To access the final edited and published work see http://dx.doi.org/101039/b823104d

Q2

Spectroelectrochemical properties of homo- and heteroleptic ruthenium and osmium binuclear complexes: intercomponent communication as a function of energy differences between HOMO levels of bridge and metal centres

Yvonne Halpin,[a] Laura Cleary,[a] Lynda Cassidy,[a] Sabine Horne,[a] Danilo Dini,[a] Wesley R. Browne†[b] and Johannes G. Vos*[a]

Received 24th December 2008, Accepted 10th March 2009
First published as an Advance Article on the web ??????
DOI: 10.1039/b823104d

A series of binuclear ruthenium and osmium complexes $[(bipy)_2Ru(qpy)Ru(bipy)_2]^{4+}$ (**1**), $[(bipy)_2$-$Os(qpy)Os(bipy)_2]^{4+}$ (**2**), $[(bipy)_2Ru(pytr\text{-}bipy)Ru(bipy)_2]^{3+}$ (**3**), $[(bipy)_2Ru(pytr\text{-}bipy)Os(bipy)_2]^{3+}$ (**4**), $[(bipy)_2Os(pytr\text{-}bipy)Ru(bipy)_2]^{3+}$(**5**) and $[(bipy)_2Os(bpbt)Os(bipy)_2]^{2+}$ (**6**) {bipy = 2,2′-bipyridyl; qpy = 2,2′:5′,5″:2″,2‴-quaterpyridyl; pytr-bipy = 3-(2,2′-bipyrid-6-yl)-5-(pyrid-2-yl)-1,2,4-triazolato, and bpbt = 5,5′-bis-(pyrid-2″-yl)-3,3′-bis-1,2,4-triazolato} are reported. Analysis of the electrochemical data focuses on structural factors and on determining the extent of electronic communication between the metal centres in the mixed valence oxidation state. Intervalence charge transfer (IT) bands could be identified in the spectra of the complexes **4** and **6** only. Analysis of their spectroelectrochemical data leads to the conclusion that the IT is superexchange mediated through the HOMO of the bridging ligand.

Introduction

Metal complexes based on polypyridyl ligands constitute versatile components for the construction of multifunctional supramolecular systems in molecular photonics and molecular electronics,[1] sensors,[2] photocatalysis,[3] solar energy conversion,[4] artificial photosynthesis,[5] non-linear optics,[6] and electrochemoluminescence[7] amongst others.[8,9] The myriad of applications are founded on the well defined chemistry of these compounds and take advantage of the versatile photophysical,[10] photochemical[11] and electrochemical[12] properties that are associated with the metal-to-ligand charge-transfer (MLCT) excitation in these metal complexes.[13]

Amongst the many multinuclear polypyridyl complexes reported,[14] an interesting subclass is represented by those binuclear systems that display additional spectroelectrochemical features due to the electronic interaction between the two metal centres in the mixed valence redox state(s).[15,16] "Communication" between metal centres where direct overlap of atomic orbitals is not possible is achieved when the bridging ligand (BL) has a system of polarisable electrons that are capable of mediating the redistribution of the electronic charge between the two metal centres.[17,18] If the BL is sufficiently capable of mediating an internuclear interaction then direct (optical) electron transfer is possible in the mixed valence state (*i.e.*, $M^{II}{}_1M^{III}{}_2 \rightarrow M^{III}{}_1M^{II}{}_2$)[19,20] and is manifested in the appearance of metal-to-metal (MM′CT) or intervalence (IT) charge transfer[21–23] absorption bands, typically in the far red and near infrared.[16,17,24] Analysis of these absorption bands[25] can provide detailed information as to the nature and extent of the interaction between the metals centres.

Recently, we reported the synthesis and characterisation of a series of homo- and hetero-binuclear ruthenium(II) and osmium(II) complexes of the general formula $[M_1(bipy)_2\text{-}BL\text{-}M_2(bipy)_2]$, where M = Ru or Os, bipy is 2,2′-bipyridyl (bipy), and BL the bridging ligands 2,2′:5′,5″:2″,2‴-quaterpyridyl (qpy), 3-(2,2′-bipyrid-6-yl)-5-(pyrid-2-yl)-1,2,4-triazolato (pytr-bipy), and 5,5′-bis-(pyrid-2″-yl)-3,3′-bis-1,2,4-triazolato (bpbt).[26]

In the present contribution, we describe in detail the electrochemical and spectroelectrochemical properties of these compounds. The goal of the present study is to evaluate the extent of electronic communication between the two metal centres as a function of the electronic properties of the bridging ligand and the positioning of the two metal centres. In particular, attention is directed towards the homo- and heterodinuclear complexes of ruthenium and osmium $[(bipy)_2Ru(qpy)Ru(bipy)_2]^{4+}$ (**1**), $[(bipy)_2Os(qpy)Os(bipy)_2]^{4+}$ (**2**), $[(bipy)_2Ru(pytr\text{-}bipy)Ru(bipy)_2]^{3+}$ (**3**), $[(bipy)_2Ru(pytr\text{-}bipy)Os(bipy)_2]^{3+}$ (**4**), $[(bipy)_2Os(pytr\text{-}bipy)Ru(bipy)_2]^{3+}$(**5**) and $[(bipy)_2Os(bpbt)Os(bipy)_2]^{2+}$ (**6**) (Fig. 1). The data obtained are compared with the electrochemical and spectroelectrochemical properties of the related binuclear complexes **7–11** with 3,5-bis(pyridin-2′-yl)-1,2,4-triazolato (bpt) as BL (Fig. 1),[16,27,28] and complexes **12–14** with isomeric quaterpyridyl BLs (Fig. 2).[11,17,29–31]

The systematic variation in the nature of the bridge and the introduction of both ruthenium and osmium metal centres allows a critical evaluation of the structural factors that affect the extent of electronic communication between the metal centres of these types of dinuclear complexes.

[a]*Solar Energy Conversion SRC, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland. E-mail: han.vos@dcu.ie; Fax: +353-1-7005503; Tel: +353-1-7005307*
[b]*Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747AG, Groningen, The Netherlands*
† Present address: Department of Chemistry, Trinity College Dublin, Dublin 2, Ireland.

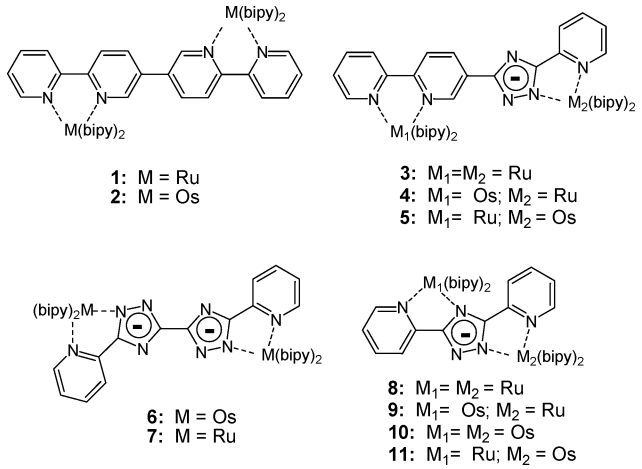


Fig. 1 Structures of binuclear complexes **1–6** and related compounds bpt[(bipy)$_2$Ru(bpbt)Ru(bipy)$_2$]$^{2+}$ (**7**), [(bipy)$_2$Ru(bpt)Ru(bipy)$_2$]$^{3+}$ (**8**), [(bipy)$_2$Ru(bpt)Os(bipy)$_2$]$^{3+}$ (**9**), [(bipy)$_2$Os(bpt)Os(bipy)$_2$]$^{3+}$(**10**) and [(bipy)$_2$Os(bpt)Ru(bipy)$_2$]$^{3+}$ (**11**).

