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Emitting Species in Chemiluminescence Reactions with Acidic Potassium Permanganate: A Re-Evaluation Based on New Spectroscopic Evidence

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Abstract The reaction of acidic potassium permanganate with a wide range of compounds is known to produce a broad red emission, and there is strong evidence for an excited manganese(II) emitting species. Nevertheless, numerous researchers have proposed other emitters for reactions with acidic potassium permanganate, particularly for systems where fluorescent compounds were present, either as enhancers or reaction products. We have examined many reactions of this type and found that, in most cases, the same red emission was produced. There were, however, some exceptions, including the oxidation of dihydralazine, certain thiols and sulphite (each in the presence of an enhancer).

Keywords Chemiluminescence spectra · Fluorescence spectra · Emitting species · Energy transfer · Potassium permanganate

Introduction

Acidic potassium permanganate has been used extensively as a chemiluminescence reagent for the determination of a wide range of analytes, including pharmaceuticals, biomolecules, antioxidants, illicit drugs, pesticides and pollutants [1, 2]. The spectral distribution of the chemiluminescence from many reactions with permanganate in acidic solution has been reported to be single broad band with a maximum between 610 and 750 nm [1]. Moreover, spectra that were corrected for the wavelength dependence of the detector response and monochromator transmission exhibited a maximum intensity at 734 ± 5 nm (or 689 ± 5 nm if sodium hexametaphosphate was added) [3]. Singlet oxygen (which is known to emit two intense bands in the visible region at 633 nm and 703 nm, and another band in the near-infrared at 1268 nm during the reaction of hydrogen peroxide and sodium hypochlorite [4, 5]) has often been postulated to be the emitting species in reactions with acidic potassium permanganate [1], but this is unlikely, because the visible spectral distribution is different and no chemiluminescence has been detected at 1268 nm [3]. We have recently shown that the characteristic red emission from reactions with acidic potassium permanganate matches the laser-induced photoluminescence ($^4T_1 \rightarrow {}^6A_1$ transition) of manganese(II) in simple aqueous solution [6], which in conjunction with previous evidence [3], confirms that the emitter is an excited manganese(II) species derived from the oxidant.

Some researchers have reported that the emission intensity from certain reactions with acidic potassium permanganate is enhanced by the addition of highly fluorescent compounds such as rhodamine B [7–9] and quinine [10–13], and proposed light-producing pathways involving energy transfer to the added fluorophore [9–11]. Others have postulated that the emission from selected reactions with acidic potassium permanganate emanates from fluorescent oxidation products of the analyte [14–17]. However, spectroscopic evidence is rarely provided to support these claims.

In this paper, we present new evidence that has enabled us to re-evaluate the nature of the emitting species in many previously reported chemiluminescence reactions involving acidic potassium permanganate. The reactions selected for investigation encompass a wide range of analytes and reagent conditions.

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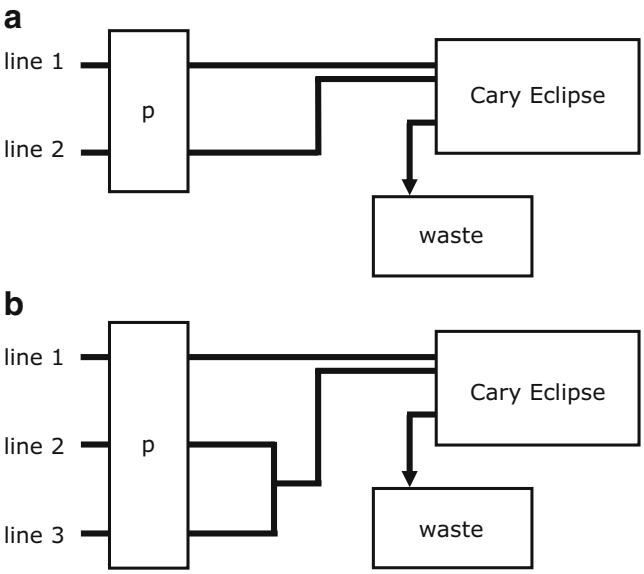

Fig. 1 Continuous flow manifolds used for the collection of chemiluminescence spectra (p: peristaltic pump)

