DALTON
FULL PAPER

Synthesis, electrochemistry and photophysics of rigid norbornylogous-bridged complexes of ruthenium and osmium

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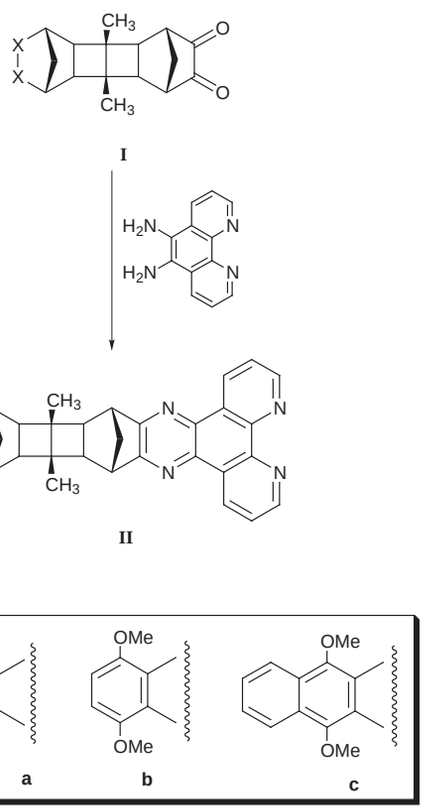
A series of rigid phenanthroline-annulated ligands incorporating fused 6-bond norbornane bicyclo[2.2.0]hexane bridges have been synthesized. The resulting dipyridoquinoxaline (dpq) ligands with covalently bound 1,4-naphthoquinone (dpq-6-NQ) or 1,4-benzoquinone (dpq-6-BQ) moieties were treated with *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ to yield the $[Ru(dpq\text{-}6\text{-}NQ\}^{2+}$ and $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ [Ru = $Ru(bipy)_2$] complexes as PF_6^- salts. The symmetric bis-annulated dpq-6-dpq ligand was similarly metallated to yield the dinuclear $[Ru(dpq\text{-}6\text{-}dpq)M]^{4+}$ [Ru = $Ru(bipy)_2$, M = $Ru(bipy)_2$ or $Os(bipy)_2$] species, whose electrochemistry and UV-Vis absorption spectra are consistent with class I or weakly coupled class II (localised) mixed-valence character and weak through-bond coupling across the norbornylogous bridge. Preliminary photophysical measurements using steady-state emission spectroscopy revealed quenching of the Ru^{II}-based ^{3}MLCT emissive state in the $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ complexes, which is assumed to arise from intramolecular electron transfer between Ru^{II}* and the electron-accepting quinone groups. In contrast, the efficient quenching of the ^{3}MLCT emissive state observed in $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ is consistent with intramolecular electronic energy transfer ($k_{EET} = 1.5 \times 10^7\ s^{-1}$) between the Ru^{II}* and Os^{II} centres.

Introduction

Much attention is currently being paid to the development of artificial photochemical molecular devices (PMDs).[1–3] Essential to the successful development of such applications is a fundamental understanding of intramolecular electron transfer (ET) and electronic excitation energy transfer (EET) processes. Rigid covalently bonded systems in which the distance and orientation between the donor and acceptor chromophores are well defined are essential for theoretical and experimental ET and EET investigations.[2,4,5] Whilst several studies of structurally rigid molecules incorporating organic acceptor and donor groups have appeared,[4,6–14] only more recently similar systems incorporating transition metal chromophores have been reported.[15–33] These metal complexes are ideal for modeling vectorial ET and EET processes, a necessary characteristic in the design of PMDs.[1,2]

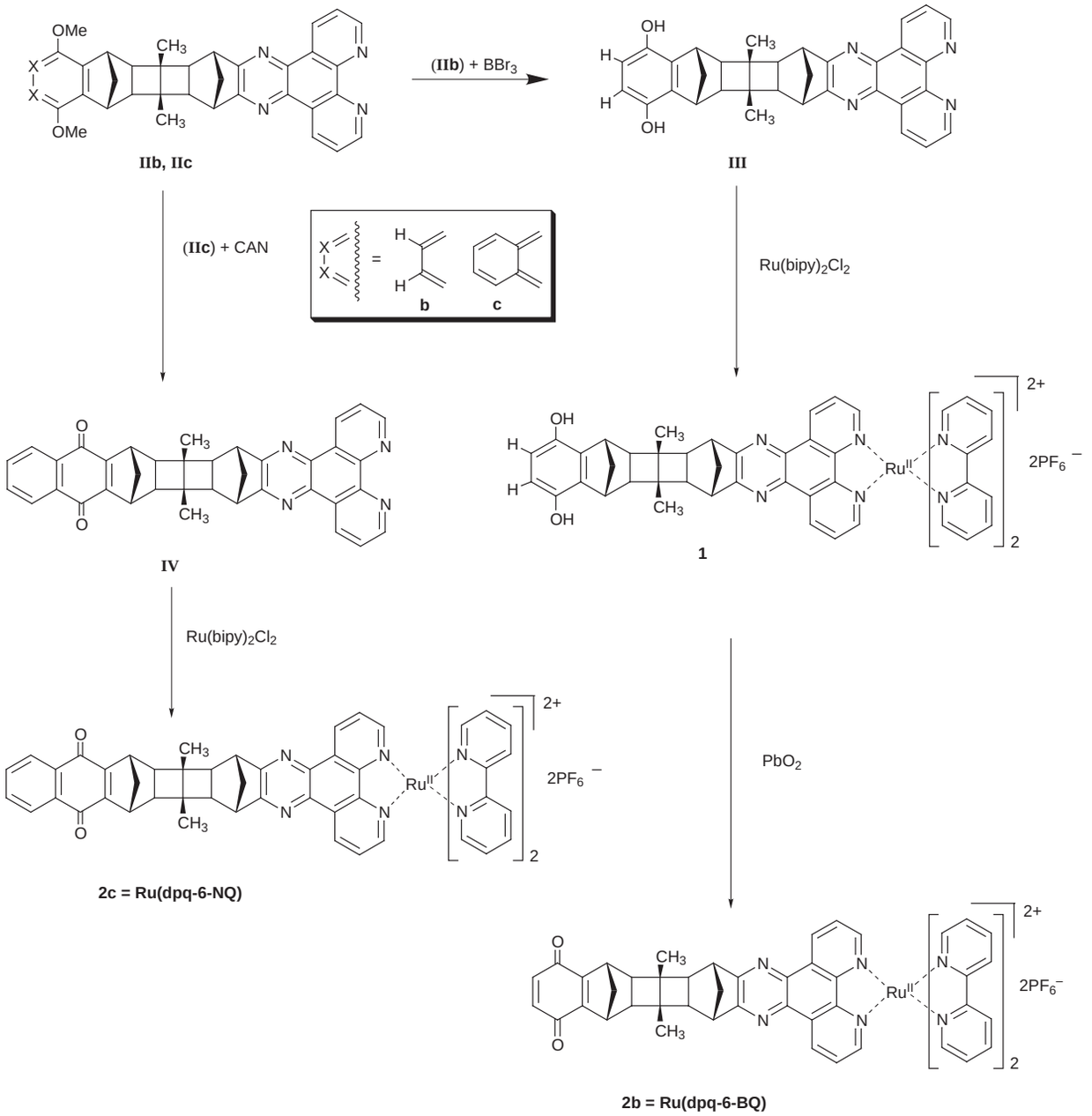
The synthesis of suitably rigid saturated hydrocarbon bridges possessing a range of well defined lengths has proved to be a significant challenge. Several conformationally rigid ligands incorporating 1,10-phenanthroline,[34,35] 4,5-diazafluorene,[29,36,37] and annulated pyridazine[32,33,36] units have been reported capable of co-ordinating luminescent transition metal polypyridine centres. Whilst some of the corresponding metallated species have been structurally characterised, only limited photophysical data have been reported.[29,30]

An initial report of the synthesis of rigid phenanthroline-annulated systems incorporating fused 6-bond norbornane bicyclo[2.2.1]hexane (norbornylogous) bridges has been developed in our laboratory.[38] The novel phenanthroline-bearing ligands were obtained *via* the condensation of 5,6-diamino-1,10-phenanthroline with norbornane-2,3-diones (*e.g.*, Scheme 1) , similar to the synthesis of the bis-phenanthroline ligand reported by Bolger *et al.*[39,40] Herein is reported the complete synthesis and characterisation of the norbornylogous ligands and two distinctly new classes of mononuclear and dinuclear bichromophoric complexes. In the first class the



Scheme 1

electron donor group is $[Ru^{II}(bipy)_2]$, which is tethered *via* the rigid norbornylogous bridge to either 1,4-naphthoquinone or 1,4-benzoquinone moieties, with quinones which are known to be moderate electron acceptors. These mononuclear complexes can be regarded as mixed inorganic–organic bichromophoric



Scheme 2

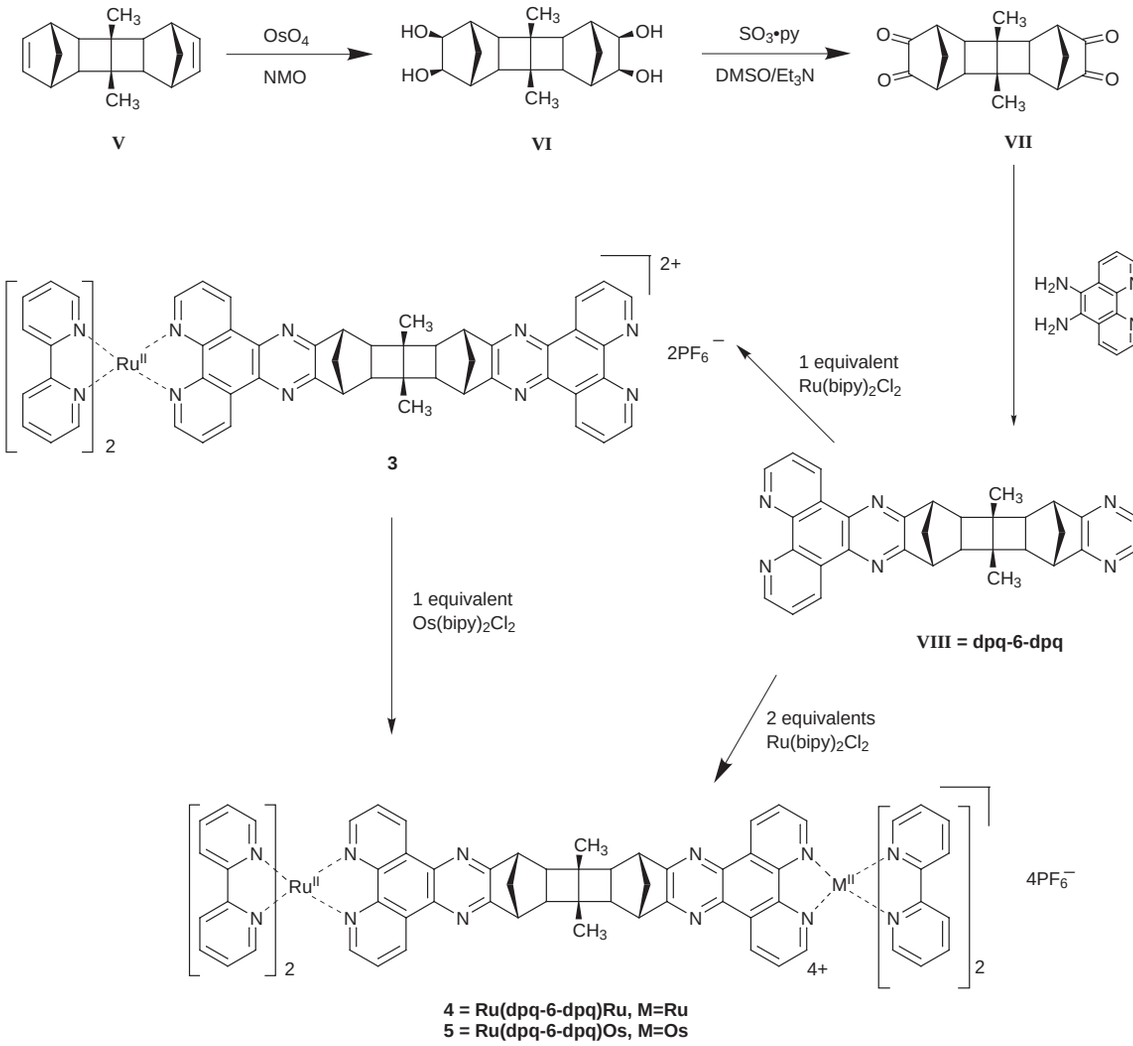
systems capable of undergoing photoinduced ET. The second class of complexes are dinuclear species consisting of $[Ru^{II}(bipy)_2]$ bridged to another $[M^{II}(bipy)_2]$ (M = Ru or Os) group. The heterodinuclear complex bearing both Ru and Os is of interest since it has the potential of undergoing intramolecular EET.[2,17,18,22,29,30] The luminescence spectroscopy of both classes of bichromophoric complexes reveal the presence of efficient ET or EET processes which are compared to relevant previously reported systems.