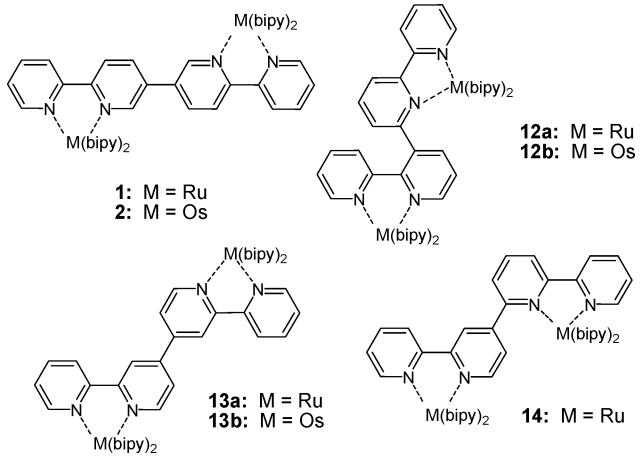


Fig. 2 Structures of quaterpyridyl bridged binuclear complexes **1**,**2**, [(bipy)$_2$M$_1$(qpy$_1$)M$_2$(bipy)$_2$]$^{4+}$ (**12**), [(bipy)$_2$M(qpy$_2$)M(bipy)$_2$]$^{4+}$ (**13**) and [(bipy)$_2$M(qpy$_3$)M(bipy)$_2$]$^{4+}$ (**14**).

Experimental

The synthesis and structural characterization of complexes **1–6** were reported previously.[26] Cyclic and differential pulse voltammetries are reported in the ESI. Potential values are referred with respect to the saturated calomel reference electrode (SCE). Glassy carbon and platinum disc electrodes were used as the working electrodes and a platinum wire was employed as the counter electrode. The electrode area was 0.07 cm^2. A solution of 0.1 M TBAPF$_6$ (Fluka, electrochemical grade) in a 50 : 50 mixture of acetonitrile (Aldrich, anhydrous, 99.8%) and dichloromethane (Aldrich, anhydrous, 99.8%) were used as the supporting electrolyte. A mixed solvent system was employed to prevent adsorption to the electrode. Analyte concentrations of typically 1 mM were used. Electrochemical experiments were carried out using a CHI750C electrochemical bipotentiostat. Prior to each experiment, the electrochemical cell was degassed for at least 10 min using argon and a blanket of argon was maintained throughout. The working electrodes were prepared by polishing with 0.05 μm alumina paste and sonicated in Millipore grade water for 5 min followed by 5 min of sonication in either acetonitrile or dichloromethane. The platinum electrodes were cleaned by polishing followed by electrochemical cleaning in 0.5 M H_2SO_4 prior to sonication in acetonitrile or dichloromethane. All cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}.

UV-vis–NIR spectroelectrochemical measurements were performed using a model CHI760C bipotentiostat (CH Instruments) and either a JASCO 630 UV-vis spectrophotometer or a JASCO 570 UV-vis NIR spectrophotometer. Analyte concentrations were typically 0.1–1.0 mM in anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). A platinum gauze working electrode, Pt wire auxiliary electrode and SCE reference electrode were employed (calibrated externally using 0.1 mM solutions of ferrocene in 0.1 M TBAPF$_6$ in acetonitrile). A custom made 2 mm path length quartz cuvette (volume: 1.2 mL) was employed for all spectroelectrochemical measurements.

Results and discussion

Redox properties

The redox properties of the dinuclear complexes **1–6** were studied by cyclic and differential pulse voltammetry (Fig. 3).

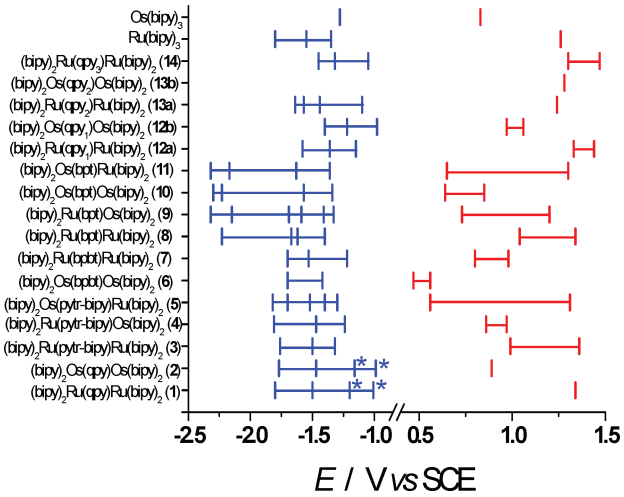


Fig. 3 Oxidation (red lines), and reduction (blue lines) formal potentials $E_{1/2}$ [$E_{1/2} = (E_{p,a} + E_{p,c})/2$] for metal complexes **1–14**, Ru(bpy)$_3$ and Os(bpy)$_3$.[16,30,32–34] For complexes **1–6** the asterisk indicates that the reduction process at that specified potential value is localized on the bridging ligand.

The half-wave potentials indicate that the oxidations and reductions of each of the six complexes are centred on the metals and ligands, respectively.[12]

The electrochemistry of the symmetric homodinuclear complex **1** is similar to that of its regioisomer [Ru(bipy)$_2$(qpy)Ru(bipy)$_2$]$^{4+}$ (**13a**), first reported by Steel and co-workers,[34] in which the bipyridyls of the BL are connected at the C4 position and not the C5 position as in the case of **1** and **2**. The oxidation potential of **1** (+1.34 V *vs.* SCE) is 100 mV more positive than that of **13a**.[34] This difference is ascribed to the change in connectivity of the two bipyridyl moieties of the BL. In fact, **13a** is linked at the C4–C4′ position giving a more impeded rotation around the C–C bond with respect to the direct linkage from C5 in **1**. In

This journal is © The Royal Society of Chemistry 2009

the latter, there is a less hindered rotation around the bond. This would diminish delocalisation across the bridge with a consequent increase in the oxidation potential for the bridged metal centres in **1** in comparison to **13a**.

Four cathodic processes are resolved in the CV of **1** and **2**, and analysis by differential pulse voltammetry indicates that these four redox waves correspond to six reduction steps with only the first two redox processes being fully resolved. Comparison with related compounds and considering the π-acceptor properties of the BL, it can be inferred that the first two reduction steps at −1.00 and −1.20 V *vs.* SCE are localised on the BL rather than on the peripheral bipyridyl ligands.[34,35] The third and fourth reduction waves, each representing two partially resolved one-electron reductions, are assigned to reduction of the four peripheral bipyridyl ligands. Comparison of the reduction potentials for the quaterpyridyl bridge in complexes **1** and **2** shows only a weak dependence of these on the nature of the coordinating metal.

