Ruthenium(II) Complexes of 6,7-Dicyanodipyridoquinoxaline: Synthesis, Luminescence Studies, and DNA Interaction

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The hexafluorophosphate and chloride salts of a series of ruthenium(II) complexes incorporating a new dipyridophenazine-based ligand, dicnq (6,7-dicyanodipyrido[2,2-*d*:2′,3′-*f*]quinoxaline), are synthesized in good-to-moderate yields. These mono ($[Ru(phen)_2(dicnq)]^{2+}$; phen = 1,10 -phenanthroline), bis ($[Ru(phen)(dicnq)_2]^{2+}$), and tris ($[Ru(dicnq)_3]^{2+}$) complexes are fully characterized by elemental analysis, infrared, FAB-MS, ^{1}H NMR, and cyclic voltammetric methods. Results of absorption titration and thermal denaturation studies reveal that these complexes are moderately strong binders of calf-thymus (CT) DNA, with their binding constants spanning the range $(1-3) \times 10^4$ M^{-1}. On the other hand, under the identical set of experimental conditions of light and drug dose, the DNA (pBR 322)-photocleavage abilities of these ruthenium(II) complexes follow the order $[Ru(phen)_2(dicnq)]^{2+} > [Ru(phen)(dicnq)_2]^{2+} \gg [Ru(dicnq)_3]^{2+}$, an order which is the same as that observed for their MLCT emission quantum yields. Steady-state emission studies carried out in nonaqueous solvents and in aqueous media with or without DNA reveal that while $[Ru(dicnq)_3]^{2+}$ is totally nonemissive under these solution conditions, both $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ are luminescent and function as "molecular light switches" for DNA. Successive addition of CT DNA to buffered aqueous solutions containing the latter two complexes results in an enhancement of the emission in each case, with the enhancement factors at saturation being approximately 16 and 8 for $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$, respectively. These results are discussed in light of the relationship between the structure-specific deactivations of the MLCT excited states of these metallointercalators and the characteristic features of their DNA interactions, and attempts are made to compare and contrast their properties with those of analogous dipyridophenazine-based complexes, including the ones reported in the preceding paper.

Introduction

Studies aimed at probing the effects of variations in the metal ion and the ligand on the abilities of metal complexes incorporating the dipyridophenazine (dppz) family of ligands to bind and photocleave DNA are of current interest in view of their relevance to various biochemical and biomedical applications.[1−5] We previously reported the effect of metal ion variation on the DNA interactions of mixed-ligand complexes of dppz.[6] The influence of variations in the dppz structure on the functions of the resulting metal complexes was demonstrated in the preceding paper, where a pair of redox-related ruthenium(II) complexes were shown to exhibit not only interesting "electro−photo switch" effects but also strong DNA-binding and -photocleavage proclivities.[7] The dppz ligand was modified by fusing it to either a quinone or a hydroquinone to create these properties. On the other hand, the unique architecture of dppz—the prototype ligand in which 2,2′-bipyridyl and phenazine subunits are brought together to give an extended aromatic π-system—permits the design of a variety "second-generation" ligands to suit individual applications.[3−5] In our continued efforts in this direction, we recently synthesized a dicyano subunit-appended ligand belonging to the dppz family, viz., 6,7-dicyanodipyrido[2,2-*d*:2′,3′-*f*]-quinoxaline (dicnq). The novel "molecular light switch" effect exhibited by a representative dicnq complex in the presence of DNA was recently reported.[8] This paper describes the syntheses, characterizations, and DNA-binding and -photocleavage properties of a series of ruthenium(II) complexes of dicnq ($[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$, and $[Ru(dicnq)_3]^{2+}$, where phen = 1,10-phenanthroline), the structures of which are shown in Figure 1. In addition, results of investigations carried out on the "molecular light switch" effects exhibited by these new complexes are also presented here.

Experimental Section

A. Materials. 1. General Details. Diaminomaleonitrile was obtained from Aldrich. All other chemicals, biochemicals, and solvents utilized in this study were obtained in their highest available purity from sources specified in the preceding paper. The solvents utilized for the spectroscopic and electrochemical work were rigorously purified before use according to standard procedures.[9] Deionized, triply distilled water was used for preparing various buffers.

2. Syntheses. 1,10-Phenanthroline-5,6-dione (phen-dione),[10] $[Ru(phen)_3]Cl_2$,[11] $[Ru(phen)_2Cl_2]$,[12] and $[Ru(phen)Cl_4]^-$ [13] were synthesized by following the reported procedures. The syntheses of dicnq and its ruthenium(II) complexes are described below.

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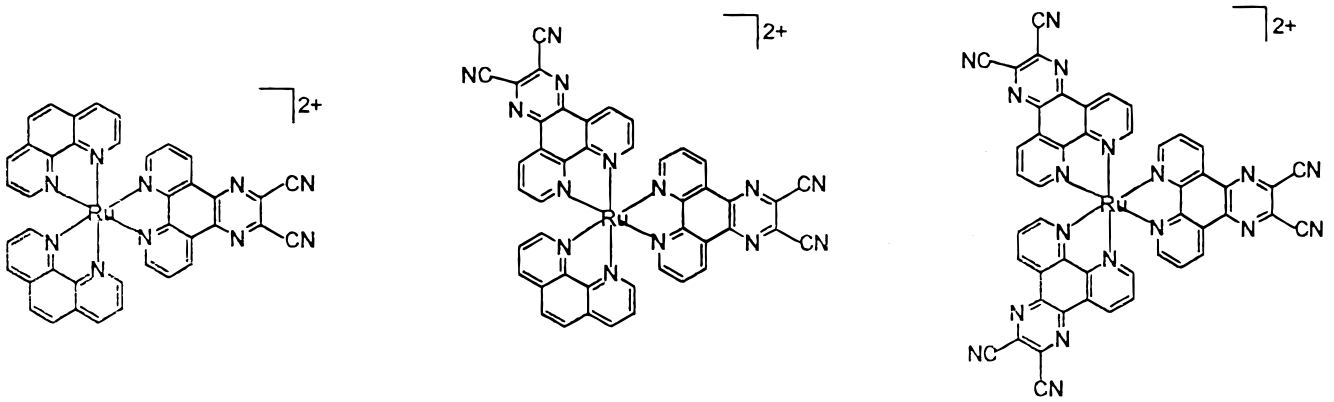

Figure 1. Structures of the three ruthenium(II) complexes investigated in this study.

dicnq (6,7-Dicyanodipyrido[2,2-*d*:2′,3′-*f*]quinoxaline). phen-dione (0.1 g, 0.5 mmol) and diaminomaleonitrile (0.1 g, 0.9 mmol) were dissolved in ethanol, and the resulting solution was refluxed for 45 min under a nitrogen atmosphere. The brownish-yellow needles that precipitated from the solution upon cooling to room temperature were filtered off, washed with cold ethanol, and suction-dried to obtain the desired product in pure form. Yield: 80%.

Anal. Found: C, 67.98; H, 2.19; N, 29.37. Calcd for $C_{16}H_6N_6$: C, 68.08; H, 2.14; N, 29.57. FAB-MS: *m*/*z* 283 (M^+). IR (KBr pellet): 742, 1373, 1504, 1583, 2239, 2337 cm^{-1}. ^1H NMR (DMSO-d_6, 200 MHz, TMS): δ 9.38 (m, 4H), 8.04 (q, 2H).

