"Electro-Photo Switch" and "Molecular Light Switch" Devices Based on Ruthenium(II) Complexes of Modified Dipyridophenazine Ligands: Modulation of the Photochemical Function through Ligand Design

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The importance of metal complexes containing polypyridine ligands, such as 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bpy), in studies related to solar energy conversion, artificial nuclease design, molecular electronic device fabrication, etc. has been well-documented in the literature.[1] In recent years, ligands derived from appropriate modification of bpy and phen have been employed so as to suit the individual application. Unique among the host of such modified ligands reported so far is dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), a near-planar, heteroaromatic entity obtained by fusing a phenazine subunit to bpy. The archetypal electronic and structural features of the complexes derived from this versatile ligand seem to have made them attractive candidates for use in studies, mainly, with DNA.[2] During our continued investigations on the DNA interactions of dppz-based complexes,[3] it occurred to us that further strategic derivatization of this ligand might serve to explore and also to modulate other interesting functions associated with the ensuing complexes. This paper reports on the synthesis, characterization, and *mutually exclusive* photochemical functions of two novel ruthenium(II) complexes which incorporate either a quinone-fused (qddpz = naphtho[2,3-*a*]dipyrido[3,2-*h*:2′,3′-*f*] phenazine-5,18-dione) or a dicyano aromatic subunit appended (6,7-dicyanodipyridoquinoxaline) dppz-based ligand.

Ligands dicnq and qdppz[4] were synthesized by reacting together 1,10-phenanthroline-5,6-dione (phen-dione) and the corresponding diammines as illustrated in Figure 1. $[Ru(phen)_2(qdppz)](PF_6)_2$ and $[Ru(phen)_2(dicnq)](PF_6)_2$ were prepared by condensing $Ru(phen)_2Cl_2$ with qdppz or dicnq. The PF_6 salts were converted to the water-soluble chloride salts by the standard procedure using TBACl. All the new ligands and their complexes investigated in the present study have been fully characterized by CHN analysis, infrared, UV−visible, FABMS, ^{1}H and ^{13}C NMR, and electrochemical methods.[5]

Both $[Ru(phen)_2(qdppz)]Cl_2$ and $[Ru(phen)_2(dicnq)]Cl_2$ bind to CT DNA with binding constants of $(4.3 \pm 0.5) \times 10^4$ and $>10^6$ M^{-1}, respectively, as determined by the absorption titration method. As is true for the analogous dppz complex,[2d] the principal mode of DNA binding by these two complexes has been identified to involve the base-pair intercalation of the bound qdppz/dicnq by the application of various physicochemical and biochemical methods.[3a] In the present paper, we present results of novel "electro-photo switch" and "molecular light switch" effects observed for the two complexes.

$[Ru(phen)_2(qdppz)]^{2+}$ was found to be weakly luminescent ($\phi \leq 10^{-4}$) in rigorously dried $CHCl_3$, CH_2Cl_2, dichloroethane, and CH_3CN and to be essentially nonluminescent in buffer A (5 mmol tris, pH 7.1, 50 mmol of NaCl), aqueous CH_3CN (10% H_2O), and anionic micellar (0.1 M SDS) solutions. The weakness of luminescence observed for the complex in nonaqueous solvents can be rationalized in terms of an intramolecular photoinduced electron transfer (PET) quenching of its MLCT state by the appended quinone fragment as was the case with $Re(qdppz)(CO)_3Cl$.[4] An additional process, which was reported previously for $[Ru(phen)_2(dppz)]^{2+}$, involving the sensitivity of the excited state to quenching by water and the subsequent increase in the nonradiative decay rate seems to be responsible for the total lack of emission observed for the complex in the aqueous environments.[2b,c,h]

$[Ru(phen)_2(hqdppz)]^{2+}$, a complex containing the hydroquinone form of the ligand,[5] could be obtained by the reduction of $[Ru(phen)_2(qdppz)]^{2+}$ with $Na_2S_2O_4$, and the process could be reversed to get back the quinone form by $Ce(NH_4)_2(NO_3)_6$. $[Ru(phen)_2(hqdppz)]^{2+}$ was found to be essentially nonluminescent in aqueous solutions with or without buffer A. However, the complex showed its MLCT luminescence ($\lambda_{em(max)} = 601$ nm) in micellar and aqueous CH_3CN (10% H_2O) solutions with quantum yields (ϕ) of approximately 0.002 and 0.01, respectively. We believe that the PET reaction, which has been proposed above for the quinone-containing complex, does not operate in this hydroquinone-containing complex. Thus, the lack of luminescence observed in water and in aqueous buffered solutions can be explained solely on the basis of a proton transfer quenching of the excited state of the complex. A "partial recovery" occurs in

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(4) While this study was in progress,[3] the synthesis of qdppz was reported by Lopez et al. (Lopez, R. B.; Loeb, B. L.; Boussie, T.; Meyer, T. J. *Tetrahedron Lett*. **1996**, *37*, 5437).