In contrast to complexes **1** and **2**, for complex **3**, two resolved reversible one-electron oxidation steps are observed, which are assigned to sequential oxidation at the two different binding sites of the asymmetric ditopic pytr-bipy ligand (Fig. 1). The two redox process can be assigned to oxidation of metal centres coordinated to the pytr (0.99 V *vs.* SCE) and bipy (1.36 V *vs.* SCE) components of the BL, respectively, by comparison with the redox potentials of related complexes.[10b,16d,e,36] The similarity of the latter redox potential with that of complex **1** (Fig. 3) is an indication of the localisation of this oxidation process at the metal centre that coordinates the bipyridyl unit of the BL in **3**. This potential is 100 mV higher than the oxidation potential of the mononuclear complex $[Ru(bipy)_3]^{2+}$ (Fig. 3).[29] This positive shift may be a consequence of electronic effects since the $Ru(bipy)_2(pytr^-)$ moiety in complex **3** is close to the positively charged moiety obtained upon oxidation of the Ru centre bonded to the triazole moiety of the BL. The least negative, one-electron, reduction process at −1.32 V is assigned to reduction of the bipy grouping on the pytr-bipy ligand of **3** (Fig. 3). The two redox waves at more negative potentials (−1.50 and −1.76 V *vs.* SCE, Fig. 3) are assigned to the first and second reduction of the peripheral bipy ligands, respectively. The second reduction step of the triazole based ligand lies outside the potential window available. Similar assignments can be made in the analysis of the reduction processes of the same BL in heterodinuclear complex **4** (Fig. 3).

The oxidation processes of the heterobinuclear complexes **4** and **5** consist of two resolved one-electron redox steps, the separation of the two redox waves being markedly different between the two complexes (Fig. 3). For **5**, assignment of the two redox processes can be made on the basis of comparison with related mononuclear complexes. The first oxidation is assigned to the pyridyl-triazolato bound osmium centre (0.56 V) while the second process at 1.31 V is assigned to the ruthenium centre bound to the bipyridyl unit of the bridging ligand.

For **4**, the assignment is less obvious since the two redox waves are separated by only 110 mV and are both close to those of their related mononuclear complexes. Assignment on the basis of comparison would suggest that the $Os(bipy)_2$-bipyridyl bound centre is the first to be oxidised followed by the $Ru(bipy)_2$-pyridyl-triazolato centre. This assignment is verifyable by spectroelectrochemistry (*vide infra*) which shows that the first oxidation is accompanied by a decrease in the intensity of the osmium ^{3}MLCT absorption bands. Overall, the difference in the half–wave potentials of the ruthenium and osmium metal centres is small in complex **4** ($\Delta E_{1/2}$, 110 mV) compared to that observed for complex **5** ($\Delta E_{1/2}$, 750 mV) (Fig. 3).

Five distinct one-electron reduction processes are observed for **5**. In analogy to $Ru(bipy)_3$, the reduction peaks at −1.30 V and −1.52 V are assigned to the reduction of the two non-bridging bipy ligands that are coordinated by Ru(II) in **5**. Similarly, the two reduction steps at −1.40 V and −1.70 V are still ascribed to the reduction of the two non-bridging bipy ligands that are coordinated by Os(II). The negative shift observed for the reduction steps of the non-bridging ligands of Os(II) is related to the presence of a negative charge in the triazolato moiety coordinated by Os(II), and, secondly, the stronger electron releasing properties of Os(II) with respect to Ru(II). The fifth reduction step at −1.82 V is assigned to the reduction of the BL in correspondence of the bipy moiety of the BL because of the closeness of this value with that of the third reduction potential of $Ru(bipy)_3$ (Fig. 3).

Complex **6**, the osmium analogue of $[(bipy)_2Ru(bpbt)Ru(bipy)_2]^{2+}$[16] exhibits two reversible one-electron oxidations at $E_{1/2} = +0.47$ and +0.56 V *vs.* SCE (Fig. 3). Despite the chemical equivalency of the Os sites in **6** (Fig. 1), two close but resolved redox waves are observed for the oxidation of the two metal centres (Fig. 3). Interestingly, for the analogous ruthenium complex $[(bipy)_2Ru(bpbt)Ru(bipy)_2]^{2+}$ (**7**), the separation (ΔE) is 100 mV, *i.e.* twice that observed for **6**. The first metal oxidation potential of **6** is 420 mV lower that the oxidation potential of the metal centres in the homobinuclear osmium complex **2** in agreement with the coordination of both metal centres to pyridyl-triazolato units. The two reduction waves of complex **6** are consistent with two bielectronic processes of reduction that are localised on bipy ligands as reported previously.[16,37]

The comproportionation constant as a measure of internuclear communication

The comproportionation constant for complexes **1** to **14**, listed in Table 1, refer to the reaction[19]

$$M^{II}{}_1M^{II}{}_2 + M^{III}{}_1M^{III}{}_2 \rightleftarrows 2M^{II}{}_1M^{III}{}_2 \quad (1)$$

and can be calculated from ΔE_{ox} (Fig. 3) at 298 K through the relationship:

$$K_c' = \exp[(\Delta E_{ox}/\mathrm{mV})/25.69] \quad (2)$$

The largest K_c' values in this series of complexes are observed for complexes **3** and **5** with calculated values of 1.8×10^6 and

Table 1 Separation between the 1st and 2nd oxidation potentials, ΔE_{ox}, and the corresponding comproportionation constant, K_c' (eqn (1)), for **1–14**

	ΔE_{ox}/mV	K_c'		ΔE_{ox}/mV	K_c'
1	0	4	**8**[14]	300	1.2×10^5
2	0	4	**9**[14]	470	8.9×10^7
3	370	1.8×10^6	**10**[14]	210	3.6×10^3
4	110	72	**11**[14]	650	9.9×10^{11}
5	750	4.8×10^{12}	**12a**[32]	11	1.5
6	90	35	**12b**[33]	9	1.4
7	180	1100	**13a,b**[14]	0	4
			14[31]	7	1.3

4.8×10^{12} for $\Delta E_{ox} = 370$ (**3**) and 750 (**5**) mV, respectively (eqn (1)). Complexes **4** and **6** present lower values of ΔE_{ox} (110 and 90 mV, respectively), and hence K_c' is 72 (**4**) and 35 (**6**), respectively. In the case of the complexes **1** and **2** and the concurrent oxidation of both metal centres indicates that the electronic coupling across the bis-bipyridyl bridge is either absent or weak and that an electrostatic interaction is absent.[14] This conclusion is supported by the absence of an intervalence transfer band in the vis–NIR spectrum of these systems (see ESI).

Generally, the observation of a separation between the metal centred oxidation potentials is taken as an indication of electrostatic interaction or ligand orbital mediated superexchange between the metal centres. It is important, however, to note that the nature of the metal centres involved also plays a role. The related comproportionation constant, K_c' (*vide supra*), calculated from the ΔE_{ox} values according to eqn (2), is therefore often taken as an indicator of the extent of electrostatic interaction and redox asymmetry between the metal centres as well as the thermodynamic stability of the mixed valence compound (Table 1).[17,18,38]

Since absorption bands assignable to IT transitions were observed for complexes **4** and **6** whereas compounds **3** and **5** showed no evidence of such absorptions (*vide infra*), the value of K_c' observed for these compounds reduces to be that of a measure of the redox asymmetry between the metal centres and/or to the degree of electrostatic interaction. It must also be taken into account that the value of K_c' is sensitive to the donor/acceptor properties of solvent and electrolyte, and varies as a result.[39]

Spectroelectrochemistry

The absorption properties of the binuclear complexes **1–6** in the divalent state are summarised in Table 2 to facilitate discussion of the spectroelectrochemical data.[26] The absorption bands in the UV are assigned to $\pi \rightarrow \pi^*$ intraligand electronic transitions.[16,40] The absorption bands in the range 400–520 nm are assigned to ^{1}MLCT transitions. For the Os(II) containing complexes additional triplet-based ^{3}MLCT absorption bands are observed between 520 and 800 nm.