Experimental

Fluorescence and chemiluminescence spectra

Fluorescence and chemiluminescence spectra were obtained using a Cary Eclipse spectrofluorometer (Varian, Australia) fitted with an R928 photomultiplier tube (Hamamatsu, Japan). For the collection of fluorescence spectra, solutions were transferred into quartz cuvettes (10 mm × 10 mm) that were placed in the cell holder. A data interval of 1 nm and a band pass of 5 nm (for both excitation and emission) were used for all experiments. For the collection of chemiluminescence spectra, the excitation source of the spectrofluorometer was turned off (Bio/Chemiluminescence mode). The reactants were continuously mixed using a flow manifold (Fig. 1a) consisting of a peristaltic pump (Gilson Minipuls 3; John Morris Scientific, Australia) with bridged PVC tubing (1 mm i.d.; Pro-Tech Group, Australia), PTFE manifold tubing (0.8 mm i.d.; Pro-Tech Group) and an integrated glass T-piece and spiral flow cell (0.5 mm i.d., 90 μL volume; Embell Scientific, Australia) mounted in front of the emission window of the spectrofluorometer. When required, a second T-piece (Cole-Palmer, Australia) was used to merge an additional solution with one of the reactant streams prior to the final confluence point (Fig. 1b). Solutions were pumped at flow rates of between 1.85 and 4.29 mL min^{-1} (per line). Spectra were an average of ten scans (1 s gate time, 1 nm data interval, 20 nm band pass) and where stated, were corrected for the wavelength dependence of the detector response and monochromator transmission [3].

Reagents

1-Naphthol, hydroxylamine hydrochloride, manganese(II) sulphate monohydrate and vanillin were purchased from Ajax (Australia). 2,4-Dinitrochlorobenzene, captopril, cysteine, L-dopa, cefadroxil, dopamine hydrochloride, epinephrine, norepinephrine bitartrate salt, perphenazine, proflavine hydrochloride, quinine hydrochloride, acriflavine, dihydralazine (1,4-dihydrazinophthalazine sulphate dihydrate), glutathione, riboflavin and amoxicillin were purchased from Sigma-Aldrich (Australia). 2,4-Dinitrophenylhydrazine, hydrazine sulfate, hydroquinone, propan-2-ol, rhodamine B and sulphuric acid were purchased from BDH Chemicals (Australia). Potassium permanganate was purchased from Chem-Supply (Australia). Benzalkonium chloride, 3-cyclohexylaminopropanesulfonic acid (CAPS) and butane-2,3-dione were purchased from Fluka (Switzerland). Formic acid was purchased from Hopkin & Williams Ltd. (UK). Formaldehyde was purchased from Selby-Biolab (Australia). Sodium sulphite was purchased from Radiometer (Denmark). Sodium sulphite solutions were prepared in deoxygenated water.

Table 1 Chemical conditions for the collection of spectra for chemiluminescence reactions enhanced with quinine

System	Ref.	Reagents	Intensity maxima[a]
A	[10]	Line 1: $KMnO_4$ (0.5 mM) in H_2SO_4 (0.5 M) Line 2: Cefadroxil (1 mM) and quinine (50 μg mL^{-1})	735 ± 5 nm
B	[11]	Line 1: $KMnO_4$ (1 mM) in H_2SO_4 (1 M) Line 2: Hydroquinone (1 mM), quinine (0.5 mM) and benzalkonium chloride (3.4 g L^{-1})	735 ± 5 nm
C	[12]	Line 1: $KMnO_4$ (0.5 mM) in H_2SO_4 (0.5 M) Line 2: Amoxicillin (1 mM) and quinine (1 mM)	735 ± 5 nm
D	[13]	Line 1: $KMnO_4$ (0.4 mM) in H_2SO_4 (1.5 M) Line 2: Cysteine, glutathione or captopril (1 mM) and quinine (1 mg mL^{-1})	458 ± 5 nm and 735 ± 5 nm

[a] Data from our investigation (not from the original paper)

