Analyst

Cite this: *Analyst*, 2012, **137**, 2766

www.rsc.org/analyst

COMMUNICATION

Chemiluminescence from osmium(II) complexes with phenanthroline, diphosphine and diarsine ligands†

Elizabeth M. Zammit,[a] Gregory J. Barbante,[a] Brenden Carlson,[b] Egan H. Doeven,[c] Neil W. Barnett,[a] Conor F. Hogan,[c] Mark M. Richter[d] and Paul S. Francis*[a]

Received 3rd April 2012, Accepted 23rd April 2012
DOI: 10.1039/c2an35446b

The reaction of various $[Os(L)_2(L')]^{2+}$ complexes (where L and L′ are phenanthroline, diphosphine or diarsine ligands) and organic reducing agents after chemical or electrochemical oxidation of the reactants produces an emission of light corresponding to MLCT transitions. In certain instances, the emission was greater than that of $[Ru(bipy)_3]^{2+}$, but the relative signals were dependent on many factors, including reagent concentration, mode of oxidation, reducing agent and the sensitivity of the photodetector over the wavelength range.

The extensive use of $[Ru(bipy)_3]^{2+}$ and its derivatives in chemiluminescence[1] and electrochemiluminescence (ECL)[2–5] detection has created great interest in alternative metal-complex reagents to improve the sensitivity of existing detection systems and develop new analytical applications.[3,6–9] Osmium complexes offer some advantages over their ruthenium counterparts: the larger crystal field strength of the heavy metal raises the energy of the non-emissive d–d states, which reduces thermal deactivation of the metal-to-ligand charge transfer (MLCT) states, imparting greater photostability.[10,11] However, tris diimine Os(II) complexes generally exhibit lower emission energies, shorter excited-state lifetimes and lower ECL efficiencies than their Ru(II) analogues[12–14] which has been attributed to differences in oxidation potentials, larger spin–orbit coupling and energy gap considerations. These shortcomings have been addressed by substituting one or more diimine ligands with stronger π-acceptors, such as diphosphine or diarsine species.[15–17] Richter *et al.* for example, showed that the ECL efficiency of $[Os(phen)_2(dppene)]^{2+}$ (phen = 1,10-phenanthroline, dppene = bis(diphenylphosphino) ethene) was double that of $[Ru(bipy)_3]^{2+}$, with tri-*n*-propylamine (TPA) in aqueous solution,[17] and further enhancements (3- to 5-fold) were obtained by incorporating a non-ionic surfactant[18] or ionic liquids.[19] In more recent studies, related Os(II) complexes in acetonitrile, acetonitrile–water and acetonitrile–dioxane solutions have exhibited greater annihilation and co-reactant ECL efficiencies than $[Ru(bipy)_3]^{2+}$.[20,21] Despite these promising preliminary investigations into osmium-based ECL, the possibility of initiating these reactions with chemical oxidants is yet to be explored. Herein, we examine the light-producing reactions of Os(II) complexes with organic reducing agents, initiated by chemical or electrochemical oxidation, to assess their potential as chemiluminescence reagents and derive new insight into their interrelated redox and luminescence properties.‡

A variety of Os(II) complexes, $[Os(bthp)_2(dmpe)]^{2+}$ (**1**), $[Os(tmep)_2(dchpe)]^{2+}$ (**2**), $[Os(tmep)_2(diars)]^{2+}$ (**3**), $[Os(tmep)_2(dmpe)]^{2+}$ (**4**), $[Os(phen)_2(dppene)]^{2+}$ (**5**), $[Os(diars)_2(bthp)]^{2+}$ (**6**) (see Fig. 1 for full ligand names and structures), were prepared as hexafluorophosphate salts as previously described.[15,22]