Upon oxidation, significant changes in the electronic absorption spectra are observed. In all cases, the intensity of the ^{1}MLCT band decreases and in the case of osmium containing complexes, the ^{3}MLCT absorption bands also decrease (see ESI). Of particular interest in the present study is the electrochemical generation of the mixed valence state (*i.e.* $M_1^{II}M_2^{III}$) to investigate potential IT absorption bands in the NIR region. The ability to generate the mixed valence form is dependent on the comproportionation constant, K_c' (Table 1).

Table 2 UV-vis absorption data[26] for $M_1^{II}M_2^{II}$ dinuclear complexes in acetonitrile at 298 K

	Absorption λ_{max}/nm (ε/10^4 $M^{-1}cm^{-1}$)
1	430 (sh[a]), 450(2.53)
2	463 (2.57) 625 (0.47)
3	447 (1.76)
4	445 (1.23) 622 (0.16)
5	456 (1.68), 501 (1.18)
6	496 (2.67) 652 (0.61)
7	478 (1.90)
$[Ru(bipy)_3]^{2+}$	450 (1.30)
$[Os(bipy)_3]^{3+}$	468 (1.11)
7[14]	330, 368 (sh), 442, 482

[a] sh = shoulder.

Table 3 λ_{max} of E_{opt} and interaction parameters α^2 (eqn (3)), $\Delta\nu_{1/2calcd}$ (eqn (5)) and $\Delta\nu_{1/2exp}$ for the mixed valence state of **4** (this work), and complexes **7–11**

	E_{opt}/cm^{-1}	$\Delta\nu_{1/2exp}$/cm^{-1}	ε/M^{-1}cm^{-1}	$\Delta\nu_{1/2calcd}$/cm^{-1}	α^2
4	5128	4636	633	3405	2.7×10^{-3}
7[16d]	5490	4690	1820	3060	7.0×10^{-3}
8[16e]	5556	3300	2400	3341	16.0×10^{-3}
9[16e]	7143	3800	1200	3650	7.0×10^{-3}
10[16e]	8333	4500	460	4170	2.7×10^{-3}
11[16e]	8772	4300	1140	3700	6.1×10^{-3}

In dinuclear complexes where $\Delta E_{ox} = 0$ mV and the redox sites are electrochemically equivalent, the statistical value of K_c' is 4 meaning that only a maximum 25% of the complex is in the mixed valance stand at the $E_{1/2}$.[19] Although for complexes **1** and **2**, oxidation of both metal centres occurs concurrently, bulk electrolysis at the $E_{1/2}$ will allow for a significant proportion of the mixed valence state to be generated and by examination of the changes in the electronic absorption spectrum as a function of applied potential, the appearance and subsequent disappearance of absorption bands can reveal the presence of IT band/s in the mixed valence state.

Oxidation of **1** leads to the appearance of low intensity broad absorption bands in the range 10450–17500 cm^{-1}, which are assigned to ligand to metal charge transfer transitions (LMCT) characteristic of bipyridyl-based Ru(III) complexes.[16] Analysis of the vis–NIR spectrum shows no evidence of an IT absorption band in the mixed valence state of complex **1** (see ESI). As for **1**, oxidation of the dinuclear Os complex **2** leads to a decrease in the intensity of the MLCT absorption bands (see ESI) and the simultaneous appearance of low intensity bands in the region 4450–5700 cm^{-1} assigned to osmium centred dπ–dπ transitions.[41] Oxidation of **3** at +1.10 V results in formation of the mixed valence species with the concomitant decrease in the intensity of the ^{1}MLCT band and the appearance of a new absorption band at *ca.* 11700 cm^{-1} (see ESI). This NIR absorption band is assigned as an LMCT transition and not as an IT absorption band since it persists in the spectrum of the fully oxidised species generated at 1.40 V (see ESI). The intensity and energy of the LMCT absorption band allows for its assignment as a LMCT transition from the electron rich triazolato to the ruthenium centre.[10b,42] Oxidation at 1.40 V results in conversion to the $Ru^{III}Ru^{III}$ state. This results in a further decrease in the ^{1}MLCT absorption band and a partial increase in intensity of the LMCT absorption band at 11 700 cm^{-1}. The increase in absorption at 16 000 cm^{-1} is characteristic of LMCT transition of a Ru^{III} polypyridyl complex. For **3**, there is no evidence for the appearance of IT absorption bands in the NIR region in the mixed valence state despite the large value of K_c' (1.8×10^6, eqn (1)), confirming that the large ΔE is due to the asymmetry of the redox centres.[17] To summarise, the $Ru(bipy)_2(pytr)^{2+}$ unit is oxidized first followed by oxidation of the $Ru(bipy)_2(bipy)^{2+}$ unit.

Oxidation of the heterodinuclear system $[(bipy)_2Ru(pytr\text{-}bipy)Os(bipy)_2]^{3+}$ (**4**) at a potential (+0.95 V) intermediate of the 1st and 2nd oxidation steps results in a decrease in the intensity of both the ^{1}MLCT and ^{3}MLCT absorption bands (Fig. 4). This indicates

This journal is © The Royal Society of Chemistry 2009

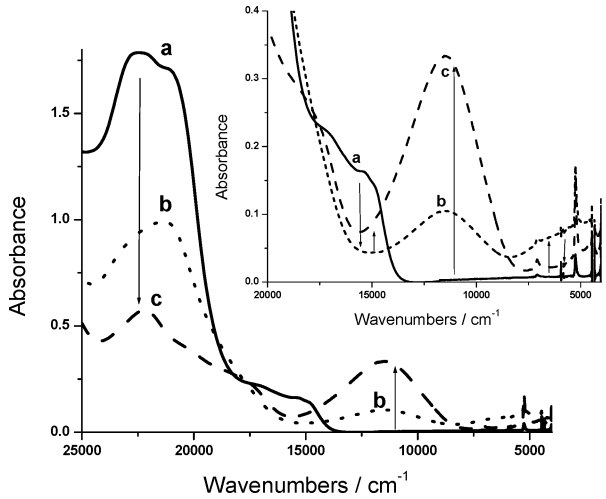


Fig. 4 UV-vis–NIR absorption spectra of $[(bipy)_2Ru(pytr\text{-}bipy)Os(bipy)_2]^{3+}$ (**4**) in 0.1 M $TBAPF_6/CH_3CN$ at (a) E = OCP, (b) $E = 0.95$ V [Os(III)-Ru(II)] and (c) $E = 1.10$ V [Os(III)-Ru(III)] *vs.* SCE.

that the $[Os(bipy)_2(bipy)]$ moiety is oxidised first. Furthermore, two new absorption bands in the NIR region appear at *ca.* 11 800 cm^{-1} and 6000 cm^{-1} (Fig. 4). Increasing the applied potential to +1.10 V resulted in the oxidation of the second metal centre and was accompanied by a further decrease in the ^{1}MLCT absorption bands and a substantial increase in the absorption band at 11 800 cm^{-1} and a decrease in the intensity of the absorption at 6000 cm^{-1} (Fig. 4). The appearance and subsequent disappearance of the band at 6000 cm^{-1} is indicative of an IT absorption band of the mixed valence state (Fig. 4). The absorption band at 11 800 cm^{-1} can be assigned to a LMCT transition of the $(bipy)_2Ru(pytr)$ unit, which is partially oxidised and fully oxidised at 0.95 and 1.10 V, respectively.

