J Incl Phenom Macrocycl Chem (2012) 73:287–293
DOI 10.1007/s10847-011-0055-y

ORIGINAL ARTICLE

Peroxyoxalate chemiluminescence of 1,4-dihydroxy-3-methyl-thioxanthone and quenching effect of *β*-cyclodextrin

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Received: 3 June 2011 / Accepted: 23 September 2011 / Published online: 4 November 2011

Abstract The chemiluminescence generated from the reaction of bis(2,4,6-trichlorophenyl) oxalate (TCPO), hydrogen peroxide and 1,4-dihydroxy-3-methyl-thioxanthone (DMT) was investigated. Effects of reacting components, solvent and concentrations of TCPO, sodium salicylate, hydrogen peroxide and DMT were studied and their optimal values were determined. In addition, the influences of *β*-Cyclodextrin (*β*-CD) on the peroxyoxalate chemiluminescence (PO-CL) system of DMT were examined at optimized condition. The results showed that the presence of *β*-CD causes both enhancing and quenching effects on PO-CL system of DMT based upon its concentration. The Stern–Volmer quenching constant (K_q) was evaluated as 2.32×10^4 M^{-1} ($R^2 = 0.991$) by creating a linear regression plot on experimentally obtained data. This study resulted in satisfactorily determination of *β*-CD in the range 5.0×10^{-6} to 1.0×10^{-4} M.

Keywords Chemiluminescence · Cyclodextrin · Peroxyoxalate · Quenching · Thioxanthone

Introduction

Chemiluminescence is production of light through a chemical reaction that is a sensitive and selective analytical technique for determination of chemical compounds [1]. The application of chemiluminescence is going to be popular in food, pharmaceutical industry and biomedical analyses owing to its simplicity and a need of simple instrumentation without a light source [2]. Peroxyoxalate chemiluminescence (PO-CL) is an indirect chemiluminescence system that among the different types of chemiluminescence shows the most efficiency. In a PO-CL system, hydrogen peroxide oxidation of an aryl oxalate ester in the presence of a fluorophore could occur. The system has to excite a large number of fluorophores through a chemically initiated electron exchange luminescence (CIEEL) mechanism. By forming of one or more energy-rich intermediate(s), which form(s) some charge transfer complex(es) with the fluorophore, the fluorophore shifts to the excited state and emits light in return to ground state [3, 4]. Considering the kinetic characteristics, the PO-CL method could be easily coupled to analytical systems such as flow injection analysis and HPLC. The advantage of a PO-CL is a wide pH range to carry out the oxidation and stability and high efficiency [5, 6]. Here, we investigated a thioxanthone derivative as a luminophore probe for PO-CL system.

Thioxanthone derivatives are an important class of heterocyclic molecules. This compounds exhibit biologically and medically significant activities that could be used in anti-cancer, anti-parasitic and anti-drugs [7–9]. Thioxanthones are also photoinitiators for photoinitiated polymerization reactions in industrial applications [10, 11].

Cyclodextrins (CDs) are a family of cyclic oligosaccharides with a hydrophilic outer surface and a lipophilic central cavity, which possess a cage-like supramolecular structure. This composition consists of six, seven and eight glucopyranose units that named *α*-, *β*- or *γ*-CD, respectively [12–14]. CDs are widely used in pharmaceutical, food and cosmetic [15].

In this work, we studied the chemiluminescence emission of the luminophore 1,4-dihydroxy-3-methyl-thioxanthone (DMT, Fig. 1) in the presence of a PO system, so the influence of reacting agents are studied in details.

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Effect of solvent on the emission of the solution is also examined. In addition, in order to use the system as a quantitative method, its selective reaction and the behavior of the PO-CL system towards β-CD was also investigated in details.

Experimental

Chemical reagents and apparatuses

Commercial reagents were obtained from Merck and were used without further purification. Bis(2,4,6-trichlorophenyl) oxalate (TCPO) was synthesized from the reaction of 2,4,6-trichlorophenol and oxalyl chloride in the presence of tri-ethylamine as described elsewhere [16]. Luminophore DMT was synthesized and purified as reported before [17] and β-CD was purchased from Fluka and used directly.

The chemiluminescence spectra and all emission intensities were recorded on a Varian Cary Eclipse fluorescence spectrophotometer.