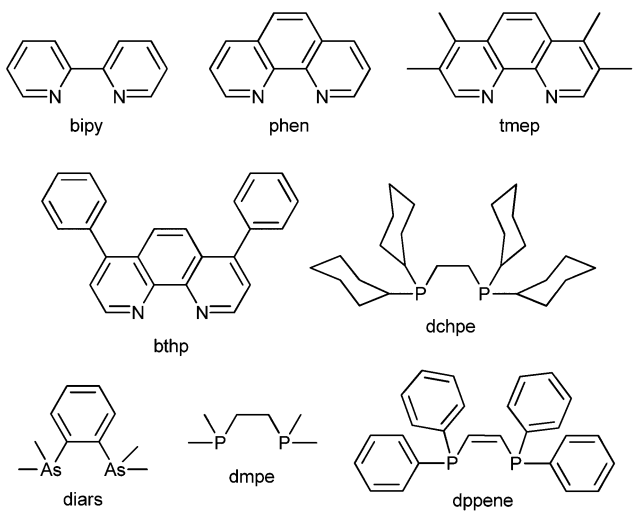

Fig. 1 Ligands. **bipy**: 2,2′-bipyridine, **phen**: 1,10-phenanthroline, **tmep**: 3,4,7,8-tetramethyl-1,10-phenanthroline, **bthp**: 4,7-diphenyl-1,10-phenanthroline (*i.e.* bathophenanthroline), **dchpe**: 1,2-bis(dicyclohexylphosphino)ethane, **diars**: 1,2-bis(dimethylarseno)benzene, **dmpe**: 1,2-bis(dimethylphosphino)ethane, and **dppene**: bis(diphenylphosphino) ethane.

[a]*School of Life and Environmental Sciences, Deakin University, Locked Bag 20000, Geelong, Victoria 3220, Australia. E-mail: paul.francis@deakin.edu.au; Tel: +61 3 5227 1294*
[b]*Department of Chemistry, University of Washington, Seattle, Washington, 98195, USA*
[c]*Department of Chemistry, La Trobe Institute for Molecular Science, LaTrobe University, Victoria 3086, Australia*
[d]*Department of Chemistry, Missouri State University, Springfield, Missouri 65897, USA*
† Electronic supplementary information (ESI) available: ECL intensity *versus* oxidation potential. See DOI: 10.1039/c2an35446b

Table 1 Selected spectroscopic and electrochemical data

Complex	PL[a]/eV	τ[a]/μs	ϕ_{PL}[a]	E°[bc]/V	ECL[cd]/eV	ECL[c]/nm
1	1.88	1.6	0.12	1.063	1.85	670
2	1.95	1.7	0.10	0.976	1.94	640
3	1.98	1.7	0.08	0.954	1.97	630
4	2.03	2.4	0.17	0.938	1.97	630
5	2.08	1.8	0.20	1.340[e]	2.00	620
6	2.09	8.9	0.36	1.464[e]	2.05	605

[a] In acetonitrile; data from ref. 22 for complexes **1**–**4** and **6**, and ref. 15 for complex **5**. [b] $M^{2+/3+}$ *vs.* Ag/AgCl. [c] In 1 : 1 (v/v) acetonitrile–aqueous phosphate buffer (0.1 M, pH 7). [d] A co-reactant concentration of 500 μM was used for all complexes, except for **6** where 10 mM co-reactant was used. [e] Peak potentials rather than formal potentials.

In contrast to $[Os(phen)_3]^{2+}$, which emits in the near-infrared (λ_{max} = 720 nm; 1.72 eV),[10] these complexes exhibited emission maxima in the visible region (Table 1). Complexes **2**–**5** (each incorporating a single diphosphine or diarsine ligand) emitted at wavelengths similar to those of $[Ru(bipy)_3]^{2+}$ (λ_{max} = 620 nm; 2.00 eV). In the case of complex **1**, the hypsochromic influence of the diphosphine ligand was somewhat off-set by the low π* energy of the bathophenanthroline ligands. DFT calculations have shown that the excited states of these complexes predominantly involve charge-transfer between the d metal orbitals and the π* of the substituted phenanthroline ligands.[22] Complex **6** (containing two diarsine ligands) exhibited the highest energy radiative transition. In this case, DFT calculations indicated significant mixing of the ligand-centred π–π* into the MLCT state, resulting in a greater quantum yield and excited state lifetime (Table 1).[22]