Oxidation of **5** at +0.90 V results in a decrease in the intensity of the ^{1}MLCT absorption band together with a disappearance of the ^{3}MLCT absorption band at *ca.* 16 000 cm^{-1} and the appearance of a new absorption band centred at 14 300 cm^{-1} and 4300 cm^{-1} assigned to Os^{III} based LMCT absorption bands (see ESI).[43] This confirms that the $Os(bipy)_2(pytr)$ unit is oxidised first as expected from analysis of the electrochemical data (Fig. 3). At +1.50 V, oxidation of the $Ru(bipy)_2(bipy)$ unit is accompanied by a further decrease in the intensity of the ^{1}MLCT absorption bands (see ESI). There is no evidence for the appearance of IT absorption bands in the mixed valence state.

$[Os(bipy)_2(pytr\text{-}pytr)Os(bipy)_2]^{2+}$ (**6**) exhibits two sets of MLCT bands in the UV-vis–NIR spectrum, the ^{1}MLCT absorption bands centred at 20 000 cm^{-1} (500 nm) and ^{3}MLCT absorption bands at 14 900 cm^{-1} (670 nm) (Fig. 5). The half-wave potential for the oxidation of the first osmium metal centre is +0.47 V and +0.56 V for oxidation of the second centre (Fig. 3). In the fully oxidised state, at +0.75 V, the intensities of both ^{1}MLCT and ^{3}MLCT absorption bands are reduced (Fig. 5). Furthermore, a new absorption band at 13 700 cm^{-1} (730 nm) can be assigned to a triazolato-based LMCT transition together with narrow lower energy absorption bands at 5800 and 4200 cm^{-1}.[44] At +0.51 V, intermediate between the $E_{1/2}$ of the first and second redox steps, the LMCT absorption band at 13 700 cm^{-1} is notably absent while the narrow low energy bands at 5800 and 4200 cm^{-1} are present

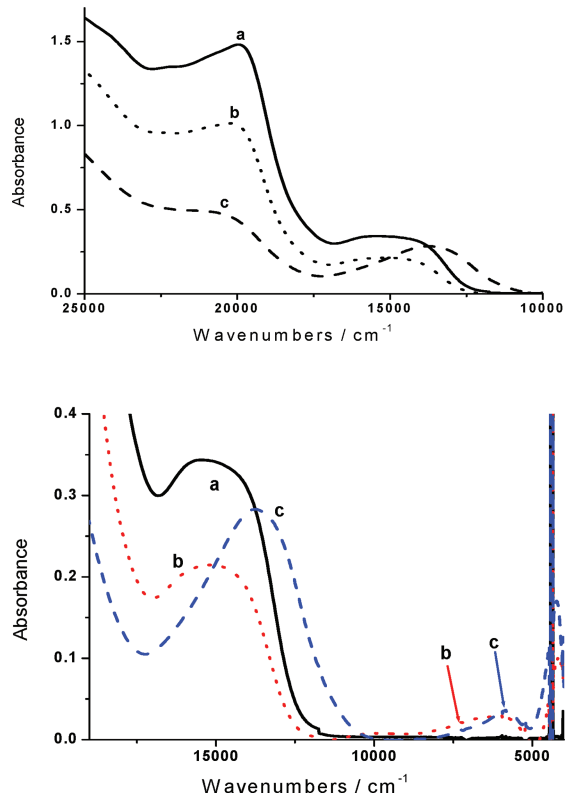


Fig. 5 UV-vis–NIR absorption spectra of $[(bipy)_2Os(bpbt)Os(bipy)_2]^{2+}$ (**6**) in 0.1 M $TBAPF_6/CH_3CN$ at (a) E = OCP, (b) E = 0.51 V [Os(III)-Os(II)] and (c) $E = 0.75$ V [Os(III)-Os(III)] *vs.* SCE. Lower graph: expansion of the 5000–19 000 cm^{-1} region.

(Fig. 5). A weak broad absorption band at *ca.* 8000 cm^{-1} can be assigned, tentatively, to an IT absorption band due to its disappearance when fully oxidised. Overall, it is apparent that there is an interaction between the two metal centres of **6** in the mixed valence state. This interaction is small as indicated by the low intensity and broadness of the putative IT band.[45] The low intensity of the proposed IT band renders the evaluation of the interaction parameters difficult (*vide infra*).[17,20–23]

Interaction parameters in mixed valence states

The four primary classifications for the electronic character of mixed valence dinuclear complexes are (i) type I (non-interacting), (ii) type II (weakly interacting), (iii) type II/III (solvent dependent interaction) and (iv) type III (strong interaction).[22,46] Depending on the extent of interaction between the metal centres in the mixed valence state, the delocalisation across both metal centres (α^2) and the electronic coupling H_{ab} between the metal centres will vary.

Frequently, the magnitude of ΔE, the separation between the first and second metal oxidation steps is taken to provide insight into the degree of interaction between metal centres. However, ΔE is dominated by contributions from redox asymmetry and electrostatic contributions and hence a large value of ΔE does not necessarily imply strong internuclear interaction, *i.e.* a large value for α^2 or H_{ab}.

The analysis of spectroelectrochemical data is essential in the evaluation of the extent of interaction between metal centres. Assignment of absorption bands of the mixed valence species to

IT transitions (optical electron transfer) is made on the basis of the absence of these bands in the fully reduced and oxidised states. In the present series of binuclear complexes **1–6** IT bands were identifiable only in the cases of $[(bipy)_2Ru(pytr\text{-}bipy)Os(bipy)_2]^{3+}$ (**4**) (Fig. 4) and $[(bipy)_2Os(bpbt)Os(bipy)_2]^{2+}$ (**6**) (Fig. 5), and for the complex $[(bipy)_2Ru(bpbt)Ru(bipy)_2]^{2+}$ (**7**).[16d]

The calculation of the interaction parameters α^2, H_{ab} and $\Delta\nu_{1/2calc}$ representing the delocalisation parameter, the coupling constant and the calculated peak width at half height for the IT band, respectively,[17,20–23] is feasible for the heteronuclear complex **4** only, since the low intensity IT band observed in the spectrum of **6** is broad and overlaps with lower energy absorption bands (Fig. 5). The interaction parameters α^2, H_{ab} and $\Delta\nu_{1/2calc}$ are defined by the relationships:[45]

$$\alpha^2 = \frac{(4.2*10^{-4})\varepsilon_{max}\Delta\nu_{1/2}}{r^2 E_{opt}} \quad (3)$$

$$H_{ab} = (\alpha^2 E^2{}_{opt})^{1/2} \text{ in cm}^{-1} \quad (4)$$

$$\Delta\nu_{1/2calc} = [2310 \times (E_{opt} - \Delta E)]^{1/2} \text{ in cm}^{-1} \quad (5)$$

where ε_{max} is the molar absorptivity (in M^{-1} cm^{-1}) of the IT band, $\Delta\nu_{1/2}$ is the experimentally determined value of the peak width at half height for the IT band (in cm^{-1}), r is the electron transfer distance (in Å), E_{opt} and ΔE the energy corresponding to the maximum of absorption for the IT band (in cm^{-1}) and the energy difference between metal sites (in cm^{-1}, see eqn (1)), respectively. The distance r is taken to be 9.5 Å,[16d] however this value corresponds to the centre-to-centre distance and does not take into account the reduction in electron transfer distance due to strong mixing between metal orbitals and BL-based orbitals.[45] Hence the calculated values for α^2 and H_{ab} represent the lower limit of the actual value. Furthermore, for **4**, the value of $\Delta\nu_{1/2}$ determined by direct measurement of the IT band is larger than the theoretical value (eqn (5)) confirming that the system is best described as type II (valence localised).[17,21] From Table 4 it is clear that the interaction in terms of delocalisation in **4** is close to complexes such as **9** in which the metals are separated by an electron rich triazolato ligand.