Procedure

At room temperature, proper amounts of stock solutions of TCPO (in ethyl acetate) and sodium salicylate (in methanol) were added into a 1-cm quartz cell containing 1.0 mL of DMT (in chloroform). The reaction would start after addition of a required amount of hydrogen peroxide, and then the chemiluminescence (a. u.) spectra or emission intensity of the mixture were recorded immediately. All solutions were freshly prepared when they were used for the measurements. All evaluated data values were of at least three repeated measurements ($n = 3$) for each case.

Results and discussion

As we could find in the literature, the familiar proposed mechanism for PO-CL reaction is as demonstrated by Eqs. 1–5, in which a CIEEL mechanism is probably responsible of the excitation [18–20]. It has been shown that the key intermediate 1,2-dioxetanedione (C_2O_4), a highly strained and unstable molecule, is produced in this mechanism. C_2O_4 forms a charge transfer complex with a fluorophore by accepting one electron from fluorophore and then a chemiluminescence light emits after the decomposition of this complex. As seen in the following steps, in an indirect chemiluminescence fashion, when hydrogen peroxide reacts with oxalate ester (here TCPO), after an intramolecular displacement, C_2O_4 is formed which will not emit but transfers its energy to a fluorophore (DMT, in this work) and release of CO_2 molecule. Afterward, the resulting sensitized fluorophore releases its energy in form of light or heat [18–21].

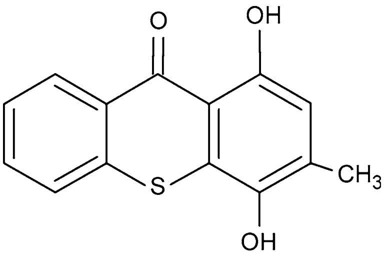

Fig. 1 The structure of 1,4-dihydroxy-3-methyl-thioxanthone (DMT)

$$2\mathrm{TCPO} + \mathrm{H_2O_2} \xrightarrow{k_1} \mathrm{C_2O_4} + 2\mathrm{HTCP} \quad (1)$$

$$\mathrm{C_2O_4} + \mathrm{DMT} \xrightarrow{k_2} [\mathrm{C_2O_4^{\bullet-}DMT^{+-}}] \quad (2)$$

$$[\mathrm{C_2O_4^{\bullet-}DMT^{+-}}] \xrightarrow{k_3} \mathrm{DMT^*} + 2\mathrm{CO_2} \quad (3)$$

$$\mathrm{DMT^*} \xrightarrow{k_4} \mathrm{DMT} + \mathrm{h}v \quad (4)$$

or

$$\mathrm{DMT^*} \xrightarrow{k_5} \mathrm{DMT} + \text{heat} \quad (5)$$

The chemiluminescence intensity depends on various factors that are investigated in the following studies. At first, in order to find a clue about the luminescence spectral properties of the luminophore DMT (1.0×10^{-3} M), the fluorescence emission spectra was taken at a proper fixed excitation wavelength 382 nm in chloroform. As demonstrated in Fig. 2, DMT acts as a highly efficient fluorophore at this exciting wavelength with maximum emission intensity at 453 nm that is indicative the presence of proper energy levels in the molecule to response towards an appropriate sensitizer.

Effect of solvent on PO-CL

The emission characteristics of a molecule often depend strongly on molecule's environment where factors such as polarity, hydrogen-bonding ability or viscosity of the solvent that may cause dramatic changes in the emission behavior of a solute. Polar solvent molecules reorient themselves in the proximity of a fluorescent molecule after excitation. Consequently, some excited-state energy is transferred from the fluorophores to the solvent [22].