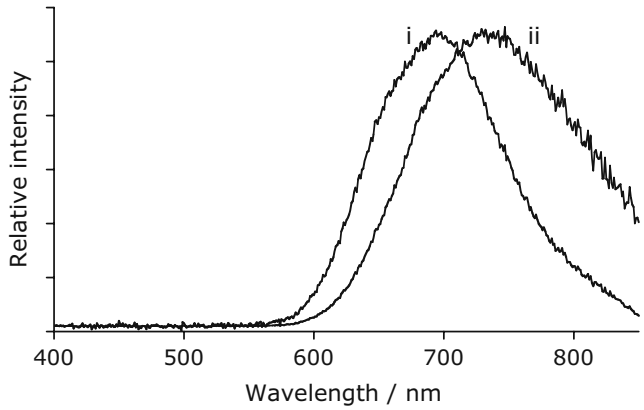

Fig. 2 Uncorrected (i) and corrected (ii) chemiluminescence spectra for System B: acidic potassium permanganate, hydroquinone, quinine and benzalkonium chloride

Results and discussion

Quinine

Quinine is a highly fluorescent molecule (particularly in dilute acid solution) and has been used to enhance the emission intensity from chemiluminescence reactions [18–20]. A mechanism of enhancement involving energy transfer from an excited intermediate leading to emission from quinine is often proposed [18–20]. Quinine has been used as an enhancer in a small number of analytical applications based on acidic potassium permanganate chemiluminescence, including the determination of cefadroxil [10], amoxicillin [12], hydroquinone [11] and thiol-containing drugs [13]. In two of these studies [10, 11], a light-producing pathway involving energy transfer to the fluorescent sensitiser was proposed. In the other papers [12, 13], the mechanism was not discussed.

To establish the nature of the emitting species in these systems, we have collected chemiluminescence spectra using a continuous flow manifold (Fig. 1a) and the reagent conditions described in each paper (Systems A — D, Table 1). Systems A, B and C each produced a single broad band with a corrected wavelength of maximum intensity at 735 nm (Fig. 2). This spectral distribution is the same as that reported for many reactions with acidic potassium permanganate and has been attributed to an excited manganese(II) species [3, 6]. In each of the three spectra collected for System D, the same red emission was observed, but a second peak at 458 nm was also detected. Prior to correction (Fig. 3a), this peak in the blue region appeared more intense, but with correction (Fig. 3b), the red emission was dominant (under these reagent conditions). The spectrum was smoothed by adjacent averaging, to remove the excessive noise above 600 nm, caused by a combination of the low signal-to-noise ratio of the uncorrected spectrum and the large correction factor above 600 nm (to compensate for the relatively poor response of the PMT). The peak at 458 nm matches the fluorescence spectrum of quinine (Fig. 3c) and it appears that System D is the only reaction under investigation in which energy transfer to quinine has occurred. It can therefore be concluded that, unlike many other analytes, certain thiol