A comparison of the ECL of these complexes dissolved in 1 : 1 v/v acetonitrile–water using potassium oxalate and ofloxacin (a tertiary amine pharmaceutical) as co-reactants revealed marked differences in intensity that did not follow the observed trends of photoluminescence quantum yield.§ In agreement with previous studies of related complexes,[20,21] several species (complexes **2**, **3**, **5**) exhibited greater intensities than $[Ru(bipy)_3]^{2+}$, which can be initiated at considerably lower electrode potentials than 1.176 V found for $[Ru(bipy)_3]^{2+}$ under these conditions. In addition to more sensitive detection,[1–4] these complexes hold great promise for application in the recently devised approach to selectively excite multiple concomitant electrochemiluminophores based on their distinct redox properties.[9] A plot of ECL intensity *versus* oxidation potential (Fig. S1 in ESI†) shows relatively intense emissions from complexes that have significantly lower or higher oxidation potentials than $[Ru(bipy)_3]^{2+}$.

Table 3 Spectroscopic properties of Ru(II)/Os(II) complexes (chloride salts) in acidic aqueous solution**

Complex	λ_{abs}[a]/nm		λ_{em}[ab]/nm	ϕ_{PL}[c]
	π–π*	MLCT		
$[Ru(bipy)_3]^{2+}$	285	427, 454	628	0.028[d]
$[Ru(phen)_3]^{2+}$	263	420, 450	606	0.027
$[Os(phen)_2(dppene)]^{2+}$	266	369, 476	620	0.070

[a] 1×10^{-5} M complex in 0.05 M sulfuric acid, in a quartz cell of 1 cm path length. [b] Excitation at 450 nm. [c] Air saturated aqueous solution at room temperature. [d] From ref. 25.

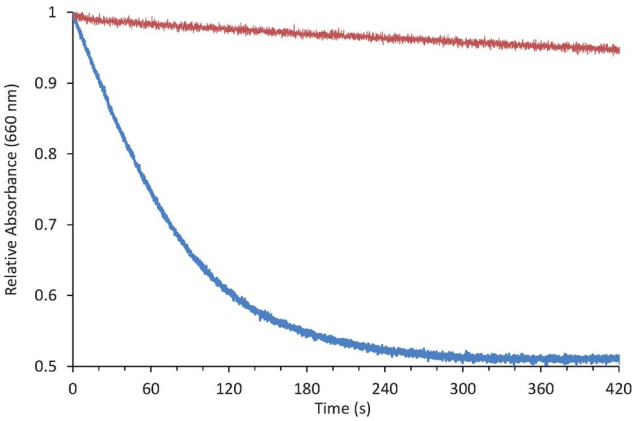

Fig. 2 Temporal stability of $[Ru(bipy)_3]^{3+}$ (red line) and $[Os(phen)_2(dppene)]^{3+}$ (blue line) in 0.05 M sulfuric acid, monitored by absorbance at 660 nm (normalised at $t = 0$). The Ru(II)/Os(II) complexes were oxidised using lead dioxide which was removed by syringe tip filter as the solutions were dispensed into the cuvette within the spectrophotometer.[24]

We examined the chemically initiated luminescence of these six Os(II) complexes (1 mM in 1 : 1 v/v acetonitrile–water) using flow injection analysis methodology,¶ where the complex was injected into a carrier stream containing ofloxacin (1×10^{-5} M in 1 : 1 v/v acetonitrile–water), which merged with an aqueous acidic oxidant solution (1 mM cerium(IV) sulfate in 0.05 M sulfuric acid), before

Table 2 ECL and chemiluminescence intensities (blank subtracted) for the osmium complexes, relative to that of $[Ru(bipy)_3]^{2+}$ under each set of chemical and instrumental conditions

	Relative ECL intensity§		Relative CL intensity¶	
	Ofloxacin[a]	Oxalate[a]	Ofloxacin[a]–cerium(IV)[b]	
Complex	Trialkali PMT[c]	Trialkali PMT[c]	Bialkali PMT[d]	Trialkali PMT[c]
1	1.31	0.93	0.06	0.76
2	4.00	4.84	0.10	0.20
3	5.16	2.59	0.14	0.07
4	0.54	0.56	0.04	0.05
5	2.45	1.54	0.88	0.48
6	0.12	0.22	0.17	0.06

[a] Co-reactant. [b] Chemical oxidant. [c] Model 9828SB. [d] Model 9124B40.