[Ru(phen)$_2$(dicnq)](PF$_6$)$_2$·2H$_2$O (Bis(1,10-phenanthroline)(6,7-Dicyanodipyrido[2,2-*d*:2′,3′-*f*]quinoxaline)ruthenium(II) Hexafluorophosphate Dihydrate). [Ru(phen)$_2$Cl$_2$] (0.1 g, 0.17 mmol) and dicnq (0.06 g, 0.2 mmol) were placed in a 100 mL round-bottom flask containing 60 mL of a methanol−water (1:1, vol/vol) mixture, and the suspension was heated to reflux for 2 h. The resulting brownish-red solution was allowed to cool to room temperature, after which it was stored at 0 °C for 1 h. A saturated aqueous solution of NH_4PF_6 was added to this solution to precipitate the crude complex, which was filtered off. The solid was washed with $CHCl_3$, recrystallized from acetone−ether, and vacuum-dried to obtain the pure product. Yield: 85%.

Anal. Found: C, 46.00; H, 2.29; N, 12.96. Calcd for $C_{40}H_{26}N_{10}O_2$: C, 45.92; H, 2.40; N, 13.10. FAB-MS: *m*/*z* 889 ($[M - PF_6]^+$), 743 ($[M - 2PF_6]^+$). IR (KBr pellet): 715, 837, 1373, 1427, 1554, 2229, 3408, 3641 cm^{-1}. ^1H NMR (DMSO-d_6, 200 MHz, TMS): δ 8.80 (dd, 4H), 8.40 (s, 4H), 8.21 (m, 2H), 8.05 (dd, 4H), 7.94 (m, 2H), 7.80 (m, 4H).

[Ru(phen)(dicnq)$_2$](PF$_6$)$_2$·2H$_2$O (Bis(6,7dicyanodipyrido[2,2-*d*:2′,3′-*f*]quinoxaline)(1,10-phenanthroline)ruthenium(II) Hexafluorophosphate Dihydrate). This complex was prepared from $[Ru(phen)Cl_4]^-$ (0.15 g, 0.34 mmol) and dicnq (0.21 g, 0.78 mmol) in a manner analogous to that employed for the synthesis of [Ru(phen)$_2$(dicnq)](PF$_6$)$_2$. Yield: 70%.

Anal. Found: C, 45.12; H, 2.04; N, 16.68. Calcd for $C_{44}H_{24}N_{14}O_2$: C, 45.11; H, 2.07; N, 16.74. FAB-MS: *m*/*z* 991 ($[M - PF_6]^+$), 845 ($[M - 2PF_6]^+$). IR (KBr pellet): 725, 841, 1371, 1429, 1554, 2237, 3645 cm^{-1}. ^1H NMR (DMSO-d_6, 200 MHz, TMS): δ 9.48 (dd, 4H), 8.80 (dd, 2H), 8.41 (s, 2H), 8.28 (m, 2H), 8.19 (dd, 4H), 7.94 (dd, 4H), 7.79 (m, 2H).

[Ru(dicnq)$_3$](PF$_6$)$_2$·2H$_2$O (Tris(6,7-dicyanodipyrido[2,2-*d*:2′,3′-*f*]-quinoxaline)ruthenium(II) Hexafluorophosphate Dihydrate). Hydrated ruthenium trichloride (0.15 g) and dicnq (0.6 g, 2.1 mmol) were refluxed in 40 mL of a methanol−water (1:1, vol/vol) mixture for 4 h. The resulting solution was allowed to cool to the room temperature and filtered. A saturated aqueous solution of NH_4PF_6 was added to the red filtrate to effect precipitation of the crude product, which was filtered off, washed with $CHCl_3$, recrystallized from acetone−ether, and vacuum-dried. Yield: 70%.

Anal. Found: C, 45.57: H, 1.64; N, 19.05. Calcd for $C_{48}H_{22}N_{18}O_2$: C, 45.46; H, 1.69; N, 19.49. FAB-MS: *m*/*z* 1093 ($[M - PF_6]^+$), 948 ($[M - 2PF_6]^+$). IR (KBr pellet): 841, 1371, 1448, 1662, 2212, 2361, 3640 cm^{-1}. ^1H NMR (DMSO-d_6, 200 MHz, TMS): δ 9.51−9.42 (m, 2H), 8.40 (dd, 2H), 8.01 (m, 2H).

The chloride salts were obtained by dissolving the above hexafluorophosphates in minimum amounts of acetone and then adding saturated solutions of tetrabutylammonium chloride in acetone, precipitating the desired products. Recovery was about 90% of the theoretical yield in each case.

B. Methods. 1. Spectroscopy and Electrochemistry. All the spectroscopic and electrochemical experiments were carried out as described in our previous work.[6−8,14−17] While the hexafluorophosphate salts of the complexes investigated in this study were employed for luminescence measurements in nonaqueous solvents, the corresponding chloride salts were used for measurements in aqueous and aqueous buffered (buffer A: 5 mM Tris, pH 7.1, 50 mM NaCl) solutions.

2. DNA-Binding and -Photocleavage Studies. Buffer A was used for absorption titration experiments and luminescence measurements. Buffer B (1 mM phosphate, pH 7.0, 2 mM NaCl) was used for thermal denaturation experiments. The chloride salts of the complexes were used in studies with DNA.

DNA melting ([DNA nucleotide phosphate] = 170 μM, [drug] = 0−7 μM) and absorption titration ([drug] = 20−30 μM and [DNA base pairs] = 0−200 μM) experiments were carried out as described in the preceding paper. Absorbance values were recorded after each successive addition of DNA solution and equilibration (ca. 10 min). The data were then fit to eq 1 to obtain the intrinsic binding constant

$$[DNA]/(\epsilon_a - \epsilon_f) = [DNA]/(\epsilon_b - \epsilon_f) + 1/K_b(\epsilon_b - \epsilon_f) \qquad (1)$$

K_b.[18] ϵ_a, ϵ_f, and ϵ_b are the apparent, free, and bound metal complex extinction coefficients, respectively. A plot of $[DNA]/(\epsilon_a - \epsilon_f)$ vs [DNA] gave a slope of $1/(\epsilon_b - \epsilon_f)$ and a *y* intercept equal to $1/K_b(\epsilon_b - \epsilon_f)$; K_b is the ratio of slope to *y* intercept.

Gel electrophoresis experiments were carried out as detailed in our previous studies with various metallointercalator- and porphyrin-based photonucleases.[6,7,16,17] Samples (preincubated in the dark, 1 h) were irradiated for 30 min inside the sample chamber of a JASCO model FP-777 spectrofluorimeter (λ_{exc} = 440 ± 5 nm, slit width = 5 nm).

