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Insights into electrochemiluminescent enhancement through electrode surface modification†

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The electrochemiluminescent (ECL) properties of a luminescent metal centre, $[\text{Ru}(\text{bpy})_3]^{2+}$, can be significantly modulated through its electronic interaction with neighbouring centres and the polymer backbone used to confine it on an electrode surface. From the perspective of ECL based sensing devices, an increase in the ECL efficiency of a metallopolymer film can result in enhanced sensor sensitivity and selectivity. This work probes the ECL properties of both conjugated, $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$, and non-conjugated, $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$, ruthenium based metallopolymer films based on a well documented reaction with sodium oxalate, where bpy is 2,2'-bipyridyl, PPyBBIM is poly[2-(2-pyridyl)-bibenzimidazole] and PVP is poly(4-vinylpyridine). Through a combination of ground state electrochemical studies and ECL measurements, the ECL efficiency for each film is determined. This study reveals that despite a dramatic influence in charge transfer rates between metal centres, as observed for the conducting polymer, mediated through the conducting polymer backbone, a corresponding increase in ECL efficiency is not always observed. The degree of communication between the adjacent excited state metal centres are an important consideration for ECL enhancement however self quenching, luminophore distribution and film porosity must also be considered.

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Introduction

ECL has been the subject of extensive study for the past three decades.^{1–6} The production of light from intermediates generated during electrolysis occurs when the energy liberated by the reaction between the electrogenerated precursors is sufficient to generate a product in an electronically excited form.⁷ Studies of inorganic ECL have been dominated by transition metal complexes,^{8–10} particularly ruthenium poly(pyridyl) species, *e.g.*, those of the general formula $\text{Ru}(\text{L})_3^{2+}$, *e.g.*, where L = 2,2'-bipyridine,^{11–13} 4,7-diphenyl-1,10-phenanthroline¹⁴ or 2,2'-bipyrazine.¹⁵ This is due to the attractive photophysical and electrochemical properties that these compounds typically exhibit.

ECL combines the inherent sensitivity, selectivity and linear range advantages of chemiluminescence methods with increased temporal and spatial control over the chemiluminescent reaction making ECL a powerful analytical tool, particularly when the surface may be modified to tune the ECL properties. Systems utilising both organic and inorganic complexes have

been developed.^{16,17} The majority of early ECL systems investigated involved species dissolved in the solution phase with emission occurring in the diffusion layer near the electrode surface. The advent of chemically modified electrodes allowed ECL to be generated in films constrained to the surface of an electrode, *e.g.* as thin layers produced by electropolymerisation of vinyl containing monomeric species or by electrostatic incorporation of the luminescent species into a preformed polymer matrix. The ability to modify electrode surfaces with ECL producing complexes has greatly increased the scope of potential ECL applications within biomedical sensor design.

Depending on the nature of the specific ECL reaction, the sensitivity of film ECL based systems may be limited by certain factors including slow rates of charge transfer (characterised by the homogeneous charge transfer diffusion coefficient, D_{CT}) through the film. A slow rate of charge transfer will lead to slow regeneration of the Ru^{3+} state that is required to react with an analyte to produce ECL. In contrast, a fast charge transfer rate will lead to a higher numbers of excited state precursors per unit time, a brighter emission and improved sensitivity. One appealing possibility is to wire the luminophores using a conjugated polymer backbone. Charge transfer between ruthenium centres in a non-conjugated metallopolymer typically consists of a through space mechanism and the introduction of a conjugated backbone is known to enhance charge transfer rates between metal centres.¹⁸ For ECL to occur it must be thermodynamically feasible, *e.g.* the reaction between the oxidised and reduced species should have a negative ΔG° value. As

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† Electronic supplementary information (ESI) available: Randles-Sevcik for $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ thin films and photoluminescence and ECL emission spectra for $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ are given here. See DOI: 10.1039/c2an36045d

the formal potential for most ruthenium polypyridyl complexes ranges between 1.4 and 0.8 eV the range of co-reactants that can produce ECL with these systems can sometimes be limited. ECL production can also be affected by film porosity. A more porous film will allow enhanced diffusion of the analyte through the film to the ruthenium metal centres. Where a film is compact, an analyte may have difficulty diffusing through that film and as such only a fraction of the film is active for ECL generation. The level of porosity in a film is highly dependent on the structure of the polymer backbone however it can also be influenced by the pH of the contacting electrolyte as well as the concentration and identity of the electrolyte present.