Results and discussion

Synthesis

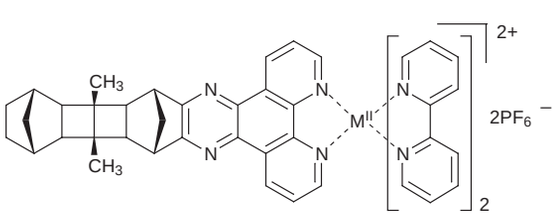
Norbornylogous ligands. The monoannulated ligands **IIa**–**IIc** were obtained in good yield (70–90%) by the condensation reaction of the norbornane-2,3-diones **Ia**–**Ic**[38] with 5,6-diamino-1,10-phenanthroline[40] in refluxing ethanol–chloroform, followed by purification on silica gel (Scheme 1). The condensation products form a new class of ligands named as dipyridoquinoxaline norbornanes (dpq). The dimethoxynaphthalene ligand **IIc** was oxidised to the naphthoquinone **IV** (in 94% yield) using an excess of ammonium cerium(IV) nitrate (CAN) (Scheme 2).[41] Direct oxidative bis-demethylation of the dimethoxybenzene ligand **IIb** to the benzoquinone could not be achieved using CAN owing to the extensive formation of dimeric products.[41] However, near quantitative conversion of **IIb** into the hydroquinone **III** was readily obtained using BBr_3 in dichloromethane.[42]

The bis-annulated dipyridoquinoxaline **VIII** (dpq-6-dpq) was synthesized starting with the known diene **V**[43] as outlined in Scheme 3. The terminal double bonds of **V** were bis-dihydroxylated using a catalytic amount of OsO_4 and *N*-methylmorpholine (NMO) in aqueous 1,4-dioxane,[44–47] to give the tetraol **VI** in 68% yield. The hydroxyl groups are assumed to be *exo* to the methylene bridge of the [2.2.1] norbornane based on the tendency for norbornanes to react on the *exo* face.[48] Further oxidation to the corresponding tetraone **VII** (in 38% yield) was achieved using pyridine–SO_3 complex in triethylamine and dimethyl sulfoxide.[49] The condensation of **VII** with an excess of 5,6-diamino-1,10-phenanthroline using a similar method to that used for the monoannulated ligands formed the bis-dipyridoquinoxaline **VIII** in 52% yield.



Scheme 3

Metal complexes. The mononuclear $[M^{II}(bipy)_2]$ (M = Ru or Os) co-ordinated complexes **1**, **2c** (Scheme 2), **6** and **7** were obtained by refluxing the corresponding norbornylogous dpq ligand with either *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (in aqueous ethanol) or *cis*-$[Os(bipy)_2Cl_2]$ (in aqueous 1,2-ethanediol) using standard methods.[40,50] Purification was afforded by size-exclusion chromatography and/or chromatography on silica gel, followed by recrystallisation. Moderate yields of between 50 and 75% were obtained. The monochromophoric complexes **6** and **7**, $[M^{II}(dpq\text{-}6)]^{2+}$ (M = Ru or Os), represent model compounds in the present study.



6 = Ru(dpq-6)
7 = Os(dpq-6)

Oxidation of the hydroquinone **III** to the corresponding benzoquinone ligand (using PbO_2)[51] followed by reaction with *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ yielded several inseparable products, consistent with earlier reports[52] of similar reactions with related benzoquinone derivatives. Hence **III** was treated with *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ directly to give the hydroquinone complex **1**. The ^{1}H NMR spectrum revealed the product to be a mixture of **1** and the benzoquinone complex **2b** (Scheme 2), with further reaction of the mixture with PbO_2 giving pure **2b**.

The homo- and hetero-dinuclear complexes **4** and **5** (Scheme 3), respectively, were synthesized using similar methods to those used for the mononuclear complexes. The reaction of **VIII** with two equivalents of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ yielded two major products, one of which was the desired bis-metallated species **4**. The other unknown product, the second orange band to be eluted during size-exclusion chromatography, was not characterised. Complex **5** (55% yield) was synthesized *via* the monometallated intermediate **3**, obtained by slow addition of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ to **VIII** in acidic 1,2-ethanediol,[53] followed by reaction with *cis*-$[Os(bipy)_2Cl_2]$. The reaction between **VIII** and *cis*-$[Os(bipy)_2Cl_2]$ resulted in a very low yield of the osmium monometallated adduct.

Absorption spectroscopy

The UV-Vis absorption data for all metal complexes and selected ligands are given in Table 1. The ground-state absorption characteristics for all the ruthenium and osmium mononuclear complexes are found to be insensitive to the nature of the dpq ligands, with similar properties found to those observed for $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$. The low-energy absorption bands at wavelengths above 400 nm are associated with $d_\pi \longrightarrow \pi^*$ MLCT transitions.[3,54,55] The more intense bands found at higher energy between 200 and 300 nm can be attri-

buted to $\pi \longrightarrow \pi^*$ ligand centred (LC) transitions originating at the bipy and dpq ligands. The less intense broad manifold occurring between 500 and 700 nm for the osmium-bearing complexes is likely to be associated with direct transitions to the MLCT triplet state.[54] The absorption bands observed for the heterodinuclear $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ complex are found to be approximately the superposition of those observed for the models $[Ru(dpq\text{-}6)]^{2+}$ and $[Os(dpq\text{-}6)]^{2+}$ (Fig. 1). This is an expected result as the ruthenium(II) and osmium(II) chromophores are likely to be electronically isolated in the ground state due to the insulating nature of the norbornylogous bridge (see below).

Electrochemistry

The electrochemical data obtained by cyclic and differential voltammetry for all metal complexes and selected ligands in MeCN and DMF are summarised in Table 2 (potentials given in V *vs.* $Fc^{+/0}$). All couples were characterised to be nearly chemically reversible based on the cathodic-to-anodic current ratios. The metal centred $M^{3+/2+}$ couples of all complexes bearing co-ordinated ruthenium are observed at 0.90 (± 0.01) V in MeCN, which compares to 0.89 V for $[Ru(bipy)_3]^{3+/2+}$. Similarly, the $M^{3+/2+}$ couples corresponding to the osmium-based couples are observed at 0.46 V in MeCN, identical[56] to that for $[Os(bipy)_3]^{3+/2+}$. This distinct insensitivity of the formal potentials of the $M^{3+/2+}$ couples to the nature of the dpq ligands is consistent with previous findings that the metal-based HOMO has little contribution from the π-acceptor ligands.[40]

Table 1 Electronic absorption spectral data for complexes and selected ligands[a]

Complex/ligand[b]	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})
$[Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$	451 (33.2), 424 (sh), 332 (sh), 286 (144), 277 (sh), 258 (97.5), 210 (80.0)
$[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$	632 (sh, ≈4.5), 572 (sh, ≈5.0), 451 (37.0), 429 (sh), 334 (sh), 288 (174), 259 (sh, ≈117)
$[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$	450 (16.9), 425 (sh), 330 (sh), 284 (77.6), 256 (65.8), 220 (sh)
$[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$	451 (14.9), 425 (sh), 330 (sh), 284 (73.5), 252 (53.3), 211 (42.4)
$[Ru(dpq\text{-}6)]^{2+}$	450 (10.6), 425 (sh), 330 (sh), 285 (47.3), 257 (32.4)
$[Os(dpq\text{-}6)]^{2+}$	626 (4.0), 580 (4.5), 480 (17.2), 437 (15.6), 392 (sh), 332 (sh), 290 (80.0), 260 (51.6), 206 (53.3)
$[Ru(bipy)_3]^{2+}$[c]	452 (14.6), 288 (76.6)
$[Os(bipy)_3]^{2+}$[d]	579 (3.3), 478 (11.1), 436 (10.7), 290 (78.0)
dpq-6-dpq[e]	348 (20.7), 335 (sh), 330 (17.2), 319 (sh), 314 (22.7), 307 (21.2), 299 (sh), 288 (sh)
dpq-6[e]	347 (8.8), 334 (sh), 329 (7.9), 319 (sh), 313 (10.8), 307 (10.3), 299 (sh), 288 (sh)

[a] In MeCN solution at 298 K. [b] Ru = {Ru(bipy)$_2$}, Os = {Os(bipy)$_2$}. [c] Ref. 55. [d] Ref. 53. [e] In DMF solution.

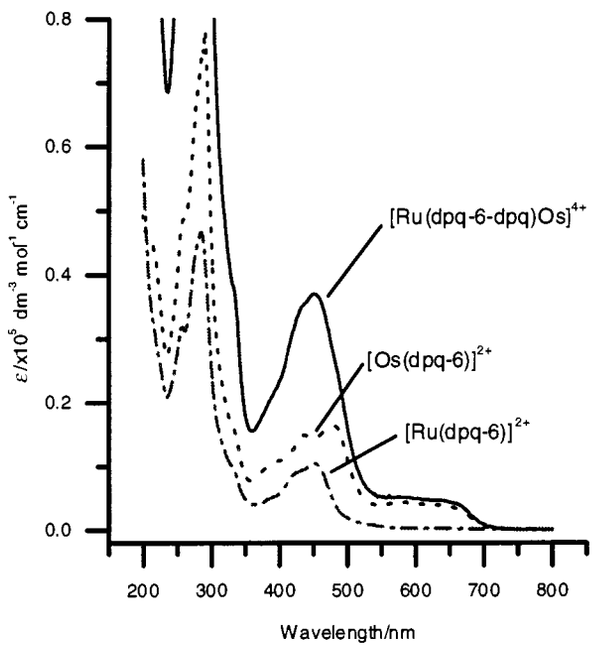


Fig. 1 The UV-Vis absorption spectra of $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ (——), $[Os(dpq\text{-}6)]^{2+}$ (. . . .) and $[Ru(dpq\text{-}6)]^{2+}$ (-.-.-) in MeCN at ambient temperature. Ru = {Ru(bipy)$_2$}.