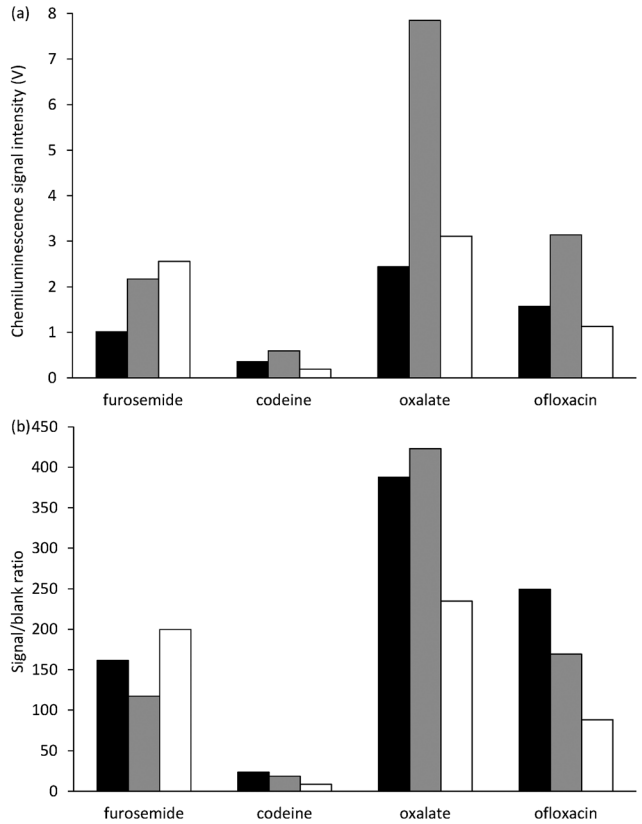

Fig. 3 Chemiluminescence signal and signal/blank ratio for the reaction of 0.1 mM $[Ru(bipy)_3]^{2+}$ (black columns), $[Ru(phen)_3]^{2+}$ (grey columns) or $[Os(phen)_2(dppene)]^{2+}$ (white columns) with cerium(IV) and various analytes (co-reactants) in acidic aqueous solution. Furosemide, codeine and potassium oxalate were at a concentration of 1×10^{-5} M and ofloxacin was at 1×10^{-6} M.

entering a coiled-tubing detection cell. Although no Os(II) complex produced a chemiluminescence signal greater than that of $[Ru(bipy)_3]^{2+}$ (with ofloxacin and cerium(IV)), large responses were observed for complex **5** and the far red emitters: complexes **1** and **2**. The emissions from these complexes occur in a region of the spectrum where the sensitivity of conventional photomultiplier tubes (PMTs) is significantly reduced. A comparison of intensities using a 'green enhanced' bialkali PMT (rather than the extended-range trialkali PMT) showed a large bias towards the complexes that emitted at lower wavelengths (Table 2). In agreement with previous studies of the chemiluminescence reactions of Ru(II) and Ir(III) complexes,[23,24] a different ratio of intensities was observed when the tertiary amine reductant was replaced with potassium oxalate (data not shown). Based on these findings, complex **5** ($[Os(phen)_2(dppene)]^{2+}$) was selected for further investigation.

The above Os(II) complexes and those utilised in previous ECL studies were prepared as hexafluorophosphate salts, which have low solubility in aqueous solution.[19] To examine the utility of $[Os(phen)_2(dppene)]^{2+}$ in this more analytically useful solvent, we therefore prepared the corresponding chloride salt.‖ Selected spectroscopic properties for $[Os(phen)_2(dppene)]^{2+}$, $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ in 0.05 M sulfuric acid are shown in Table 3. These values are in good agreement with previously reported data for these complexes in acetonitrile and aqueous solutions.[10,25]

Similar to observations for Ru(III) complexes containing phenanthroline ligands,[24] the oxidised $[Os(phen)_2(dppene)]^{3+}$ complex was found to be less stable in aqueous solution than $[Ru(bipy)_3]^{3+}$ (Fig. 2).** However, the *in situ* oxidation of reactants with cerium(IV) using flow injection analysis ensured reproducible mixing of solutions and avoided problems associated with the alternative approach of off-line oxidation with lead dioxide.[26]

