solution have been observed in some cases. See: (a) Warren, R. M. L.; Tatehata, A.; Lappin, A. G. *J. Chem. Soc., Dalton Trans.* **1994**, *11*, 1655. (b) Warren, R. M. L.; Lappin, A. G.; Mehta, B. D.; Neumann, H. M. *Inorg. Chem.* **1990**, *29*, 4185.

(58) Krotz, A. H.; Kuo, L. Y.; Barton, J. K. *Inorg. Chem.* **1993**, *32*, 5963.

(59) Turro, C. Unpublished results.

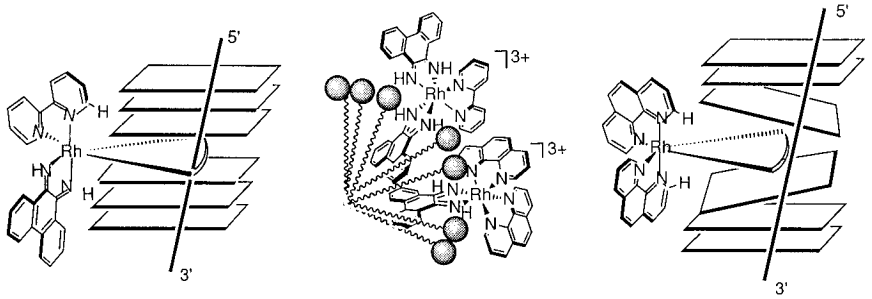


Figure 7. Models for binding of $Rh(phi)_2bpy^{3+}$ (left) and $Rh(phen)_2phi^{3+}$ (right) binding to DNA and SDS micelles (center). Due to steric clashes of the 2,9 phen protons with major groove substituents, intercalation of $Rh(phen)_2phi^{3+}$ into DNA occurs preferentially at base steps which are opened in the major groove, resulting in reduced basestacking at the binding site. No such steric interactions inhibit binding of $Rh(phi)_2bpy^{3+}$, and thus binding is largely sequence-neutral and the base pairs are well-stacked with the intercalating phi ligand.[24,25,29] The more disordered binding of Rh(III) complexes to SDS micelles suggests that the two acceptors will bind equivalently.

have occurred between $*Ru(phen)_2dppz^{2+}$ and $Rh(phen)_2phi^{3+}$. If cooperative binding were important, then quenching would be different for the two acceptors and likely would be static; in other words, no changes in Ru(II) emission lifetime would be observed. While it is known that $Rh(phen)_2phi^{3+}$ binds to DNA with greater sequence-selectivity than $Rh(phi)_2bpy^{3+}$ (iii), differences in binding affinity between sites is small compared to the concentrations used in these experiments, and therefore all sites on the DNA should be sampled. Additionally, there is no evidence for large sequence preferences for $Ru(phen)_2dppz^{2+}$ binding to B-form DNA.[12]

Photocleavage and binding studies[21−29] provide an explanation for the lack of DNA-mediated quenching by $Rh(phen)_2phi^{3+}$. Figure 7 illustrates a thoroughly investigated model for the intercalation of $Rh(phen)_2phi^{3+}$ and $Rh(phi)_2bpy^{3+}$ into B-form DNA.[25,29] Comparisons of photocleavage and crystal structures of several DNA oligonucleotides indicate that there is a strong correlation between the binding of $Rh(phen)_2phi^{3+}$ and the degree of opening in the major groove. This opening of the major groove results in a destacking of the base pairs and, presumably, separation of the base step from the electronically well-coupled π-stack. The shape-selective binding of $Rh(phen)_2phi^{3+}$ but not $Rh(phi)_2bpy^{3+}$ is also responsible for the increased sequence-selectivity of $Rh(phen)_2phi^{3+}$ compared to $Rh(phi)_2bpy^{3+}$. Finally, the notion that $Rh(phen)_2phi^{3+}$ and $Rh(phi)_2bpy^{3+}$ are stacked differently is consistent with the observed hypochromicity of the phi ligands upon binding to DNA; $Rh(phen)_2phi^{3+}$ shows 40% hypochromicity in the phi bands, while $Rh(phi)_2bpy^{3+}$ shows 60% for the intercalated ligand (30% for the complex).[25]

We therefore propose a model whereby intercalative binding affords access to the purported DNA π-way, and this intimate coupling of the donor and acceptor into the DNA helix depends sensitively on stacking of the intercalator. Poor stacking of the intercalating guest with the DNA host limits DNA-mediated quenching, as in the case of Λ-$Ru(phen)_2dppz^{2+}$, or abolishes such quenching, as for $Rh(phen)_2phi^{3+}$. The SDS micelle affords a medium for dynamic quenching through collision but offers no comparable π-stacked array, as in a DNA duplex, to mediate fast electron-transfer chemistry.

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Supporting Information Available: UV−visible spectra of Rh(III) complexes in water and bound to SDS micelles and Stern−Volmer plots showing the quenching of $*Ru(phen)_2dppz^{2+}$ by Rh(III) complexes in micelles in pH 8.5 buffer (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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