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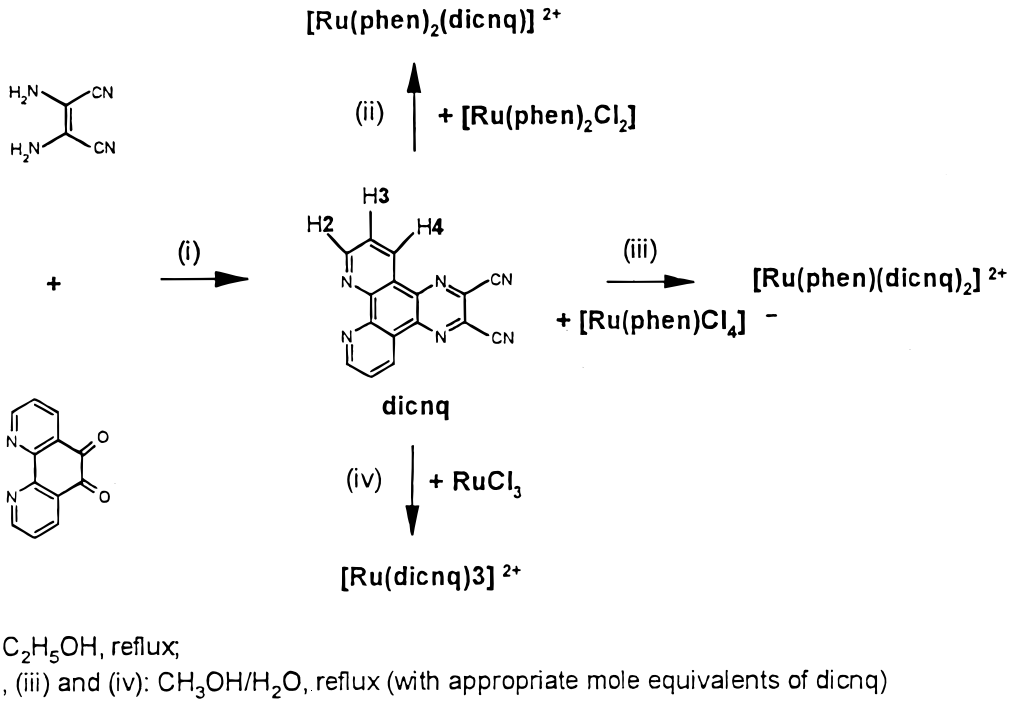

Figure 2. Scheme leading to the syntheses of dicnq and its mono, bis, and tris ruthenium(II) complexes.

Results and Discussion

The new ligand dicnq, while retaining the basic "dppz" structure, also possesses strongly electron withdrawing cyano groups in its architecture. Thus, dicnq is expected to be an easily reducible ligand having a strong DNA-binding ability, as is the case with the quinone-fused, dppz-based ligand naphtho[2,3-*a*]dipyrido[3,2-*h*:2′,3′-*f*]phenazine-5,18-dione (qdppz) reported in the previous paper. However, important differences exist between the complexes of dicnq and qdppz (and also other dppz-based ligands) with regard to their properties, especially those related to their DNA interactions. An attempt is made here to allude to this aspect in discussing the DNA-binding, DNA-photocleavage, and luminescence properties of our dicnq series of ruthenium(II) complexes.

A. Synthesis. Schemes leading to the syntheses of dicnq and its ruthenium(II) complexes are illustrated in Figure 2. The ligand was synthesized by the condensation of phen-dione with diaminomaleonitrile in ethanol in a manner similar to that reported for the preparation of dppz.[19] The condensation proceeded smoothly, providing the pure sample in 80% yield. Ruthenium(II) complexes containing dicnq were synthesized by refluxing this ligand and the appropriate mole ratios of the precursor complexes in methanol−water mixtures and precipitating the products as the PF_6 salts. The yields were good to moderate in each case. The corresponding chloride salts were prepared with ease by a standard method.

B. Spectral and Electrochemical Characterization. dicnq and its complexes were characterized, initially, by elemental analysis, infrared spectroscopy, and FAB-MS methods (see the Experimental Section). The uncomplexed ligand gave a satisfactory elemental analysis and the expected CN stretching frequency at 2239 cm^{-1} in its infrared spectrum. Elemental analysis data also indicated the dihydrate nature of each of the ruthenium(II) complexes investigated in this study. In the FAB-MS studies, dicnq showed a base peak at *m*/*z* 283 ascribable to its mass (M^+), but only the peaks due to $[M - PF_6]^+$ and $[M - 2PF_6]^+$ fragments were seen in the mass spectra of the new complexes, as is the case for the PF_6 salts of other ruthenium(II) polypyridyls reported previously.[20]

The ^1H NMR spectrum of dicnq could be easily analyzed on the basis of the positions and the integrated intensities of the resonance peaks. While the resonances of the H-4 and H-2 aromatic protons appear as a multiplet (m) around 9.38 ppm, the resonance due to the H-3 proton appears as a quatret (q) at 8.04 ppm (see Figure 2 for proton identification). In comparison, the H-4, H-2, and H-3 proton signals of phen are located at 9.11 (doublet of doublet, dd), 8.51 (dd), and 7.78 (q) ppm, respectively. The downfield shifts observed for these protons on dicnq, in comparison with the corresponding protons on phen, are consistent with the electron-withdrawing nature of the cyano groups. Figure 3 compares the ^1H NMR spectra of $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$, and $[Ru(dicnq)_3]^{2+}$ with the spectrum of $[Ru(phen)_3]^{2+}$. In these spectra, resonances due to the protons of bound phen and dicnq are seen to be shifted (to both downfield and upfield regions) compared to those of free ligands, indicating complexation. In addition, there is a progressive decrease in the intensity of the peaks due to phen concomitant with an increase in the intensity of the peaks due to dicnq as one moves from $[Ru(phen)_3]^{2+}$ to $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$, and $[Ru(dicnq)_3]^{2+}$ in that order.

In DMF containing 0.1 M $(TBA)PF_6$, uncomplexed dicnq shows a well-defined reversible one-electron-reduction wave at −0.66 V vs SCE.[21] A reduction wave for the complexed dicnq in $[Ru(phen)_2(dicnq)]^{2+}$ occurs at −0.81 V (reversible one-electron transfer) followed by the successive phen reductions at −1.29 and −1.48 V under similar experimental conditions

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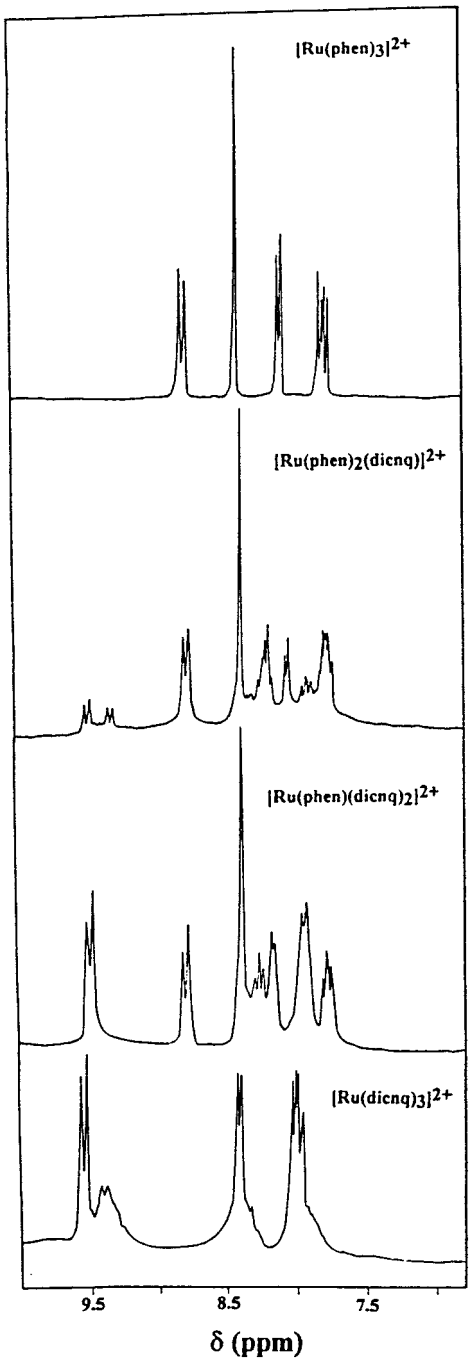

Figure 3. ^{1}H NMR spectra of $[Ru(phen)_3]^{2+}$, $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$, and $[Ru(dicnq)_3]^{2+}$ in DMSO-d_6.

