Study of binuclear complexes with two $[Ru^{II}(bpy)_2]^{2+}$ moieties coordinated by a bridging binucleating ligand (L) bearing two bidentate chelating sites.

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Three series, each of four sets, of binuclear ruthenium(II) complexes of the type $[(bpy)_2Ru^{II}(L)\ Ru^{II}(bpy)_2](ClO_4)_2 2H_2O$; (L = binucleating ligand, bearing two 2-hydroxy-4-(*n*-alkoxy)benzaldimino moieties bound to $(CH_2)_2$, $(CH_2)_3$ or 1, 4-disubstitutedbenzene bridge and, bpy = 2,2′-bipyridine), have been synthesised and characterised. The complexes are diamagnetic and comparative ^1H NMR spectral studies of the complexes and the ligands establish the binuclear composition of the complexes. All the complexes display four metal-to-ligand charge transfer transitions in the visible region of the electronic spectra. In acetonitrile the complexes show one reversible oxidation process in the potential range 0.57–0.60 V, due to the oxidation of the ruthenium(II) centres to ruthenium(III). The complexes are non-luminescent at room temperature and are catalytically inactive to oxygenation reactions.

Keywords: ruthenium complex, binuclear complex, bis-(bipyridyl)ruthenium(II) moiety

Interest in the chemistry of Ru(II) polypyridyl complexes is largely due to their photo redox properties.[1-7] The coordination environment around ruthenium plays a key role in stabilising its different oxidation states and hence directs the redox properties of Ru(II) complexes. In this context a large variety of ruthenium-bpy complexes have been prepared and studied, with the aim of modulating the ground and excited state energies of the complexes. The basic strategies behind all these activities are: to introduce different groups within the bpy moiety of $[Ru(bpy)_3]^{2+}$, to obtain complexes where one or two bpy molecule(s) of $[Ru(bpy)_3]^{2+}$ core is/are substituted by other types of bidentate donor sites, or to use a suitable bridging ligand to bring together two or more $[Ru(bpy)_2]^{2+}$ moieties in polynuclear arrangement.[8,9] Although mononuclear systems have been extensively studied, the development of newer classes of polynuclear complexes, in which Ru(II)-bpy fragments are connected by bridging ligands, is of continuing interest, because of their outstanding electrochemical and luminescence properties.[10-13] The related photo-activity pattern of polynuclear species essentially depends on the nature of the bridging group, which can facilitate the flow of electrons and energy between the molecular components,[14] indicating the extent of interaction between the two metal centres. It has also been reported that the presence of a long aliphatic chain on the ligand in a photosensitiser ruthenium bpy complex can suppress its aggregation on the TiO_2 in solar cells.[15] Ruthenium complexes have also been observed to act as efficient oxygenation catalysts.[16]

In the present work, we have synthesised a new class of binuclear ruthenium-bpy complexes. The aim of the study is to investigate the influence of substitution of one bpy in $[Ru(bpy)_3]^{2+}$ complex by another ligand with a long side chain, on the stability of the oxidation state of ruthenium. The syntheses, characterisation, spectral and electrochemical properties of a group of binuclear complexes, where two $[Ru(bpy)_2]^{2+}$ moieties are coordinated by two chelating 2-aldiminophenolate moieties of a potential binucleating tetradentate ligand, with long side chains, are described. The catalytic and luminescence properties of these complexes have been studied, but no activity was observed.

Experimental

Materials: Commercially available ruthenium trichloride (SRL, India) was converted to $RuCl_3.3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. The complex *cis*-$[Ru(bpy)_2Cl_2].2H_2O$ was prepared, according to the reported prodecure.[17] 1,2-Diaminoethane and 1,3-diaminopropane (Loba, India) were used after distillation over KOH, while 1,4-diaminobenzene (Loba, India) was used without further purification. Alkylbromides (Sisco Chem, India) were also used after distillation. All other chemicals and solvents were of reagent grade commercial materials and were used as received. Tetraethylammonium perchlorate (TEAP), for electrochemical studies, was prepared as reported in the literature.[18]