In a mixture including 1 mL of DMT (1.0×10^{-3} M) in the desired solvent, 0.5 mL TCPO (1.0×10^{-3} M), 0.5 mL sodium salicylate (1.0×10^{-3} M) and 50 µL H_2O_2 (1.0 M), the chemiluminescence of the system was monitored in the presence of common solvents DMSO, chloroform, acetonitrile, DMF, THF and acetone. The results are shown in Fig. 3. As this figure indicates, the intensity of

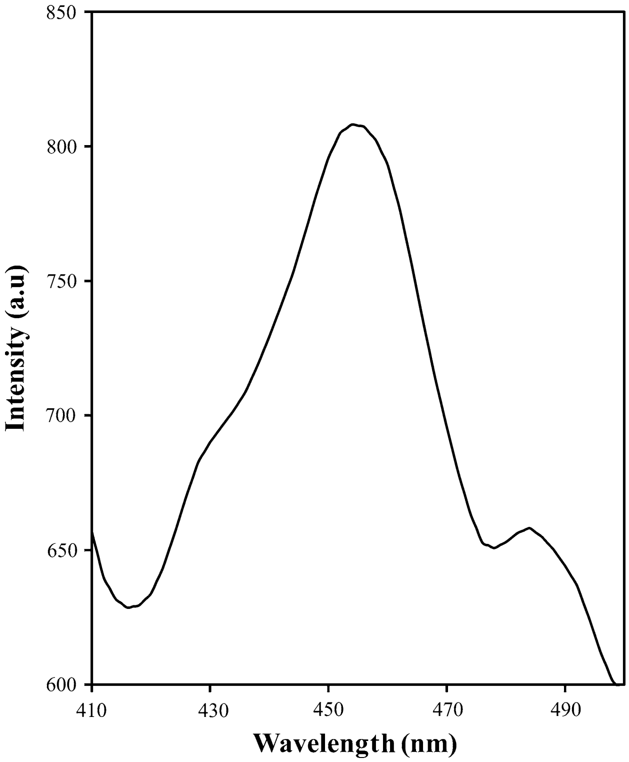

Fig. 2 The fluorescence emission spectra of DMT (1.0×10^{-3} M, in chloroform) when excited at fixed excitation wavelength 382 nm

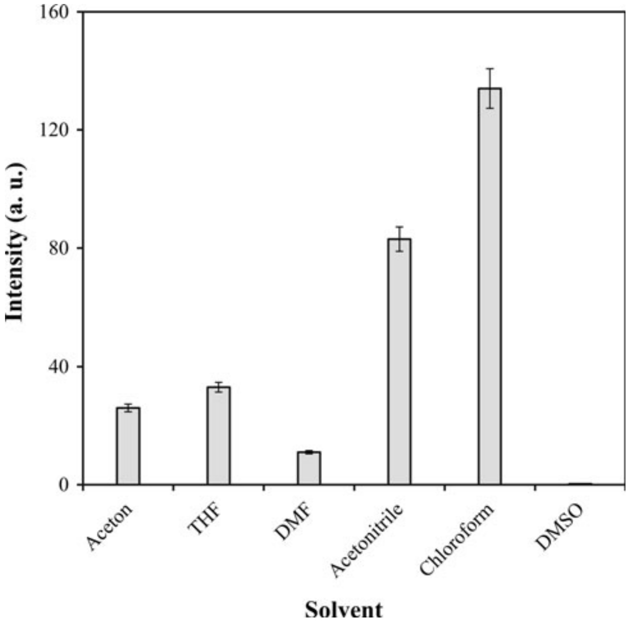

Fig. 3 The effect of type of solvent on DMT/PO-CL system for a solution containing DMT (1.0×10^{-3} M, in 1 mL of each solvent), TCPO (0.5 mL, 1.0×10^{-3} M), sodium salicylate (0.5 mL, 1.0×10^{-2} M) and H_2O_2 (50 μL, 1.0 M). The percentage bars display the error bars for the selected data with 5% value

PO-CL system is at the highest value for the case of chloroform among all the solvents used. We found that chloroform could serve as the best solvent for the PO-CL system of interest. An explanation for this increase in intensity of the emission is, generally, both polarity and viscosity strongly influence emission. The solutions viscosities are only slightly different but the dielectric constant of chloroform is much lower than that of others and has a low donor number [23]. Since the excited species are electrically polar, they could be affected by a polar medium that facilitates the energy transfer from the excited molecule to the solvent. In contrast, based on the conditions provided by chloroform it would be expected to show higher emission quantum yield [24].