(5) Representative data are as follows. **qdppz:** FABMS (*m*/*z*) 413, $[M^+]$; ^{1}H NMR ($CDCl_3$, 200 MHz, TMS) δ (ppm) 9.85 (d, 1H), 9.65 (d, 1H), 9.35 (d, 2H), 8.71 (dd, 2H), 8.32 (q, 2H), 7.88 (m, 4H); $E_{1/2}$ (DMF, 0.1 M $TBAPF_6$, V vs SCE) −0.46, −1.48. **$[Ru(phen)_2(qdppz)]^{2+}$:** FABMS (*m*/*z*) 1019, $[M-PF_6]^+$, 874, $[M-2PF_6]^+$; ^{1}H NMR (DMSO-d_6, 200 MHz, TMS) δ (ppm) 9.5 (br, 2H), 8.81 (m, 6H), 8.41 (s, 4H), 8.32 (d, 2H), 8.23 (d, 4H), 8.10 (d, 4H), 7.82 (m, 6H); ^{13}C NMR (CD_3CN/10% D_2O, 200 MHz, TMS) δ (ppm) 182.8 and 183.5; $E_{1/2}$ (CH_3CN, 0.1 M $TBAPF_6$, V vs SCE) +1.36, (DMF, 0.1 M $TBAPF_6$, V vs SCE) −0.37, −1.27, −1.49. **$[Ru(phen)_2(hqdppz)]^{2+}$:** UV−vis ($CH_3CN$/10%$H_2O$) λ_{max}, nm (log ϵ) 442 (4.28), 348 (4.22), 300 (sh, 4.74), 263 (5.06); ^{13}C NMR (CD_3CN/10% D_2O, 200 MHz, TMS) δ (ppm) 156.5 and 157.6. **dicnq:** FABMS (*m*/*z*) 283, $[M^+]$; ^{1}H NMR (DMSO-d_6, 200 MHz, TMS) δ (ppm) 9.38 (m, 4H), 8.04 (q, 2H). **$[Ru(phen)_2(dicnq)]^{2+}$:** FABMS (*m*/*z*) 889, $[M-PF_6]^+$; 743, $[M-2PF_6]^+$; ^{1}H NMR (DMSO-d_6, 200 MHz, TMS) δ (ppm) 8.80 (dd, 4H), 8.40 (s, 4H), 8.21 (m, 2H), 8.05 (dd, 4H), 7.94 (m, 2H), 7.80 (m, 4H); $E_{1/2}$ (DMF, 0.1 M $TBAPF_6$, V vs SCE) −0.83, −1.29, −1.48.

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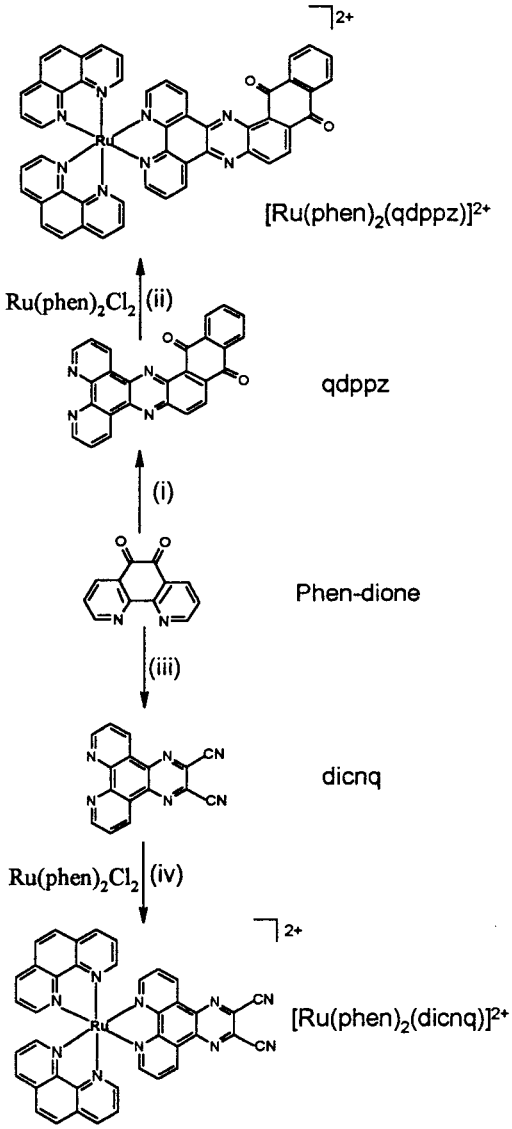

Figure 1. Scheme leading to the synthesis of $[Ru(phen)_2(qdppz)]^{2+}$ and $[Ru(phen)_2(dicnq)]^{2+}$: (i) 1,2-diaminoanthraquinone, C_2H_5OH, 5 h (72%); (ii) ethylene glycol, reflux; (iii) diaminomaleonitrile, C_2H_5OH, 45 min (80%); (iv) CH_3OH/H_2O, reflux.