This work describes how different polymeric surface confinement strategies can be utilised to modify the ECL properties to facilitate sensor development. Each approach has been evaluated based on charge transport and regeneration times within the film, ECL production and ECL efficiencies.

Experimental section

Materials and reagents

The metallopolymers, $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$, were prepared as described previously.^{19–21} For electrochemical measurements LiClO_4 purchased from Sigma Aldrich was used as the supporting electrolyte and made up to volume with MilliQ water (18 M Ω cm). All solvents used were of spectroscopic grade and were stored over activated molecular sieves. Working electrodes were prepared by polishing with alumina (1.0–0.3 μm) on a felt pad, followed by sonication in distilled deionized water for 30 min. Where appropriate, working electrodes were modified by applying a drop ($\approx 15 \mu\text{L}$) of an ethanolic solution of the metallopolymer or a $[\text{Ru}(\text{bpy})_3]^{2+}$:Nafion film to the electrode surface. Stock solutions of Nafion- $[\text{Ru}(\text{bpy})_3]^{2+}$ were prepared by dissolving 1 mg of $[\text{Ru}(\text{bpy})_3]^{2+}$ in 2 mL methanol. Then, 200 μL of this solution was diluted in 1.8 mL of methanol and 200 μL of Nafion (5% w/v mixture of low molecular weight alcohols) was added. The mediator was found to precipitate at higher concentrations. The modified electrodes were then allowed to dry in the dark for 10 to 12 hours. The surface coverage, Γ , was determined by graphical integration of background corrected cyclic voltammograms ($<5 \text{ mV s}^{-1}$). In all cases the surface coverage ranged from 1.4×10^{-8} to $3.1 \times 10^{-8} \text{ mol cm}^{-2}$. All solutions were deoxygenated using nitrogen or argon prior to measurement.

Apparatus

Electrochemical experiments were performed in a standard electrochemical cell using a CH instruments (Memphis TN.) model 660 potentiostat. Cyclic voltammetry experiments were carried out using a 3 mm diameter glassy carbon working electrode in a conventional three electrode assembly using a platinum flag as the counter electrode. Potentials were measured *versus* a standard Ag/AgCl aqueous reference electrode (3 M KCl). Measurements involving simultaneous detection of light and current utilized a CH instrument model 760B connected to an Oriel 70680 photomultiplier tube (PMT). The

PMT was biased at -850 V by a high voltage power supply (Oriel, model 70705) and an amplifier/recorder (Oriel, model 70701) was used in all the experiments. During the experiments, the cell was kept in a light-tight box in a specially designed holder where the working electrode was positioned directly opposite to the fibre optic bundle, the other end of which was coupled to the PMT. An Oriel model IS520 gated intensified CCD operated at $-20 \text{ }^\circ\text{C}$, coupled to an Oriel model MS125 spectrograph, was used to acquire ECL spectra. Where necessary, thin film emission spectra were smoothed using an eight-point Savitsky–Golay algorithm.

All measurements were made at room temperature ($20 \text{ }^\circ\text{C}$). For all ECL experiments 0.5 mM $\text{Na}_2\text{C}_2\text{O}_4$ (pH 6) was used as the co-reactant. All other reagents used were of analytical grade, and all solutions were prepared in milli-Q water (18 m Ω cm).