Physical measurements: Microanalyses were carried out using a Perkin-Elmer 240C elemental analyser. I.R spectra were obtained on a Perkin-Elmer 783 spectrophotometer, as KBr pellets. ^1H NMR spectra were obtained using a 300 MHz varian FT-spectrophotometer in $CDCl_3$ solution, using TMS as the internal standard. Electronic spectra were recorded on a Shimadzu UV-240 UV-visible spectrophotometer. Magnetic susceptibilities were measured with the help of a PAR 155 vibrating sample magnetometer. Thermogravimetric studies of complexes were carried out using a DT30 thermal analyser and cyclic voltametric studies were carried out using a PC controlled EG&G/PAR 273A electrochemistry system. A glassy carbon working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode, were used in three electrode configuration. TEAP was the supporting electrolyte and the concentration of the solution was ~10^{-3} M. Gas chromatography analyses were carried out on a Shimadzu G.C. 14B instrument, equipped with an oracle 3 computing integrator, using 10% SE 30 with 1% QF on chromosorb column (2M) and nitrogen as carrier gas. Emission spectra were recorded on F-4500 Hitachi fluorescence spectrophotometer. The room temperature fluorescence spectra were obtained in acetonitrile solution, using 1 cm path length quartz cell.

Preparation of ligands and complexes

Synthesis of aldehyde: The ligands 2-hydroxy-4-(*n*-alkoxy) benzaldehydes, were synthesised following a reported method,[19-20] by reacting alkyl bromide with 2,4-dihydroxybenzaldehyde, in presence of $KHCO_3$ in anhydrous acetone. The products were purified by flash column chromatography, using hexane ethylacetate (96:4 v/v) as the eluent. The purity of the product obtained was checked by TLC.

The ligand L_1–L_3 were prepared by condensing 2-hydroxy-4-(*n*-alkoxy)benzaldehyde, with appropriate dimines, in a 2:1 mole ratio, in dry methanol. The yellow-coloured compound precipitated on stirring at room temperature and was filtered, washed with methanol and dried in air.

Caution: Although no problems were encountered in the present study, perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities.

Synthesis of $[(bpy)_2Ru^{II}(L_1)Ru^{II}(bpy)_2](ClO_4)_2.2H_2O$ (Series **1**): The starting complex, $[Ru(bpy)_2Cl_2]2H_2O$ 100 mg, (0.19 mmol) was dissolved in ethanol (40 cm^3) and $AgNO_3$ 65 mg (0.38 mmol) was added. The mixture was refluxed for 1 h. The initial violet solution changed to orange-red. The mixture was then cooled and filtered through a Gooch (G-4) sintered glass funnel. The ligand L_1, [1,2-bis(2-hydroxy-4-(*n*-alkoxy)benzaldiaminoethane] (0.095 mmol) and NaOH 15 mg (0.19 mmol) were then added to the above filtrate. The resulting solution was refluxed for 6 h. The volume of the solution was reduced by distillation to 5 ml and solid sodium perchlorate was added, followed by 100 ml water. The precipitate, thus formed, was filtered and washed thoroughly with water and dried *in vacuum*. The resulting solid was redissolved in minimum volume of dichloromethane and was subjected to column chromatography,