Table 2 Electrochemical data for complexes and selected ligands[a]

Complex/ligand[b]	Solvent	$M^{3+/2+}$ couple(s)		Ligand-based couples				
$[Ru(dpq\text{-}6)]^{2+}$	MeCN	0.89 (71)			−1.67 (101)	−1.89		
	DMF	0.82 (106)			−1.55 (62)	−1.75 (68)	−1.98 (94)	≈ −2.3[c]
$[Os(dpq\text{-}6)]^{2+}$	MeCN		0.46 (57)		−1.62 (63)	[d]		
	DMF		0.41 (96)		−1.63 (61)	−1.81 (63)	−2.13 (93)	−2.38 (121)
$[Ru(dpq-6\text{-}BQ)]^{2+}$	MeCN	0.90 (62)		−0.90 (59)	[d]			
	DMF	0.82 (81)		−0.92 (57)	≈−1.6[d]			
$[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$	MeCN	0.91 (63)		−1.08 (69)	[d]			
	DMF	0.83 (73)		−1.10 (58)	≈−1.6[d]			
$[Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$	MeCN	0.90 (58)			−1.68 (55)	[d]		
	DMF	0.84 (78)			−1.66 (70)	−1.88 (75)	−2.12 (81)	−2.43 (144)
$[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$	MeCN	0.90 (60)	0.46 (59)		−1.65 (119)	[d]		
	DMF	0.83 (104)	0.39 (79)		−1.66 (101)	−1.85 (146)	−2.13[c]	−2.20[c]
$[Ru(bipy)_3]^{2+}$	MeCN	0.89 (62)			−1.70 (59)	−1.89 (83)	−2.14 (57)	
	DMF[e]				−1.76	−1.92	−2.14	
$[Os(bipy)_3]^{2+}$[f]	MeCN		0.46 (80)		−1.63 (80)	−1.81 (70)	−2.11 (70)	
$[Ru(dppz)]^{2+}$	MeCN[g]	0.86			−1.40	−1.82	−2.05	−2.45
	DMF[h]				−1.36	−1.79	−1.99	−2.31
dpq-6-dpq	DMF				−2.20 (110)	[i]		
dpq−6	DMF				−2.22 (65)	[i]		
dppz-6-BQ[j]	MeCN			−0.95	−1.85[h]	−2.05[h]		

[a] Formal reduction potentials in V *vs.* $Fc^{+/0}$ measured at ambient temperature with solvent–0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ peak–peak separations (ΔE_p/mV) in cyclic voltammogram for chemically reversible processes given in parentheses (ΔE_p = 61 mV for $FC^{+/0}$). [b] Ru = {Ru(bipy)$_2$}, Os = {Os(bipy)$_2$}. [c] Cyclic voltammogram distorted. [d] Couple not resolved adsorption spike observed. [e] Ref. 63 at −54 °C. [f] Ref. 56. [g] Ref. 64. [h] Ref. 84. [i] Irreversible multi-electron process, E_{pc} = *ca.* −2.8 V. [j] Ref. 52; dppz-6-BQ = 11,11a,11b,11c,12,13,16,17,17a,17b,17c,18-dodecahydro-11b,17b-dimethyl-11,18;12,17-dimethanonaphtho[2‴,3‴:3″,4″]cyclobuta[1″,2″:3′,4′]cyclobuta[1′,2′:4,5]benzo[1,2-*i*]dipyrido[3,2-*a*:3-*c*]phenazine-13,16-dione. [k] Quasi-reversible couple.

The more negative reduction potentials of the $Os^{3+/2+}$ couples in $[Os(dpq\text{-}6)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ reflect the greater reducing nature of the osmium centre.[57]

The similarity in peak-to-peak separations (ΔE_p) in the cyclic voltammograms of the $M^{3+/2+}$ couples (≈60 mV) compared with those of $[Ru(bipy)_3]^{3+/2+}$ and $Fc^{+/0}$ indicate that all couples involve a single-electron process. The exception to this is in the oxidation of $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$ at 0.90 V ($\Delta E_p = 58$ mV) in MeCN. This couple is assumed to arise from two coincident single-electron processes. Under normal circumstances, ΔE_p is predicted to be 58 and 29 mV for one- and two-electron processes, respectively.[58] However, in the case of class I or weakly coupled class II mixed-valence complexes such as $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{5+}$ the statistical factor ($K_c \approx 4$) would lead to a ≈35 mV difference in the potentials of the $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{5+/4+}$ and $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{6+/5+}$ couples.[59,60] Hence the observed ΔE_p value and the occurrence of only a single oxidation wave for $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$ is consistent with the weak through-bond coupling expected across the insulating dpq-6-dpq ligand in this complex, as well as in $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$.

The electrochemical reductions of the metal complexes in MeCN revealed distortions in the cyclic voltammograms (excluding the first reduction processes), which are most likely due to electrode adsorption.[40,61,62] The electrochemistry in DMF was less complicated, allowing the formal potentials to be obtained for the ligand-based processes (Table 2). The formal potentials of the first reduction processes for $[Ru(dpq\text{-}6)]^{2+}$, $[Os(dpq\text{-}6)]^{2+}$, $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$ and $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ in MeCN are all very similar (*ca.* −1.65 V), and are only slightly more positive than that for $[Ru(bipy)_3]^{2+}$ (−1.70 V). It is inconclusive as to whether the first ligand-based reduction occurs at the dpq unit of the bridge or at bipy. The situation is somewhat different for $[Ru(bipy)_2(dppz)]^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine), where the first reduction occurs ≈0.4 V more positive than that for $[Ru(bipy)_3]^{2+}$.[64] The first reduction processes observed for $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ occur at significantly more positve potentials (by ≈0.5–0.7 V) than for all other metal couples without quinone functionalities, and correspond to reduction of benzoquinone and naphthoquinone, respectively.[65]

Luminescence spectroscopy

The steady-state emission spectra of the three relevant bichromophoric complexes in MeCN are shown in Fig. 2, along with that of the model compound $[Ru(dpq\text{-}6)]^{2+}$. The observed bands correspond to emission from what is assumed to be a Ru^{II}-based ^{3}MLCT excited state, similar to that observed[54] for $[Ru(bipy)_3]^{2+}$. The reduction in emission intensities of the three bichromophoric complexes relative to $[Ru(dpq\text{-}6)]^{2+}$ is indicative of intramolecular quenching of the ^{3}MLCT emissive state. Under the experimental conditions used for the luminescence measurements (concentration ≤ 10^{-5} mol dm^{-3}) intermolecular quenching through ET and EET processes may be disregarded.[27,30]

The emission band maxima, quantum yields and selected excited-state lifetimes of the ruthenium complexes are given in Table 3. From the data it is apparent that the Ru^{II} excited-state emission is quenched by 10, 65 and 97% in $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$, $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$, respectively. As expected, the quantum yield of the homodinuclear complex $[Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$ is identical to that of the mononuclear $[Ru(dpq\text{-}6)]^{2+}$ model, indicating negligible electronic interaction across the norbornylogous bridge in the excited state. The excited state lifetime (τ) for $[Ru(dpq\text{-}6)]^{2+}$ (874 ns) is found to be similar to that observed for $[Ru(bipy)_3]^{2+}$ (850 ns),[66] indicating that substitution of a single bipy ligand by dpq-6 has only a small effect on the lifetime of the ^{3}MLCT emissive state. For $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ no lower-energy emission band emanating from the $[Os^{II}(bipy)_2]$ moiety could be detected upon scanning to longer wavelengths. A lower intensity Os^{II}-based emission at *ca.* 740 nm, akin to that observed for $[Os(bipy)_3]^{2+}$,[67] could not be detected owing to limitations in the source and detector of the spectrofluorimeter used in the present study.

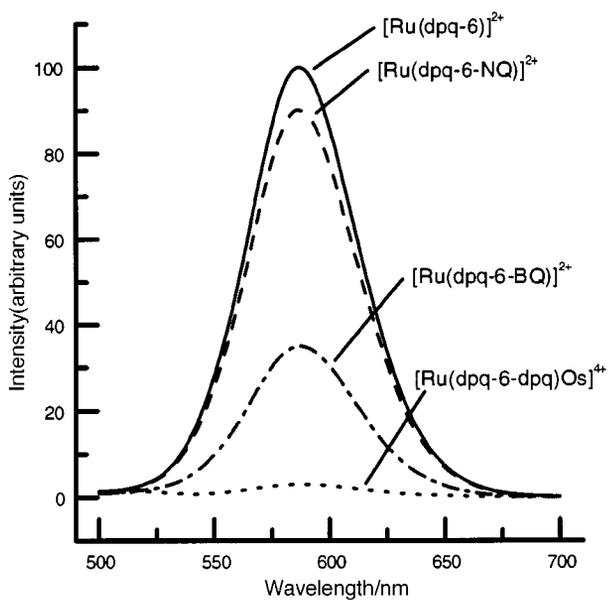


Fig. 2 Steady-state emission spectra of $[Ru(dpq\text{-}6)]^{2+}$ (——), $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ (----), $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ (-.-.-), and $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ (.....) in MeCN at ambient temperature ($\lambda_{exc} = 450$ nm, spectra are normalised for absorbance). Ru = $\{Ru(bipy)_2\}$, Os = $\{Os(bipy)_2\}$.

Table 3 Luminescence properties of complexes[a]

Complex[b]	λ_{em}/nm	τ[c]/ns	$10^2\varphi_{em}$[d]	(φ_{rel})	$10^{-6}\,k$[e]/s^{-1}	$-\Delta G°$/eV
$[Ru(dpq\text{-}6)]^{2+}$	587	874 ± 1	7.2	(100)		
$[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$	587		6.5	(90)	0.12 (ET)	0.09[f]
$[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$	588		2.5	(35)	2.2 (ET)	0.28[f]
$Ru(dpq\text{-}6\text{-}dpq)Ru]^{4+}$	587		7.1	(100)		
$[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$	588		0.21[g]	(3)	15.0[g,h] (EET)	0.36[i]
$[Ru(bpy)_3]^{2+}$	612					
	620[j]	850[j,k]	6.2[i,l]	(87)		
$[Os(dpq\text{-}6)]^{2+}$	[m]					
$[Os(bpy)_3]^{2+}$	740[n]					

[a] In deoxygenated MeCN solution (298 K) with $\lambda_{exc} = 450$ nm. [b] Ru = $\{Ru(bipy)_2\}$, Os = $\{Os(bipy)_2\}$. [c] Excited-state lifetime. [d] Quantum yield of Ru^{II}-based emission (±8%); value in parentheses is φ_{em} relative to $[Ru(dpq\text{-}6)]^{2+}$ as a percentage. [e] Rate constant for ET or EET from eqn. (1). [f] Free energy for ET calculated from eqn. (2). [g] Error = ±33%. [h] Corrected for absorption of [Os(dpq-6)] chromophore at 450 nm. [i] Spectroscopic energy change for EET. [j] From Ref. 66 at 296 K. [k] Error = ±5%. [l] Error = ±15%. [m] Not available. [n] From ref. 67.