Results and discussion

Electrochemical properties of $\text{Ru}^{2+/3+}$ redox couple

ECL production is highly dependent upon the rate of charge transfer (D_{CT}). A fast rate of charge transfer ensures sufficient Ru^{3+} will be present to react with a given analyte and produce ECL. An insufficient amount of Ru^{3+} will result in decreased ECL emission and hence decreased sensitivity. The redox metallopolymers that have typically been used for ECL suffer from relatively slow charge transport compared to recently developed conducting metallopolymers.²²

Metallopolymers currently utilised for ECL production such as $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ consist of electrochemically active sites at each ruthenium metal centre tethered to a electrochemically *inactive* backbone. The ruthenium metal d-orbitals are isolated from one another and as such charge transfer occurs *via* a “through space mechanism” requiring polymer chain movement to allow the metal centres to collide. By incorporating a conjugated backbone the electronic interactions between the polymers π -system and the metals d-orbitals can modulate the properties of both components in interesting and potentially useful ways. One of the anticipated benefits is fast cycles of Ru^{3+} production and subsequent reaction with co-reactant which is typically present in excess. A faster rate of charge transfer would thereby significantly increase the production of ECL leading to enhanced sensitivity. This increase coupled with an increased luminescence yield should lead to favourable characteristics necessary for enhanced ECL production. This faster regeneration of the Ru^{3+} species in the $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_n]^{2+}$ metallopolymers arises from enhanced communication through the conjugated π -system and may increase the ECL intensity.¹⁸ This development could impact greatly on sensor design, as the faster regeneration of the Ru^{3+} species should drastically improve the sensitivity of systems involving a ruthenium redox centre. The rate of charge transfer can be conveniently addressed by determining the homogeneous charge transfer diffusion coefficient, D_{CT} , of each metallopolymer, Fig. 1. Fig. S1, shown in ESI,[†] shows that for $0.1 \leq \nu \leq 0.5 \text{ V s}^{-1}$, the voltammetric peak currents, i_p , increase linearly with increasing scan rate. This behavior is consistent with semi-infinite linear

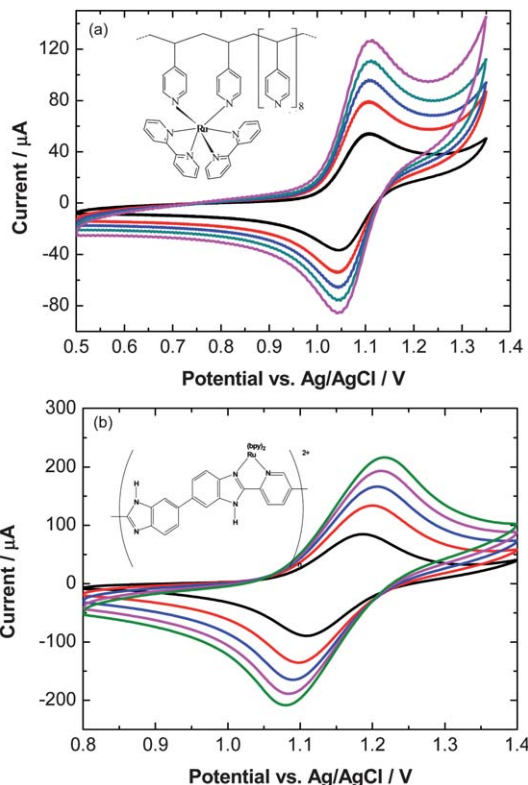


Fig. 1 Scan rate dependency for thin films of (a) $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$, and (b) $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ ($\Gamma = (2.1 \pm 0.2) \times 10^{-8} \text{ mol cm}^{-2}$), in 0.1 M LiClO_4 , $100 < \nu < 500 \text{ mV s}^{-1}$. Analysis was performed at pH 6.0. Structures of each metallopolymer are also provided.