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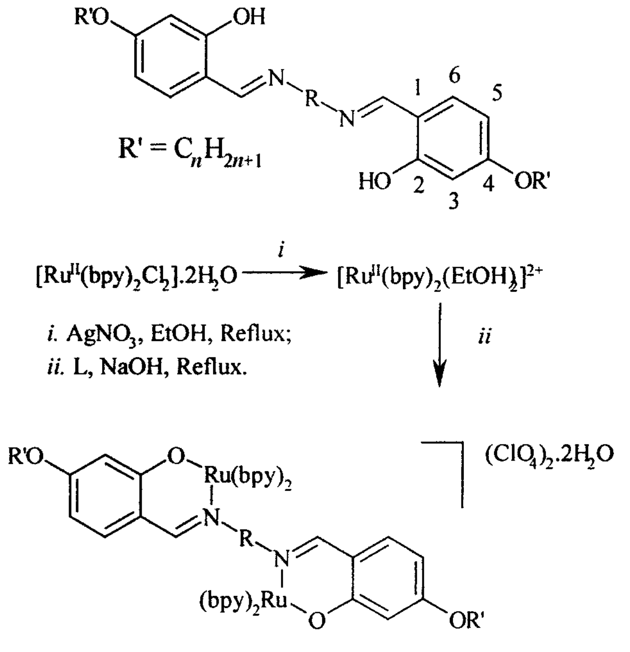
using silica gel (60–120) mesh, Acmey, India). The initial yellow band, due to the unreacted ligand, was eluted out by pure benzene. The orange-red band, due to the pure desired complex, was eluted out by using benzene-acetonitrile mixture (3:1 v/v).

The complexes $[(bpy)_2Ru^{II}(L_2)Ru^{II}(bpy)_2](ClO_4)_2 2H_2O$ Series **2** and $[(bpy)_2Ru^{II}(L_3)Ru^{II}(bpy)_2](ClO_4)_2 2H_2O$ Series **3** were synthesised following the same method, as described for the complexes of Series **1** using equivalent amount of L_2 and L_3, respectively, instead of L_1.

Results and discussion



n	R	Ligand	Complex
6	$(Ch_2)_2$	$L_{1(6)}$	**1**
10		$L_{1(10)}$	**2**
14		$L_{1(14)}$	**3**
18		$L_{1(18)}$	**4**
6	$(Ch_2)_3$	$L_{2(6)}$	**5**
10		$L_{2(10)}$	**6**
14		$L_{2(14)}$	**7**
18		$L_{2(18)}$	**8**
6	1,4-disubstituted benzene	$L_{3(6)}$	**9**
10		$L_{3(10)}$	**10**
14		$L_{3(14)}$	**11**
18		$L_{3(18)}$	**12**

Scheme 1

The Schiff's bases formed from two equivalents of 2-hydroxy-4-(*n*-alkoxy)benzaldehyde with either of two aliphatic diamines or one aromatic diamine, have been used to form binuclear ruthenium complexes, in the present study. Individual ligands and their abbreviations are shown in Scheme 1.

The ligands gave satisfactory elemental analyses and further characterisation has been done by IR and ^1H NMR spectral studies. In the IR spectra of the free ligands, the $\nu_{C=N}$ stretching frequency appears at *ca.* 1640 cm^{-1} and the OH stretching band of the phenolic hydroxyl group appears at *ca* 3250 cm^{-1}.

The ^1H NMR spectra of two representative ligands $L_{1(10)}$ and $L_{3(10)}$ were recorded in $CDCl_3$. In the spectrum of $L_{1(10)}$, the singlet, which integrate to two protons due to the two equivalent aldimine protons appears at δ 9.7. The signals due to the aromatic protons, H^5 and H^6 of the two equivalent 2-hydroxy-4-(*n*-alkoxy)benzaldimino moieties appear at δ 6.37 and 7.08 respectively, as two doublets which integrate to two protons each, while the signal due to H^3 appears at δ 8.19 as a singlet, integrating to two protons. The triplet, which integrates to four protons at δ 4.0 has been assigned to the four equivalent protons of two equivalent methylene groups of the 1,2-diaminoethane moiety of the ligand. The signals due to the protons of the alkoxy chain appear within the range δ 1.2–1.8 as complex multiplet which integrates to the required 42 protons. In the spectrum of $L_{3(10)}$ the signals due to the aromatic protons of the two 2-hydroxy-4-(*n*-alkoxy)benzaldimino moieties appear in a similar region with minor shifts in the δ values, while the signal due to the two equivalent aldimine protons appears as a singlet at δ 13.1. The doublet at δ 7.67, integrating to four protons, has been assigned to the four equivalent aromatic protons of the 1,4-diaminobenzene moiety.