Ruthenium–quinone intramolecular quenching. The excited-state quenching observed for both $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ can be attributed to photoinduced ET from the sensitised $[(bipy)_2Ru^{II*}]$ chromophore to the quinone moieties. The rate constants for the ET reactions (k_{ET}) were obtained using eqn. (1).[31] where φ_{em}^0 and τ^0 are the emission

$$k_{ET} = (\varphi_{em}^0 - \varphi_{em})/\varphi_{em}\tau^0 \quad (1)$$

quantum yield and lifetime of the unquenched ruthenium chromophore (in this case $[Ru(dpq\text{-}6)]^{2+}$), respectively, and φ_{em} is the quantum yield of the bichromophoric complex. The intramolecular k_{ET} values for $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ are given in Table 3. The Gibbs free energy or driving force for ET ($-\Delta G^\circ_{ET}$) for the quinone complexes is given in Table 3, and can be calculated from the Weller;[68,69] eqn. (2)

$$-\Delta G^0_{Et} = E_{0\text{-}0}(Ru^{II*}) - E(D^{+/0}) + E(A^{0/-}) + \frac{14.45 q_1 q_2}{\varepsilon R_c} \quad (2)$$

where $E_{0\text{-}0}(Ru^{II*})$ is the Ru^{II}-based excited-state energy, $E(D^{+/0})$ and $E(A^{0/-})$ are the ground-state reduction potentials for the donor and acceptor couples, respectively; and the final term represents the coulombic attraction energy between D^+ and A^- given by charges q_1 and q_2, whilst ε and R_c are the relative permittivity of the solvent and the centre-to-centre distance between D and A in angstroms, respectively. The $E_{0\text{-}0}(Ru^{II*})$ term is best approximated[27,66] from the emission band maxima of relevant reference compounds at 77 K. For the related $[Ru(bipy)_2(phen)]^{2+}$ complex in 4:1 (v/v) ethanol–methanol matrix at 77 K,[70] $\lambda_{em} = 575$ nm which corresponds to $E_{0\text{-}0}(Ru^{II*}) = 2.16$ eV. The $E(D^{+/0})$ and $E(A^{0/-})$ terms for both $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ are obtained directly from the electrochemical data in Table 2. The coulombic term is calculated to be *ca.* −0.08 eV for both quinone complexes, assuming formation of $[Ru^{III}(dpq\text{-}6\text{-}Q^-)]^{2+}$ (Q = quinone) and R_c of ≈14 Å.

For both $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$, $-\Delta G^\circ_{ET}$ is positive and indicates that intramolecular ET is exergonic and should take place. The ET rate for $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ is faster than that for $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ (by an order of magnitude) and this is consistent with ET occurring within the Marcus[71,72] normal region. This follows from the driving force data where $-\Delta G^\circ_{ET}$ for $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ (0.28 eV) is greater than that in $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ (0.09 eV). Molecular modeling of the dpq-6-BQ ligand at the AM1 level reveals an edge-to-edge separation of 7.03 Å between the dpq and benzoquinone rings, and over such distances the exited-state emission quenching is consistent with through-bond ET. The quenching in $[Ru(dpq\text{-}6\text{-}BQ)]^{2+}$ and $[Ru(dpq\text{-}6\text{-}NQ)]^{2+}$ is most likely due to ET rather than triplet–triplet EET, since the triplet states of benzoquinone and naphthoquinone lie *ca.* 0.2 and 0.34 eV, respectively, above the emissive ^{3}MLCT state.[73]

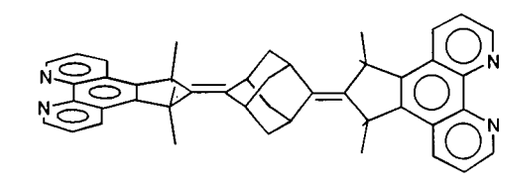
Ruthenium–osmium intramolecular quenching. The steady-state emission spectrum of $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ in MeCN reveals 97% quenching of the Ru^{II}-based emission at 588 nm [$\varphi_{em} = (2.1 \pm 0.7) \times 10^{-3}$]. However, the [Os(dpq-6)] chromophore also absorbs at 450 nm, which corresponds to a corrected quenching of 93%, and an effective quantum yield for the dinuclear complex of 5.0×10^{-3}. Using this corrected value for φ_{em} and eqn. (1), the rate of intramolecular quenching of the ^{3}MLCT state in $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ is calculated to be $(1.5 \pm 0.5) \times 10^7$ s^{-1}.

The observed quenching is most likely due to energy transfer rather than to electron transfer since oxidative quenching to form $[Ru^{I}(dpq\text{-}6\text{-}dpq)Os^{III}]^{4+}$ is calculated to be weakly endergonic ($-\Delta G^\circ_{ET}$ = *ca.* −0.06 eV), as is reductive quenching to form $[Ru^{III}(dpq\text{-}6\text{-}dpq)Os^{I}]^{4+}$ ($-\Delta G^\circ_{ET}$ = *ca.* −0.35 eV).†[29,74] By contrast, quenching due to intramolecular EET would be exergonic ($-\Delta G^\circ_{EET}$ = *ca.* 0.36 eV),‡[17,29] eqn. (3).

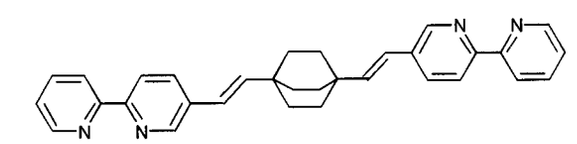
$$[Ru^{II*}(dpq\text{-}6\text{-}dpq)Os^{II}]^{4+} \longrightarrow [Ru^{II}(dpq\text{-}6\text{-}dpq)Os^{II*}]^{4+} \quad (3)$$

Quenching due to intramolecular EET is also highly likely based upon the direct overlap of the $[Ru^{II}(dpq\text{-}6)]$-based emission ($\lambda_{em} = 588$ nm) and ground-state absorption of $[Os^{II}(dpq\text{-}6)]$ ($\lambda_{max} = 572$ nm, $\varepsilon \approx 5$ dm^3 mol^{-1} cm^{-1}). It is most likely that the EET observed in the $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ system takes place by a through-bond rather than through-space mechanism on the grounds of precedent in related systems incorporating organic donor–acceptor groups.[11] However, confirmation must await distance dependence studies of the dynamics of EET in systems possessing variable bridge length.

It is interesting to compare k_{EET} for $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ with the corresponding values measured for relevant literature systems. For the rigid complex $[(bipy)_2Ru^{II}(PAP)Os^{II}(bipy)_2]^{4+}$ of Belser and co-workers,[30,35] $k_{EET} = 5.2 \times 10^7$ s^{-1} at 298 K in MeCN.§ A more detailed analysis on the semi-rigid $[(bipy)_2Ru^{II}(bipy\text{-}S\text{-}bipy)Os^{II}(bipy)_2]^{4+}$ by De Cola *et al.*[17] reported $k_{EET} = 5.0 \times 10^7$ s^{-1} under similar conditions; EET involving the ^{3}MLCT levels was postulated to occur predominantly by a Dexter[75] (exchange) mechanism. A similar mechanism is inferred for the excited-state emission quenching observed in $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$, although elucidation of the exact mechanism will require further photophysical studies.



PAP



bipy-S-bipy

Experimental

General

The solvents methanol, acetone, anhydrous diethyl ether, tetrahydrofuran and chloroform were all AR grade and used as received. Acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide were HPLC grade. Solvents were purchased from either Aldrich or Rhône-Poulenc. Ethanol, dichloromethane and triethylamine were distilled before use using literature methods.[76] Doubly distilled water was used throughout. *N*-Methylmorpholine (NMO), pyridine–sulfur trioxide complex (pyridine-SO_3), ammonium cerium(IV)

† Driving force values calculated using excited state properties and ground state reduction potentials of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$.

‡ Calculated from the difference in $E_{0\text{-}0}(Ru^{II*})$ and $E_{0\text{-}0}(Os^{II*})$ energies, *ca.* 2.16 and 1.8 eV, respectively. The $E_{0\text{-}0}(Os^{II*})$ value was derived from the emission band of $[Os(phen)_3]^{2+}$ in 1:4 (v/v) ethanol–methanol at 77 K.[66]

§ It is interesting to consider the similarity in k_{EET} values (*ca.* 10^7) observed between the totally rigid $[Ru(dpq\text{-}6\text{-}dpq)Os]^{4+}$ and $[Ru(PAP)Os]^{4+}$ complexes, considering the longer bridge length in the latter. Energy minimisation calculations at the AM1 level on the dpq-6-dpq (C_{2v} symmetry) and PAP ligand (D_{2d} symmetry) of Belser and co-workers[30,35] yielded edge-to-edge separations of 7.29 and 10.75 Å, respectively.

nitrate (CAN), lead(IV) dioxide, boron tribromide and ammonium hexafluorophosphate were AR grade (Aldrich) and used as received. Osmium tetraoxide (OsO_4) catalytic solution was prepared according to the procedure of Sharpless and Akashi.[77] The complex *cis*-[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (99%, bipy = 2,2′ bipyridine) was purchased from Strem Chemicals. 5,6-Diamino-1,10–phenanthroline,[40] [Ru(bipy)$_3$][PF$_6$]$_2$,[78] *cis*-[Os(bipy)$_2$Cl$_2$],[50] 6-dione (**Ia**),[38] DMB-6-dione (**Ib**),[38] DMN-6-dione (**Ic**),[38] and 6-diene (**V**)[43] were prepared according to literature procedures. The salt [NBu$^n_4$][PF$_6$] was prepared according to a literature procedure[79] and recrystallised from ethanol–diethyl ether.

Microanalyses were conducted by ANU Microanalytical Laboratories and by Dr. R. Finlayson of the University of New South Wales. The ^{1}H NMR spectra were obtained on a Bruker AC300F (300 MHz) spectrometer with chemical shifts downfield from TMS (from residual solvent signal). ^{13}C NMR spectra were obtained on the same spectrometer (75.5 MHz) with chemical shifts reported downfield from TMS. Assignments were determined with aid of 90 and 135° DEPT experiments. Matrix assisted laser desorption ionisation linear time-of-flight (MALDI) mass spectra were recorded on a Finnigan Lasermat 2000 spectrometer. Sample solutions were mixed with matrix solutions of either 2-cyano-4-hydroxycinnamic acid or 2,5-dihydroxybenzoic acid and allowed to dry at room temperature. Electrospray mass spectra were recorded on a VG Quattro mass spectrometer with an ion source temperature of 60 °C, a capillary voltage of 4 kV and a counter electrode voltage of 1 kV. Samples were dissolved in a mixture of aqueous acetonitrile (MeCN–water, 1 : 1) with 1% acetic acid added.

General synthetic procedures

All syntheses were conducted under an argon atmosphere (high purity, CIG). Column chromatography was carried out using Silica Gel 60 (0.040–0.063 mesh, Merck 9385). For purification of neutral ligands, unless otherwise stated, the eluting solvent was methanol–dichloromethane–aqueous ammonia (3 : 100 : 0.33, v/v). Size-exclusion chromatography was carried out using Sephadex LH-20 resin (Pharmacia) and methanol–MeCN (2 : 1, v/v) as the eluting solvent, with the complex isolated by removal of solvent under reduced pressure (≈50 °C). Metal complexes were isolated as hexafluorophosphate salts *via* metathesis with [NH$_4$][PF$_6$] using the following method: saturated aqueous [NH$_4$][PF$_6$] (1 cm^3) was added and the solution volume reduced to ≈2–5 cm^3 under reduced pressure (≈50 °C); the resulting precipitate was filtered off and washed with cold water (5 cm^3) followed by diethyl ether (3 × 50 cm^3) and air dried under suction. Complexes were recrystallised from acetone–water–saturated aqueous [NH$_4$][PF$_6$]. All purified ligands and metal complexes were dried *in vacuo* over P$_2$O$_5$ and stored in the dark.

