Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 109, No. 2, April 1997, pp. 155–158.

Redox-activated luminescence and light-induced nuclease activity of a new mixed-ligand ruthenium(II) complex

S AROUNAGUIRI[a], APARNA DATTAGUPTA[b]
and BHASKAR G MAIYA*[a]
[a]School of Chemistry, and
[b]School of Life Sciences, University of Hyderabad, Hyderabad 500 046, India

MS received 30 November 1996

Abstract. The new metallointercalator 1, a mixed-ligand ruthenium(II) complex incorporating a quinone-fused dipyridophenazine ligand, effects an efficient cleavage of the supercoiled plasmid DNA upon activation with visible light. In addition, the quinone/hydroquinone redox couple 1/2 represents a molecular light-switching device displaying interconversion between non-luminescent state 1 and luminescent state 2.

Keywords. Metallointercalator; DNA-binding and photocleavage; redox-switching of luminescence.

1. Introduction

Currently, a great deal of attention is being paid to DNA interactions of mixed-ligand ruthenium(II) complexes containing 1,10-phenanthroline (phen) and modified phen ligands, with the latter being specially designed to augment intercaltive interaction by the complexes (Murphy and Barton 1993; Holmlin and Barton 1995; Jacquet *et al* 1995; Liu *et al* 1995; Schoch *et al* 1996). Such complexes can also be employed in research related to molecule-based electronic devices and solar energy conversion processes (Balzani 1987; Harriman and Ziessel 1996; Constable *et al* 1996). During our recent studies (Arounaguiri and Maiya 1996) on the DNA interactions of nickel(II) and cobalt(III) complexes containing dipyrido[3,2-*a*:2′,3′-*c*]-phenazine (dppz, a modified phen ligand), it occurred to us that further derivatization of this ligand with appropriate functional group/s might not only accentuate DNA-binding and photocleavage efficiencies of the ensuing complexes but also serve to explore other interesting functional aspects associated therein. Towards this end, we have now synthesized a novel mixed-ligand complex 1, containing a quinone-fused di-pyridophenazine ligand (10,11-[1,4-naphthalene-dione]dipyrido[3,2-*a*:2′,3′- *c*] phenazine, Aqphen). The quinone moiety has been specifically chosen here owing to its known intercalating ability and rich redox chemistry (Bhattacharya and Mandal 1996; Breslin and Schuster 1996). Indeed, as will be demonstrated in this communication, complex 1 is not only an avid binder of CT-DNA but is also an efficient photocleaving agent of supercoiled pBR 322 DNA. In addition, results of combined coulometry and fluorescence studies reveal that the redox (quinone/hydroquinone) couple 1/2 unites an electroactive component with a light emitting centre and that it

*For correspondence

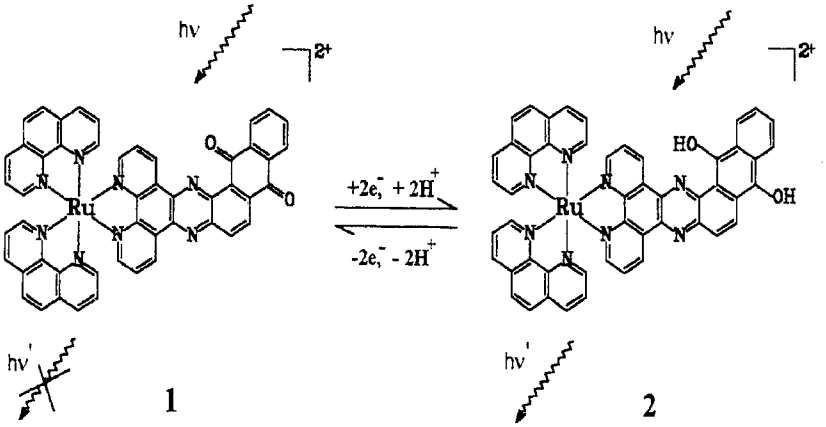

Figure 1. Structures of redox-related ruthenium complexes 1 and 2.

can, in principle, be used in redox-activated optical signal generation and allied applications (figure 1).

It should be noted here that, while this manuscript was being prepared, synthesis and characterization of Aqphen and a rhenium complex containing it (Re(Aqphen)(CO)$_3$Cl) have been reported by Lopez et al (1996). However, the focal theme of their paper was entirely different from that envisaged in the present study.

