

Synthesis, Photophysical Properties and DNA Binding Studies of Novel Luminescent Rhenium(I) Complexes. X-Ray Crystal Structure of [Re(dppn)(CO)₃(py)](OTf)

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Two novel luminescent rhenium(I) complexes, [Re(dppz)(CO)₃(py)](OTf) **1** and [Re(dppn)(CO)₃(py)](OTf) **2** are synthesized and their photophysical properties studied; X-ray structural studies of **2** reveal a highly planar dppn ligand which may account for the interaction of **1** and **2** with double-stranded calf thymus DNA.

Rhenium(I), ruthenium(II) and copper(I) diimine complexes have long been found to possess metal-to-ligand charge-transfer (MLCT) excited states.¹ Owing to the fact that charge separation is involved in the excited state, complexes of this type are usually very sensitive to their environment. They can therefore be viewed as efficient reporters of their surroundings. These complexes often exhibit solvatochromism² and with specially designed ligands, they can also act as alkali and alkaline earth metal ion probes.³ The interactions of these metal complexes with DNA have also been widely investigated.⁴ However, while most work has been done on Ru^{II}^{4a-e} and Cu^I^{4f,g} diimine complexes, comparatively little attention has been focused on luminescent Re^I compounds.^{4h} In view of this, together with our recent interest in luminescent MLCT excited states^{5a-e} and transition metal-DNA interactions,^{5f} we have synthesized two novel luminescent rhenium(I) complexes, [Re(dppz)(CO)₃(py)](OTf) **1** and [Re(dppn)(CO)₃(py)](OTf) **2**, with extended planar ligands dppz (dipyridophenazine) and dppn (benzodipyridophenazine). Their binding to calf thymus DNA has also been investigated.

The ligands and complexes were synthesized by modified literature procedures.[†] Both **1** and **2** gave satisfactory elemental analyses and were characterized by ¹H NMR and positive ion FAB-MS.[‡] The crystal structure of **2** has also been determined by X-ray crystallography.[§]

The perspective drawing of the cation of **2** with atomic numbering and the stereoview of the unit cell are depicted in Fig. 1. The Re^I centre adopts a distorted octahedral geometry with the carbonyl groups coordinated in a *facial* manner. The average bond distances and angles are comparable to typical values of similar Re^I diimine complexes.^{6a,b} As expected, all the atoms of the dppn ligand lie on an essentially perfect plane, with the distance from the benzo edge of this plane to the metal centre being *ca.* 12.5 Å. Owing to this extended planarity, it is not surprising to find that the rings of the dppn ligands in **2** show some stacking interactions [Fig. 1(b)]. The distance between the ideal ring planes of the two dppn ligands on adjacent cations was found to be *ca.* 3.4 Å, packed in a head-to-tail fashion, similar to the base pair stacking distance in DNA^{6c} and the intercalator-base pair stacking distance in oligonucleotide intercalator complexes.^{6d,e} Similar observations have also been reported for [Ru(OH₂)(dppz)(tpy)]²⁺.^{6f}

The photophysical properties of **1** and **2** are summarized in Table 1. Both complexes exhibit low energy absorptions at *ca.* 380–450 nm. These absorptions are tentatively assigned as admixtures of d(Re) → π* (diimine) MLCT and π → π* (diimine) intra-ligand (IL) transitions, considered the fact that both the free ligands dppz and dppn absorb at quite low energies (*e.g.* dppn absorbs at *ca.* 413 and 391 nm in CH₂Cl₂). The

observation that the electronic absorptions of **2** occur at lower energies than those of **1** is in accordance with the more extended π conjugation in dppn, rendering the π* orbital of the ligand to be more stabilized. In 5% aqueous buffered (20 mmol dm⁻³ Tris-HCl, pH 7.0) methanol solutions, the low energy absorption bands of **1** and **2** exhibit hypochromism upon addition of double-stranded calf thymus DNA, suggesting binding of the complexes to the biopolymers.⁴ Small bathochromic shifts were observed concomitant with the hypochromicity, and the electronic absorption spectra revealed clear isosbestic points at *ca.* 402 and 438 nm for **1** and **2**, respectively.