Synthesis

12,15-Dimethoxy-10b,16b-dimethyl-10,10a,10b,10c,11,16,16a,16b,16c,17-decahydro-10,17 : 11,16-dimethanonaphtho-[2″,3″ : 3′,4′]cyclobuta[1′,2′ : 3,4]cyclobuta[1,2-*l*]dipyrido[3,2-*a* : 2′,3′-*c*]phenazine IIb (dpq-6-DMB). A solution of compound **Ib**[38] (0.36 g, 0.95 mmol) in chloroform (2 cm^3) was added dropwise to a stirring suspension of 5,6-diamino-1,10-phenanthroline (0.22 g, 1.05 mmol) in ethanol (25 cm^3) heated to reflux. The resulting solution was heated at reflux for 4 h in the dark. The mixture was cooled and the solvent removed under reduced pressure. To remove any unchanged 5,6-diamino-1,10-phenanthroline, the mixture was redissolved in chloroform (40 cm^3), filtered and the solvent removed once more under reduced pressure. The crude product was dissolved in the minimum volume of dichloromethane and chromatographed on silica gel, affording compound **IIb** (dpq-6-DMB) (465 mg, 88%). Owing to its extreme insolubility satisfactory elemental analysis could not be obtained. However, the identity of the compound was unambiguously determined from its spectroscopic properties. MALDI mass spectrum: *m/z* 554, [*M* + H]$^+$. ^{1}H NMR (CDCl$_3$): δ 9.63 (2 H, d, *J* = 8.1), 9.41 (2 H, d, *J* = 3.9), 7.90 (2 H, dd, *J* = 7.8, 4.5), 6.56 (2 H, s), 3.76 (6 H, s), 3.69 (2 H, s), 3.58 (2 H, s), 2.27 (1 H, br d, *J* = 10.5), 2.23 (2 H, s), 2.05 (1 H, br d, *J* = 10.8), 2.00 (2 H, s), 1.83 (1 H, br d, *J* = 9.6), 1.64 (1 H, br d, *J* = 9.3 Hz) and 1.13 (6 H, s). ^{13}C NMR (CDCl$_3$): δ 163.27 (C$_q$), 150.85 (CH), 147.77 (C$_q$), 145.19 (C$_q$), 137.12 (C$_q$), 136.33 (C$_q$), 133.45 (CH), 127.75 (C$_q$), 123.87 (CH), 109.13 (CH), 56.03 (CH), 49.73 (CH), 48.30 (CH), 44.40 (CH), 43.55 (CH$_2$), 43.20 (C$_q$), 40.97 (CH$_2$), 40.32 (CH) and 9.49 (CH$_3$).

12,17-Dimethoxy-10b,18b-dimethyl-10,10a,10b,10c,11,18,18a,18b,18c,19-decahydro-10,19 : 11,18-dimethanoanthra-[2″,3″ : 3′,4′]cyclobuta[1′,2′ : 3,4]cyclobuta[1,2-*l*]dipyrido[3,2-*a* : 2′,3′-*c*]phenazine IIc (dpq-6-DMN). The annulation of compound **Ic**[38] (170 mg, 0.40 mmol) with 5,6-diamino-1,10-phenanthroline (100 mg, 0.48 mmol) in ethanol–chloroform (6 cm^3: 2 cm^3) was performed according to the above procedure. Purification on silica gel afforded **IIc** (185 mg, 77%). Similar to compound **IIb** above, the identity of the compound was unambiguously determined from its spectroscopic properties. MALDI mass spectrum: *m/z* 603, [*M* + H]$^+$. ^{1}H NMR (CDCl$_3$): δ 9.49 (2 H, dd, *J* = 8.1, 2.1), 9.23 (2 H, dd, *J* = 3.9, 1.6), 8.04 (2 H, dd, *J* = 6.3, 3.3), 7.75 (2 H, dd, *J* = 8.4, 4.5), 7.41 (2 H, dd, *J* = 6.6, 3.3), 3.95 (6 H, s), 3.76 (2 H, s), 3.72 (2 H, s), 2.35–2.25 (3 H, br m), 2.21 (2 H, s), 2.09–2.02 (2 H, br m), 1.79 (1 H, br d, *J* = 10 Hz) and 1.19 (6 H, s). ^{13}C NMR (CDCl$_3$): δ 162.65 (C$_q$), 151.29 (CH), 146.50 (C$_q$), 144.32 (C$_q$), 137.35 (C$_q$), 134.67 (C$_q$), 132.58 (CH), 127.80 (C$_q$), 127.39 (C$_q$), 125.06 (CH), 123.54 (CH), 121.94 (CH), 61.78 (CH), 50.66 (CH), 44.34 (CH), 43.66 (C$_q$), 42.79 (CH$_2$), 40.84 (CH$_2$), 40.55 (CH) and 9.62 (CH$_3$).

10b,18b-Dimethyl-10,10a,10b,10c,11,18,18a,18b,18c,19-decahydro-10,19 : 11,18-dimethanoanthra[2″,3″ : 3′,4′]cyclobuta-[1′,2′ : 3,4]cyclobuta[1,2-*l*]dipyrido[3,2-*a* : 2′,3′-*c*]phenazine-12,17-dione, IV (dpq-6-NQ). A solution of aqueous saturated CAN (≈0.5 cm^3) was added dropwise to a stirring solution of compound **IIc** (112 mg, 0.19 mmol) in tetrahydrofuran (5 cm^3) and MeCN (10 cm^3) until no further colour change was observed. After stirring the solution for 1 h a second aliquot of saturated CAN (≈0.5 cm^3) was added, and the mixture stirred for 1 h. Water (20 cm^3) was added and the mixture extracted into chloroform (50 cm^3). The organic extract was washed with brine (30 cm^3), dried over anhydrous Na$_2$SO$_4$ and the solvent removed under reduced pressure. The crude product was dissolved in the minimum volume of dichloromethane and chromatographed on silica gel affording **IV** (100 mg, 94%) as a bright yellow solid. Similar to compound **IIb** above, the identity of **IV** was unambiguously determined from its spectroscopic properties. MALDI mass spectrum: *m/z* 573, [*M* + H]$^+$. ^{1}H NMR (CDCl$_3$): δ 9.46 (2 H, dd, *J* = 8.2, 2.1), 9.20 (2 H, dd, *J* = 4.1, 1.5), 7.97 (2 H, dd, *J* = 5.6, 3.0), 7.72 (2 H, dd, *J* = 8.1, 4.6), 7.60 (2 H, dd, *J* = 5.7, 2.8), 3.69 (2 H, s), 3.62 (2 H, s), 2.28–2.16 (3 H, m), 2.12–2.00 (3 H, m), 1.75 (1 H, d, *J* = 9.8), 1.61 (1 H, d, *J* = 9.8 Hz) and 1.11 (6 H, s). ^{13}C NMR (CDCl$_3$): δ 181.61 (C$_q$), 162.55 (C$_q$), 154.07 (C$_q$), 151.31 (CH), 146.50 (C$_q$), 137.36 (C$_q$), 133.28 (CH), 132.86 (C$_q$), 132.65 (CH), 127.37 (C$_q$), 126.19 (CH), 123.58 (CH), 48.60 (CH), 48.49 (CH), 44.39 (CH), 43.36 (C$_q$), 41.60 (CH$_2$), 41.44 (CH), 40.89 (CH$_2$) and 9.40 (CH$_3$).

10b,14b-Dimethyl-10,10a,10b,10c,11,12,13,14,14a,14b,14c,15-dodecahydro-10,15 : 11,14-dimethanobenzo[3′,4′]cyclobuta-[1′,2′ : 3,4]cyclobuta[1,2-*l*]dipyrido[3,2-*a* : 2′,3′-*c*]phenazine hydrate IIa (dpq-6·H$_2$O). The annulation of compound **Ia**[38] (193 mg, 0.71 mmol) with 5,6-diamino-1,10-phenanthroline

(165 mg, 0.78 mmol) in ethanol–chloroform (6 cm^3 : 2 cm^3) was performed according to the procedure for **IIb** above. Purification on silica gel, using methanol–dichloromethane–aqueous ammonia (4 : 100 : 0.33, v/v), afforded **IIa** (231 mg, 73%) (Found: C, 78.58; H, 6.13; N, 12.14. Calc. for $C_{30}H_{30}N_4O$: C, 77.89; H, 6.54; N, 12.11%). MALDI mass spectrum: *m*/*z* 445, $[M + H]^+$. ^{1}H NMR ($CDCl_3$): δ 9.51 (2 H, dd, J = 10.5, 2.0), 9.24 (2 H, dd, J = 4.5, 1.5), 7.76 (2 H, dd, J = 7.0, 4.1), 3.62 (2 H, s), 2.29 (2 H, s), 2.23–2.13 (3 H, m), 2.02–1.95 (3 H, m), 1.53–1.45 (2 H, br m), 1.29 (1 H, br d, J= 10 Hz), 1.09–1.01 (2 H, m) and 0.98 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 163.02 (C_q), 151.31 (CH), 146.56 (C_q), 137.34 (C_q), 132.66 (CH), 127.54 (C_q), 123.61 (CH), 52.49 (CH), 48.54 (CH), 44.40 (C_q), 44.30 (CH), 40.79 (CH_2), 36.24 (CH), 35.06 (CH_2), 28.46 (CH_2) and 9.57 (CH_3).

10b,22b-Dimethyl-10,10a,10b,10c,11,22,22a,22b,22c,23-decahydro-10,23 : 11,22-dimethanodipyrido[3′′′,2′′′ : 6″,7″; 2′′′′,3′′′′ : 8″,9″]phenazino[2″,3″ : 3′,4′]cyclobuta[1′,2′ : 3,4]cyclobuta[1,2-*l*]dipyrido[3,2-*a* : 2′,3′-*c*]phenazine tetrahydrate VIII (dpq-6-dpq·4H_2O). An OsO_4 solution (2.4 cm^3, 0.05 mmol) was added to a stirred suspension of compound **V**[43] (1 g, 4.2 mmol) and NMO (2.4 g, 21 mmol) in 1,4-dioxane (10 cm^3) and water (≈0.25 cm^3), and the resulting solution stirred at room temperature for 48 h. Dichloromethane (20 cm^3) was added, followed by aqueous $Na_2S_2O_5$ (3 g in 30 cm^3, 16 mmol). The white precipitate was filtered off and washed with water (50 cm^3), dichloromethane (40 cm^3), ethyl acetate (80 cm^3), and diethyl ether (80 cm^3), affording **VI** (0.87 g, 68%), which was used without further purification. ^{1}H NMR [$(CD_3)_2SO$]: δ 4.63 (br s, OH), 3.36 (4 H, s), 1.82 (8 H, br s), 1.66 (2 H, d, J = 10.2), 1.23 (2 H, d, J = 10.7 Hz) and 0.64 (6 H, s). ^{13}C NMR [$(CD_3)_2SO$]: δ 73.47 (COH), 47.18 (CH), 43.50 (CH), 43.08 (C_q), 28.85 (CH_2) and 10.02 (CH_3).