These ligands, containing long alkoxy chains, have been used to study the effect of a long chain on the electrochemical, luminescent and catalytic properties of the binuclear ruthenium(II) complexes. Twelve binuclear ruthenium complexes, having the general formula $[(bpy)_2Ru^{II}(L)Ru^{II}(bpy)_2]^{2+}$, have been synthesised from $[Ru(bpy)_2Cl_2]2H_2O$, following the synthetic route shown in Scheme 1. The reddish-brown coloured cationic complexes were precipitated directly from the respective reaction mixture, as dihydrated perchlorate salts, $[(bpy)_2Ru^{II}(L)Ru^{II}(bpy)_2](ClO_4)_2.2H_2O$. The pure complexes were obtained by column chromatography.

The micro-analytical data (C, H, N) for the binuclear ruthenium complexes, as collected in Table 1, correspond to the expected composition. Magnetic susceptibility measurements show that these complexes are diamagnetic, as expected for the complexes of ruthenium(II) (low spin d^6, S=0).

The $\nu_{C=N}$ stretching frequency of the free ligands was found to be shifted to *ca* 1614 cm^{-1} in the complexes, supporting the coordination of the azomethine function to the metal ions.[21] Further, the OH stretching band of the phenolic hydroxyl group of free ligands disappeared in the IR spectra of the complexes, supporting the deprotonation of phenolic hydroxyl groups of the ligand during complexation. The strong bands, near *ca* 1089 and 623 cm^{-1} are observed for all the complexes, due to the presence of non-coordinated perchlorate.[22]

The ^1H NMR spectra of two representative complexes, **2** and **10** were recorded in $CDCl_3$ to compare with the same of the corresponding ligands $L_{1(10)}$ and $L_{3(10)}$. All the signals of the ligand protons are retained only with minor shift in the positions in the ^1H NMR spectra of the complexes. The aromatic region of the ^1H NMR spectra of the complexes appears complicated owing to the significant overlap of the signals due to the aromatic protons of the 2,2'-bipyridine and ligands, L. However, the signals in the aromatic region integrate to the required number of protons of both the ligands. This supports the metal to ligand ratio Ru(II) : L : bpy = 2 : 1 : 4, in the complex.

Electronic spectral studies: The complexes are highly soluble in ethanol, methanol, dichloromethane, acetonitrile, chloroform and benzene. Solution electronic spectra of the complexes were recorded in acetonitrile solution. The spectral data are collected in Table 1 and a representative spectrum is shown in Fig. 1. All the complexes display four intense absorptions, one in the visible region and three in the UV region. On the basis of high value of the extinction coefficients, these bands are assigned to the metal-to-ligand charge transfer transition (MLCT) and $\pi \rightarrow \pi^*$ intraligand transitions. The band at 290 nm is assigned to the $\pi \rightarrow \pi^*$ intraligand transition of the bpy, as observed in $[Ru(bpy)_3]^{2+}$. The lowest energy MLCT band at 500 nm is assigned to the $d\pi Ru(II) \rightarrow \pi^*$ MLCT transition, where π^* is essentially ligand, bpy centred orbital.[23] The other two high intensity bands at 375 and 300 nm, not seen in $[Ru(bpy)_3]^{2+}$, may be assigned to $\pi \rightarrow \pi^*$ (L) and $d\pi Ru(II) \rightarrow \pi^*$ (L) transitions, where L is Schiff's-base ligand.

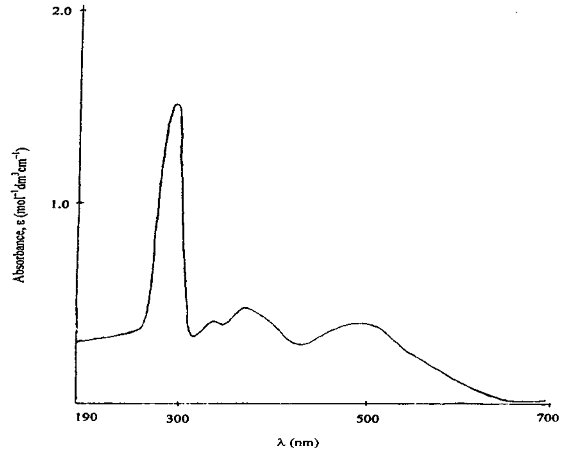


Fig 1. Representative UV-visible spectrum of **10** in acetonitrile.