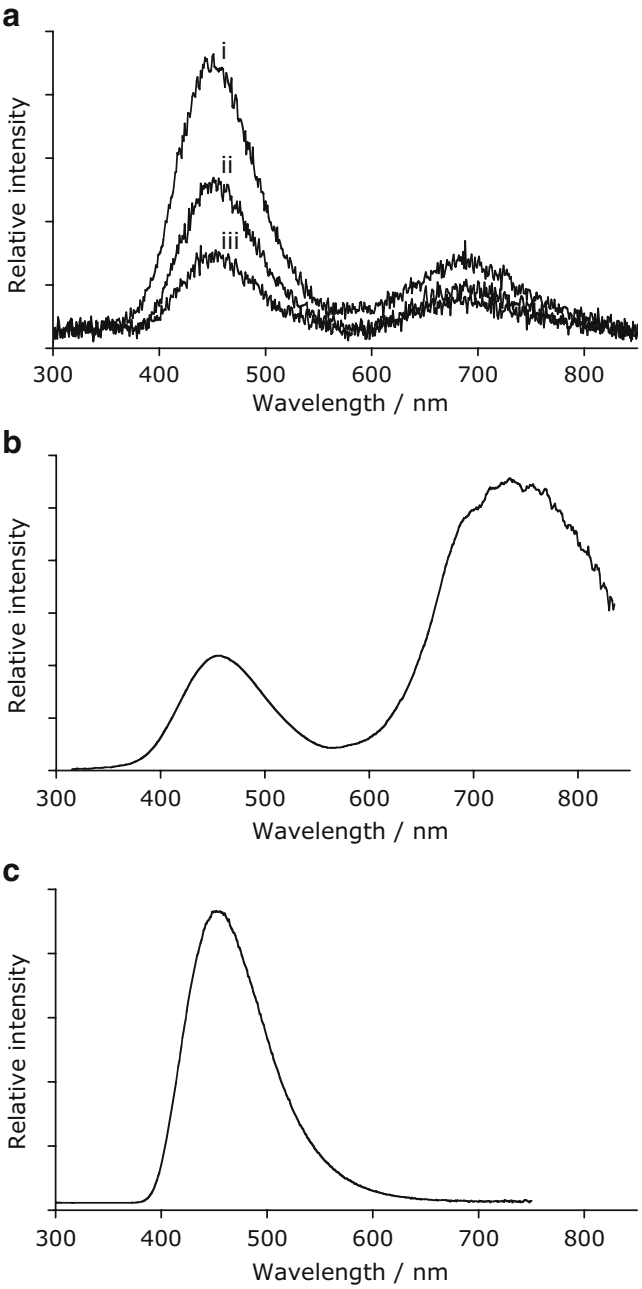

Fig. 3 **a** Uncorrected chemiluminescence spectra for System D: acidic potassium permanganate, quinine and captopril (i), cysteine (ii) or glutathione (iii). **b** Corrected chemiluminescence spectrum (smoothed) for acidic potassium permanganate, quinine and captopril. **c** Corrected fluorescence emission spectrum for quinine (λ_{ex} = 382 nm)

compounds (such as cysteine, glutathione and captopril) react with acidic potassium permanganate to produce high-energy intermediates that are capable of exciting added fluorophores. This finding is consistent with previous studies that have shown that the reaction of thiol compounds with other oxidants (e.g. cerium(IV) or bromate) and various fluorophores (e.g. quinine, rhodamine B and rhodamine 6G) evokes chemiluminescence with sufficient intensity for the determination of the thiols [18, 21, 22].

Rhodamine B

Rhodamine B is another highly fluorescent molecule that has been used to enhance the emission intensity from a range of chemiluminescence reactions [23–26]. As with quinine, it is often assumed that rhodamine B accepts energy from an excited intermediate, leading to its characteristic emission [24–26]. Rhodamine B has been used as an enhancer in a relatively small number of chemiluminescence reactions with acidic potassium permanganate published in the open literature [1]. Al-Tamrah and Townshend reported that rhodamine B enhanced the chemiluminescence reaction between acidic potassium permanganate and various naphthols [7], but they did not discuss the emitting species. Using the reagent conditions described in that paper, we were unable to establish the spectral distribution. However, using the modified conditions shown in Table 2 (System E), a spectrum was obtained. Townshend and Wheatley used rhodamine B in the determination of several nitrogen nucleophiles with acidic potassium permanganate [8]. The authors attributed the emission to excited analyte oxidation products: nitrogen oxide from hydroxylamine, and dinitrogen from phenylhydrazines. Under the chemical conditions described by Townshend and Wheatley [8], spectra were obtained for the oxidation of hydroxylamine (System F) and 2,4-dinitrophenylhydrazine in 20% (v/v) propan-2-ol (System G) using the continuous flow manifold shown in Fig. 1b. The spectra obtained for Systems E, F and G (Table 2) each showed a single broad band with a maximum at 735 nm (corrected), which matched that obtained for Systems A – C (Fig. 2).

Yang and co-workers reported the determination of dihydralazine with acidic potassium permanganate and rhodamine B [9]. Based on a wavelength of maximum intensity at approximately 575 nm (established using interference filters) they concluded that the chemiluminescence emanated from rhodamine B after energy transfer from an excited oxidation product of dihydralazine. We have collected the chemiluminescence spectrum for this reaction (System H, Table 2) using the continuous flow manifold shown in Fig. 1a. In agreement with the work of Yang and co-workers [9], the chemiluminescence from this reaction (Fig. 4) had a similar spectral distribution to the orange fluorescence of rhodamine B (Fig. 4). However, a weak shoulder at 650–750 nm was observed in the chemiluminescence spectrum, but not in the fluorescence spectrum. This indicates that the light-producing pathway that was dominant in Systems A – C and E – G also contributed to the total emission in System H. Additional evidence for this notion was obtained by adding sodium polyphosphate (1% w/v), which has been previously shown to enhance the characteristic red emission from reactions with acidic potassium permanganate [1]. This doubled the intensity at 650–750 nm, but reduced the peak at 591 nm by approximately 40%. Furthermore, repeating the reaction without rhodamine B produced only the weak red emission, which again could be enhanced by adding sodium polyphosphate to the permanganate reagent.