Effect of reacting components on PO-CL

In order to study the catalytic effect of sodium salicylate on the PO-CL system [18], we measured the emission intensities of PO-CL when the fixed concentrations of TCPO, H_2O_2, DMT and varying initial concentrations of sodium salicylate (4.13×10^{-4} to 9.36×10^{-3} M) were used. As can be seen from Fig. 4, the chemiluminescence intensity increases after addition of sodium salicylate to the system that confirms the catalytic effect of sodium salicylate on the reaction. Addition of sodium salicylate at higher concentrations (>0.004 M) dramatically decreases the intensity of the emitted light. This is probably due to the quenching effect of the sodium salicylate at higher concentrations because of decomposition of the reactive

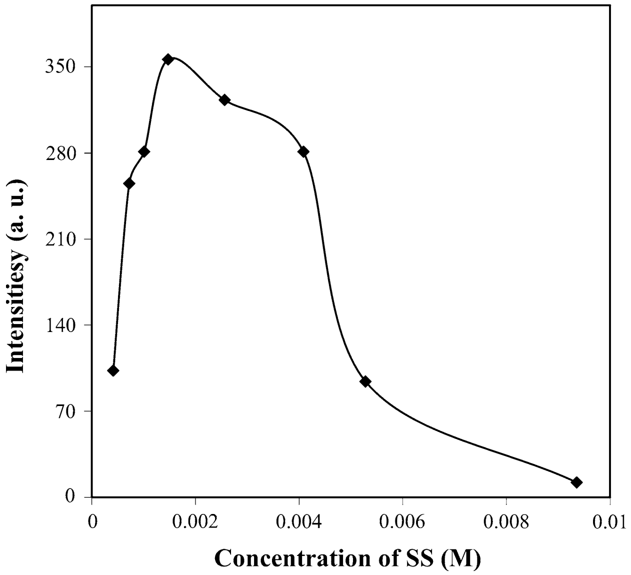

Fig. 4 The effect of sodium salicylate concentration (a 0.5 mL series, 4.13×10^{-4} to 9.36×10^{-3} M) on the PO-CL system in the presence of DMT (1.0×10^{-3} M, in 1 mL chloroform), TCPO (0.5 mL, 1.0×10^{-3} M), and H_2O_2 (50 μL, 1.0 M)

intermediate 1,2-dioxetanedione. Thus, a (2.56 ± 0.03) × 10^{-3} M of sodium salicylate was used as the optimal concentration in subsequent studies.

Investigating the effect of hydrogen peroxide concentration on PO-CL showed that the chemiluminescence intensity of the system increases until the added H_2O_2 concentration reaches to 0.025 M, after which the intensity of the emitted light is almost constant, as demonstrated in Fig. 5. For this case, constant concentrations of other reactants (1 mL 1.0 × 10^{-3} M of DMT, 0.5 mL 1.0 ×10^{-3} M of TCPO and the optimal concentration 2.56 × 10^{-3} M of sodium salicylate) were used and then the emission intensities of PO-CL measured from the solutions with different concentrations of H_2O_2 (6.60 ×10^{-3} to 5.66 × 10^{-2} M). We selected (5.06 ± 0.01) × 10^{-2} M as an optimal concentration of H_2O_2 for next reaction mixtures.

Figure 6 shows a typical response curves for the PO-CL system in the presence of the constant amount of DMT (1 mL, 1.0 × 10^{-3} M) and optimal concentrations of sodium salicylate (2.56 × 10^{-3} M), H_2O_2 (5.06 × 10^{-2} M) and various initial concentrations of TCPO (4.87 × 10^{-5} to 2.07 × 10^{-4} M). As shown in this figure, there is a linear relationship between the chemiluminescence intensities and the TCPO concentrations. Choosing (1.14 ± 0.02) × 10^{-4} M of TCPO, as an optimal concentration of this reagent, resulted in reasonable consequences.

