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COMMUNICATION

Green chemiluminescence from a bis-cyclometalated iridium(III) complex with an ancillary bathophenanthroline disulfonate ligand†

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The reaction of a fluorinated iridium complex with cerium(IV) and organic reducing agents generates an intense emission with a significant hypsochromic shift compared to contemporary chemically-initiated luminescence from metal complexes.

The chemiluminescent reduction of tris(2,2′-bipyridine)ruthenium(III) ($[Ru(bipy)_3]^{3+}$) has been widely used to detect amines of medical, forensic and industrial importance.[1,2] In these reactions, the stable $[Ru(bipy)_3]^{2+}$ precursor is initially oxidised to $[Ru(bipy)_3]^{3+}$, which is then reduced by the analyte to the electronically excited $[Ru(bipy)_3]^{2+*}$ species responsible for the emission.[3] The reactive Ru(III) state can be generated either chemically or electrochemically, where the overall process is classified as chemiluminescence (CL),[1,2] or electrochemiluminescence (ECL).[4–7] The ECL of biomolecules labelled with $[Ru(bipy)_3]^{2+}$, in the presence a co-reactant such as tripropylamine, has been utilised for exceedingly sensitive detection in commercial immunoassay systems for clinical diagnostics, food and water testing, and biodefence applications.[6–8]

The success of $[Ru(bipy)_3]^{2+}$ CL/ECL has stimulated considerable interest in developing new metal-complex reagents,[9] although research to date has predominantly focussed on ECL. One of the most promising areas of investigation is cyclometalated iridium(III) complexes, which exhibit relatively high photoluminescence efficiencies, appropriate ground and excited state redox potentials, and a diverse range of emission wavelengths.[5,6,10] The ECL of numerous such complexes has been explored in both aqueous and organic solvents.[11–16] For example, Kapturkiewicz *et al.* reported very high efficiencies for annihilation and organic co-reactant ECL of $Ir(ppy)_3$ and $L_2Ir(acac)$ complexes (where L are various ligands with N and C2′ chelating atoms) in 1 : 1 acetonitrile:dioxetane.[11,12]‡ Richter's group, however, found that the ECL efficiencies of $Ir(ppy)_3$ and $(btp)_2Ir(acac)$ were orders of magnitude lower in more analytical useful acetonitrile:water (1 : 1) and water solvents (with tripropylamine as co-reactant), in which these neutral complexes have very limited solubility.[13,14]

Kim *et al.* reported that ECL intensities for cationic $[(ppy)_2Ir(bipy)]^+$ and $[(ppy)_2Ir(phen)]^+$ complexes (prepared as PF_6^- salts) were six- and twelve-times greater than that of $Ir(ppy)_3$ in polar organic solvents using tripropylamine as a co-reactant,[15] and we subsequently utilised the more water-soluble chloride salts of these complexes, and the sodium salt of the corresponding 4,7-diphenylphenanthroline-disulfonate (bathophenanthroline disulfonate) derivative, $[(ppy)_2Ir(BPS)]^-$ (Fig. 1), in the first demonstration of chemically initiated luminescence of cyclometalated iridium complexes.[17] The $[(ppy)_2Ir(BPS)]^-$ complex in particular produced far greater chemiluminescence intensities than $[Ru(bipy)_3]^{2+}$, arising from reaction of the oxidised $[(ppy)_2Ir(BPS)]^0$ species with both analyte and solvent.[17] A related approach to improve the solubility in aqueous solution for co-reactant ECL was recently described by Li *et al.*,[18] who utilised a bis-cyclometalated iridium complex containing a bipyridine ligand appended with two sugar moieties. The $[(pq)_2Ir(bipy\text{-}sugar)]^+$ complex was evaluated using tripropylamine at a Pt electrode, and found to produce an emission five-fold greater than that of $[Ru(bipy)_3]^{2+}$.