Triethylamine (6 cm^3, 43 mmol), followed by compound **VI** (0.83 g, 2.71 mmol), were added sequentially to a stirred solution of pyridine–SO_3 (4.3 g, 27.1 mmol) in dimethyl sulfoxide (16 cm^3). The resulting yellow-orange solution was stirred for 90 min in the dark. Dichloromethane (20 cm^3) was added and the reaction quenched with water (30 cm^3). The aqueous layer was neutralised (to pH ≈6) using HCl (0.2 M). The solution was filtered and the filtrate extracted with dichloromethane (150 cm^3). The green-brown residue was washed with water (30 cm^3), followed by dichloromethane (80 cm^3). The combined dichloromethane fractions were washed with HCl (0.2 M, 2 × 80 cm^3), followed by aqueous brine (3 × 80 cm^3) and dried (anhydrous Na_2SO_4). The solvent was removed by distillation under high vacuum (50 °C) for 2 h, affording the crude dione **VII** (0.30 g, 38%) as a yellow solid which was used in the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 0.94 (s, largest CH_3 peak).

A stirred solution of 5,6-diamino-1,10-phenanthroline (94 mg, 0.45 mmol) in ethanol (1.5 cm^3) was heated to reflux for 5 min. To this, tetraone **VII** (55 mg, 0.18 mmol) in chloroform (2 cm^3) was added dropwise. The resulting mixture was heated at reflux in the dark for 20 h. The solvent was removed under reduced pressure, the crude product dissolved in dichloromethane and chromatographed on silica gel. Elution with methanol–dichloromethane–aqueous ammonia (2 : 100 : 0.33 v/v; increasing to 5 : 100 : 0.33), afforded **VIII** (dpq-6-dpq·4H_2O) (62 mg, 52%) as a light solid. Similar to compound **IIb** above, the identity of **VIII** was unambiguously determined from its spectroscopic properties. MALDI mass spectrum: *m*/*z* 647, $[M + H]^+$. ^{1}H NMR ($CDCl_3$): δ 9.49 (4 H, dd, J = 8.4, 1.6), 9.22 (4 H, dd, J = 4.1, 1.5), 7.75 (4 H, dd, J = 8.2, 4.6), 3.76 (4 H, s), 2.34 (4 H, s), 2.31 (2 H, d, J = 10.8), 2.12 (2 H, d, J = 10.8 Hz) and 1.25 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 162.46 (C_q), 151.41 (CH), 146.53 (C_q), 137.48 (C_q), 132.67 (CH), 127.37 (C_q), 123.64 (CH), 48.54 (CH), 44.44 (CH), 43.84 (C_q), 41.03 (CH_2) and 9.71 (CH_3).

[Ru_2(dpq-6-BQ)][PF_6]$_2$·4H_2O (2b) [Ru = Ru(bipy)$_2$]. A solution of 25% (w/v) boron tribromide–dichloromethane (2.2 cm^3, 2.2 mmol of BBr_3) was slowly added dropwise to a solution of compound **IIb** (200 mg, 0.36 mmol) in dichloromethane (20 cm^3) at 0 °C. The resulting solution was slowly warmed to room temperature and stirred for 16 h in the dark. It was cooled to 0 °C, water added (10 cm^3), and the pH adjusted to 7–8 with saturated $NaHCO_3$. The resulting mixture was heated to reflux for 15 min, cooled to room temperature and the dichloromethane removed under reduced pressure. The aqueous solution was filtered and the crude product washed with water (20 cm^3) and dichloromethane (10 cm^3), affording **III** (187 mg, 98%). ^{1}H NMR [$(CD_3)_2SO$]: δ 9.39 (2 H, br d, J = 8), 9.16 (2 H, br s), 8.34 (br s, OH), 7.88 (2 H, br s), 6.26 (2 H, br s), 3.67 (2 H, br s), 3.47 (2 H, br s), 2.25–2.00 (4 H, br m), 1.87 (2 H, br s), 1.72 (1 H, br d, J = 8), 1.44 (1 H, br d, J = 9 Hz) and 1.06 (6 H, br s).

A stirred suspension of compound **III** (50 mg, 0.095 mmol) and *cis*-[Ru(bipy)$_2$$Cl_2$]·2$H_2O$ (55 mg, 0.105 mmol) in ethanol–water (1 : 1, 8 cm^3) was heated at reflux for 15 h in the dark. It was diluted to ≈40 cm^3 with ethanol–water (1 : 1), filtered, and the crude complex isolated by metathesis with [NH_4][PF_6]. Initial purification was afforded by size-exclusion chromatography, with the desired product corresponding to the main orange band. The complex was further purified by chromatography on silica gel eluting with MeCN–water–saturated KNO_3 (100 : 10 : 1, R_f = 0.33). Metathesis with [NH_4][PF_6] afforded complex **1** (72 mg, 62%) as an orange solid. Electrospray mass spectrum: *m*/*z* 1083, $[M - PF_6]^+$; 468, $[M - 2PF_6]^{2+}$.

A suspension of complex **1** (62 mg, 0.050 mmol) and lead(IV) dioxide (1.5 g, 5.8 mmol) in dichloromethane (10 cm^3) was stirred for 8 h in the dark. The lead(IV) dioxide was removed by filtration and the residue washed with dichloromethane (10 cm^3). The organic fractions were combined and the solvent was removed under reduced pressure. The complex was recrystallised affording **2b** (34 mg, 55%) as a red microcrystalline solid (Found: C, 49.88; H, 3.36; N, 8.34. Calc. for $C_{54}H_{50}F_{12}N_8O_6P_2Ru$: C, 49.97; H, 3.88; N, 8.63%). Electrospray mass spectrum: *m*/*z* 1081, $[M - PF_6]^+$; 468, $[M - 2PF_6]^{2+}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.61 (2 H, d, J = 8.2), 8.86-8.77 (4 H, m), 8.48 (2 H, d, J = 5.1), 8.28–7.93 (10 H, m), 7.66–7.58 (2 H, m), 7.40–7.30 (2 H, m), 6.58 (2 H, s), 3.81 (2 H, s), 3.45 (2 H, s), 2.36 (1 H, d, J = 10.8), 2.28 (2 H, s), 2.16 (1 H, d, J = 10.3), 1.77 (1 H, d, J = 9.8), 1.59 (1 H, d J = 9.8 Hz) and 1.15 (6 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 184.48 (C_q), 165.92 (C_q), 158.43 (C_q), 158.20 (C_q), 154.05 (CH), 153.15 (CH), 153.02 (CH), 152.23 (C_q), 149.29 (C_q), 139.11 (CH), 138.97 (CH), 138.04 (C_q), 137.09 (CH), 133.99 (CH), 131.30 (C_q), 128.82 (CH), 128.62 (CH), 127.91 (CH), 125.39 (CH), 125.32 (CH), 49.40 (CH), 49.18 (CH), 45.37 (CH), 44.15 (C_q), 42.49 (CH_2), 41.89 (CH), 41.72 (CH_2) and 9.51 (CH_3).

[Ru(dpq-6-NQ)][PF_6]$_2$·H_2O 2c [Ru = Ru(bipy)$_2$]. A suspension of compound **IV** (50 mg, 0.087 mmol) with *cis*-[Ru(bipy)$_2$$Cl_2$]·2$H_2O$ (50 mg, 0.096 mmol) in ethanol–water (1 : 1, 8 cm^3) was heated at reflux for 15 h in the dark. It was diluted to ≈40 cm^3 with ethanol–water (1 : 1), filtered, and the crude complex isolated by metathesis with [NH_4][PF_6]. Initial purification was afforded by size-exclusion chromatography, with the desired product corresponding to the main orange band. The complex was further purified by chromatography on silica gel eluting with MeCN–water–saturated KNO_3 (100 : 10 : 1, R_f = 0.30). Metathesis with [NH_4][PF_6], followed by recrystallisation, afforded **2c** (55 mg, 50%) as a red microcrystalline solid (Found: C, 53.84; H, 3.67; N, 8.58. Calc. for $C_{58}H_{46}F_{12}N_8O_3P_2Ru$: C, 53.83; H, 3.58; N, 8.66%). Electrospray mass spectrum: *m*/*z* 1131, $[M - PF_6]^+$; 493, $[M - 2PF_6]^{2+}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.60 (2 H, dd, J = 8.2, 1.0), 8.88–8.74 (4 H, m), 8.49 (2 H, dd, J = 5.4, 1.0), 8.28–8.20 (2 H, m), 8.20–7.92

(10 H, m), 7.82–7.73 (2 H, m), 7.67–7.57 (2 H, m), 7.41–7.25 (2 H, m), 3.82 (2 H, s), 3.59 (2 H, s), 2.37 (1 H, d, J = 10.8), 2.29 (2 H, s), 2.18 (1 H, d, J = 10.3), 2.11 (2 H, s), 1.83 (1 H, d, J = 9.2), 1.68 (1 H, d, J = 10.3 Hz) and 1.18 (6 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 181.83 (C_q), 165.84 (C_q), 158.35 (C_q), 158.11 (C_q), 158.04 (C_q), 154.70 (CH), 153.97 (CH), 153.09 (CH), 152.94 (CH), 149.22 (C_q), 139.02 (CH), 138.90 (CH), 138.84 (CH), 137.95 (C_q), 134.31 (CH), 133.88 (CH), 131.22 (C_q), 128.74 (CH), 128.55 (CH), 127.81 (CH), 126.62 (CH), 125.30 (CH), 49.40 (CH), 49.14 (CH), 45.29 (CH), 44.19 (C_q), 42.21 (CH), 41.65 (CH_2) and 9.49 (CH_3).

[Ru(dpq-6-dpq)Ru$_2$][PF$_6$]$_4$·2Me$_2$CO·2H$_2$O 4 [Ru = Ru(bipy)$_2$]. A mixture of *cis*-[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (68 mg, 0.13 mmol) and compound **VIII** (40 mg, 0.062 mmol) in ethanol–water (1 : 1, 8 cm^3) was heated at reflux for 24 h in the dark. The reaction mixture was cooled to room temperature and the crude complex isolated by metathesis with [NH_4][PF_6] (see general method). It was initially purified by size-exclusion chromatography, with the desired product corresponding to the inital orange band. Further purification was afforded by chromatography on silica gel eluting with MeCN–water–saturated KNO_3 (20 : 2 : 1 v/v, R_f = 0.26). Metathesis with [NH_4][PF_6], followed by recrystallisation, afforded complex **4** (52 mg, 41%) as a red microcrystalline solid (Found: C, 47.73; H, 2.64; N, 9.46. Calc. for $C_{44}H_{39}F_{12}N_8O_2P_2Ru$: C, 47.92; H, 3.47; N, 10.16%). Electrospray mass spectrum: *m*/*z* 882, [M − 2PF$_6$]$^{2+}$; 539, [M − 3PF$_6$]$^{3+}$; 369, [M − 4PF$_6$]$^{4+}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.60 (2 H, d, J = 7.7), 9.59 (2 H, d, J = 7.7), 8.89–8.71 (8 H, m), 8.51–8.43 (4 H, m), 8.29–8.19 (2 H, m), 8.19–7.87 (18 H, m), 7.65–7.57 (4 H, m), 7.40–7.32 (2 H, m), 7.29–7.22 (2 H, m), 3.86 (4 H, s), 2.45 (2 H, d, J = 10.7), 2.37 (4 H, s), 2.10 (2 H, d, J = 10.2 Hz) and 1.33 (6 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 165.75 (C_q), 158.45 (C_q), 158.22 (C_q), 158.08 (C_q), 154.04 (C_q), 153.13 (CH), 153.05 (CH), 149.31 (C_q), 139.11 (CH), 138.98 (CH), 138.12 (C_q), 133.99 (CH), 131.36 (C_q), 131.30 (C_q), 128.80 (CH), 128.65 (CH), 127.90 (CH), 125.37 (CH), 125.25 (CH), 49.24 (CH), 45.50 (CH), 44.86 (C_q), 41.80 (CH_2) and 9.78 (CH_3).