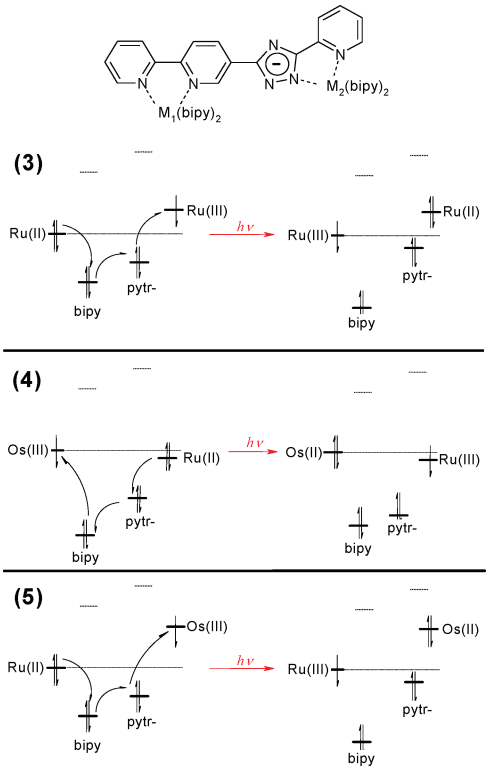
Comparison of pytpytr bridged complexes 6 and 7

Complexes **6** and **7**[16] are bridged by the same bis-(pyridyl-triazolato) ligand but differ in the metal centres (*i.e.* osmium *vs.* ruthenium). The magnitude of ΔE for **6** is less and the intensity and energy of the IT band of the mixed valence state indicate that both the delocalisation (α^2) and interaction parameters H_{ab} possess lower values and hence the internuclear communication can be considered to be weaker. Previously, the interaction mechanism in the mixed valence state for complex **7** was assigned as being *via* HOMO mediated superexchange by the electron rich triazolato ligands. Hence the less positive oxidation potentials of the metal centres of **6** compared with **7** imply that mixing with the HOMO orbitals of the bridging ligand will be reduced. This would explain the decreased interaction strength in **6**.

Comparison of bpypytr bridged complexes 3–5

Complexes **3–5** incorporate the same bridging ligand (pytr-bipy) but differ in the metal centres (*i.e.* ruthenium *vs.* osmium). The variation of the redox properties of **3**, **5** and **4** are in the first instance due to the difference in the redox potentials of the ruthenium and the corresponding osmium units and secondly the difference in the coordination properties of the pyridine-triazolato and bipyridyl components of the ditopic bridging ligand. In complexes **3** and **5**, the metal coordinated to the pyridyl-triazolato unit is oxidised first, whereas for complex **4** it is the metal centre coordinated to the bipyridyl unit that is oxidised first followed closely by oxidation of the second metal centre.

Surprisingly, an IT absorption band, which indicates significant internuclear interaction, is observed for complex **4** and not for complexes **3** and **5**. This is counter intuitive considering that for symmetric dinuclear compounds an increase in the separation between the first and second oxidation potential (ΔE) typically indicates increased interaction strength (where the separation is not due to electrostatic interactions or asymmetry). The internuclear separation between the metal centres precludes either electrostatic interaction or direct metal orbital overlap between the osmium(III) and ruthenium(II) metal centres and hence the interaction strength manifested in the IT absorption band can be ascribed to HOMO superexchange mediated interaction between the metal centres. The increased interaction observed for **4** compared with **3** and **5** can be rationalised by considering the nature of the optical electron transfer in terms of the energy of the 'donor' and 'acceptor' metal centres. For **4**, the optical transition, Os(III)Ru(II) → Os(II)Ru(III) involves a conversion to a state, which is relatively close in energy to the ground state compared with the corresponding transition for complex **3** and **5** (Scheme 1). Furthermore, if an electron hopping model is considered then in the case of complexes **3** and **5** the optical transfer of an electron formally results in an increase in



Scheme 1 HOMO mediated superexchange in complexes **3–5** in the mixed valence states.

This journal is © The Royal Society of Chemistry 2009

the energy difference of the HOMO orbitals of the bridging ligand (bpy and pytr$^-$) in the optically excited state whilst in the case of **4** these states move closer together in energy.

Hence it can be concluded that the dominant interaction in the mixed valence state of **4** is that of a dπ(M^{III})–π(L) mixing with π-orbitals of the bridging ligand (HOMO mediated superexchange).[17] By comparison of the reduction potentials of **4** with those of **1** and **2** (Fig. 3), it can be seen that the π^* (LUMO) of BL in **4** is higher in energy than that of both **1** and **2**. This additional consideration supports the conclusion that the mechanism of internuclear interaction in **4** is HOMO mediated and not LUMO mediated superexchange.

Conclusions

The spectroelectrochemical properties of symmetrically and asymmetrically bridged binuclear complexes of ruthenium and osmium **1–6** have been determined in the UV-vis–NIR range. The oxidation potential of the metal centres in quaterpyridyl bridged species **1** and **2** has a weak dependence on the type of quaterpyridyl isomer (compare complexes **12–14**), that bridges the two metal centres and first oxidation does not provide evidence for intermetallic communication in **1** and **2**. Within the group of pytr-bipy bridged complexes **3–5** only **4** exhibits spectroelectrochemical features in its mixed valence state, which could be assigned unambiguously to an IT transition. It is found that the overall change in energy involved in the IT transition (*i.e.* the difference in oxidation potentials of the metal centres), and the effect of the electron transfer on the relative energies of the HOMO orbitals associated to the binding units of the bridging ligand constitute the critical factors for the occurrence of IT. In the sole case of **4** the ligand mediated electron transfer Ru(II)-[pytr-bipy]-Os(III) $\rightarrow$ Ru(III)-[pytr-bipy]-Os(II) is possible because of the larger electron-withdrawing strength of the binding moiety (bipy) that is coordinated by the oxidised metal centre (Os). This implies a HOMO (of the bridging ligand) mediated superexchange mechanism where the energy differences between the HOMOs of the binding sites and the gap between these and the energy levels of the coordinating metals are the critical parameters.

Compound **6** displays an IT transition also, which occurs *via* a HOMO (of the bridging ligand) mediated superexchange mechanism. The common structural factors that accompany such an electronic event in **4** and **6** are the presence of osmium as metal centre, and the presence of at least one triazole moiety in the bridging ligand. In the case of complexes **6** and **7** differing only in the nature of the metal centres, the weaker intermetallic interaction of osmium complex **6** in comparison to the analogous ruthenium complex **7**, is due to the larger gap between the energy of the metal orbitals of Os with respect to Ru, and the HOMO of the binding unit of the ligand.

Acknowledgements

The authors thank the Irish Research Council (IRCSET, LC) the Netherlands Organisation for Scientific Research (NWO-vidi, WRB) and Science Foundation Ireland (grant 06/RFP/029 and Solar Energy Conversion SRC) (LC, YH, DD, and JGV) for supporting this work.

Notes and references

1 B. J. Coe and N. R. M. Curati, *Comments Inorg. Chem.*, 2004, **25**, 147; W. R. Browne, N. M. O'Boyle, J. J. McGarvey and J. G. Vos, *Chem. Soc. Rev.*, 2005, **34**, 641; V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26; C. A. Mirkin and M. A. Ratner, *Annu. Rev. Phys. Chem.*, 1992, **43**, 719; M. D. Todd, K. V. Mikkelsen, J. T. Hupp and M. A. Ratner, *New J. Chem.*, 1991, **15**, 97; J. G. Vos and J. M. Kelly, *Dalton Trans.*, 2006, 4869.