In contrast to the limited emission wavelengths available for ruthenium polypyridine chelates,[19] cyclometalated iridium complexes can be 'tuned' across a wide spectral range, as demonstrated in several elegant photoluminescence studies.[20–22] The ability to tune spectroscopic and redox properties through subtle changes in ligand structure is of great interest in CL/ECL analysis, in order to manipulate the selectivity, shift emission wavelengths to more sensitive regions of the photodetector, and enable simultaneous detection of

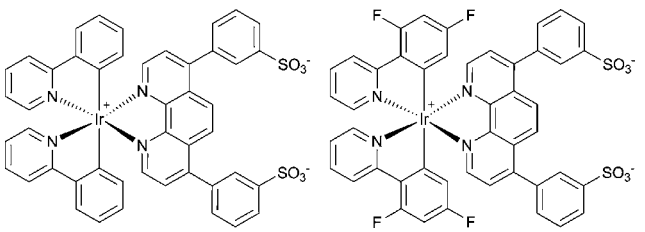

Fig. 1 Structure of $[(ppy)_2Ir(BPS)]^-$ and $[(df\text{-}ppy)_2Ir(BPS)]^-$ complexes.

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† Electronic supplementary information (ESI) available: Absorption and photoluminescence emission spectra for $[(df\text{-}ppy)_2Ir(BPS)]^-$, $[(ppy)_2Ir(BPS)]^-$, and $[Ru(bipy)_3]^{2+}$, intensity *versus* time profiles for the chemiluminescence reactions of $[(df\text{-}ppy)_2Ir(BPS)]^-$ and $[Ru(bipy)_3]^{2+}$ with cerium(IV) and ofloxacin, and NMR characterisation of $[(df\text{-}ppy)_2Ir(BPS)]^-$ and $[(ppy)_2Ir(BPS)]^-$. See DOI: 10.1039/c1an15315c

complementary chemiluminophores, for internal standardisation or multi-analyte detection.[13,14,19]

Although the archetypal tris-cyclometalated iridium complex $Ir(ppy)_3$ exhibits green luminescence (λ_{max} = 517 nm, uncorrected) in acetonitrile at room temperature,[13] substitution of one phenylpyridine for bipyridine or other diimine ligand results in a significant bathochromic shift,[17,18,23,24] and thus complexes such as $[(ppy)_2Ir(bipy)]^+$ and $[(ppy)_2Ir(BPS)]^-$ emit orange light in a similar region to that of $[Ru(bipy)_3]^{2+}$. In contrast, the incorporation of electron-withdrawing substituents such as fluorine on the cyclometalating ring causes a hypsochromic shift, by stabilising the HOMO level.[10,21,22,25] We have therefore adopted this strategy to prepare an iridium-based chemiluminescence reagent, $[(df\text{-}ppy)_2Ir(BPS)]^-$ (Fig. 1), with much shorter emission wavelengths than the conventional $[Ru(bipy)_3]^{2+}$ complex.§

The presence of the fluorine groups on $[(df\text{-}ppy)_2Ir(BPS)]^-$ lowered the solubility of the complex in aqueous solution, and therefore the reagents were prepared in 1 : 1 acetonitrile:water. The UV-vis absorption spectra of $[(df\text{-}ppy)_2Ir(BPS)]^-$, $[(ppy)_2Ir(BPS)]^-$, and $[Ru(bipy)_3]^{2+}$ in this solvent mixture are included in the ESI (Fig. S1).† The spectra were similar to those of the analogous complexes without sulfonate substituents, $[(df\text{-}ppy)_2Ir(dpp)]^+$ and $[(ppy)_2Ir(dpp)]^+$, dissolved in acetonitrile,[26] for which the strong bands below 300 nm were attributed to intra-ligand π–π* transitions and the weaker, poorly defined bands above 300 nm were ascribed to metal-to-ligand charge transfer transitions. The photoluminescence of $[(ppy)_2Ir(BPS)]^-$ in 1 : 1 acetonitrile:water was similar to that of $[Ru(bipy)_3]^{2+}$, but the emission from $[(df\text{-}ppy)_2Ir(BPS)]^-$ was hypsochromically shifted (Table 1 and Fig. S1 in ESI†). The photoluminescence quantum yields of $[(ppy)_2Ir(BPS)]^-$ and $[(df\text{-}ppy)_2Ir(BPS)]^-$ were 3.4- and 2.5-fold that of $[Ru(bipy)_3]^{2+}$.¶