To further examine the light-producing pathway in the reaction of acidic potassium permanganate, dihydralazine and rhodamine B, the oxidant was replaced with cerium(IV) sulfate (2 mM in 0.25 M sulphuric acid). In this case, the spectrum matched the characteristic fluorescence of rhodamine B (the shoulder at 650–750 nm was not observed).

Table 2 Chemical conditions for the collection of spectra for chemiluminescence reactions enhanced with rhodamine B

System	Ref.	Reagents	Intensity maxima[a]
E[b]	[7]	Line 1: $KMnO_4$ (0.4 mM) in H_2SO_4 (1.5 M) Line 2: 1-Naphthol (1 mM) and rhodamine B (0.02 mM)	735 ± 5 nm
F	[8]	Line 1: $KMnO_4$ (0.05 mM) in H_2SO_4 (50 mM) Line 2: Hydroxylamine (1 mM) Line 3: Rhodamine B (0.01 mM) in formic acid (1 M)	735 ± 5 nm
G	[8]	Line 1: $KMnO_4$ (0.05 mM) in H_2SO_4 (50 mM) Line 2: 2,4-Dinitrophenylhydrazine (1 mM) in propan-2-ol (20% v/v) Line 3: Rhodamine B (0.01 mM) in formic acid (1 M)	735 ± 5 nm
H	[9]	Line 1: $KMnO_4$ (0.2 mM) in H_2SO_4 (0.1 M) Line 2: Dihydralazine (1 mM) in rhodamine B (0.08 mM)	591 ± 5 nm

[a] Data from our investigation (not from the original paper)

[b] Conditions modified from original paper

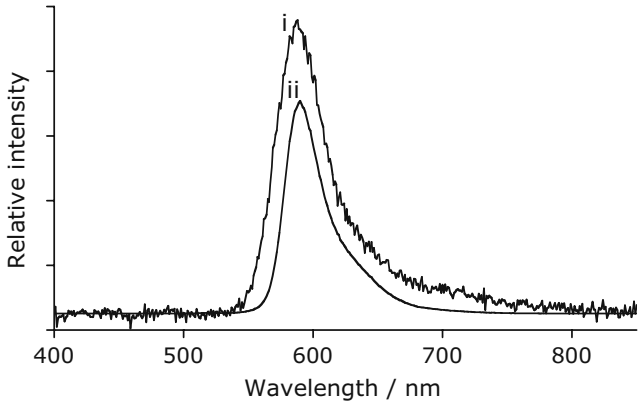

Fig. 4 (i) Chemiluminescence spectrum (uncorrected) for System H: acidic potassium permanganate, dihydralazine and rhodamine B. (ii) Fluorescence emission spectrum (uncorrected) for rhodamine B (λ_{ex}= 257 nm)

Without dihydralazine, the reaction of either oxidant (cerium(IV) or permanganate) with rhodamine B produced a very weak emission with a maximum emission at 591 nm. It is interesting to note that the oxidation of another hydrazine species, 2,4-dinitrophenylhydrazine, by acidic permanganate in the presence of rhodamine B (System G), elicited only the red emission attributed to manganese(II) (*i.e.* energy transfer to rhodamine B was not observed).

Fluorescent oxidation products

There are numerous examples of chemiluminescence reactions where an organic molecule is oxidised to form an electronically excited fluorescent product that is responsible for the emission [27–29]. Similarly, the chemiluminescence elicited from several reactions with acidic potassium permanganate has been attributed to an emission from a fluorescent oxidation product of the analyte. Examples include the oxidation of acriflavine or proflavine [14], catecholamines [15], perphenazine [16] and vanillin [17]. We have collected chemiluminescence spectra for these reactions (Systems I – L, Table 3) and found, in all four cases, a broad emission with a maximum intensity at 735 nm (corrected), which matched the spectral distribution from Systems A – C (Fig. 2) and Systems E – G. This provides strong evidence that the light-producing pathways proposed for these reactions [14–17] were incorrect.