Finally, the obtained results shown in Fig. 7 reveal a linear correlation between the chemiluminescence intensities of the system and amount of the luminophore (DMT), from 2.5 × 10^{-4} to 5.6 × 10^{-4} M. Properly, (4.52 ± 0.01) × 10^{-4} M DMT was used in subsequent reactions. So far, we revealed that DMT can be used as a useful chemiluminescence probe and determined the optimal concentrations

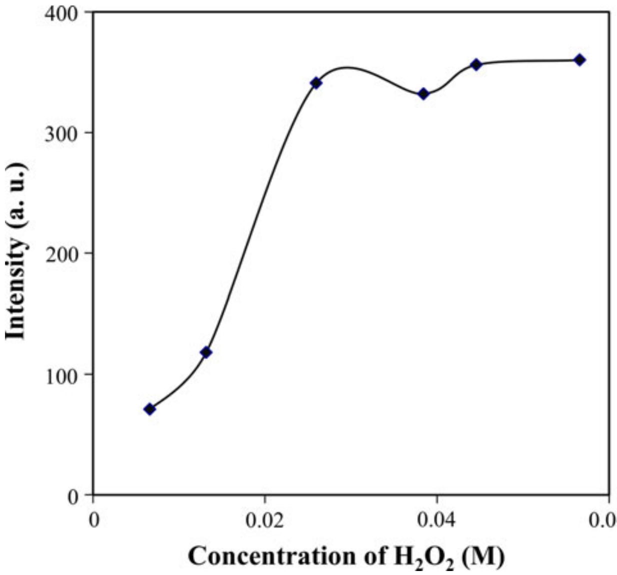

Fig. 5 The effect of H_2O_2 concentration (50 μL, 6.60 × 10^{-3} to 5.66 × 10^{-2} M) on the CL intensity of 1 mL DMT (1.0 × 10^{-3} M, in chloroform), 0.5 mL TCPO (1.0 × 10^{-3} M) and sodium salicylate (2.56 × 10^{-3} M)

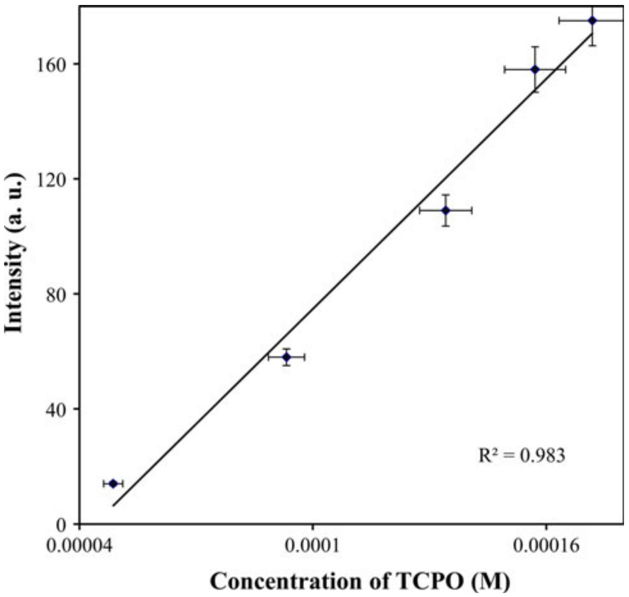

Fig. 6 The influence of varying concentration of TCPO (4.87 × 10^{-5} to 2.07 × 10^{-4} M) on the PO-CL system with 5.06 × 10^{-2} M of H_2O_2, 2.56 × 10^{-3} M of sodium salicylate, and 1 mL 1.0 × 10^{-3} M of DMT (in chloroform). The percentage bars display the error bars for the selected data with 5% value

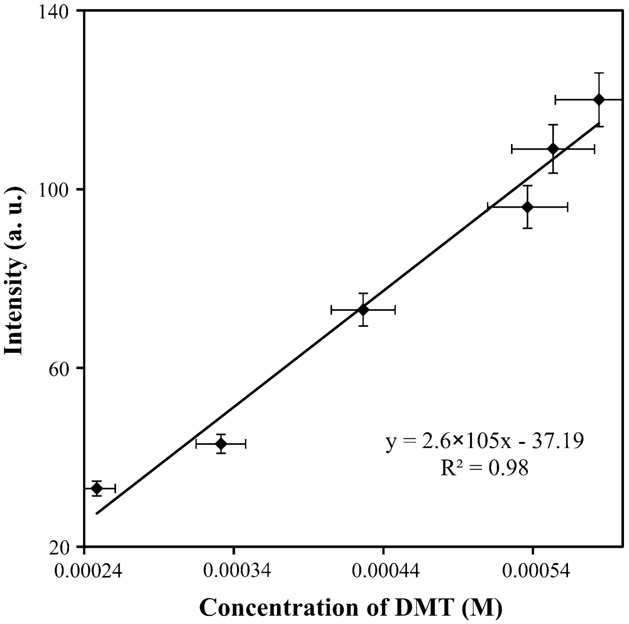

Fig. 7 The effect of DMT concentration (a 1 mL series in chloroform, 2.40 × 10^{-4} M to 5.84 × 10^{-4} M) on the chemiluminescence intensity of DMT/PO-CL system in the presence of the TCPO, H_2O_2 and sodium salicylate, 1.14 × 10^{-4} M, 5.06 × 10^{-2} M and 2.56 × 10^{-3} M, respectively. The percentage bars display the error bars for the selected data with 5% value