2. Results and discussion

2.1 *Synthesis and characterization*

Refluxing an ethanol solution (250 ml) containing readily accessible 1,10-phenanthroline-5,6-dione (0·21 g, 1 mmol) and 1,2-diamino anthraquinone (0·23 g, 1 mmol) for 5 h and evaporation of the solvent gave a greenish-brown residue which was taken up in 100 ml $CHCl_3$ and warmed to $\approx 50°C$. The solution was cooled and filtered, and a yellow precipitate obtained upon addition of diethyl ether to the filtrate. It was vacuum dried, after washing thoroughly with diethyl ether, to give the pure sample of Aqphen in $\approx 70\%$ yield. Complex $\underline{1}\cdot(PF_6)_2$ was prepared by condensing $Ru(phen)_2Cl_2$ and Aqphen in refluxing diethylene glycol. Addition of NH_4PF_6 precipitated crude $\underline{1}\cdot(PF_6)_2$, which was purified by recrystallization (acetone–diethyl ether, yield > 80%). The PF_6 salt was converted to the water-soluble chloride salt $\underline{1}\cdot Cl_2$, by the standard procedure using tetrabutylammonium chloride (TBACl). Both Aqphen and 1 were characterized by elemental analysis, FAB-MS, IR, UV-Vis, NMR and cyclic voltammetric methods.†

---

† *Selected data for Aqphen, and 1*

Aqphen: Analysis: Found: C, 73·02; H, 3·16; N, 11·75%, Calcd. for $C_{26}H_{12}N_4O_2$: C, 73·73; H, 2·98; N, 12·59%; IR (KBr pellet): 1670, 1585, 1462 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{nm}(log ε): 410 (4·13), 394 (4·13), 281 (4·58). 259(4·62). ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 9·85 (*d*, 1H), 9·65 (*d*, 1H), 9·35 (*d*, 2H), 8·71 (*dd*, 2H), 8·32 (*q*, 2H), 7·88(*m*, 4H).

$\underline{1}\cdot(PF_6)_2$: Analysis: Found: C, 50·86; H, 2·37; N, 9·22%; calcd. for $C_{50}H_{32}N_8O_4P_2F_{12}Ru$: C, 50·06, H, 2·49; N, 9·34%; IR (KBr pellet): 1670, 1589, 1427, 837 cm^{-1} UV-Vis (CH_3CN) λ_{nm}(log ε): 438 (4·29), 388(4·32), 302(4·83), 278(4·92), 263(5·09). ^{13}C NMR (200 MHz, CD_3CN/10% D_2O, 298 K): δ 181 (ArC=O)

lex $\underline{1}\cdot(PF_6)_2$ showed its characteristic MLCT band at 438 nm and bands ıe intra-ligand transitions at 388 (Aqphen) and 263 (phen) nm in the UV-Vis ı. The well-defined cyclic voltammetric responses seen at +1·36 and for the complex can be ascribed to Ru^{III}/Ru^{II} and Aqphen/Aqphen^{-} respectively. The complex was found to be weakly luminescent ($\phi < 10^{-4}$) in ·ganic solvents, presumably due to an intramolecular photoinduced electron (PET) quenching of its MLCT state by the appended quinone fragment. The and redox characteristics of $\underline{1}\cdot Cl_2$ were found to be essentially similar to $\underline{1}\cdot(PF_6)_2$. In aqueous buffered or aqueous CH_3CN (4–5% H_2O) solutions, ›ride salt was found to be totally non-fluorescent.

√A-binding and photocleavage

inding by $\underline{1}\cdot Cl_2$ was monitored by absorption titration (MLCT band, buffer M tris, *p*H 7·1, 50 mM NaCl), thermal denaturation (monitoring A_{260} of DNA, ; = 1 mM phosphate, *p*H 7·0, 2 mM NaCl) and differential pulse voltammetric ɔ reduction peak, buffer A) methods. In the presence of increasing amounts of nus (CT) DNA, the complex showed bathochromic shifts (maximum: 4 ± 1 nm) ›sochromism (maximum: 25 ± 3%) in the UV-Vis spectrum, diminution of peak (maximum: 40 ± 5%) and cathodic shifts of the peak potential (maximum: nV) in differential pulse voltammograms and increase in the DNA melting ıture (4 ± 1°C at $[DNA]_{phosphate}/[\underline{1}] = 25$) in thermal denaturation experiments. ›bservations are reminiscent of those reported earlier for various metallointerca- ncluding the metal-dppz complexes and suggest that the complex $\underline{1}\cdot Cl_2$ binds / to DNA by an intercalative mode (Gupta *et al* 1992; Murphy and Barton 1993; ı and Barton 1995; Arounaguiri and Maiya 1996). It was not possible to eva- ıe accurate binding constant (K_b) for DNA intercalation by $\underline{1}$ by the absorption ı method because the complex was found to bind too strongly (stoichiometric ;) even at micromolar concentrations of DNA as was the case with the previously dppz complexes (Hiort *et al* 1993; Arounaguiri and Maiya 1996).

garose gel electrophoresis experiments, control runs suggested that untreated ł pBR 322 DNA (supercoiled form, 100 μM in nucleotides) does not show any :ible cleavage in the dark and even upon irradiation by 440 ± 5 nm light for 2 h sample chamber of a Jasco model 777 spectrofluorimeter (slit width 5/5 nm). ·ly, DNA nicking was not observed for the plasmid treated with $\underline{1}\cdot Cl_2$ (10 μM) dark run. On the other hand, irradiation of DNA in the presence of the :x for 25 min caused complete conversion of the supercoiled form (form I), ting relaxed circular DNA (form II) under similar experimental conditions.