Other species

Several other light-producing pathways have been proposed for reactions involving acidic potassium permanganate. Zhu and co-workers postulated that the oxidation of butane-2,3-dione in the presence of manganese(II) led to an emission from the organic reactant [30], and Liu *et al*. suggested molecular nitrogen as the emitter in the reaction of permanganate with a mixture of 2,4-dinitrochlorobenzene and hydrazine after it was heated for 90 mins [31]. We obtained chemiluminescence spectra for these reactions (Systems M and N, Table 4) using the continuous flow manifold shown in Fig. 1a. Both spectra matched those observed for Systems A – C, E – G and I – L, which suggests a common emitter that is independent of the analyte, and disproves the previously proposed light-producing pathways [30, 31].

The reaction of sulphite with oxidising agents such as permanganate, cerium(IV) and hydrogen peroxide in acidic solution is known to produce chemiluminescence [32]. Stauff and Jaeschke reported that the emission occurred between 450 and 600 nm, and proposed a light-producing pathway involving emission from sulphur dioxide [33], but this is yet to be confirmed. A range of compounds can enhance the chemiluminescence generated by the oxidation of sulphite [34–39]. In the case of fluorescent compounds, the mechanism of enhancement is often postulated to involve energy transfer from an excited reaction intermediate and subsequent emission from the efficient fluorophore [34–37]. However, several non-fluorescent enhancers have also been reported [35, 36, 38]. Al-Tamrah and co-workers investigated the effect of

Table 3 Chemical conditions for the collection of spectra for chemiluminescence reactions previously thought to involve energy transfer to fluorescent analytes or analyte oxidation products

System	Ref.	Reagents	Intensity maxima[a]
I	[14]	Line 1: $KMnO_4$ (0.3 mM) in H_2SO_4 (50 mM) Line 2: Acriflavine or proflavine (1 mM)	735 ± 5 nm
J	[15]	Line 1: $KMnO_4$ (0.5 mM) in H_2SO_4 (1 M) Line 2: Epinephrine, norepinephrine, dopamine or L-dopa (1 mM) in formaldehyde (0.8 M)	735 ± 5 nm
K	[16]	Line 1: $KMnO_4$ (394 ppm) in H_2SO_4 (0.3 M) Line 2: Perphenazine (1 mM)	735 ± 5 nm
L	[17]	Line 1: $KMnO_4$ (0.2 mM) in H_2SO_4 (2.5 M) Line 2: Vanillin (1 mM) in H_2SO_4 (2.5 M)	735 ± 5 nm

[a] Data from our investigation (not from the original paper)

Table 4 Chemical conditions for the collection of spectra for several miscellaneous chemiluminescence reactions with acidic permanganate where emitters other than manganese(II) species were previously proposed

System	Ref.	Reagents	Intensity maxima[a]
M	[30]	Line 1: $KMnO_4$ (2 mM) in H_2SO_4 (15 mM) Line 2: Butane-2,3-dione (0.1 M) and manganese(II) sulfate (1 mM)	735 ± 5 nm
N	[31]	Line 1: $KMnO_4$ (0.1 mM) in H_2SO_4 (0.18 M) Line 2: 2,4-Dinitrochlorobenzene (0.125 mg mL^{-1}; 50 mL) and hydrazine sulfate (5 mg mL^{-1}; 100 mL) heated in boiling water bath for 90 mins	735 ± 5 nm
O[b]	[35]	Line 1: $KMnO_4$ (0.075 mM) in H_2SO_4 (10 mM) Line 2: Sodium sulphite (0.5 mM) Line 3: Riboflavin (0.2 mM)	539 ± 5 nm
P[b]	[35]	Line 1: $KMnO_4$ (0.05 mM) in H_2SO_4 (10 mM) Line 2: Sodium sulphite (1 mM) Line 3: CAPS (1 mM)	475 ± 5 nm

[a] Data from our investigation (not from the original paper)

[b] Conditions modified from original paper

riboflavin and 3-cyclohexylaminopropanesulfonic acid (CAPS) on the reaction between acidic potassium permanganate and sodium sulphite [35]. They attributed the enhancement from riboflavin to a mechanism involving energy transfer, but a chemiluminescence spectrum was not collected to confirm this proposal. The same research group later suggested that the enhancement by non-fluorescent cyclohexyl compounds such as CAPS might be due to the formation of β-sultines [40].