Visual inspection of the reaction of $[(df\text{-}ppy)_2Ir(BPS)]^-$ with cerium(IV) and a pharmaceutical (ofloxacin) when the reactants were continuously merged within a serpentine flow-cell[27] revealed a striking green emission (Fig. 2).‖ Subsequent investigations were performed using flow-injection analysis (FIA), where the reagent was injected into a carrier stream containing an analyte, which merged with the oxidant solution, before entering a coiled-tubing detection cell.**

Using a reagent concentration (1×10^{-3} M) within the range previously utilised for $[Ru(bipy)_3]^{2+}$ (1×10^{-4} M to 2.5×10^{-3} M[28–34]), greater chemiluminescence signals were obtained using at least one of the two iridium complexes for each analyte (Table 2). However, the 'blank' responses (resulting from reaction of the oxidised complexes with the solvent[33]) were also larger, resulting in inferior signal/blank ratios. Interestingly, at lower reagent concentrations, this discrepancy was much smaller (Table 3), and in the case of furosemide, the signal/blank ratio using $[(df\text{-}ppy)_2Ir(BPS)]^-$ was superior to that obtained using $[Ru(bipy)_3]^{2+}$.

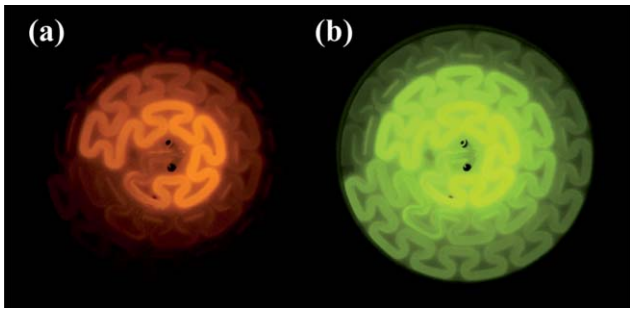

Fig. 2 Chemiluminescence from the reactions of (a) $[(ppy)_2Ir(BPS)]^-$ and (b) $[(df\text{-}ppy)_2Ir(BPS)]^-$, with cerium(IV) and ofloxacin within a dual-inlet serpentine flow-cell. Photographs taken using a Nikon D700 digital camera, with 42 s and 30 s exposure time, respectively.

The competing reactions of the reagent with target analyte and solvent were further explored by monitoring the chemiluminescence under stopped-flow conditions.** At a reagent concentration of 1×10^{-3} M, emission intensities for the reactions of 1×10^{-5} M ofloxacin with $[Ru(bipy)_3]^{2+}$ and $[(df\text{-}ppy)_2Ir(BPS)]^-$ (and 1×10^{-3} M cerium (IV)) peaked at 6.9 s and 2.2 s from the initiation of the reaction, and similar maxima were observed for the corresponding blank signals (see ESI, Fig. S2a and S2b).† Lowering the reagent concentration to 1×10^{-5} M (and the analyte to 1×10^{-6} M) had little effect on the shape of the profiles for $[Ru(bipy)_3]^{2+}$ (other than a large decrease in overall intensity). In the case of $[(df\text{-}ppy)_2Ir(BPS)]^-$, the profile for the analyte signal was similar to that obtained at higher reagent conditions, but the blank reponse contained a small initial sharp peak and a relativly slow rise and decay over the next 80 s (Fig. S2c and S2d).† It should be borne in mind that the light detected in an FIA system (such as those reported in Tables 2 and 3) is only a portion of the entire emisssion profile, dependant on the kinetics of the light-producing pathway, the solution flow rates, and the volume and geometry of the detection flow-cell. As the flow rates were optimised for the greatest signal/blank ratios, the improved relationship at low reagent concentrations can in part be explained by the relative rates of reaction.