diffusion and under these conditions the response can be described by the Randles–Sevcik equation;

$$i_p = 2.65 \times 10^5 n^{3/2} A D_{\text{CT}} \nu^{1/2} C \quad (1)$$

where n is the number of electrons transferred, A is the area of the working electrode, D_{CT} is the diffusion coefficient, and C is the concentration of the redox centers. The concentration of ruthenium centers within the metallopolymer has been determined from density measurements in non-swelling solvents as 0.8 M. Thus, eqn (1) allows D_{CT} to be estimated for both the oxidation and reduction processes of each metallopolymer. Table 1 shows the D_{CT} values for the oxidation process for each metallopolymer. As expected the fastest rate of charge transfer is obtained for the $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ metallopolymer being an order of magnitude faster than that obtained for the Nafion– $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ films. Based on these D_{CT} values it

Table 1 D_{CT} for thin films based on results from Fig. 1^a

Modified surface	D_{CT} ($\text{cm}^2 \text{ s}^{-1}$)
Nafion– $[\text{Ru}(\text{bpy})_3]^{2+}$	$2.3 \pm 0.8 \times 10^{-11}$
$[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$	$9.2 \pm 1.1 \times 10^{-11}$
$[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$	$4.79 \pm 0.8 \times 10^{-10}$

^a All values based on averaged results from 5 independent measurements.

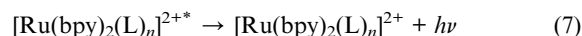
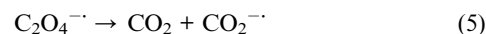
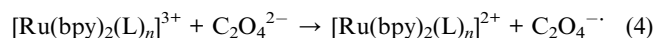
is possible to predict the regeneration rates of the Ru^{3+} species within each film according to the equation;²¹

$$t = \delta^2 / \pi D_{\text{CT}} \quad (2)$$

where δ is the minimum dry thickness and using D_{CT} calculated from eqn (2) which indicates the time taken to fully oxidise the film and regenerate the Ru^{3+} mediating centres was $\sim 10 \text{ s}$ for the PVP metallopolymer and just under 5 s for the conducting PPyBBIM film. Generally, this faster regeneration rate would indicate a possible increase in ECL intensity with a subsequent decrease in detection limits.²¹

Ruthenium-oxalate system

Previous work on imidazole metallopolymer has identified useful properties that may lead to an improvement in ECL sensor design.¹⁶ Therefore, the production of ECL has been probed using oxalate^{23,24} as the co-reactant. High oxalate concentrations in the blood or urine are associated with renal failure, vitamin deficiencies, intestinal deficiencies, hyperoxaluria²⁵ and have also been implicated in the formation of kidney stones. As such, selective and precise methods for the determination of oxalate are important. ECL *via* the reaction of sodium oxalate with the Ru^{3+} excited state is a well documented system.^{1–4,12,19} Ruthenium containing metallopolymer immobilised on an electrode surface such as $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ have also been shown to produce ECL upon reaction with oxalic acid. All ECL studies were carried out at pH 6.0. This pH was chosen as a near neutral pH is highly desirable for biological applications. The reaction scheme for the generation of ECL between a ruthenium containing metallopolymer and oxalic acid has been well documented^{14–16,24} and occurs according to the reaction scheme;^{5,12,19}



In this catalytic route, oxidation of oxalate is mainly through ruthenium mediated reaction. Direct oxidation of oxalate at the electrode, although thermodynamically possible, is known to be kinetically slow.²⁶ This behaviour arises because a significant overpotential must be applied before oxalic acid can be oxidized at a bare electrode. Therefore, the direct oxidation of oxalate is generally considered to contribute little to the ECL emission in either solution phase or immobilized ruthenium/oxalate systems.^{27–29} Fig. 2 shows the current responses obtained when thin films of Nafion– $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ are placed in 0.1 M phosphate buffer solution containing 0.5 mM $\text{Na}_2\text{C}_2\text{O}_4$ (pH 6). Significant increases in current are observed for each composite film. This enhanced current arises from the mediated oxidation of oxalic acid by