[Ru(dpq-6-dpq)Os][PF$_6$]$_4$·3H$_2$O 5 [Ru = Ru(bipy)$_2$, Os = Os(bipy)$_2$]. A suspension of *cis*-[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (48 mg, 0.093 mmol) in ethanol–chloroform (15 cm^3: 3 cm^3) was added dropwise to a solution of compound **VIII** (60 mg, 0.093 mmol) in 1,2-ethanediol–HCl (0.2 M) (9 cm^3: 1 cm^3) which was heated at reflux for 60 min. Excess of chloroform was removed by purging the mixture with argon for 5 min (solution volume reduced to ≈10 cm^3). The stirred solution was heated to 120 °C in the dark for 3 h, after which it was red. The solution was cooled to room temperature, water added (5 cm^3) and the solution filtered. The crude complex was isolated by metathesis using [NH_4][PF_6] and purified by size-exclusion chromatography. The second orange band corresponded to the desired product, **3** (38 mg, 31%). ^{1}H NMR [$(CD_3)_2CO$]: δ 9.53–9.43 (2 H, m), 9.41–9.34 (2 H, m), 8.99–8.91 (2 H, m), 8.85–8.70 (4 H, m), 8.47–8.42 (2 H, m), 8.25–7.89 (10 H, m), 7.81–7.70 (2 H, m), 7.66–7.56 (2 H, m), 7.40–7.34 (1 H, m), 7.27–7.20 (1 H, m), 3.86 (2 H, s), 3.79 (2 H, s), 2.48–2.37 (6 H, m), 2.22 (2 H, d, J = 10.3 Hz) and 1.33 (6 H, s). Complex **3** was used in the next step without further purification.

A stirred suspension of complex **3** (38 mg, 0.028 mmol) and *cis*-[Os(bipy)$_2$Cl$_2$] (18 mg, 0.031 mmol) in aqueous 1,2-ethanediol (5% v/v, 3 cm^3) was protected from light and heated to 150 °C for 2 h. The temperature was lowered to 120 °C and the solution heated at this temperature for 14 h. The mixture was cooled to room temperature and the crude complex isolated by metathesis using [NH_4][PF_6]. It was purified by size-exclusion chromatography, with the main green band corresponding to the desired product, followed by recrystallisation, affording **5** (32 mg, 55%) as a black microcrystalline solid (Found: C, 44.71; H, 2.55; N, 10.05. Calc. for $C_{82}H_{68}F_{24}N_{16}O_3OsP_4Ru$: C, 44.84; H, 3.12; N, 10.20%). Electrospray mass spectrum: *m*/*z* 926, [M − 2PF$_6$]$^{2+}$; 569, [M − 3PF$_6$]$^{3+}$; 391, [M − 4PF$_6$]$^{4+}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.60 (1 H, d, J = 8.2), 9.59 (1 H, d, J = 8.7), 9.37 (1 H, d, J = 8.2), 9.36 (1 H, d, J = 8.2), 8.86–8.71 (8 H, m), 8.48–8.43 (2 H, m), 8.41–8.35 (2 H, m), 8.26–8.18 (2 H, m), 8.18–7.77 (18 H, m), 7.64–7.57 (2 H, m), 7.54–7.48 (2 H, m), 7.39–7.33 (1 H, m), 7.28–7.22 (2 H, m), 7.19–7.12 (1 H, m), 3.86 (4 H, s), 2.44 (2 H, d, J = 10.7), 2.37 (4 H, s), 2.21 (2 H, d, J = 10.3 Hz) and 1.32 (6 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 165.17 (C_q), 160.31 (C_q), 160.11 (C_q), 159.97 (C_q), 158.42 (C_q), 158.20 (C_q), 158.05 (C_q), 154.03 (CH), 153.22 (CH), 153.11 (C_q), 153.02 (CH), 152.98 (C_q), 152.28 (CH), 152.21 (CH), 152.16 (CH), 152.10 (CH), 151.56 (C_q), 149.27 (C_q), 139.08 (CH), 138.97 (C_q), 138.91 (CH), 138.45 (CH), 138.33 (CH), 138.23 (C_q), 138.19 (C_q), 138.13 (C_q), 138.09 (C_q), 133.95 (CH), 133.53 (CH), 131.54 (C_q), 131.48 (C_q), 131.31 (C_q), 131.26 (C_q), 129.24 (CH), 129.08 (CH), 128.79 (CH), 128.62 (CH), 128.15 (CH), 127.88 (CH), 125.54 (CH), 125.44 (C_q), 125.36 (CH), 125.25 (CH), 49.21 (CH), 45.37 (CH), 44.83 (C_q),.41.77 (CH_2) and 9.75 (CH_3).

[Ru(dpq-6)][PF$_6$]$_2$·H$_2$O 6 [Ru = Ru(bipy)$_2$]. The reaction of compound **IIa** (50 mg, 0.11 mmol) with *cis*-[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (64 mg, 0.124 mmol) was performed according to the procedure for complex **2c** above. Size-exclusion chromatography, followed by recrystallisation, afforded **6** (79 mg, 61%) as a red microcrystalline solid (Found: C, 51.81; H, 4.04; N, 9.35. Calc. for $C_{50}H_{46}F_{12}N_8OP_2Ru$: C, 51.51; H, 3.98; N, 9.61%). Electrospray mass spectrum: *m*/*z* 1003, [M − PF$_6$]$^+$; 429, [M − 2PF$_6$]$^{2+}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.62 (2 H, d, J = 8.2), 8.88–8.73 (4 H, m), 8.49 (2 H, d, J = 5.1), 8.30–7.88 (10 H, m), 7.67–7.55 (2 H, m), 7.40–7.30 (2 H, m), 3.70 (2 H, s), 2.33–2.12 (5 H, m), 2.12–2.05 (unresolved, m), 1.69 (1 H, d, J = 10.3), 1.50 (2 H, d, J = 7.2), 1.31 (1 H, d, J = 9.2 Hz) and 1.12–1.04 (unresolved, m) and 1.02 (6 H, s). ^{13}C NMR (CD_3CN): δ 166.11 (C_q), 158.24 (C_q), 158.00 (C_q), 153.83 (CH), 152.98 (CH), 149.05 (C_q), 138.91 (CH), 138.79 (CH), 138.05 (C_q), 133.89 (CH), 131.40 (C_q), 128.58 (CH), 128.41 (CH), 127.69 (CH), 125.28 (CH), 125.21 (CH), 53.35 (CH), 49.23 (CH), 45.30 (C_q), 45.22 (CH), 41.59 (CH_2), 37.15 (CH), 35.68 (CH_2), 29.12 (CH_2) and 9.76 (CH_3).

[Os(dpq-6)][PF$_6$]$_2$·3H$_2$O 7 [Os = Os(bipy)$_2$]. The reaction of compound **IIa** (40 mg, 0.09 mmol) with *cis*-[Os(bipy)$_2$Cl$_2$] (57 mg, 0.099 mmol) in aqueous 1,2-ethanediol (5% v/v, 4 cm^3) was performed according to the procedure for complex **2c** above. Size-exclusion chromatography, followed by recrystallisation, afforded **7** (84 mg, 75%) as a dark green microcrystalline solid (Found: C, 46.27; H, 3.27; N, 8.67. Calc. for $C_{50}H_{50}F_{12}N_8O_3OsP_2$: C, 46.51; H, 3.90; N, 8.68%). Electrospray mass spectrum: *m*/*z* 1093, [M − PF$_6$]$^+$; 474, [M − 2PF$_6$]$^{2+}$. ^{1}H NMR [$(CD_3)_2CO$]: δ 9.40 (2 H, d, J = 7.7), 8.82 (2 H, d, J = 8.2), 8.78 (2 H, d, J = 8.2), 8.41 (2 H, d, J = 5.6), 8.12–7.84 (10 H, m), 7.57–7.50 (2 H, m), 7.31–7.23 (2 H, m), 3.70 (2 H, s), 2.35–2.16 (5 H, m), 2.12–2.06 (unresolved, m), 1.70 (1 H, d, J = 9.5), 1.51 (2 H, d, J = 7.7), 1.31 (1 H, d, J = 10.3 Hz), 1.10–1.05 (unresolved, m) and 1.02 (6 H, s). ^{13}C NMR [$(CD_3)_2CO$]: δ 165.95 (C_q), 160.37 (C_q), 160.15 (C_q), 153.23 (CH), 152.30 (CH), 152.24 (CH), 152.19 (CH), 151.53 (C_q), 138.50 (CH), 138.37 (CH), 138.17 (C_q), 133.60 (CH), 131.62 (C_q), 129.28 (CH), 129.13 (CH), 128.18 (CH), 125.54 (CH), 53.42 (CH), 49.31 (CH), 45.30 (C_q), 45.19 (CH), 41.54 (CH_2), 37.09 (CH), 35.66 (CH_2), 29.05 (CH_2) and 9.74 (CH_3).

Electrochemistry

Cyclic staircase voltammetry and differential pulse voltammetry (DPV) were conducted using a BAS-100B electrochemical analyser employing a three-electrode system, using

electronic *iR* compensation. The working electrode was a 1.5 mm radius glassy carbon inlaid disk (BAS). A 0.5 mm radius platinum electrode (Cypress) was also used. All experiments employed a platinum wire counter electrode, and a Ag–AgCl–saturated KCl reference electrode (gel type with Vycor™ frit, BAS). The conditions for DPV experiments were as follows: pulse amplitude = +50 (oxidation) or −50 mV (reduction), sample width = 17 ms, pulse period = 1000 ms, and scan rate = 4 mV s^{-1}. The working electrode was regularly polished using a suspension of alumina (0.04 μm, Struers) and distilled water on suede polishing cloth (Buehler, microcloth). The electrolyte used was 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$, with the electroactive species at *ca.* 1×10^{-3} mol dm^{-3}. All formal reduction potentials were internally referenced *versus* the IUPAC standard ferrocinium–ferrocene ($Fc^{+/0}$) couple (V *vs.* $Fc^{+/0}$),[80,81] with the latter found at 0.38 V *vs.* SCE. Where possible, formal potentials were obtained from both cyclic and differential pulse voltammetric measurements, with an error of ±0.01 V. All electrochemical samples were initially deoxygenated by purging with argon for 20 min, and kept under an argon atmosphere for the duration of experiments. The argon was pretreated using a water/oxygen purification system consisting of the following as a mounted assembly: an indicating moisture trap (5 Å molecular sieves with Dryerite™, Activon); a high-capacity coil oxygen trap (Alltech), an indicating oxygen trap (Alltech); and a low flow-rate gas flowmeter (Cole-Palmer). The purified argon was presaturated with MeCN by passing through a solvent bubbler.