The chemiluminescence of $[Os(phen)_2(dppene)]^{3+}$ with cerium(IV) and various organic compounds in aqueous solution was compared to that of $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ under identical conditions (Fig. 3).¶†† Previous investigations of the chemiluminescence of Ru(II) and Ir(III) complexes have revealed several species that produce more intense emissions than $[Ru(bipy)_3]^{2+}$.[27,28] However, these complexes also produced much greater 'blank' responses, due to reaction between complex and solvent, which has a deleterious effect when the intention is to detect the co-reactant. In contrast, 0.1 mM $[Os(phen)_2(dppene)]^{2+}$ gave comparable signal and blank responses to the conventional Ru(II) complexes (Fig. 3). In the case of furosemide, $[Os(phen)_2(dppene)]^{2+}$ gave double the intensity of $[Ru(bipy)_3]^{2+}$ and a higher signal/blank ratio.

Ofloxacin elicited the greatest responses of the four analytes (the results shown in Fig. 3 were obtained with ofloxacin at an order of magnitude lower concentration than the other compounds). Limits of detection for ofloxacin using 0.1 mM $[Ru(bipy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$ and $[Os(phen)_2(dppene)]^{2+}$ were 4.5×10^{-9} M, 1.7×10^{-9} M and 1.8×10^{-9} M, respectively, which are comparable with those previously reported for this analyte using $[Ru(bipy)_3]^{2+}$–Ce(IV) chemiluminescence (between 1×10^{-9} M and 6×10^{-7} M).[28–33] By increasing the concentration of the complexes to 1 mM, the signals became approximately 10-fold larger, but the signal/blank ratios decreased. This effect (previously ascribed to the relative reaction rates of the complex with analyte and solvent and the portion of the total emission detected by the flow injection analysis detector[28]) was more prominent for $[Ru(phen)_3]^{2+}$ and $[Os(phen)_2(dppene)]^{2+}$ than $[Ru(bipy)_3]^{2+}$.

Conclusions

Osmium(II) complexes that incorporate combinations of diimine and diphosphine or diarsine ligands are promising alternatives to traditional tris-diimine ruthenium(II) complexes for chemiluminescence and ECL detection. These complexes provide convenient control of redox and luminescence properties using a variety of readily available ligands.

Acknowledgements

This research was funded by the Australian Research Council (FT100100646).

Notes and references

‡ Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate was obtained from Strem Chemicals (Newbury, Minnesota, USA). Sulfuric acid was purchased from Merck (Kilsyth, Victoria, Australia). Cerium(IV) sulfate, 1,10-phenanthroline, ethylene glycol, Sephadex LH-20, furosemide, hydrochlorothiazide and ofloxacin were obtained from Sigma-Aldrich (Castle Hill, New South Wales, Australia). Codeine was donated by GlaxoSmithKline (Port Fairy, Victoria, Australia). Potassium oxalate was purchased from BDH Chemicals (Poole, England) and lead dioxide from Ajax Finechem (Sydney, Australia).

§ Electrochemical experiments were performed using μ-AUTOLAB electrochemical workstation potentiostat (MEP Instruments, North Ryde, NSW, Australia) with General Purpose Electrochemical Systems (GPES) software (version 4.9). The electrochemical cell consisted of a cylindrical glass container with a quartz base and Teflon cover with spill tray, and was encased in a custom-built light-tight faraday cage. The three-electrode configuration consisted of a glassy carbon 3 mm diameter working electrode shrouded in Teflon (CH Instruments, Austin, TX, USA), a 1 cm^2 platinum gauze auxiliary electrode and a Ag/AgCl reference electrode. Emission intensities were measured with an extended range photomultiplier tube (PMT; Electron Tubes model 9828B) positioned against the base of the cell. ECL spectra were obtained by replacing the PMT with a fibre optic cable (1 m) connected to a spectrometer with CCD detector (model QE6500, Ocean Optics). The spectrometer software was triggered by the potentiostat using a HR 4000 Break-Out box. The complexes were prepared at a concentration of 0.1 mM in 1 : 1 v/v acetonitrile–water, with 0.1 M phosphate buffer (pH 7) as the supporting electrolyte. Prior to each experiment, the working electrode was polished using 0.3 μm and then 0.05 μm alumina with Milli-Q water on a felt pad, rinsed in freshly distilled acetonitrile and dried with a stream of nitrogen. The working electrode was then positioned at an appropriate distance (~2 mm) from the bottom of the cell for detection of the ECL signal, and the solution was purged with argon for 5 min. The complexes were then electrochemically cycled to their respective oxidative potentials to generate the Ru(III)/Os(III) forms in the presence of 10 μM ofloxacin or potassium oxalate. All intensities were compared to that of $[Ru(bipy)_3]^{2+}$.