(Figure 4). On the other hand, reduction of both dicnq ligands in $[Ru(phen)(dicnq)_2]^{2+}$ occurs at −0.51 V, followed by the reduction of phen at −1.34 V. Electron addition to all the three dicnq ligands in $[Ru(dicnq)_3]^{2+}$ occurs at −0.47 V. Thus, the relative ease of reduction of the bound dicnq follows the order $[Ru(phen)_2(dicnq)]^{2+} > [Ru(phen)(dicnq)_2]^{2+} > [Ru(dicnq)_3]^{2+}$. An analysis of these data suggests that the π^* orbital of dicnq lies lower than that of phen and, probably, that the added electron is delocalized equally on the π^* levels of the dicnq ligands rather than on only one ligand.[22,23] This latter supposition is not in line with DeArmond's[24] proposal that the electron is

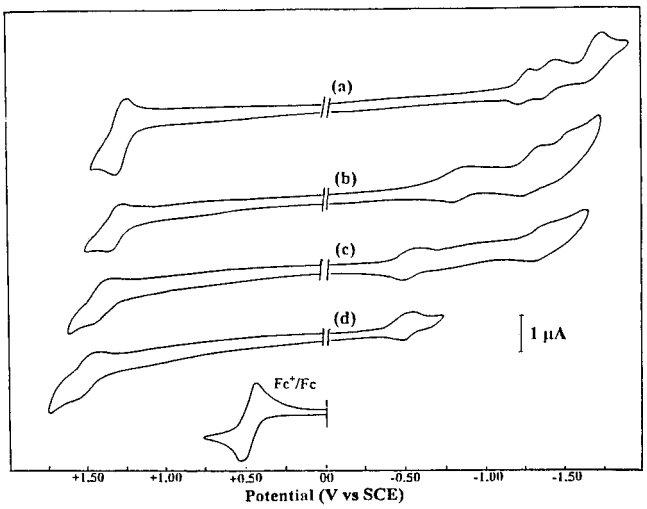

Figure 4. Cyclic voltammograms of (a) $[Ru(phen)_3]^{2+}$, (b) $[Ru(phen)_2(dicnq)]^{2+}$, (c) $[Ru(phen)(dicnq)_2]^{2+}$, and (d) $[Ru(dicnq)_3]^{2+}$, for oxidation in CH_3CN, 0.1 M $(TBA)PF_6$ and reduction in DMF, 0.1 M $(TBA)PF_6$. (Fc = ferrocene; scan rate = 100 mV s^{-1}).

localized in the π^* levels of one ligand rather than being delocalized over the whole ligand π system in $[Ru(bpy)_3]^{2+}$. However, it is consistent with the electrochemical data for $[Ru(dppz)_3]^{2+}$, wherein reductions of all three complexed dppz ligands have been reported to occur at the same potential.[22]

No oxidation wave was discernible for both phen and dicnq in CH_3CN, 0.1 M $(TBA)PF_6$ when the potential was scanned up to +1.8 V. On the other hand, oxidations of the ruthenium centers in $[Ru(phen)_2(dicnq)]^{2+}$, $[Ru(phen)(dicnq)_2]^{2+}$, and $[Ru(dicnq)_3]^{2+}$ occur at +1.31, +1.41, and +1.51 V, respectively, under similar experimental conditions of solvent and supporting electrolyte (see Figure 4).[25] Thus, electron abstraction from the metal center is more difficult in these complexes than it is from $[Ru(phen)_3]^{2+}$ (1.26 V), due to the presence of electron-withdrawing cyano groups on dicnq. Interestingly, the sequential substitution of phen in $[Ru(phen)_3]^{2+}$ with dicnq increases the oxidation potential of ruthenium steadily, resulting in an overall anodic shift of 0.25 V for $[Ru(dicnq)_3]^{2+}$ compared to $[Ru(phen)_3]^{2+}$. Such monotonic increase in the metal-centered oxidations with the number of electron-withdrawing ligands in metallopolypyridyls has been well-documented in the literature.[26]

UV−visible data for dicnq and its ruthenium(II) complexes are summarized in Table 1. The absorption spectrum of dicnq shows bands in the 220−400 nm region with the most intense band being located at 265 nm. This intense peak observed for dicnq is similar to that observed, at the same wavelength, for phen. On the other hand, additional peaks appearing at 305, 347, and 365 nm in the spectrum of dicnq indicate that the corresponding transitions could arise from the "quinoxaline" portion of this ligand.[27] In the UV−visible spectra of the three complexes (Figure 5), the ultraviolet regions show intense bands

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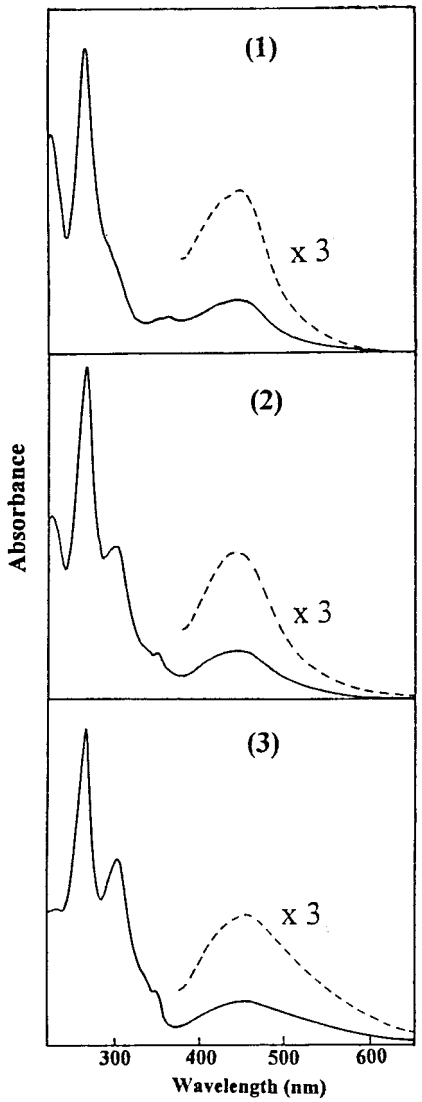

Figure 5. UV−visible spectra of (1) $[Ru(phen)_2(dicnq)]^{2+}$, (2) $[Ru(phen)_2(dicnq)]^{2+}$, and (3) $[Ru(dicnq)_3]^{2+}$ in CH_3CN.