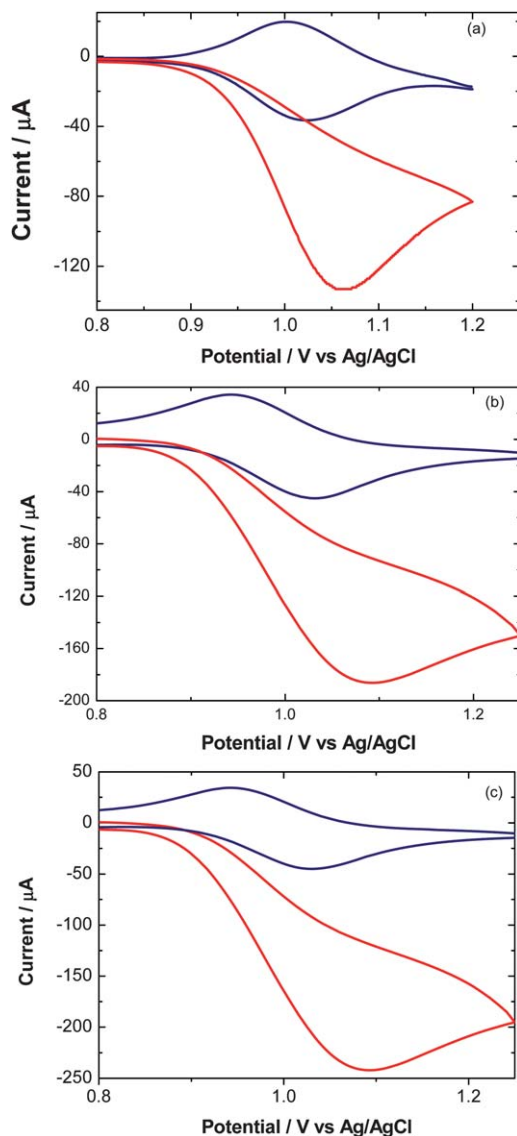


Fig. 2 Current responses for (a) Nafion-[Ru(bpy)₃]²⁺, (b) [Ru(bpy)₂(PVP)₁₀]²⁺, and (c) [Ru(bpy)₂(PPyBBIM)₁₀]²⁺ recorded in 0.1 M phosphate buffer solution supporting electrolyte: (blue line) without the addition of 0.5 mM Na₂C₂O₄; (red line) with the addition of 0.5 mM Na₂C₂O₄; analysis was performed at pH 6.

Ru³⁺ centres within the film. The current response increases with time due to the slow rate of equilibration upon addition of oxalate. The large increase in current at *circa* 1.1 V vs. Ag/AgCl, on addition of the substrate clearly demonstrates that oxalate is oxidised at potentials when Ru³⁺ sites exist within the metallopolymer film.

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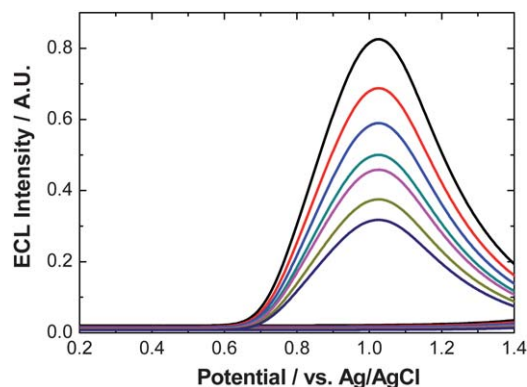


Fig. 3 ECL response of [Ru(bpy)₂(PVP)₁₀]²⁺ metallopolymer film on the concentration of [Na₂C₂O₄] at a scan rate of 100 mV s⁻¹ over the potential range 0.2 V ≤ ν ≤ 1.4 V vs. Ag/AgCl.

concentration of sodium oxalate. ECL occurs at a potential of approximately 1.1 V vs. Ag/AgCl as with the current response, (Fig. 3), and increases linearly with increasing concentration of oxalate. This linear range is observed for both metallopolymer films. The Nafion composite film, however, is less reproducible and seems to plateau at $\sim 1 \times 10^{-3} \text{ M}$, as can be seen in Fig. 4. Unlike the metallopolymer films, the ruthenium in the Nafion film is not covalently bound to the polymer but rather held in place due to electrostatic interactions. This results in ruthenium leaching from the modified layer into solution thereby reducing the amount available for reaction with oxalate at the electrode surface, thus leading to the plateau observed in Fig. 4.