¶ For the examination of chemiluminescence intensities, flow injection analysis was used to reproducibly combine the reacting species. The manifold was constructed as previously described.[34] The distance between the final confluence point and the beginning of the detection coil was ~10 mm. The photodetector was an Electron Tubes photomultiplier tube (ETP, NSW, Australia), model 9124B40 operated at 0.9 kV, or 9828SB operated at 1.3 kV. The Os(II)/Ru(II) complex (dissolved in either 1 : 1 v/v acetonitrile–water or aqueous 0.05 M H_2SO_4) was injected (70 μL) into a carrier line containing the co-reactant/analyte (in the same solvent), which merged with the oxidant (1×10^{-3} M cerium(IV) sulfate in 0.05 M H_2SO_4) before entering the detection flow-cell. For each complex/co-reactant combination, flow rates of 1 and 3.5 mL min^{-1} per line were compared. Blank signals were obtained under the same conditions, except that the co-reactant/analyte solution was replaced by deionised water.

‖ The synthesis of $[Os(phen)_2(dppene)]Cl_2$ followed the procedures of Kober and co-workers.[16] 1H NMR 8.554–8.585 (dd, 2H), 8.366–8.388 (dd, 2H), 8.347 (s, 2H), 8.179–8.210 (dd, 2H), 8.106–8.136 (2H), 8.014–8.036 (dd, 2H), 7.955–7.985 (2H), 7.492–7.641 (m, 12H), 7.129–7.175 (q, 2H), 6.905–6.959 (m, 2H), 6.596–6.649 (t, 4H), 6.072–6.099 (d, 4H), yield 0.958 g (28.3%).

** Absorbance and photoluminescence measurements were performed using a Cary 300 Bio UV-Vis Spectrophotometer and Cary Eclipse Spectrofluorimeter (Varian Analytical Instruments, Australia). Emission spectra were corrected as previously described.[35] The stability of the Ru(III)/Os(III) complexes in acidic aqueous solution and the relative photoluminescence quantum yields of the Ru(II)/Os(II) complexes were established as previously described.[24,36] Quantum yield experiments were performed at room temperature without degassing, using the literature value of 0.028 for $[Ru(bipy)_3]^{2+}$ in air-saturated aqueous solution.[25]

†† In an initial optimisation of conditions, the Os(II)/Ru(II) complexes were tested at concentrations of 0.1, 0.5 and 1 mM. The greatest intensities were observed using 1 mM, but 0.1 mM tended to give superior signal-to-blank ratios.