2 A. P. Doherty, M. A. Stanley and J. G. Vos, *Analyst*, 1995, **120**, 2371; C. Mallins, S. Fanni, H. G. Glever, J. G. Vos and B. D. MacCraith, *Anal. Commun.*, 1999, **36**, 3; R. Grigg and W. D. J. Amilaprasadh Norbert, *J. Chem. Soc., Chem. Commun.*, 1992, 1300; G. De Ruiter, T. Gupta and M. E. Van der Boom, *J. Am. Chem. Soc.*, 2008, **130**, 2744; A. Ghosh, B. Ganguly and A. Das, *Inorg. Chem.*, 2007, **46**, 9912; J. F. Fernandez-Sanchez, R. Cannas, S. Spichiger, R. Steiger and U. E. Spichiger-Keller, *Anal. Chim. Acta*, 2006, **566**, 271; S. A. Trammell, H. M. Goldston, P. T. Tran, L. M. Tender, D. W. Conrad Benson and H. W. Hellinga, *Bioconjug. Chem.*, 2001, **12**, 643.

3 S. Rau, D. Walther and J. G. Vos, *Dalton Trans.*, 2007, 915; E. Cano–Yelo and A. Deronzier, *J. Chem. Soc., Perkin Trans. II*, 1984, 1093; M. A. Ischay, M. E. Anzovino, J. Du and T. P. Yoon, *J. Am. Chem. Soc.*, 2008, **130**, 12886; H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, 1972, **94**, 8238.

4 F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Graetzel, *J. Am. Chem. Soc.*, 2008, **130**, 10720; H. J. Snaith, C. S. Karthikeyan, A. Petrozza, J. Teuscher, J. E. Moser, M. K. Nazeeruddin, M. Thelakkat and M. Graetzel, *J. Phys. Chem. C*, 2008, **112**, 7562; M. Graetzel, *Nature*, 2001, **414**, 338; A. Hagfeldt and M. Graetzel, *Acc. Chem. Res.*, 2000, **33**, 269; P. Liska, N. Vlachopoulos, M. K. Nazeeruddin, P. Comte and M. Graetzel, *J. Am. Chem. Soc.*, 1988, **110**, 3686.

5 T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163; E. Baranoff, J. P. Collin, L. Flamigni and J. P. Sauvage, *Chem. Soc. Rev.*, 2004, **33**, 147; L. Sun, L. Hammarstroem, B. Akermark and S. Styring, *Chem. Soc. Rev.*, 2001, **30**, 36; V. Balzani, F. Barigelletti and L. De Cola, *Top. Curr. Chem.*, 1990, **158**, 31.

6 C. Feuvrie, O. Maury, H. Le Bozec, I. Ledoux, J. P. Morrall, G. T. Dalton, M. Samoc and M. G. Humprey, *J. Phys. Chem. A*, 2007, **111**, 8980; C. Girardot, B. Cao, J. C. Mulatier, P. L. Baldeck, J. Chauvin, D. Riehl, J. A. Delaire, C. Andraud and G. Lemercier, *ChemPhysChem*, 2008, **9**, 1531; O. Maury and H. Le Bozec, *Acc. Chem. Res.*, 2005, **38**, 691; H. Le Bozec and T. Renouard, *Eur. J. Inorg. Chem.*, 2000, 229.

7 H. Wei and E. Wang, *Trends Anal. Chem.*, 2008, **27**, 447; B. A. Gorman, P. S. Francis and N. W. Barnett, *Analyst*, 2006, **131**, 616; D. Dini, *Chem. Mater.*, 2005, **17**, 1933; V. Balzani and A. Juris, *Coord. Chem. Rev.*, 2001, **211**, 97.

8 K. Sone and M. Yagi, *Electrochim. Acta*, 2008, **53**, 6535; R. J. Mortimer, A. L. Dyer and J. J. Reynolds, *Displays*, 2006, **27**, 2; D. H. Oh and S. G. Boxer, *J. Am. Chem. Soc.*, 1990, **112**, 8161.

9 K. Szacilowski, W. Macyk, A. Drzewiecka-Matuszek, M. Brindell and G. Stochel, *Chem. Rev.*, 2005, **105**, 2647; M. C. De Rosa and R. J. Crutchley, *Coord. Chem. Rev.*, 2002, **233–234**, 351.

10 S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini and V. Balzani, *Top. Curr. Chem.*, 2007, **280**, 117; A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von Zelewsky, *Coord. Chem. Rev.*, 1989, **84**, 85; K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159; J. N. Demas and D. G. Taylor, *Inorg. Chem.*, 1979, **18**, 3177; G. D. Hager and G. A. Crosby, *J. Am. Chem. Soc.*, 1975, **97**, 7031.

11 M. Hissler, A. Harriman, A. Khatyr and R. Ziessel, *Chem.–Eur. J.*, 1999, **5**, 3366; A. Harriman, F. M. Romero, R. Ziessel and A. C. Benniston, *J. Phys. Chem. A*, 1999, **103**, 5399; R. L. Cleary, K. J. Byrom, D. A. Bardwell, J. C. Jeffery, M. D. Ward, G. Calogero, N. Armaroli, L. Flamigni and F. Barigelletti, *Inorg. Chem.*, 1997, **36**, 2601; R. J. Shaw, W. F. Wacholtz, C. K. Ryu and R. H. Schmehl, *New J. Chem.*, 1996, **20**, 749; X. Y. Zhang and M. A. J. Rodgers, *J. Phys. Chem.*, 1995, **99**, 12797; M. Ruthkosky, C. A. Kelly, F. N. Castellano and G. J. Meyer, *Coord. Chem. Rev.*, 1998, **171**, 309; M. Tsushima, N. Ikeda, A. Yoshimura, K. Nozaki and T. Ohno, *Coord. Chem. Rev.*, 2000, **208**, 299.

12 M. Marcaccio, F. Paolucci, C. Paradisi, S. Roffia, C. Fontanesi, L. J. Yellowlees, S. Serroni, S. Campagna, G. Denti and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 10081; S. Stagni, A. Palazzi, S. Zacchini, B. Ballarin, C. Bruno, M. Marcaccio, F. Paolucci, M. Monari, M. Carano and A. Bard, *Inorg. Chem.*, 2006, **45**, 695; M. Marcaccio, F. Paolucci, C. Paradisi, M. Carano, S. Roffia, C. Fontanesi, L. J. Yellowlees, S.