SDS solutions where the complex can, in principle, reside in a more hydrophobic micellar environment and the dipyridophenazine ligand is protected from water. There is a further enhancement of luminescence in aqueous CH_3CN solutions due to the presence of less water in solution.[2b,c,h]

In aqueous CH_3CN (4−5% H_2O) solutions containing 0.1 M $TBAPF_6$, $[Ru(phen)_2(qdppz)](PF_6)_2$ could be reduced at −0.26 V (cyclic voltammetry). Exhaustive coulometric reduction of the complex conducted in deaerated, aqueous CH_3CN at −0.5 V generated $[Ru(phen)_2(hqdppz)](PF_6)_2$ as identified by its UV−visible and NMR spectra. The solution containing this reduced complex showed an oxidation wave at +0.92 V, and the bulk exhaustive coulometry conducted at +1.1 V was seen to regenerate $[Ru(phen)_2(qdppz)]^{2+}$. The redox cycle was repeated three to four times with <5% loss of the material. In addition, while the quinone form was found to be almost nonluminescent, the electrochemically generated hydroquinone form of the complex showed

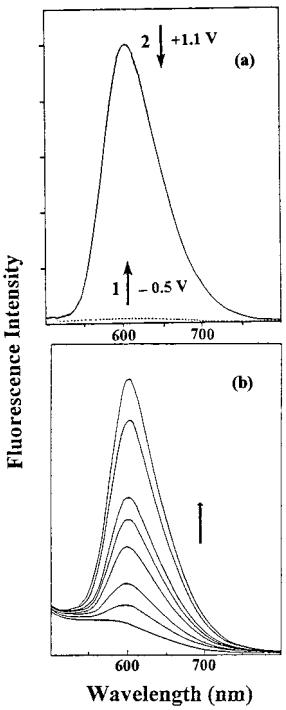

Figure 2. (a) Luminescence spectra (CH_3CN/5% H_2O, 0.1 M $TBAPF_6$, λ_{exc} = 440 nm) of $[Ru(phen)_2(qdppz)]^{2+}$ (**1**) and $[Ru(phen)_2(hqdppz)]^{2+}$ (**2**) as obtained by exhaustive electrolyses at the indicated potentials in each case. The arrows refer to the reversible changes observed upon electrochemical interconversion of these complexes. (b) Luminescence enhancement observed for $[Ru(phen)_2(dicnq)]^{2+}$ upon addition of CT DNA. [Ru] = 10 μM and [DNA nucleotide phosphate] = 0−370 μM (buffer A; λ_{exc} = 440 nm).

the MLCT luminescence at 601 nm (ϕ = 0.02), Figure 2a. Thus, the $2e^-/2H^+$ couple $[Ru(phen)_2(qdppz)]^{2+}/[Ru(phen)_2(hqdppz)]^{2+}$, which combines an electroactive component with a light-emitting center, represents a redox-activated luminescence on/off switching device.[7] On the other hand, $[Ru(phen)_2(dicnq)]^{2+}$ was seen to be a "luminescence reporter" of DNA as described below.

Steady state emission spectra of 10 μM solutions of $[Ru(phen)_2(dicnq)]Cl_2$ in buffer A showed an increase in the emission intensity with successive addition of CT DNA and reached a maximum (~16 times) at a [DNA nucleotide phosphate]/[Ru] ratio of 36, Figure 2b. This emission enhancement is quite impressive in comparison with the enhancement observed for $[Ru(phen)_3]^{2+}$ (enhancement factor is 2 even at a [DNA nucleotide phosphate]/[Ru] ratio of ~80), but it is relatively less pronounced compared to the strong "molecular light switch" effect reported[2] for $[Ru(phen)_2(dppz)]^{2+}$. The emission enhancement observed here for $[Ru(phen)_2(dicnq)]^{2+}$ in the presence of DNA can be interpreted in terms of protection of the imine nitrogens of the dicnq ligand from attack by water and a consequent decrease in the nonradiative processes upon intercalation.[2b,c,h]

In summary, we have demonstrated in this study that while the redox couple $[Ru(phen)_2(qdppz)]^{2+}/[Ru(phen)_2(hqdppz)]^{2+}$ represents an "electro-photo switch", $[Ru(phen)_2(dicnq)]^{2+}$ is an efficient "molecular light switch" for DNA, *the functions exhibited by the two complexes reported here being mutually exclusive*. Thus, these results testify to the importance of the architectural intricacies and electronic structures of the new dppz-based ligands in dictating the useful photochemical functions of their complexes.

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(6) Interestingly, both $[Ru(phen)_2(qdppz)]^{2+}$ and $[Ru(phen)_2(hqdppz)]^{2+}$ (10 μM) remain essentially nonluminescent in the presence of excess DNA. Further studies are in progress.

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