The complexes **1** and **2** display orange luminescence upon irradiation of light with λ > 350 nm. These emissions are assigned as originating from MLCT excited state although its intra-ligand character cannot be entirely ruled out.⁷ Both **1** and

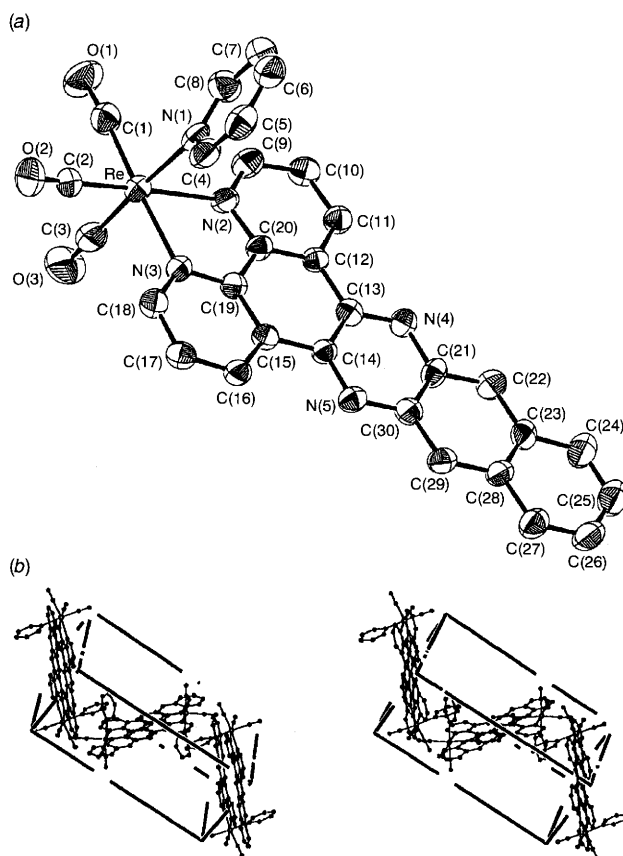


Fig. 1 (a) The perspective view of the cation of **2** with atomic numbering, showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Re(1)–N(1) 2.206(6), Re(1)–N(2) 2.186(5), Re(1)–N(3) 2.175(5), Re(1)–C(1) 1.928(8), Re(1)–C(2) 1.931(8), Re(1)–C(3) 1.937(8); N(1)–Re(1)–N(2) 82.2(2), N(1)–Re(1)–N(3) 87.0(2), N(1)–Re(1)–C(1) 94.2(3), N(1)–Re(1)–C(2) 90.9(2), N(1)–Re(1)–C(3) 176.7(2), N(2)–Re(1)–N(3) 75.3(2), N(2)–Re(1)–C(1) 100.5(2), N(2)–Re(1)–C(2) 170.0(2), N(2)–Re(1)–C(3) 94.9(3), N(3)–Re(1)–C(1) 175.5(2), N(3)–Re(1)–C(2) 97.2(2), N(3)–Re(1)–C(3) 80.8(2), C(1)–Re(1)–C(2) 87.1(3), C(1)–Re(1)–C(3) 87.9(3). (b) The stereoview of the unit cell of **2**. Hydrogen atoms and anions are omitted for clarity.