Table 1. Absorption and Emission Data Obtained in CH_3CN[a]

compound	absorption: λ_{max}, nm (log ϵ)	emission λ_{em}, nm	emission ϕ_{em}
dicnq	265 (4.64), 305 (4.40), 347 (3.93), 365 (3.83)		
$[Ru(phen)_2(dicnq)]^{2+}$	263 (5.12), 292 (4.64), 349 (4.15), 362 (4.18), 445 (4.33)	613	0.012
$[Ru(phen)(dicnq)_2]^{2+}$	264 (5.15), 300 (4.80), 346 (4.24), 441 (4.31)	610	0.004
$[Ru(dicnq)_3]^{2+}$	266 (5.13), 302 (4.88), 348 (4.34), 452 (4.29)		

[a] Error limits: λ, ±1 nm; ϵ, ±7%; ϕ_{em}, ±10%.

arising from the intraligand transitions due to the coordinated phen and dicnq. While both $[Ru(dicnq)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ show intense absorption bands at 266 and 263 nm, respectively, the former complex additionally displays relatively less intense transitions at 302 and 348 nm. Thus, both phen and dicnq absorb at shorter wavelengths in these complexes and the bands at 302 and 348 nm are ascribable exclusively to intraligand transitions involving the coordinated dicnq. Accordingly, in the spectra of the mixed-ligand complexes, $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$, the ultraviolet regions are dominated by the transitions due to both phen (263/264 nm) and dicnq (263/264 292/300 and 346/349 nm). In addition, the ratio of the absorbance at ~266 nm (phen + dicnq) to that at ~300 nm (dicnq) decreases with an increasing number of dicnq ligands in the complexes as 3.0 ($[Ru(phen)_2(dicnq)]^{2+}$) > 2.2 ($[Ru(phen)(dicnq)_2]^{2+}$) > 1.8 ($[Ru(dicnq)_3]^{2+}$ (also, compare the corresponding ϵ values in Table 1).

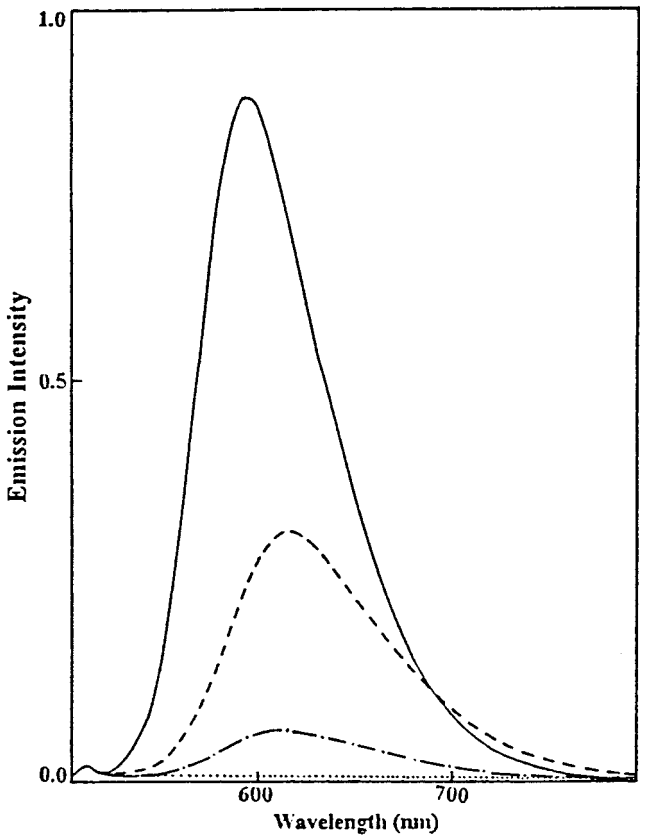

Figure 6. Luminescence spectra of equiabsorbing (OD = 0.2) $[Ru(phen)_3]^{2+}$ (—), $[Ru(phen)_2(dicnq)]^{2+}$ (- - -), $[Ru(phen)(dicnq)_2]^{2+}$ (—·—), and $[Ru(dicnq)_3]^{2+}$ (···) in CH_3CN (λ_{exc} = 440 nm).

The visible region of the spectrum of each new complex investigated in the present study is characterized by the presence of a broad d(π-π^*) MLCT transition located between 441 and 452 nm (see Figure 5, dashed lines), close to the corresponding transition of $[Ru(phen)_3]^{2+}$ (446 nm). Thus, although the electrochemical data suggest that the π^* orbital of dicnq lies lower than the phen π^* (vide supra), we believe that the MLCT absorptions of these new complexes could probably result from an overlap of Ru(dπ) → dicnq(π^*) and Ru(dπ) → phen(π^*) transitions, as is the case with various mixed-ligand complexes of the type $[Ru(LL)_n(LL')_{3-n}]^{2+}$ where LL = bpy or phen and LL′ is a heterocyclic ligand other than bpy/phen.[28−30] Finally, presence of only the MLCT band for these complexes of dicnq in the visible regions is similar to the observation made for $[Ru(phen)_2(hqdppz)]^{2+}$ but is in contrast to the appearance of both the MLCT and quinone $\pi-\pi^*$ bands for $[Ru(phen)_2(qdppz)]^{2+}$.[7]

Figure 6 compares the luminescence spectra of the three complexes with the spectrum of $[Ru(phen)_3]^{2+}$ (λ_{exc} = 440 nm; dry CH_3CN); Table 1 summarizes the relevant data. As seen, while the mono- and bis-dicnq complexes are luminescent with

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(29) Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3863.
(30) Yam, W. V.; Lee, W. V.; Ke, F.; Siu, K. M. *Inorg. Chem.* **1997**, *36*, 2124.

their emission maxima appearing at 616 and 612 nm, respectively, the tris-dicnq complex is nonemissive. The band maxima of these dicnq complexes are red-shifted in comparison with that of $[Ru(phen)_3]^{2+}$ under similar experimental conditions of solvent and excitation wavelength. This situation is quite similar to that of $[Ru(phen)_2(dppz)]^{2+}$, whose ^{3}MLCT emission band maximum has been reported at 618 nm in CH_3CN.[31] Data given in Table 1 also reveal that emission quantum yields of the complexes investigated here are lower than that of $[Ru(phen)_3]^{2+}$ ($\phi_{em} = 0.028$ in dry CH_3CN) and vary as $[Ru(phen)_2(dicnq)]^{2+} > [Ru(phen)(dicnq)_2]^{2+} \gg [Ru(dicnq)_3]^{2+}$. A variety of excited-state processes, including enhanced internal conversion and intersystem crossing, ion association, excitation energy transfer (EET), photoinduced electron transfer (PET), etc., are thought to be operative in the emission quenchings observed for the complexes in dry CH_3CN.[32] Among these, the possibility of an intramolecular PET from the ruthenium center to the easily reducible dicnq ligand is discussed here. A rough estimate of free energies (ΔG) for the PET reactions illustrated in eq 2 can be made using eq 3, where $E_{1/2}$(ox) and $E_{1/2}$(red) are the

$$^3[Ru^{II}(phen)_n(dicnq)_{3-n}]^{2+} \rightarrow [Ru^{III}(phen)_n(dicnq^{\bullet -})_{3-n}]^{2+} \quad (2)$$

$$\Delta G = E_{1/2}(ox) - E_{1/2}(red) - E_{0-0} \quad (3)$$

oxidation and reduction potentials, respectively, and E_{0-0} is the energy of the ^{3}MLCT state of each complex.[33] These calculations reveal that the ΔG values for $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ are approximately $+0.10$ and -0.10 eV, respectively. Assuming that E_{0-0} of $[Ru(dicnq)_3]^{2+}$ is close to that of $[Ru(phen)(dicnq)_2]^{2+}$,[33] a rough value of ΔG for an intramolecular PET for this complex can be estimated to be ~ -0.05 eV. Thus, intramolecular PETs of the type shown in eq 2 are, in principle, possible in these complexes in dry CH_3CN solutions, but they are only moderate, unlike the case for $[Ru(phen)_2(qdppz)]^{2+}$ ($\phi < 10^{-4}$ in CH_3CN) discussed in the preceding paper. In addition, we note that it is not generally correct to consider exclusively a PET-based mechanism only on the basis of thermodynamic criteria. As stated earlier, other *intramolecular* processes as reported for a series of ruthenium(II) complexes containing the polyazaaromatic ligand tap or hat (tap = 1,4,5,8-tetraazaphenanthrene; hat = 1,4,5,8,9,12-hexaazatriphenylene)[34] and for $[Ru(phen)_2(dppz)]^{2+}$ in polar, aprotic solvents cannot be ruled out altogether.[35] Therefore, it is reasonable to expect that PET-based mechanisms do contribute to the excited-state decays of these donor−acceptor type complexes. This interpretation is consistent with a similar interpretation made earlier for $[Ru(bpy)_2(NOP)]^{2+}$ (NOP = 2-(4-nitrophenyl)imidazo[4,5-*f*][1,10]phenanthroline), where a photoelectron transfer from the ruthenium(II) center to the electron-deficient ligand NOP has been invoked to explain the strong luminescence quenching.[36]