Serroni, S. Campagna and V. Balzani, *J. Electroanal. Chem.*, 2002, **532**, 99; S. Roffia, R. Casadei, F. Paolucci, C. Paradisi, C. A. Bignozzi and F. Scandola, *J. Electroanal. Chem.*, 1991, **302**, 157.
13 J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, 1971, **93**, 1800; M. H. V. Huynh, D. M. Dattelbaum and T. J. Meyer, *Coord. Chem. Rev.*, 2005, **249**, 457; G. Lemercier, A. Bonne, M. Four and L. M. Lawson-Daku, *C. R. Chimie*, 2008, **11**, 709; A. Vogler and H. Kunkely, *Coord. Chem. Rev.*, 1998, **177**, 81.
14 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
15 K. C. Gordon, A. K. Burrell, T. J. Simpson, S. E. Page, G. Kelso, M. I. J. Polson and A. Flood, *Eur. J. Inorg. Chem.*, 2002, 554; K. D. Demadis, G. A. Neyhart, E. M. Kober and T. J. Meyer, *J. Am. Chem. Soc.*, 1998, **120**, 7121; M. Haga, T. Matsumura-Inoue and S. Yamabe, *Inorg. Chem.*, 1987, **26**, 4148; D. M. D'Alessandro, P. H. Dinolfo, M. S. Davies, J. T. Hupp and F. R. Keene, *Inorg. Chem.*, 2006, **45**, 3261; N. Chanda, R. H. Laye, S. Chakraborty, R. L. Paul, J. C. Jeffery, M. D. Ward and G. K. Lahiri, *J. Chem. Soc., Dalton Trans.*, 2002, 3496.
16 R. Hage, A. H. J. Dijkhuis, J. G. Haasnoot, R. Prins, J. Reedijk, B. E. Buchanan and J. G. Vos, *Inorg. Chem.*, 1988, **27**, 2185; R. Hage, J. G. Haasnoot, J. Reedijk, R. Wang and J. G. Vos, *Inorg. Chem.*, 1991, **30**, 3263; R. Hage, H. E. B. Lempers, J. G. Haasnoot, J. Reedijk, F. M. Weldon and J. G. Vos, *Inorg. Chem.*, 1997, **36**, 3139; C. Di Pietro, S. Serroni, S. Campagna, M. Gandolfi, R. Ballardini, S. Fanni, W. R. Browne and J. G. Vos, *Inorg. Chem.*, 2002, **41**, 2871; R. Hage, J. G. Haasnoot, H. A. Nieuwenhuis, J. Reedijk, D. J. A. De Ridder and J. G. Vos, *J. Am. Chem. Soc.*, 1990, **112**, 9245; W. R. Browne, N. M. O'Boyle, W. Henry, A. L. Guckian, S. Horn, T. Fett, C. M. O'Connor, M. Duati, L. De Cola, C. G. Coates, K. L. Ronayne, J. J. McGarvey and J. G. Vos, *J. Am. Chem. Soc.*, 2000, **127**, 1229.
17 W. R. Browne, R. Hage and J. G. Vos, *Coord. Chem. Rev.*, 2006, **250**, 1653; M. D. Ward and F. Barigelletti, *Coord. Chem. Rev.*, 2001, **216–217**, 127; A. Beyeler and P. Belser, *Coord. Chem. Rev.*, 2002, **230**, 29; M. M. Richter and K. J. Brewer, *Inorg. Chem.*, 1993, **32**, 2827; H. P. Hughes and J. G. Vos, *Inorg. Chem.*, 1995, **34**, 4001; B. Schlicke, P. Belser, L. De Cola, E. Sabbioni and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 4207; B. Gholamkass, K. Nozaki and T. Ohno, *J. Phys. Chem. B*, 1997, **101**, 9010; E. A. Fellows and F. R. Keene, *J. Phys. Chem. B*, 2007, **111**, 6667.
18 D. E. Richardson and H. Taube, *Coord. Chem. Rev.*, 1984, **60**, 107.
19 C. Creutz, in *Progress of Inorganic Chemistry*, ed. S. J. Lippard, Wiley: 1983, New York, vol. 30.
20 C. Creutz, M. D. Newton and N. J. Sutin, *Photochem. Photobiol. A*, 1994, **82**, 47.
21 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
22 N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391.
23 D. M. D'Alessandro and F. R. Keene, *Pure Appl. Chem.*, 2008, **80**, 1; D. M. D'Alessandro and F. R. Keene, *Chem. Rev.*, 2006, **106**, 2270; J. P. Launay, *Chem. Soc. Rev.*, 2001, **30**, 386.
24 K. A. Goldsby and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 3002; M. Haga, M. M. Ale, S. Koseki, A. Yoshimura, K. Nozaki and T. Ohno, *Inorg. Chim. Acta*, 1994, **226**, 17.
25 D. M. D'Alessandro and F. R. Keene, *Chem. Soc. Rev.*, 2006, **35**, 424; K. D. Demadis, G. A. Neyhart, E. M. Kober, P. S. White and T. J. Meyer, *Inorg. Chem.*, 1999, **38**, 5948.
26 L. Cassidy, S. Horne, L. Cleary, W. R. Browne, and J. G. Vos, *Dalton Trans.*, 2009, in press.
27 L. De Cola, F. Barigelletti, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Chem. Phys. Lett.*, 1991, **178**, 491.
28 F. Barigelletti, L. De Cola, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chem.*, 1991, **30**, 641.
29 M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1994, 3095.
30 Y. Q. Fang, M. I. J. Polson and G. S. Hanan, *Inorg. Chem.*, 2003, **42**, 5.
31 M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1993, 1321.
32 D. A. Bardwell, F. Barigelletti, R. L. Cleary, L. Flamigni, M. Guardigli, J. C. Jeffery and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 2438.
33 V. Balzani, D. A. Bardwell, F. Barigelletti, R. L. Cleary, L. Flamigni, M. Guardigli, J. C. Jeffery, T. Sovrani and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1995, 3601.
34 A. J. Downard, G. E. Honey, L. F. Phillips and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 2259; P. Rillema and K. B. Mack, *Inorg. Chem.*, 1982, **21**, 3849.
35 C. M. Elliott and E. J. Hershenhart, *J. Am. Chem. Soc.*, 1982, **104**, 7519; J. B. Cooper, D. B. MacQueen, J. D. Petersen and D. W. Wertz, *Inorg. Chem.*, 1990, **29**, 3701.
36 T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, 1975, **58**, 401; T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, 1975, **60**, 1; W. R. Browne, C. M. O'Connor, H. P. Hughes, R. Hage, O. Walter, M. Doering, J. F. Gallagher and J. G. Vos, *J. Chem. Soc., Dalton Trans*, 2002, 4048; T. M. Pappenfus and K. R. Mann, *Inorg. Chem.*, 2001, **40**, 6301.
37 G. Orellana, M. L. Quiroga and A. M. Braun, *Helv. Chim. Acta*, 1987, **70**, 2073; R. Hage, J. G. Haasnoot, D. J. Stufkens, T. L. Snoeck, J. G. Vos and J. Reedijk, *Inorg. Chem.*, 1989, **28**, 1413.
38 D. E. Richardson and H. Taube, *Inorg. Chem.*, 1981, **20**, 1278.
39 W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch and B. L. Feringa, *Chem.–Eur. J.*, 2005, **11**, 6414.
40 A. Juris, S. Campagna, V. Balzani, G. Gremaud and A. Von Zelewsky, *Inorg. Chem.*, 1988, **27**, 3652.
41 M. Haga, M. Ali and R. Arakawa, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 76.
42 M. Duati, S. Tasca, F. C. Lynch, H. Bohlen, J. G. Vos, S. Stagni and M. D. Ward, *Inorg. Chem.*, 2003, **42**, 8377.
43 J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
44 P. Passaniti, W. R. Browne, F. C. Lynch, D. Hughes, M. Nieuwenhuyzen, P. James, M. Maestri and J. G. Vos, *J. Chem. Soc., Dalton Trans.*, 2002, 1740; M. K. Nazeeruddin, S. M. Zakeeruddin and K. Kalyanasundaram, *J. Phys. Chem.*, 1993, **97**, 9607.
45 K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655.
46 N. S. Hush, *Electrochim. Acta*, 1968, **13**, 1005.

 This journal is © The Royal Society of Chemistry 2009