Calibrations for furosemide and ofloxacin using FIA with 0.01 mM $[(df\text{-}ppy)_2Ir(BPS)]^-$ gave limits of detection that were an order of magnitude superior to those obtained with the same concentration of $[Ru(bipy)_3]^{2+}$ (Table 4), although in the case of

Table 1 Spectroscopic data

		λ_{PL} (nm)[a]		λ_{CL} (nm)[b]	
Complex	λ_{Abs} (nm)[a]	uncorr.	corr.	uncorr.	corr.
$[Ru(bipy)_3]^{2+}$	286, 451	611	623	609	622
$[(ppy)_2Ir(BPS)]^-$	280	598	621	604	628
$[(df\text{-}ppy)_2Ir(BPS)]^-$	278	530	545	529	547

[a] Absorption and photoluminescence emission spectra obtained using 10 μM complex in 1 : 1 acetonitrile:water. [b] Chemiluminescence spectra obtained by continuously merging a solution of reagent (0.5 mM) and analyte (5 μM) with a solution of cerium(IV) (1 mM in 0.05 M H_2SO_4) within a coiled reaction flow-cell mounted against the emission window of a fluorescence spectrophotometer.

Table 2 Chemiluminescence signal (V) and signal/blank ratio (shown in parentheses) for the reaction of 1 mM reagent with 1 mM Ce(IV) and 10 μM analyte

Analyte	$[Ru(bipy)_3]^{2+}$		$[(ppy)_2Ir(BPS)]^-$		$[(df-ppy)_2Ir(BPS)]^-$	
Oxalate	16	(319)	75	(4.8)	13	(3.5)
codeine	14	(205)	19	(1.3)	7	(2.1)
furosemide	4	(75)	21	(1.5)	120	(35)
ofloxacin	85	(1695)	37	(2.6)	304	(88)

Table 3 Chemiluminescence signal (mV) and signal/blank ratio for the reaction of 10 μM reagent with 1 mM Ce(IV) and 1 μM analyte

Analyte	$[Ru(bipy)_3]^{2+}$		$[(ppy)_2Ir(BPS)]^-$		$[(df\text{-}ppy)_2Ir(BPS)]^-$	
oxalate	0.8	(10)	2.3	(1.2)	0.1	(1.0)
codeine	0.4	(6)	5.1	(0.9)	0.1	(1.0)
furosemide	1.3	(17)	6.8	(3.6)	5.3	(73)
ofloxacin	3.2	(45)	6.2	(3.3)	1.9	(27)

Table 4 Limits of detection (blank + 3σ) for two pharmaceuticals using flow injection analysis with chemiluminescence detection

Reagent[a]		ofloxacin (M)	furosemide (M)
$[Ru(bipy)_3]^{2+}$	1 mM	1.1×10^{-9}	4.3×10^{-7}
	0.01 mM	3.0×10^{-8}	1.1×10^{-7}
$[(df\text{-}ppy)_2Ir(BPS)]^-$	1 mM	1.9×10^{-8}	2.5×10^{-8}
	0.01 mM	5.2×10^{-9}	1.1×10^{-8}

[a] Reagent injected into the analyte stream and merged with cerium(IV).

ofloxacin, the best figure was obtained using 1 mM $[Ru(bipy)_3]^{2+}$. These limits of detection were comparable to those previously reported for ofloxacin[28–32] and furosemide[33–35] using $[Ru(bipy)_3]^{2+}$–Ce(IV) chemiluminescence, which ranged from 1×10^{-9} M to 6×10^{-7} M, and from 8×10^{-9} M to 2×10^{-7} M, respectively.

Conclusions

A heteroleptic iridium complex soluble in an analytically useful polar solvent and exhibiting efficient green luminescence was attained through a combination of fluorinated phenylpyridine and sulfonated diphenylphenanthroline ligands. The $[(df\text{-}ppy)_2Ir(BPS)]^-$ complex was successfully utilised in chemiluminescence reactions with cerium(IV) and organic analytes. Exploration of reaction conditions revealed that the optimum reagent concentration is lower than that of the conventional $[Ru(bipy)_3]^{2+}$ complex, in part arising from differences in the kinetics of their light-producing pathways. Modification of ligand structure also influenced the relative sensitivity of the reagents towards each analyte (for example, using 1×10^{-5} M $[Ru(bipy)_3]^{2+}$, the response for ofloxacin was 2.6-fold that for furosemide, but the relationship was reversed using 1×10^{-5} M $[(df\text{-}ppy)_2Ir(BPS)]^-$), which demonstrates the potential to tune not only the photophysical properties of the reagent, but also its reactivity towards the target analyte, to further enhance the sensitivty and selectivity of chemiluminescence detection.