ECL emission and enhancement studies

Emission spectra have been recorded in order to probe the nature of the electrochemically generated electronically excited state.

Fig. 5 shows an ECL spectrum of the ruthenium composite films in contact with a solution containing 0.1 M PBS and 0.5 mM Na₂C₂O₄ (pH 6) generated at +1.1 V. The optically and electrochemically stimulated spectra are very similar in shape suggesting that both arise from the ³MLCT excited state, shown in

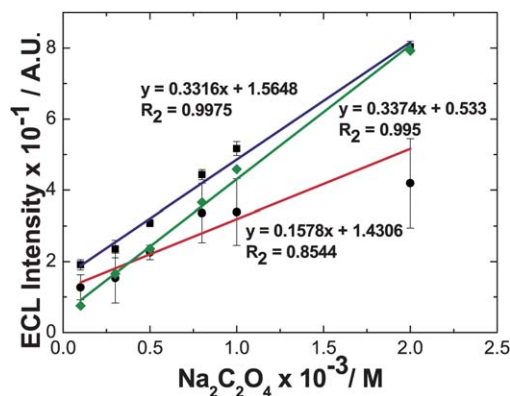


Fig. 4 Linear dependence of ECL intensity as a function of [Na₂C₂O₄] for (red line) Nafion-[Ru(bpy)₃]²⁺ film; (blue line) [Ru(bpy)₂(PVP)₁₀]²⁺ metallopolymer and (green line) [Ru(bpy)₂(PPyBBIM)₁₀]²⁺ films on GC electrodes. Error bars represent triplicate data.

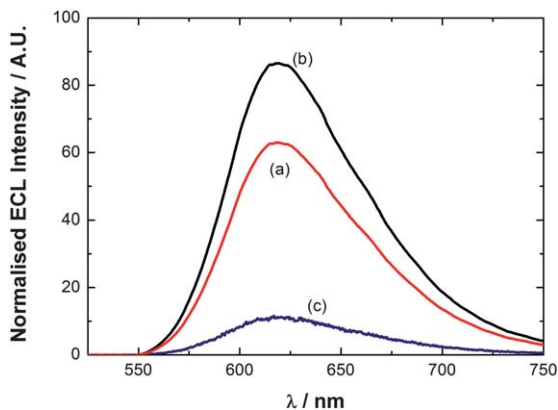


Fig. 5 ECL spectra of (a) Nafion- $[\text{Ru}(\text{bpy})_3]^{2+}$ modified electrode, (b) $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ and (c) $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ films on ITO electrodes. The ECL spectra were generated via the co-reactant pathway using 0.5 mM $\text{Na}_2\text{C}_2\text{O}_4$ in 0.1 M PBS at pH 6 as the co-reactant. The potential was held at 1100 mV. The spectra were normalized for the concentration of ruthenium centers present in the films using absorbance correction.

Fig S2.^{†24} However, as can be seen from Fig. 5 the wavelength of maximum emission for the ECL spectrum is slightly shifted to longer wavelengths by approximately 10 nm compared to the photo-excited spectrum. This behaviour has been observed previously for thin films of metallopolymers containing $[\text{Ru}(\text{N}_6)]^{2+}$ and indicates that the difference in energy between the ground and excited states is approximately 7 kJ mol^{-1} smaller in the case of ECL.²³ This slightly decreased energy difference may arise because of the different species initially present before excitation in the two experimental conditions, *i.e.*, Ru^{2+} in the case of optical excitation compared to Ru^{3+} in ECL. The magnitude of the shift in wavelength of maximum absorbance appears reasonable given the small inner sphere reorganization energy between Ru^{2+} and Ru^{3+} arising from the insensitivity of the bond lengths and angles to oxidation state in these systems. The ECL efficiency was calculated for each polymer matrix and is displayed in Table 2. The overall ECL efficiency (ϕ_{ECL}) is defined as the number of photons emitted per faradaic electron passed during the chemiluminescent reaction.³⁰ It is the product of the efficiency of populating the excited state (ϕ_{EX}) and the quantum yield of emission from that excited state (ϕ_{P}). $[\text{Ru}(\text{bpy})_3]^{2+}$ was used as a relative standard for all experiments. The relative efficiency was obtained using the relation:³¹