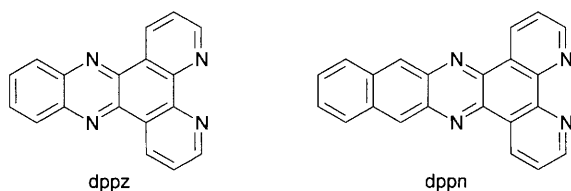


Table 1 Photophysical data for **1** and **2**

Complex	Electronic absorption λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	Medium (T/K)	Emission λ/nm^a
1	384 (12900), 366 (13045), 328 sh (16950), 287 (64595)	CH ₂ Cl ₂ (298)	556, 598 sh
		MeCN (298)	558, 594 sh
		Solid (298)	642
	382 (11700), 363 (11685), 280 (58955)	Solid (77)	620, 655 sh
		Glass ^b (77)	541, 586
		Me ₂ CO (298)	556, 590 sh
		MeOH (298)	558, 596 sh
		5% aq. MeOH ^c (298)	560, 603 sh
		5% aq. MeOH with DNA ^d (298)	565, 609 sh
2	426 (9080), 404 (9555), 382 sh (8925), 336 (49565), 279 sh (29975), 257 (35465)	CH ₂ Cl ₂ (298)	588
		MeCN (298)	595
		Solid (298)	640
	419 (11735), 398 (10945), 373 sh (9455), 324 (68860), 278 sh (32190), 263 (40565), 242 (41485)	Solid (77)	664
		Glass ^b (77)	514, 550
		Me ₂ CO (298)	595
		MeOH (298)	600
		5% aq. MeOH ^c (298)	603
		5% aq. MeOH with DNA ^d (298)	590

^a All emission values were uncorrected for instrumental response. ^b EtOH–MeOH (4:1) mixture. ^c 5% Aqueous MeOH in 20 mmol dm⁻³ Tris-HCl buffer, pH 7.0. ^d Conditions: [1] = 49 $\mu\text{mol dm}^{-3}$ [DNA-P]/[1] = 6.3; [2] = 68 $\mu\text{mol dm}^{-3}$, [DNA-P]/[2] = 9.1.

2 exhibit vibronic-structured emissions in rigid glass, with progressional spacings in the range *ca.* 1300–1800 cm⁻¹, typical of aromatic C–C and C–N stretches. In aqueous MeOH–buffer solutions, the emission intensities of both **1** and **2** indicate an obvious enhancement upon addition of double-stranded calf thymus DNA. The titration curves are shown in Fig. 2. These increments, together with the hypochromicity observed in the UV–VIS absorption spectra, can be ascribed to the intercalation of the complexes to the double helix, as similar observations have also been reported in other Ru^{II}^{4a–e} and Cu^I^{4f,g} metal-ligand intercalators. The emission intensity of **1** grows steadily to *ca.* 13 times larger and saturates at a [DNA–phosphate]:[Re] ratio of *ca.* 4.5:1. However, the DNA binding properties of **2** are significantly different. The emission intensity drops at low [DNA–phosphate]:[Re] ratio (minimum at around 0.4:1) before it gradually approaches saturation with an overall gain of approximately 1.3 times. Similar findings have been observed with [Ru(dppn)(phen)₂]²⁺.^{4e} It is envisaged that, in such a polar medium, the cations of **2** would tend to self-associate as a result of the highly hydrophobic nature of the species.⁸ Addition of polyelectrolytes such as DNA has been suggested to induce ion aggregation,^{4g} associated with the suppression of the emission intensity of **2**. Similar phenomena have also been reported in other comparatively hydrophobic intercalators.⁹ The intensity enhancement which occurred at the later stage is likely to be the consequence of intercalation of the complex into the DNA, with

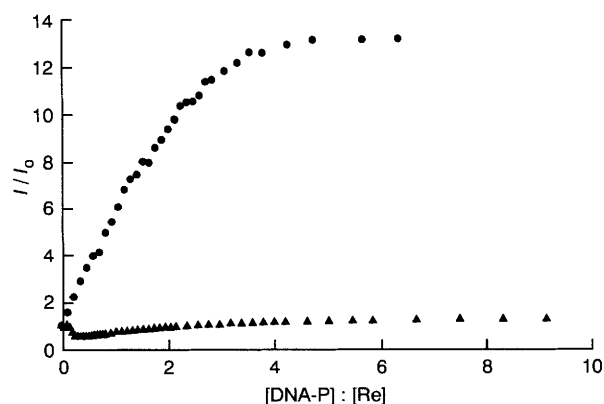


Fig. 2 The emission titration curves for **1** (●) and **2** (▲) with calf thymus DNA in aqueous buffered methanol (20 mmol dm⁻³ Tris-HCl, pH 7.0). I_0 = emission intensity in the absence of DNA; I = emission intensity after addition of DNA. Excitation wavelength = 350 nm. The emission intensities were monitored at 565 and 590 nm for **1** and **2**, respectively. [Re]: **1** = 49 $\mu\text{mol dm}^{-3}$, **2** = 68 $\mu\text{mol dm}^{-3}$.

the extended planar ligand stacked in between the base pairs of the duplex.