C. DNA Binding. Bindings of the chloride salts of the three new complexes synthesized in this study with CT DNA were monitored by thermal denaturation, absorption titration, and luminescence methods. These results are summarized in this section, which also discusses aspects related to the abilities of these complexes to act as "molecular light switches" for DNA.

CT DNA was seen to melt at 60 ± 1 °C in the absence of any added drug under our experimental conditions (2 mM NaCl, 1 mM phosphate). The melting temperature (T_m) of DNA is increased by 5, 4, and 3 (±1) °C in the presence of $[Ru(phen)_2(dicnq)]^{2+}$ (Figure 7a), $[Ru(phen)(dicnq)_2]^{2+}$, and $[Ru(dicnq)_3]^{2+}$, respectively, at a [DNA nucleotide phosphate]/[complex] ratio of 25 in each case. In the absorption titration experiments, each ruthenium(II) complex showed the presence of isosbestic points, hypochromicity, and red-shifted absorption maxima with increasing additions of DNA, as illustrated for $[Ru(phen)(dicnq)_2]^{2+}$ in Figure 7b. For $[Ru(dicnq)_3]^{2+}$, wavelengths at the isosbestic points, magnitudes of bathochromic shifts in the absorbance maximum, and the percent hypochromicity (at saturation) are 485 and 358 nm, 4 nm, and 12%, respectively. The analogous parameters for $[Ru(phen)(dicnq)_2]^{2+}$/$[Ru(phen)_2(dicnq)]^{2+}$ are 482 and 352/480 and 351 nm, 5/6 nm, and 17/16%, respectively. All of these observations are consistent with intercalative modes of binding by these complexes with the duplex.[37−40] Data obtained from the absorption titration experiments were fit to eq 1 to give binding constants (K_b) of $(3.3 \pm 0.5) \times 10^4$, $(3.0 \pm 0.5) \times 10^4$, and $(9.7 \pm 0.5) \times 10^3$ M^{-1} for $[Ru(phen)(dicnq)_2]^{2+}$, $[Ru(phen)_2(dicnq)]^{2+}$, and $[Ru(dicnq)_3]^{2+}$, respectively. These K_b values are thus are close to that of $[Ru(phen)_3]^{2+}$ [41] but are low in comparison with the strong DNA binding ($K_b > 10^6$ M^{-1}) exhibited by $[Ru(phen)_2(dppz)]^{2+}$ and other dppz-based complexes[42−51] and also by $[Ru(phen)_2$-

(31) Hartshorn, R. M.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 5919.

(32) Obviously, it is not going to be easy to estimate the contribution from each of these excited-state processes only on the basis of the steady-state emission data. However, an intramolecular EET from the ^{3}MLCT state to the bound dicnq ligand is less likely to occur, and hence, the contribution of this process to the overall decrease in the ϕ_{em} values is considered to be the minimum. The extent of ion association is expected to be dependent on the solvent properties and also on the charge on the luminophore. In this regard, it should be noted that all these complexes are dipositive, with the same counterion (PF_6) balancing the charge. The weakness of luminescence of these complexes rendered an accurate determination of their ϕ_{em} values in various solvents difficult.

(33) The E_{0-0} values for $[Ru(phen)_2(dicnq)]^{2+}$ (2.02 ± 0.05 eV) and $[Ru(phen)_2(dicnq)]^{2+}$ (2.03 ± 0.05 eV) are taken to be the same as their MLCT emission maxima. Estimation of an accurate E_{0-0} for $[Ru(dicnq)_3]^{2+}$ is not possible because this complex is essentially nonluminescent.

(34) The excited-state decays of this category of complexes are known to occur mainly by three mechanisms: (i) nonradiative deactivation of the ^{3}MLCT states directly to the ground state, (ii) thermally activated crossing from the ^{3}MLCT state to the ^{3}MC (metal-centered) state, and (iii) a mechanism that is intermediate between the prior two. See: Masschelein, A.; Jacquet, L.; Mesmaeker, A. K.; Nasielski, J. *Inorg. Chem.* **1990**, *29*, 855. Lecomte, J.-P.; Kirsch-De Mesmaeker, A. *J. Phys. Chem.* **1994**, *98*, 5382.

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(41) K_b for the binding of $[Ru(phen)_3]^{2+}$ to CT DNA is $\sim 4 \times 10^4$ M^{-1}, as determined by the absorption titration method (Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2172), although a lower value has been obtained by a subsequent equilibrium dialysis experiment (Pyle, A. M.; Rehmann, A. P.; Meshoyrer, R.; Kumar, C. V.; Turro, C. V.; Barton, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 3051).

(42) Carlson, D. L.; Hutchital, D. H.; Mantilla, E. J.; Sheardy, R. D.; Murphy, W. R., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 6424.

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(44) Holmlin, R. E.; Barton, J. K. *Inorg. Chem.* **1995**, *34*, 7.

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(46) Linncoln, B.; Broo, A.; Norden, B. *J. Am. Chem. Soc.* **1996**, *118*, 2644.