$$\phi_{\text{ECL}} = \phi_{\text{ECL}}^0 (IQ_{\text{f}}^0/Q_{\text{f}} I^0) \quad (8)$$

where ϕ_{ECL}^0 is the ECL efficiency of $[\text{Ru}(\text{bpy})_3]^{2+}$ (1 mM and 0.1 M TBABF₄/ACN) via annihilation, taken as 5.0%,^{32,33} I and I^0 are the integrated photomultiplier tube responses for the polymer and $[\text{Ru}(\text{bpy})_3]^{2+}$ respectively, and Q_{f} and Q_{f}^0 are the faradaic charges passed for the sample and standard.

It is important to note that as $[\text{Ru}(\text{bpy})_3]^{2+}$ itself cannot be immobilized directly in a thin film, the ECL efficiencies of the films are compared to 100 μM $[\text{Ru}(\text{bpy})_3]^{2+}$ in solution. Table 2 reveals that the greatest ECL efficiency is obtained from the $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ film. Interestingly the ECL emission intensity for the conjugated $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ metallopolymer

Table 2 ECL efficiencies of modified films compared to solution phase $[\text{Ru}(\text{bpy})_3]^{2+}$

Material	ϕ_{ECL}
$[\text{Ru}(\text{bpy})_3]^{2+}$ solution phase	5.0
Nafion- $[\text{Ru}(\text{bpy})_3]^{2+}$	0.089
$[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$	0.152
$[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$	0.011

^a All values based on averaged results from 5 independent measurements.

was significantly lower than that obtained for the non conjugated $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ metallopolymer despite displaying faster rates of charge transfer. There are two dominant processes that could contribute to this behaviour. Firstly, the ECL may be quenched by energy or electron transfer to the conducting polymer backbone, although further analysis is required to confirm this. Secondly, the benzimidazole film may be more compact limiting access of the co-reactant into the film. The more porous $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}]^{2+}$ metallopolymer allows increased penetration of the oxalate at the outer most layers of the film leading to increased contact between the ruthenium metal centres and the oxalate. In contrast, the ruthenium metal centres in the rigid $[\text{Ru}(\text{bpy})_2(\text{PPyBBIM})_{10}]^{2+}$ metallopolymer only contact the oxalate at the extreme outer layer, whereby despite displaying enhanced rates of charge transport through the polymer film there is a reduction in overall amount of ECL produced.

Conclusions

As with all sensors there is a constant drive to improve sensitivity and selectivity. The future health care industry in conjunction with point of care health monitoring will demand the detection of life threatening diseases before critical stages have been reached. As such there much research focused on improving the sensitivities and selectivities of current biomedical sensors including ECL based systems. To date the primary inhibitor of ECL based systems has been the generation of the electroactive oxidised species which in turn is limited by charge transfer rates. By tethering the complex to different polymeric backbones this work demonstrated that enhanced rates of charge transport do not necessarily translate into enhanced ECL emission. Indeed, the enhanced transfer rate can, in fact, lead to a decrease in the sensitivity of an ECL system.

In conclusion, this work demonstrates that there may be a trade off between enhancement of charge transfer rates and the efficiency of ECL which is of the utmost importance if these materials are to be utilised in superior ECL sensors. Several factors, including, self-quenching, excited state transfer rates and luminophore distribution, in addition to improved charge transfer must also be considered.

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