It is likely that the interaction between **1** and **2** with DNA is intercalative in nature. The present work demonstrates the ability of luminescent rhenium(I) complexes to be utilized as efficient DNA sensors. Detailed mechanistic studies on the binding modes and further investigation into the design of site-specific binding and photocleavage agents are under way.

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Footnotes

† The ligand dppz was prepared by literature methods.^{10a} The ligand dppn was synthesized similarly by refluxing 1,10-phenanthroline-5,6-dione and 1,2-diaminonaphthalene in ethanol for 4 h. The crude product was recrystallized from chloroform and light petroleum. ¹H NMR (270 MHz, CDCl₃, 298 K) δ 9.6 (dd, 2H), 9.3–9.2 (dd, 2H), 8.9 (s, 2H), 8.2 (m, 2H), 7.8–7.7 (dd, 2H), 7.6 (m, 2H). EI-MS m/z at 332. The complexes **1** and **2** were synthesized and purified in a similar method to that reported for related Re^I diimine complexes.^{10b} They were subsequently recrystallized from CH₂Cl₂–MeCN–diethyl ether.

‡ Selected spectroscopic data for **1**: ¹H NMR (270 MHz, [²H₆]acetone, 298 K) δ 10.1–10.0 (m, 4H, dppz), 8.7 (m, 2H, pyridyl Hs), 8.5 (m, 4H, dppz), 8.2 (m, 2H, dppz), 8.0–7.9 (m, 1H, pyridyl Hs), 7.4 (m, 2H, pyridyl Hs); positive ion FAB-MS: ion clusters at m/z 631 [Re(dppz)(CO)₃(py)]⁺, 603 [Re(dppz)(CO)₂(py)]⁺, 552 [Re(dppz)(CO)₃]⁺, 524 [Re(dppz)(CO)₂]⁺, 496 [Re(dppz)(CO)]⁺. For **2**: ¹H NMR (270 MHz, [²H₆]acetone, 298 K) δ 10.1–10.0 (dd, 2H, dppn), 10.0–9.9 (dd, 2H, dppn), 9.2 (s, 2H, dppn), 8.7 (m, 2H, pyridyl Hs), 8.5 (dd, 2H, dppn), 8.5–8.4 (m, 2H, dppn), 8.0–7.9 (m, 1H, pyridyl Hs), 7.8 (m, 2H, dppn), 7.5–7.4 (m, 2H, pyridyl Hs); positive ion FAB-MS: ion clusters at m/z 681 [Re(dppn)(CO)₃(py)]⁺, 653 [Re(dppn)(CO)₂(py)]⁺, 602 [Re(dppn)(CO)₃]⁺, 574 [Re(dppn)(CO)₂]⁺, 518 [Re(dppn)]⁺.

§ Crystal data for ReN₅C₃₀H₁₇O₃⁺ CF₃SO₃⁻; M_r = 830.77, crystal dimensions 0.15 × 0.07 × 0.25 mm, monoclinic, space group $P2_1/n$, a = 8.896(2), b = 20.494(2), c = 16.276(3) Å, β = 101.17(2)°, V = 2911.0(6) Å³, Z = 4, D_c = 1.896 g cm⁻³, μ (Mo-K α) = 43.23 cm⁻¹, $F(000)$ = 1616, T = 298 K, 424 parameters, 4230 data measured, no. of data used in calculation 3195 [$I > 3\sigma(I)$], R = 0.030, wR = 0.042, $w = 4 F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.038 F_o^2)^2]$. The maximum and minimum residues in the final ΔF synthesis were 1.66 and -0.53 e Å⁻³, respectively. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-K α radiation (λ = 0.71073 Å) to $2\theta_{\text{max}}$ = 45°. Intensity data were corrected for Lorentz and polarization

effects and decay. The space group was determined from systematic absences and the solution of the structure by heavy-atom Patterson methods and expanded using Fourier techniques¹¹ and refinement by full-matrix least-squares methods using the MSC-Crystal Structure Package TEXSAN on a Silicon Graphics Indy computer. All 47 non-hydrogen atoms were refined anisotropically and hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached carbon atoms were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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