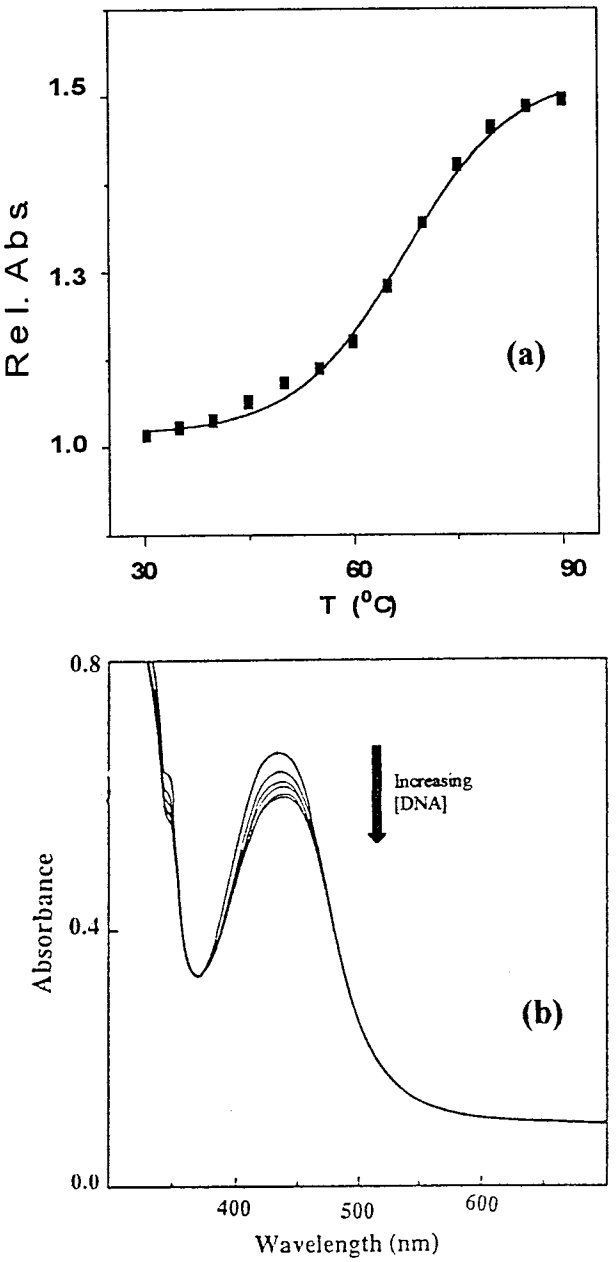

Figure 7. (a) Melting curve for $[Ru(phen)_2(dicnq)]^{2+}$ in buffer B. [DNA base pair] = 170 μM; [Ru] = 7 μM. (b) UV−visible spectra of $[Ru(dicnq)_3]^{2+}$ (25 μM) in the absence (top) and presence of increasing additions of CT DNA (bottom) in buffer A (25, 35, 45, 60, 75, and 150 μM base pairs).

$(qdppz)]^{2+}$ described in the preceding paper. Obviously, dicnq is not as extended a π system as dppz is, nor does its architecture contain the strongly intercalating quinone moiety as in the case of qdppz.

It is remarkable that even seemingly minor changes in the ligand architecture and electronic structure can lead to profound effects on DNA binding by the dipyridophenazine family of ligands. This is in contrast with a recent report by Ji and coworkers[36] that electron-donating/withdrawing groups on the imidazole ring of imidazo[4,5-*f*][1,10]phenanthroline have no significant effect on the modes of binding between DNA and the ruthenium(II) complexes.[52,53] Thus, it is possible that the weaker binding affinity of the dicnq-based complexes in comparison with the analogous dppz complexes is related to the differential groove access of these metallointercalators (i.e., minor/major).[1,54] More studies are clearly needed to resolve this crucial issue, and such studies are being planned. An equally important concern that arises at this juncture regards the identity of the ligand, dicnq or phen, that is involved in the DNA binding by $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$. Results of our attempts to identify this ligand are discussed below.

First, we recall that the strengths of DNA binding by these new dicnq complexes are, by and large, similar and are also in the same range as that of $[Ru(phen)_3]^{2+}$. Because the UV−visible method employed here for the estimation of binding constants does not monitor exclusive properties of the individual ligands in these mixed-ligand complexes, the above observation can be interpreted in terms of DNA binding by either dicnq or phen in both $[Ru(phen)(dicnq)_2]^{2+}$ and $[Ru(phen)_2(dicnq)]^{2+}$. An approach that is prescribed to help resolve such dichotomies involves the application of methods other than absorption spectroscopy to monitor DNA binding.[38] In our previous work, we resorted to the differential-pulse voltammetric method to determine that complexed qdppz (and not phen) is involved in the interaction of $[Ru(phen)_2(qdppz)]^{2+}$ within the DNA base pairs.[7] This was possible because of the low, reversible reduction potential of the quinone-bearing ligand in that complex. In the present case, however, aqueous buffered solutions of all three dicnq complexes showed ill-defined voltammograms under our experimental conditions. Thus, the DNA interactions of these complexes could not be probed by electrochemical methods. On the other hand, luminescence spectroscopy was found to be helpful for this purpose, as described below.

Steady-state emission spectra of 10 μM solutions of $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ in Tris buffer (5 mM Tris, 50 mM NaCl, pH 7.1) were recorded in the absence and presence of increasing concentrations of DNA. The spectral profiles and emission maxima were not markedly affected by additions of DNA to the complex solutions. On the other hand, there were increases in the emission intensities with successive additions of CT DNA. Figure 8 illustrates this effect. As seen, luminescence due to $[Ru(phen)_2(dicnq)]^{2+}$ increases steadily with increasing additions of CT DNA and reaches a maximum (~16 times) at a [DNA nucleotide phosphate]/[Ru] ratio of 36. In the case of $[Ru(phen)(dicnq)_2]^{2+}$, luminescence increases initially at low [DNA nucleotide phosphate]/[Ru] ratios but

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(52) On the other hand, DNA binding by $[Ru(bpy)_2(pip)]^{2+}$ (pip = 2-phenylimidazo[4,5-*f*][1,10]phenanthroline) is stronger than that by $[Ru(bpy)_2(ip)]^{2+}$ (ip = imidazo[4,5-*f*][1,10]phenanthroline), consistent with the greater planar area and extended π system of the pip ligand.[53]
(53) Wu, J.-Z.; Ye, B.-H.; Ji, L.-N.; Zhou, J.-Y.; Li, R.-H.; Zhou, Z.-Y. *J. Chem. Soc., Dalton Trans.* **1997**, 1395.
(54) In this regard, it may be noted that $[Ru(phen)_2(dpq)]^{2+}$, where dpq = dipyrido[2,2-*d*:2′,3′-*f*]quinoxaline, a closely related analogue of dicnq (i.e., dicnq without the cyano groups), binds DNA from the minor-groove side (Collins, J. G.; Sleeman, A. D.; Aldrich-Wright, J. R.; Greguic, I.; Hambley, T. W. *Inorg. Chem.* **1998**, *37*, 3133) whereas most available data indicate that $[Ru(phen)_2(dppz)]^{2+}$ binds through the major groove.[1] In addition, factors such as net charge of the molecule, nature of the ligand, and overall shape of the complex are all known to influence the propensity of a given ruthenium complex for intercalative binding with DNA (Morgan, R. J.; Chatterjee, S.; Baker, A. D.; Strekas, T. C. *Inorg. Chem.* **1991**, *30*, 2687 (and references therein)).

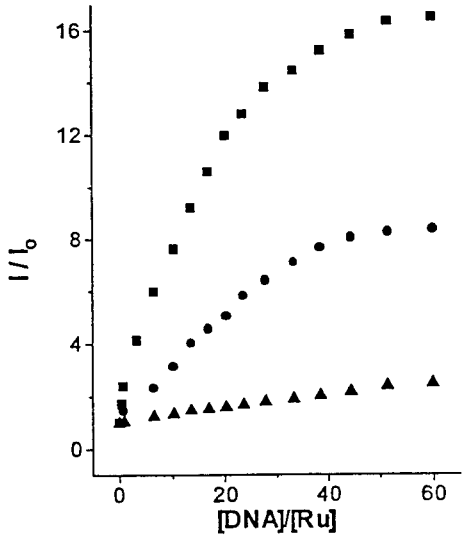

Figure 8. Plots of I/I_0 (I_0 and I refer to luminescence intensities in the absence and presence of DNA) for 10 μM solutions (buffer A) of $[Ru(phen)_2(dicnq)]^{2+}$ (■), $[Ru(phen)(dicnq)_2]^{2+}$ (●), and $[Ru(phen)_3]^{2+}$ (▲) versus increasing [DNA nucleotide phosphate]/[Ru] ratios.