Static absorption and luminescence spectroscopy

The UV-Vis absorption spectra were obtained using a CARY 5 spectrophotometer in dual-beam mode, with a spectral bandwidth of 2 nm, and a signal averaging time of 0.1 s. The wavelengths at maximum absorption (λ_{max}) are accurate to ± 2 nm, with the absorption coefficient accurate to ±5%. Optically matched quartz cells (Starna) were used throughout. Absorbance (A) values at the excitation wavelength of solutions used for excited-state emission experiments were obtained photometrically using repeated measurements with a signal averaging time of 2 s. Steady-state emission spectra were recorded using a Perkin-Elmer LS-50B spectrofluorimeter. All ruthenium-based emission spectra were measured with an excitation wavelength (λ_{exc}) of 450 nm, with the emission scanned between 500 and 750 nm. The excitation and emission spectral bandwidth was set to 15 nm, and spectra obtained at a scan speed of 20 nm min^{-1}. Luminescence measurements were conducted in deoxygenated MeCN solutions, as outlined for the electrochemical measurements described above. Solutions were prepared with absorbance values between 0.05 and 0.1, minimising quenching due to inner-cell effects.[82,83] Radiative quantum yields (φ_{em}) were reported relative to that measured for a standard solution of $[Ru(bipy)_3][PF_6]_2$ in MeCN ($\varphi_{std} = 0.062$),[66] and were calculated according to[82] eqn. (4)

$$\varphi_{em} = \varphi_{std} \frac{F_{unk}}{F_{std}} \frac{q_{std}}{q_{unk}} \frac{A_{std}}{A_{unk}} \quad (4)$$

where F is the integrated emission intensity, q the photon output of the source at λ_{exc}; A the absorbance at λ_{exc}; and unk and std refer to the unknown and standard solutions, respectively. As emission intensities of standard and unknown solutions were measured under identical instumental conditions with λ_{exc} = 450 nm, q_{std}/q_{unk} reduces to unity. The precision of the emission intensities (2σ) was obtained from repeated measurements of duplicate solutions. The absolute accuracy is estimated to be in the order of ±15%, on the basis of the literature[66] uncertainty in φ_{em} for $[Ru(bipy)_3][PF_6]_2$. Integration of emission spectra was performed using Perkin-Elmer FLDM software, and corrected for MeCN background emission. Emission spectra were uncorrected for source response. All spectroscopic and electrochemical measurements were conducted at ambient temperature (298 ± 5 K).

Time-resolved luminescence (lifetime) measurements were carried out on dilute solutions using time-correlated single photon counting detection. The excitation source was the frequency doubled output (295 nm) from a synchronously pumped dye laser (Rhodamine 6G), cavity dumped at a repetition rate of 80 kHz. Emission was monitored at 574 nm.

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References

1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.
2 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
3 D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum, New York, 1994.
4 M. N. Paddon-Row, *Acc. Chem. Res.*, 1994, **27**, 18.
5 M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435.
6 H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 3258.
7 K. W. Penfield, J. R. Miller, M. N. Paddon-Row, E. Cotsaris, A. M. Oliver and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 5061.
8 A. M. Oliver, M. N. Paddon-Row, J. Kroon and J. W. Verhoeven, *Chem. Phys. Lett.*, 1992, **191**, 371.
9 J. Kroon, A. M. Oliver, M. N. Paddon-Row and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1990, **112**, 4868.
10 G. D. Scholes, K. P. Ghiggino, A. M. Oliver and M. N. Paddon-Row, *J. Am. Chem. Soc.*, 1993, **115**, 4345.
11 G. D. Scholes, K. P. Ghiggino, A. M. Oliver and M. N. Paddon-Row, *J. Phys. Chem.*, 1993, **97**, 11871.
12 J. M. Warman, M. P. de Haas, M. N. Paddon-Row, E. Cotsaris, N. S. Hush, H. Oevering and J. W. Verhoeven, *Nature* (*London*), 1986, **320**, 615.
13 M. N. Paddon-Row and J. W. Verhoeven, *New J. Chem.*, 1991, **15**, 107.
14 G. L. Closs and J. R. Miller, *Science*, 1988, **240**, 440.
15 C. A. Stein, N. A. Lewis and G. Seitz, *J. Am. Chem. Soc.*, 1982, **104**, 2596.
16 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 942.
17 L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank and F. Vögtle, *Inorg. Chem.*, 1993, **32**, 5228.
18 F. Vögtle, M. Frank, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1643.
19 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable and A. M. W. Cargill Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7692.
20 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage and A. Sour, *New J. Chem.*, 1995, **19**, 793.
21 A. Harriman and R. Ziessel, *Chem. Commun.*, 1996, 1707.
22 M. Frank, M. Nieger, F. Vögtle, P. Belser, A. von Zelewsky, L. De Cola, V. Balzani, F. Barigelletti and L. Flamigni, *Inorg. Chim. Acta*, 1996, **242**, 281.
23 F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 1996, **35**, 136.
24 L. Hammarström, F. Barigelletti, L. Flamigni, N. Armaroli, A. Sour, J.-P. Collin and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1996, **118**, 11972.
25 V. Grosshenny, A. Harriman, F. M. Romero and R. Ziessel, *J. Phys. Chem.*, 1996, **100**, 17472.

26 M. T. Indelli, F. Scandola, L. Flamigni, J.-P. Collin, J.-P. Sauvage and A. Sour, *Inorg. Chem.*, 1997, **36**, 4247.
27 F. Barigelletti, L. Flamigni, J.-P. Collin and J.-P. Sauvage, *Chem. Commun.*, 1997, 333.
28 A. C. Benniston, A. Harriman, V. Grosshenny and R. Ziessel, *New J. Chem.*, 1997, **21**, 405.
29 L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser and S. Bernhard, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, 534.
30 V. Balzani, F. Barigelletti, P. Belser, S. Bernhard, L. De Cola and L. Flamigni, *J. Phys. Chem.*, 1996, **100**, 16786.
31 K. S. Schanze and K. Sauer, *J. Am. Chem. Soc.*, 1988, **110**, 1180.
32 A. Golka, P. J. Keyte and M. N. Paddon-Row, *Tetrahedron*, 1992, **48**, 7663.
33 A. Golka, D. C. Craig and M. N. Paddon-Row, *Aust. J. Chem.*, 1994, **47**, 101.
34 R. N. Warrener, M. A. Houghton, A. C. Schultz, F. R. Keene, L. S. Kelso, R. Dash and D. N. Butler, *Chem. Commun.*, 1996, 1151.
35 P. Belser and S. Bernhard, *Synthesis*, 1996, 192.
36 R. N. Warrener, A. B. B. Ferreira, A. C. Schultz, D. N. Butler, F. R. Keene and L. S. Kelso, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2485.
37 R. N. Warrener, A. C. Schultz, M. A. Houghton and D. N. Butler, *Tetrahedron*, 1997, **53**, 3991.
38 P. T. Gulyas, S. J. Langford, N. R. Lokan, M. G. Ranasinghe and M. N. Paddon-Row, *J. Org. Chem.*, 1997, **62**, 3038.
39 J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *J. Chem. Soc., Chem. Commun.*, 1995, 1799.
40 J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *Inorg. Chem.*, 1996, **35**, 2937.
41 P. Jacob, P. S. Callery, A. T. Shulgin and N. Castagnoli, *J. Org. Chem.*, 1976, **41**, 3627.
42 J. L. Y. Kong and P. A. Loach, *J. Heterocyc. Chem.*, 1980, **17**, 737.
43 R. N. Warrener, I. G. Pitt and D. N. Butler, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 1340.
44 E. N. Jacobsen, I. Markó, W. S. Mungall, G. Schröder and K. B. Sharpless, *J. Am. Chem. Soc.*, 1988, **110**, 1968.
45 C. Y. J. Tu and D. Lednicer, *J. Org. Chem.*, 1987, **52**, 5624.
46 K. Shishido, K. Takahashi, K. Fukumoto, T. Kanetani and T. Honda, *J. Org. Chem.*, 1987, **52**, 5704.
47 V. Van Rheenen, R. C. Kelly and D. Y. Cha, *Tetrahedron Lett.*, 1976, 1973.
48 M. N. Paddon-Row, E. Cotsaris and H. K. Patney, *Tetrahedron*, 1986, **42**, 1779.
49 R. G. Harvey, S. H. Goh and C. Cortez, *J. Am. Chem. Soc.*, 1975, **97**, 3468.
50 G. A. Lawrance, P. A. Lay, A. M. Sargeson and H. Taube, *Inorg. Synth.*, 1986, **24**, 257.
51 K. N. Ganesh and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1611.
52 A. L. Golka-Bartlett, Ph.D. Thesis, University of New South Wales, 1996.
53 P. Belser, A. von Zelewsky, M. Frank, C. Seel, F. Vögtle, L. De Cola, F. Barigelletti and V. Balzani, *J. Am. Chem. Soc.*, 1993, **115**, 4076.
54 T. J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193.
55 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
56 V. Balzani, D. A. Bardwell, F. Barigelletti, R. L. Cleary, M. Guardigli, J. C. Jeffery, T. Sovrani and M. D. Ward, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3601.
57 W. D. Harman and P. A. Lay, *Adv. Inorg. Chem.*, 1991, **37**, 219.
58 A. J. Bard and L. R. Faulkner, *Electrochemical Methods - Fundamentals and Applications*, Wiley, New York, 1980.
59 C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1.
60 M. D. Ward, *Chem. Soc. Rev.*, 1995, 121.
61 A. J. Downard, G. E. Honey, L. F. Phillips and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 2259.
62 M. M. Richter and K. J. Brewer, *Inorg. Chem.*, 1993, **32**, 2827.
63 Y. Ohsawa, M. K. DeArmond, K. W. Hanck and D. E. Morris, *J. Am. Chem. Soc.*, 1983, **105**, 6522.
64 E. Amouyal, A. Homsi, J.-C. Chambron and J.-P. Sauvage, *J. Chem. Soc., Dalton Trans.*, 1990, 1841.
65 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1986, 165.
66 E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1985, **24**, 2755.
67 E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722.
68 D. Relm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834.
69 A. Weller, *Z. Phys. Chem.*, *Neue Folge,* 1982, **133**, 93.
70 W. H. Elfring, Jr. and G. A. Crosby, *J. Am. Chem. Soc.*, 1981, **103**, 2683.
71 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
72 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.
73 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993.
74 V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, *Top. Curr. Chem.*, 1978, **75**, 1.
75 D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836.
76 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, New York, 1988.
77 K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, 1976, **98**, 1986.
78 N. C. Thomas and G. B. Deacon, *Inorg. Synth.*, 1989, **25**, 107.
79 D. A. Stephens and J. M. Williams, *Inorg. Synth.*, 1986, **24**, 141.
80 G. Gritzner and J. Kûta, *Pure Appl. Chem.*, 1984, **56**, 461.
81 I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters and L. Phillips, *J. Phys. Chem.*, 1998, submitted for publication.
82 G. G. Guildbault (Editor), *Practical Fluorescence*, Marcel Dekker, New York, 1990.
83 N. H. Damrauer, T. R. Boussie, M. Devenney and J. K. McCusker, *J. Am. Chem. Soc.*, 1997, **119**, 8253.
84 J. Fees, W. Kaim, M. Moscherosch, W. Matheis, J. Klíma, M. Krejcík and S. Záliš, *Inorg. Chem.*, 1993, **32**, 166.

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