Table 1 Characterisation data

Complexes	Micro analytical data/%[a]			Electronic spectral data[b] λ nm (ε, mol^{-1} dm^3 cm^{-1c})	Cyclic voltammetric data[d] E^0_{298}, V (ΔE_p, mV) Ru$^{II–III}$
	C	H	N		
1	53.01 (53.43)	4.75 (4.80)	9.50 (9.16)	290(966292); 330(259675); 375(201212); 500(119850)	0.598
2	55.25 (55.64)	5.53 (5.49)	8.83 (8.54)	290(717335); 330(113862); 375(125249); 500(113862)	0.567
3	57.09 (57.56)	5.71 (5.82)	7.65 (7.99)	295(131644; 330(22354); 375(29806); 495(27322)	0.596
4	58.70 (58.72)	6.38 (6.63)	7.43 (7.61)	295(79182); 330(15235); 375(166028); 495(15325)	0.572
5	53.65 (53.71)	4.80 (4.93)	9.00 (9.08)	290(976222); 330(205363); 375(201214); 500(116445)	0.570
6	56.07 (55.89)	5.26 (5.56)	8.24 (8.46)	290(989737); 330(168705); 375(202446); 500(134964)	0.570
7	57.91 (57.79)	6.07 (6.11)	7.86 (7.93)	290(411230); 330(70584); 370(82318); 500(58621)	0.576
8	58.34 (58.93)	6.44 (6.69)	7.31 (7.55)	295(122277); 375(25210); 330(20169); 495(22689)	0.604
9	54.97 (54.85)	4.39 (4.69)	8.66 (8.86)	290(110471); 330(218758); 375(251572); 500(437243)	0.572
10	56.40 (56.90)	5.19 (5.33)	8.20 (8.29)	290(138128); 330(366753); 375(427726); 500(366753)	0.574
11	58.56 (58.69)	5.94 (5.89)	7.65 (7.78)	290(813397); 330(127591); 370(140300); 500(127559)	0.595
12	60.08 (60.28)	6.26 (6.38)	6.98 (7.32)	295(682504); 330(80290); 375(107059); 495(11375)	0.605

[a]Calculated values in parentheses; [b]in acetonitrile solution; [c]extinction coefficient; shoulder; [d]conditions: solvent, acetonitrile; supporting electrolyte, $(\mathrm{Net_4})\mathrm{ClO_4}$; reference electrode, Ag/AgCl; solute concentration, 10^{-3} M; working electrode, glassy carbon. Cyclic voltammetric data: scan rate 100 mVs^{-1}; $E^o = 0.5(E_{pc} + E_{pa})$ where E_{pc} and E_{pa} are the cathodic and anodic peak potential respectively.

The transition energy of the lowest energy $d\pi$Ru(II) $\rightarrow \pi^*$ MLCT band of complexes is affected, depending on the nature of the third ligand. The lowest energy MLCT band of $[\mathrm{Ru(bpy)_3}]^{2+}$ appears at 452 nm[24] and may be compared with the lowest energy band obtained in the electronic spectra of the complexes reported here. Each mononuclear moiety, $[\mathrm{Ru^{II}(bpy)_2(L)_{1/2}}]^+$ of the binuclear complexes can be considered as $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$ with one of the coordinated bpy being replaced by $(\mathrm{L})_{1/2}$. Thus the replacement of one bpy by an asymmetric bidentate chelating site $(\mathrm{L})_{1/2}$, of the tetradentate bridging ligand L, results in a shift of the band at 452 nm of $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$ to 500 nm in the present complexes. The bidentate chelating site $(\mathrm{L})_{1/2}$ being less π–acidic compared to the π-acidic nature of bpy, the energy separation between the metal centred orbital and the lowesr energy π* orbital of $(\mathrm{L})_{1/2}$ is reduced in each $[\mathrm{Ru^{II}(bpy)_2(L)_{1/2}}]^+$ moiety, compared to $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$, and this is reflected in the appearance of the lowest energy MLCT band at *ca* 500 nm.[17]