reaches a plateau with an apparent enhancement factor of ~8 at higher [DNA nucleotide phosphate]/[Ru] ratios. $[Ru(phen)_3]^{2+}$ also shows an intensity enhancement in the presence of DNA but only a weak one; the enhancement factor is 2 for this complex even at [DNA nucleotide phosphate]/[Ru] ratios of ~80. Similar weak intensity enhancements (<3) have been reported for mixed-ligand ruthenium(II) complexes containing the ligands pip (2-phenylimidazo[4,5-*f*][1,10]phenanthroline) and ip (imidazo[4,5-*f*][1,10]phenanthroline), which are somewhat structurally analogous to dicnq.[53] On the other hand, $[Ru(phen)_2(dppz)]^{2+}$ was reported to show a $>10^4$ times enhancement of emission in the presence of DNA. In this case, emission enhancement was ascribed to the protection of the imine nitrogens from attack by water and a consequent decrease in the nonradiative processes upon intercalation.[55−59] It is reasonable to expect that, with dicnq being a quinoxaline ligand bearing imine nitrogens, the increase in emission intensity observed for $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ in the presence of DNA is also a consequence of a decrease in the nonradiative deactivation process of each excited complex due to the protection of this ligand upon intercalation.[60]

Interestingly, although the DNA-binding constants of $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ are similar (vide supra), the former complex shows relatively higher emission enhancement compared to the latter upon addition of DNA. It should be noted here that, in the event that one dicnq ligand in $[Ru(phen)(dicnq)_2]^{2+}$ is intercalated with DNA, the second, nonintercalating, spectator dicnq ligand in this complex is essentially exposed to water. Being "unprotected", this ligand is susceptible to attack by the surrounding water molecules, resulting in the nonradiative luminescence quenching mentioned above. On the other hand, intercalation by the quinoxaline ligand in $[Ru(phen)_2(dicnq)]^{2+}$ leaves only the two "innocuous", ancillary phenanthrolines exposed to the surrounding aqueous medium. This analysis strongly suggests that dicnq is involved in the DNA intercalations by both $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$.

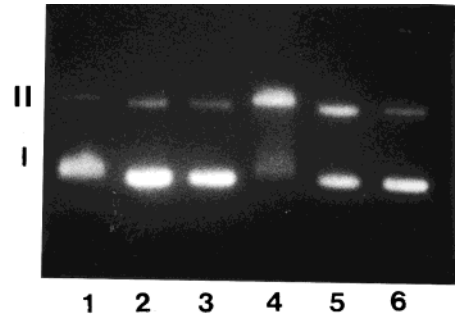

Figure 9. Photograph showing the electrophoretic behaviors of pBR 322 DNA in the presence of ruthenium(II) complexes. Lanes 1−3 (dark experiments): pBR 322 (100 μM nucleotide phosphate) + $[Ru(phen)_2(dicnq)]^{2+}$ (12), $[Ru(phen)(dicnq)_2]^{2+}$ (12), and $[Ru(dicnq)_3]^{2+}$ (12), respectively. Lanes 4−6 (light experiments): pBR 322 + $[Ru(phen)_2(dicnq)]^{2+}$ (75), $[Ru(phen)(dicnq)_2]^{2+}$ (33), and $[Ru(dicnq)_3]^{2+}$ (15), respectively. Numbers in parentheses refer to the percent of form II DNA. In each case, [DNA nucleotide phosphate]/[drug] = 10.

Finally, there was no emission enhancement for $[Ru(dicnq)_3]^{2+}$ in the presence of DNA. In fact, not only does this tris complex not emit in aqueous and aqueous buffered solutions but it is also nonemitting in various dry nonaqueous solvents such as CH_3CN, CH_2Cl_2, dichloroethane, CH_3OH, etc. (PF_6 salt). These observations can be rationalized as follows: (i) In aqueous and aqueous buffered solutions, there exists a distinct possibility of luminescence quenching for this complex via the attack of water at the quinoxaline nitrogens of the three bound dicnq ligands and subsequent enhancement in nonradiative decay. The same process can be thought to be operative even in the presence of DNA. Notwithstanding the fact that one of the dicnq ligands in $[Ru(dicnq)_3]^{2+}$ is involved in intercalation within the base pairs and protected from water, there are two additional such quinoxaline ligands exposed to water in the DNA medium. (ii) As far as the nonaqueous solvents are concerned, we believe that an intramolecular electron transfer involving the ^{3}MLCT state and the electron acceptor ligand is the major cause for the apparent nonemissive nature of this complex. The same PET mechanism is an obvious additional deactivation mechanism in aqueous and aqueous buffered media with or without DNA because these media are more polar than CH_3CN and are expected to promote an electron-transfer-based mechanism.

D. DNA Photocleavage. Irradiation of samples containing pBR 322 DNA and each of these complexes was carried out in a manner described previously,[6,7,16,17] and the effects were monitored by the agarose gel electrophoresis method. Control experiments suggested that photolysis of untreated plasmid does not produce form II from the native form I upon irradiation of the sample at 440 nm. In addition, both phen and dicnq (dissolved in 10% DMF) are not detectably active either in the dark or upon irradiation. Figure 9 shows the gel electrophoresis pattern of the plasmid pBR 322 DNA in the presence of the three metal complexes (10 μM) investigated in this study. Lanes 1−3 refer to the dark experiments and lanes 4−6 to the light experiments. In the dark experiments, no DNA nicking was perceptible for the plasmid in the presence of each of these complexes but the strong binding of $[Ru(phen)_2(dicnq)]^{2+}$ with DNA can be seen from the increased streaking and retardation

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(59) Moucheron, C.; Kirsch-De Mesmaeker, A.; Choua, S. *Inorg. Chem.* **1997**, *36*, 584.
(60) Indeed, luminescence quenching was observed upon addition of water (ca. 5−10%) to dry CH_3CN solutions of these two complexes.

of DNA mobility.[38,61,62] In the light experiments, $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ cause single-strand nicking with the conversion of form I to form II, the former complex being more active; however, $[Ru(dicnq)_3]^{2+}$ shows no appreciable photocleavage. This result may not reflect the binding strengths of these complexes if one considers the fact that their K_b values are similar (vide supra). Rather, it is probably a consequence of the influence of the number of "unprotected" dicnq ligands present in each complex in its DNA-bound state. The presence of more such nonintercalating ligands in a given DNA-bound complex causes a more efficient deactivation of its photochemically active MLCT excited state, resulting in diminished DNA-photocleavage efficiency.

Conclusions

This work is an example of a rarely encountered study wherein the syntheses, characterizations, and DNA interactions of mono, bis, and tris octahedral ruthenium(II) complexes of a given ligand are reported. Here, a series of ruthenium(II) complexes containing the new modified dipyridophenazine ligand dicnq have been synthesized and fully characterized by various physical methods. Results of absorption and fluorescence titration, thermal denaturation, and agarose gel electrophoresis experiments suggest that these complexes bind to DNA with moderate strengths, probably via an intercalative mode. The DNA-photocleavage efficiencies of the three complexes follow the order $[Ru(phen)_2(dicnq)]^{2+} > [Ru(phen)(dicnq)_2]^{2+} \gg [Ru(dicnq)_3]^{2+}$. Both $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ are luminescent in organic solvents, but $[Ru(dicnq)_3]^{2+}$ is totally nonluminescent. Finally, detailed luminescence studies reveal that $[Ru(phen)_2(dicnq)]^{2+}$ and $[Ru(phen)(dicnq)_2]^{2+}$ are moderately efficient "molecular light switches" for DNA.

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