1 B. A. Gorman, P. S. Francis and N. W. Barnett, *Analyst*, 2006, **131**, 616–639.
2 M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003–3036.
3 W. Miao, *Chem. Rev.*, 2008, **108**, 2506–2553.
4 L. Hu and G. Xu, *Chem. Soc. Rev.*, 2010, **39**, 3275–3304.
5 A. J. Bard, *Electrogenerated Chemiluminescence*, Marcel Dekker, New York, 2004.
6 M. M. Richter, in *Optical Biosensors*, ed. F. S. Ligler and C. Rowe Taitt, Elsevier, Amsterdam, 2nd edn, 2008, pp. 317–384.
7 R. J. Forster, P. Bertoncello and T. E. Keyes, *Annu. Rev. Anal. Chem.*, 2009, **2**, 359–385.
8 A. Kapturkiewicz, in *Electrochemistry of Functional Supramolecular Systems*, ed. P. Ceroni, A. Credi and M. Venturi, Wiley-Interscience, Hoboken, N.J., 2010, pp. 477–522.
9 E. H. Doeven, E. M. Zammit, G. J. Barbante, C. F. Hogan, N. W. Barnett and P. S. Francis, *Angew. Chem., Int. Ed.*, 2012, DOI: 10.1002/anie.201200814, in press.
10 E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1985, **24**, 2755–2763.
11 J. N. Demas and B. A. DeGraff, *Anal. Chem.*, 1991, **63**, 829A–837A.
12 C. Creutz, M. Chou, T. L. Netzel, M. Okumura and N. Sutin, *J. Am. Chem. Soc.*, 1980, **102**, 1309–1319.
13 F. Bolletta, M. Ciano, V. Balzani and N. Serpone, *Inorg. Chim. Acta*, 1982, **62**, 207–213.
14 H. D. Abruña, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **175**, 321–326.
15 E. M. Kober, B. P. Sullivan, W. J. Dressick, J. V. Caspar and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 7383–7385.
16 E. M. Kober, J. V. Caspar, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 4587–4598.
17 D. Bruce, M. M. Richter and K. J. Brewer, *Anal. Chem.*, 2002, **74**, 3157–3159.
18 J. Walworth, K. J. Brewer and M. M. Richter, *Anal. Chim. Acta*, 2004, **503**, 241–245.
19 J. Roop, M. Nothnagel, M. Schnuriger, M. M. Richter and G. A. Baker, *J. Electroanal. Chem.*, 2011, **656**, 34–40.
20 G. Angulo, A. Kapturkiewicz, S.-Y. Chang and Y. Chi, *Inorg. Chem. Commun.*, 2009, **12**, 378–381.
21 N. S. Pennington, M. M. Richter and B. Carlson, *Dalton Trans.*, 2010, **39**, 1586–1590.
22 B. Carlson, B. E. Eichinger, W. Kaminsky, J. P. Bullock and G. D. Phelan, *Inorg. Chim. Acta*, 2009, **362**, 1611–1618.
23 R. V. Kiran, E. M. Zammit, C. F. Hogan, B. D. James, N. W. Barnett and P. S. Francis, *Analyst*, 2009, **134**, 1297–1298.
24 M. M. Cooke, E. H. Doeven, C. F. Hogan, J. L. Adcock, G. P. McDermott, X. A. Conlan, N. W. Barnett, F. M. Pfeffer and P. S. Francis, *Anal. Chim. Acta*, 2009, **635**, 94–101.
25 K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697–2705.
26 G. P. McDermott, P. Jones, N. W. Barnett, D. N. Donaldson and P. S. Francis, *Anal. Chem.*, 2011, **83**, 5453–5457.
27 G. P. McDermott, E. M. Zammit, E. K. Bowen, M. M. Cooke, J. L. Adcock, X. A. Conlan, F. M. Pfeffer, N. W. Barnett, G. A. Dyson and P. S. Francis, *Anal. Chim. Acta*, 2009, **634**, 222–227.
28 E. M. Zammit, N. W. Barnett, L. C. Henderson, G. A. Dyson, M. Zhou and P. S. Francis, *Analyst*, 2011, **136**, 3069–3072.
29 G.-H. Wan, H. Cui, Y.-L. Pan, P. Zheng and L.-J. Liu, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.*, 2006, **843**, 1–9.
30 P. S. Francis and J. L. Adcock, *Anal. Chim. Acta*, 2005, **541**, 3–12.
31 F. A. Aly, S. A. Al-Tamimi and A. A. Alwarthan, *Talanta*, 2001, **53**, 885–893.
32 J. A. Murillo, A. Alanon Molina, A. Munoz de la Pena, I. Duran Meras and A. Jimenez Giron, *J. Fluoresc.*, 2007, **17**, 481–491.
33 Y.-M. Liu, Y.-X. Jia and W. Tian, *J. Sep. Sci.*, 2008, **31**, 3765–3771.
34 J. L. Adcock, N. W. Barnett, J. W. Costin, P. S. Francis and S. W. Lewis, *Talanta*, 2005, **67**, 585–589.
35 P. S. Francis, J. L. Adcock and N. W. Barnett, *Spectrochim. Acta, Part A*, 2006, **65**, 708–710.
36 G. J. Barbante, C. F. Hogan, D. J. D. Wilson, N. A. Lewcenko, F. M. Pfeffer, N. W. Barnett and P. S. Francis, *Analyst*, 2011, **136**, 1329–1338.