Electrochemical study: The electrochemical properties of the complexes were studied in acetonitrile (0.1 MTEAP) by cyclic voltammetry. The voltammetric data are presented in Table 1. Each complex shows a reversible response, due to ruthenium(II)–ruthenium(III), in the potential range 0.57–0.60 V. The ΔE_p values of these complexes lie in the range 60–70 mV, which do not change with change in the scan rate and the i_{pa}/i_{pa} (i_{pa} = anodic peak current and i_{pc} = cathodic peak current) ratio is close to 1.0 as expected for a reversible couple. Under identical experimental condition the ruthenium(III)-ruthenium(II) reduction potential of $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$ appears at 1.29 V.[25-28] Thus the substitution of one bpy ligand from the $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$ by a 2-aldiminophenolate moiety of the binucleating ligand L, results in a decrease of Ru(III)–Ru(II) potential by 0.70 V. This is because the ligands L are less π acidic than bpy and hence the electron density on the Ru(II) metal centre in $[\mathrm{Ru(bpy)_2L}]^+$ is more than in $[\mathrm{Ru(bpy)_3}]^{2+}$ and hence the former is oxidised at a less positive potential. Further, the decrease in overall charge per mononuclear moiety, compared to the charge of $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$, provides further electrostatic stabilisation of the oxidised species, which possibly has been reflected in the high Ru(III)–Ru(II) potential of the binuclear complexes. To study the effect of the side alkoxy chain OR' on the redox potential cyclic volumetric study of the corresponding binuclear complex with no alkoxy chains, $[(\mathrm{bpy})_2\mathrm{Ru^{II}(salen)\ Ru^{II}(bpy)_2}](\mathrm{ClO_4})_2.2\mathrm{H_2O}$, was studied. The ruthenium(II)–ruthenium(III) oxidation of this binuclear complexes appears at 0.635 V. Thus the alkoxy substituents decrease the Ru(II)–Ru(III) potential of the ruthenium centres by 30–68 mV, indicating that the alkoxy substituents being electron donating, destabilise the +2 oxidation state of the ruthenium centres by 30–68 mV.

Catalytic study: The complexes were found to be catalytically inactive towards the oxygenation of the olefin by the oxidant, iodosyl benzene. However, other binuclear Ru(III) and Ru(II) complexes have been shown to be good oxygenation catalysts.[16]

The catalytic oxygenation reaction is known to proceed through the formation of high valent metal-oxo species and subsequent transfer of oxygen to the substrate olefin.[29] Since in the present complexes the Ru(II) centres are coordinately saturated, formation of oxo cation does not take place. This may be the probable reason for the absence of catalytic activity of the complexes.

Fluorescence spectral studies: The complexes were found to be non-luminescent. As both the centres in the binuclear complex are expected to be luminescent, from MLCT excited states, in principle multiple emissions should have been observed. However, in the complexes of the type $[\mathrm{Ru(bpy)_2L}]$, where L is a σ bonding ligand, a relatively weak ligand field is created, compared to that in $[\mathrm{Ru(bpy)_3}]$. Hence, at the $[\mathrm{Ru(bpy)_2L}]$ centres, the lowest energy excited MLCT state, normally centred at the ligand π* orbital, is very low lying. Further, the electron releasing OR' groups on the binucleating Schiff's base ligand L, stabilise the low-lying MLCT state.[30] Hence, the separation between the metal centred HOMO and the ligand centred LUMO is reduced. Thus, there is a fast radiationless transition and the luminescence could not be observed at room temperature.[30,31]

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References

1 J.P. Collin, R. Kayshanian. J.P. Sauvage, G. Calogero. F. Barigelletti. A.D. Cian and V. Fischer, *J. Chem. Soc., Chem. Commun*., 1997, 775.
2 B.J. Coe, D.A. Friesen. D.W. Thompson and T.J. Meyer, *Inorg. Chem*., 1996, **35**, 4575.
3 M.D. Ward, *Inorg. Chem*., 1996, **35**, 1712.
4 S.C. Rasmussen, D.W. Thompson, V. Sing and J.D. Peterson. *Inorg. Chem.*, 1996, **35**, 3449.