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Notes and references

‡ bipy = 2,2′-bipyridine, ppy = 2-phenylpyridine anion, acac = acetylacetonate anion, btp = 2-benzo[b]thien-2-yl-pyridine anion, phen = 1,10-phenanthroline, pq = 2-phenylquinoline anion, df-ppy = 2-(2,4-difluorophenyl)pyridine anion).

§ To prepare the sodium salt of (4,7-diphenyl-1,10-phenanthroline disulfonate-κ*N*1,κ*N*10)bis[3,5-difluoro-2-(2-pyridinyl-κ*N*)phenyl-κ*C*]iridate(1-) (Na[(df-ppy)$_2$Ir(BPS)]), the dichloro-bridged dimer: di-μ-chlorobis[3,5-difluoro-2-(2-pyridinyl-κ*N*)phenyl-κ*C*]diiridium (from Suna-Tech), was refluxed with 4,7-diphenyl-1,10-phenanthroline disulfonate in 90 : 10 ethanol:water for 6 h. The solvent was then removed and the product purified using a Sephadex LH-20 column (15 cm long, 1.5 cm i.d., 1 : 1 ethanol:water eluent). Yield: 91%. HRMS-ESI (*m*/*z*) [$C_{46}H_{28}F_4IrN_4O_6S_2^+$] calcd 1065.1010, found 1065.1014. NMR spectra (^1H, ^{13}C, COSY, HSQC, HMBC) were obtained (in CD_3OD) using a Bruker Avance AV400 NMR spectrometer, and the peaks assigned through analysis of these spectra (Table S1†) were in agreement with those previously reported.[36] Na[(ppy)$_2$Ir(BPS)] was synthesised in the same manner,[17] from the corresponding dimer.[37] Yield: 81%. HRMS-ESI (*m*/*z*) [$C_{46}H_{32}IrN_4O_6S_2^+$] calcd 993.1387, found 993.1351. NMR data included in ESI.† $[Ru(bipy)_3]Cl_2 \cdot H_2O$ was purchased from Strem (MA, USA). The position of the sulfonate groups on the BPS ligand was discussed in ref. 33 and 36. The commercially available BPS used in this study was found to predominantly contain the *m*–*m*′ isomer.[33]

¶ Photoluminescence emission spectra were obtained with a Cary Eclipse fluorescence spectrophotometer and corrected for the wavelength dependence of the detector response and monochromator transmission.[38] Relative photoluminescence quantum yields were established as previously described.[19] Experiments were performed at room temperature (21 ± 3 °C), without degassing (*i.e.* under identical conditions to chemiluminescence experiments), using an excitation wavelength of 450 nm.

‖ As a part of this preliminary investigation, we used the reaction between $[(df\text{-}ppy)_2Ir(BPS)]^-$ (1×10^{-5} M in aqueous solution with 1% ethanol), cerium(IV) and a fluoroquinolone (ofloxacin or enrofloxacin) as an example of a fast chemiluminescence system to examine the influence of mixing channel geometry in detection flow-cells.[39]

** Flow injection analysis methodology was used to reproducibly combine the reacting species. The manifold was constructed as previously described,[40] except that the distance between the confluence point and the beginning of the detection coil was ~10 mm, and the photodetector was a Electron Tubes model 9124SB photomultiplier tube (ETP, NSW, Australia). Chemiluminescence intensities were established by injecting 70 μL of each iridium/ruthenium complex (dissolved in 1 : 1 acetonitrile: water) into a carrier line containing the analyte, 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 reagent/analyte combination, flow rates were optimised between 1 and 3.5 mL min^{-1} per line, to achieve the greatest signal/blank ratio. Stopped-flow experiments were performed using a manifold constructed as previously described.[41] The sample loop was filled with a 1 : 1 acetonitrile:water solution containing both reagent and analyte. The pump was then activated to dispense 120 μL of carrier (1 : 1 acetonitrile:water) and oxidant (1×10^{-3} M in 0.05 M H_2SO_4) solutions at a rate of 10 mL min^{-1} per line, which rapidly merged the three reactants in a dual-inlet serpentine flow cell,[27] where the emission was monitored over time.

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