Using the instrument manifold shown in Fig. 1b, we obtained chemiluminescence spectra for the reaction of acidic potassium permanganate and sodium sulphite enhanced by riboflavin (System O, Table 4) and by CAPS (System P). Similar spectral distributions were observed for System O and the fluorescence of riboflavin (Fig. 5), which supports the mechanism proposed by Al-Tamrah and co-workers [35]. System P produced a broad emission with maximum intensity at 475 ± 5 nm (Fig. 6), which was unlike the other chemiluminescence spectra collected in this investigation.

Conclusions

As shown in previous publications [1], the reaction of acidic potassium permanganate with a wide range of analytes leads to a broad red emission that is thought to arise from an excited manganese(II) species [3, 6]. We have detected the same characteristic red emission from several chemiluminescence reactions involving acidic potassium permanganate in which fluorescent compounds were present (either as enhancers or reaction products). Although emission from the fluorescent species has often been proposed for reactions of this type, it appears that the

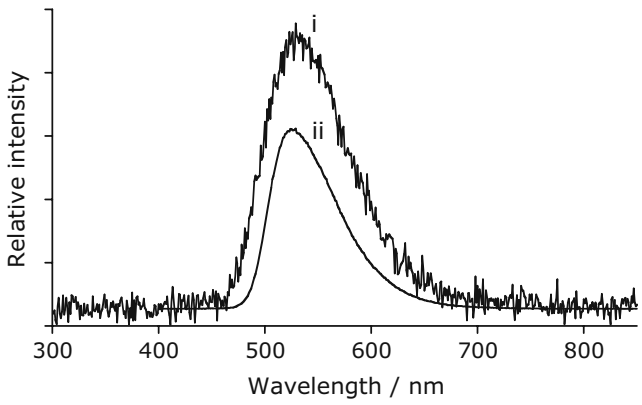

Fig. 5 (i) Chemiluminescence spectrum (uncorrected) for System O: acidic potassium permanganate, sodium sulphite and riboflavin. (ii) Fluorescence emission spectrum (uncorrected) for riboflavin (λ_{ex} = 359 nm)

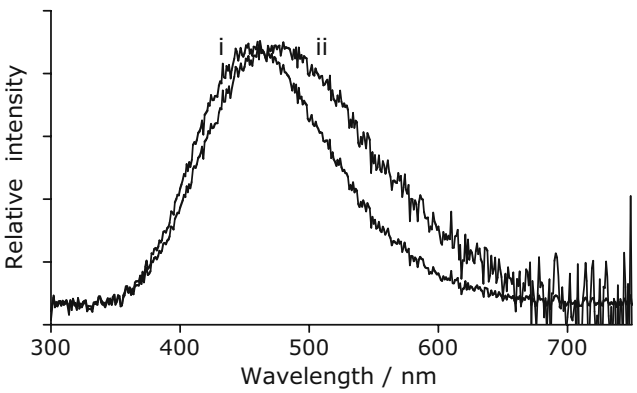

Fig. 6 Uncorrected (i) and corrected (ii) chemiluminescence spectra for System P: acidic potassium permanganate, sodium sulphite and CAPS

majority of these reactions lead to a common emitter derived from the permanganate oxidant.

There are, however, exceptions. The reaction of permanganate with certain thiols in the presence of quinine led to an emission from the fluorescent enhancer. Similarly, the oxidation of dihydralazine and rhodamine B evoked an emission that matched the characteristic fluorescence of the dye. In these cases, it appears that excited intermediates capable of transferring energy were formed, but it should be noted that the red emission attributed to manganese(II) was also observed, and therefore both of these systems involve more than one light-producing pathway. The reaction of permanganate with sulphite and riboflavin also led to an emission that matched the characteristic fluorescence of the enhancer. The chemiluminescence from the oxidation of sulphite in the presence of CAPS (a non-fluorescent enhancer) occurred in a similar spectral region to that reported for the same reaction without an enhancer, but in spite of much speculation, the nature of the species responsible for this emission is yet to be fully elucidated.

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