5 K.D. Keerthi, B.K. Santra and G.K. Lahiri, *Polyhedron*, 1998, **17**, 1387.

6 B.K. Santra, M. Menon, C.K. Pal and G.K. Lahiri, *J. Chem. Soc. Dalton Trans*. 1997, 1387.

7 M.D. Ward, *Chem. Soc. Rev.*, 1995. 121.

8 N.A. Lewis and W. Pan, *Inorg. Chem.*, 1995, **34**, 2244.

9 M.R. Wasielewski. *Chem. Rev*. 1992, **92**, 435.

10 V. Balzali, A. Zuris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996. **96**. 759.

11 E.S. Dodsworth, A.A. Vleck and A.B.P. Lever, *Inorg Chem.*, 1994, **33**, 1045.

12 R. Argazzi, C.A. Bignozzi. G.M. Hasselman and G.J. Meyer, *Inorg. Chem.*, 1998, **37**, 4533.

13 F. Barigelletti and L. Flamigini. *Chem. Soc. Rev.*, 2000, **29**, 1.

14 R.J. Crutchley, *Adv. Inorg. Chem*., 1994, **41**, 273.

15 A. Islam, H. Sugihara. M. Yanagida. K. Hara, G. Fugihasha, Y. Tachibana. R. Katoh. S. Murata and H. Arakawa. *New J. Chem*., 2002, **26**, 966.

16 T. Naota, H. Takaya and S-l. Murahashi, *Chem. Rev.*, 1998, **98**, 2599.

17 B.P. Sullivan, D.J. Salmon and T.J. Meyer, *Inorg Chem.*, 1978, **17**, 3334.

18 D.T. Sawyer and J.L. Roberts Jr. *Experimental Electrochemistry for Chemists*, pp 167-215, Wiley, New York. 1974.

19 M. Artigas, M. Marcos, E. Melendez and J.L. Serrano, *Mol. Cryst. Liq. Cryst.*, 1985, **130**. 337.

20 M. Marcos, E. Melendez and J.L. Serrano, *Mol. Cryst. Liq. Cryst*., 1983, **91**, 157.

21 R. Hariram, B.K. Santra and G.K. Lahiri., *J. Organomet. Chem.*, 1997, **155**, 540.

22 J. Chakravarty and S. Bhattacharya. *Polyhedron*, 1996, **15**, 1047.

23 K. Kalyansundaram, *Coord. Chem. Rev.*, 1982, **46**, 159.

24 G.M. Brown, T.R. Weaver, F.R. Keene and T.J. Meyer, *Inorg Chem.*, 1976, **15**, 190.

25 A. Ceulemansm and L.G. Vanquickenborne, *J. Am. Chem. Soc.*, 1981, **103**, 2238.

26 M.J. Root and E.Deutsch, *Inorg. Chem.* 1985, **14**, 1464.

27 R. Alsfasser and R.V. Elidik, *Inorg. Chem.* 1996, **35**, 628.

28 B.J. Coe, T.J. Meyer and P.C. White, *Inorg. Chem.* 1995, **34**, 593.

29 J.T. Groves and G.A. McClusky, *J. Am. Chem. Soc*., 1976, **98**, 859.

30 C. Metcalfe, S. Spey, H. Adams and J.A. Thomas, *J. Chem. Soc., Dalton Trans.*, 2002, 4732.

31 J-P. Sauvage, J-P. Collin, J-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Slamigni, *Chem. Rev.*, 1994, **94**, 993.