Redox-switching of luminescence

.stive coulometric reduction of $\underline{1}$ in deaerated, aqueous (4–5% H_2O) CH_3CN)·5 V (0·1 mol dm^{-3} $TBAPF_6$, Pt working electrode; $\underline{E}_{1/2}(red)\,\underline{1} = -0.27$ V) ıted $\underline{2}$ as identified by its UV-Vis, NMR and IR spectra.† The same electrolytic

---

ed data for $\underline{2}$

$_5)_2$: UV-Vis(CH_3CN/10%H_2O) λ_{nm}(log ε): 442(4·28), 348(4·22), 300 (*sh*, 4·74), 263(5·06); MR (200 MHz, CD_3CN/10% D_2O, 298 K): δ 153 ($\underline{Ar}C$–OH).

solution containing the hydroquinone complex could be reoxidized to obtain 1 by exhaustive coulometry at +1·1 V ($E_{1/2}$(ox) 2 = +0·92 V) and the redox-cycle was repeated thrice with < 10% loss of the material. Whereas, as stated earlier, the quinone form 1 was found to be almost non-luminescent, the electrochemically (or chemically, by $Na_2S_2O_4$) generated hydroquinone form 2 showed the MLCT luminescence at 601 nm ($\phi = 0{\cdot}018 \pm 0{\cdot}03$). Thus the couple 1/2, which combines an electroactive component with a light-emitting centre (figure 1), represents a redox activated luminescence on/off switching device with its function being similar to that exhibited by $[Ru(bpy)_2(bpy\text{-}BQ)]^{2+}$-a covalently-linked, Ru(II) complex-benzoquinone system reported previously (Goulle *et al* 1993).

3. Conclusion

In summary, the new ruthenium(II) complex 1 endowed with a novel, quinone-fused, dipyridophenazine ligand exhibits three interesting properties: (i) it strongly binds to DNA, (ii) it efficiently photocleaves DNA, and (iii) the redox couple 1/2 represents an 'electro-photoswitch'. These characteristics testify to the utility of this complex as a photonuclease and also as a molecule-based photodevice. Detailed studies investigating these aspects of complexes 1 and 2 are currently in progress.

Acknowledgements

We are grateful to the Indo-French Centre for Promotion of Advanced Research (Centre Franco-Indien Pour la Promotion de la Recherche Avancee). New Delhi for the financial assistance of this work. S A acknowledges a research fellowship received from the University Grants Commission, New Delhi.

References

Arounaguiri S and Maiya B G 1996 *Inorg. Chem.* **35** 4267
Balzani V (ed.) 1987 *Supramolecular photochemistry* (Boston: D Reidel)
Bhattacharya S and Mandal S S 1996 *J. Chem. Soc., Chem. Commun.* 1515
Breslin D T and Schuster G B 1996 *J. Am. Chem. Soc.* **118** 2311
Constable E C, Harverson P and Oberholzer M 1996 *J. Chem. Soc., Chem. Commun.* 1821
Goulle V, Harriman A and Lehn J -M 1993 *J. Chem. Soc., Chem. Commun* 1034
Gupta N, Grover N, Neyhart G A, Liang W, Singh P and Thorp H H 1992 *Angew. Chem., Int. Ed. Engl.* **31** 1048
Harriman A and Ziessel R 1996 *J. Chem. Soc., Chem. Commun.* 1707
Hiort C H, Lincoln P and Norden B 1993 *J. Am. Chem. Soc.* **115** 3448
Holmlin R E and Barton J K 1995 *Inorg. Chem.* **34** 7
Jacquet L, Kelly J M and Mesmaeker K-D 1995 *J. Chem. Soc., Chem. Commun.* 913
Liu H Q, Peng S-M and Che C M 1995 *J. Chem. Soc., Chem. Commun.* 509
Lopez R B, Loeb B L, Boussie T and Meyer T J 1996 *Tetrahedron Lett.* **37** 5437
Murphy C J and Barton J K 1993 *Methods Enzymol.* **226** 576
Schoch T K, Hubbard J L, Zoch C R, Yi G -B and Sorlie M 1996 *Inorg. Chem.* **35** 4383