of all reaction components required to produce the PO-CL system of interest as TCPO, sodium salicylate, DMT and hydrogen peroxide $1.14 \times 10^{-4}, 2.56 \times 10^{-3}, 4.52 \times 10^{-4}$ and 5.06×10^{-2} M, respectively.

Now, as an extension of our research on the chemiluminescence of DMT/PO-CL system, we are interested in reporting the results of using the proposed PO-CL system on the study of host/guest inclusion phenomena between β-CD and DMT.

The quenching effect of β-cyclodextrin

As stated in the introduction section, these molecules (CDs) have capability to enclose small hydrophobic molecules into their cavity and consequently to form host/guest complex(es) in solution [25]. We investigated the shielding effect of β-CD on light emitting of the guest molecule. There are typical reports on β-CD inclusion complexation with some xanthone and thioxanthone derivatives [26]. So the following mechanism could be proposed for encapsulation of DMT when reacts with β-CD in the solution. The inclusion complexation is stabilized by formation of hydrogen bonds between the hydrogens of peripheral hydroxide groups on the rim of the host (β-CD), both sulfur and oxygen of carbonyl group substituted on the guest (DTM). Here, DMT is encapsulated by β-CD, partially. Hence, the rigidity of the environment of the light emitter somewhat enhances while the emitting moieties of the guest is protected by the inclusion process. The results for DMT when reacts with β-CD is schematically illustrated in Fig. 8.

Here, effects of the different concentrations of β-CD (1.0×10^{-7} to 1.1×10^{-4} M) on the proposed PO-CL system were examined. Fortunately, the lifetime of the emitting system in the presence of β-CD was high enough (20 s) to determine measureable intensities. We found that the emitted light somewhat enhances at first and then to be quenched considerably. This fact could be attributed to the resulted rigidity and initial preventing the luminal system from the collision with the environment and later to more complexation of the excited DMTs by encapsulators β-CDs. Figure 9 shows the quenching effect of β-CD on the DMT/PO-CL system, for some points where changes of chemiluminescence of the system are linear.

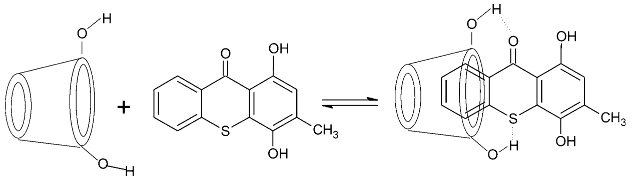

Fig. 8 Schematic diagram of encapsulation of DMT when reacts with β-CD in the solution. The inclusion complexation is stabilized by formation of hydrogen bonds between the hydrogens of peripheral hydroxide groups on the rim of the host (β-CD), both sulfur and oxygen of carbonyl group substituted on the guest (DTM). As can be seen, DMT is encapsulated by β-CD, partially

As we know, determination of Stern–Volmer quenching coefficients is important in many areas of chemistry and many quantitative analytical methods that are based on efficient quenching of a reagent by an analyte of interest [27]. Form the Stern–Volmer's method we can determine the measurable concentration range of the quencher in the solution.

From a steady-state kinetics calculation, the chemiluminescence intensity of a luminophore C in the absence (I_0) and the presence of a quencher (I) can be written as Eqs. 6 and 7, respectively:

$$I_0 = \frac{k^*}{k_{nr}}[C] \tag{6}$$

$$I = \frac{k^*[C]}{k_{nr} + k_q[Q]} \tag{7}$$

where k_{nr} describes the k value for nonradiative deactivation processes, k_q is the quenching rate constant and Q denotes the quencher β-CD. A plot of chemiluminescence

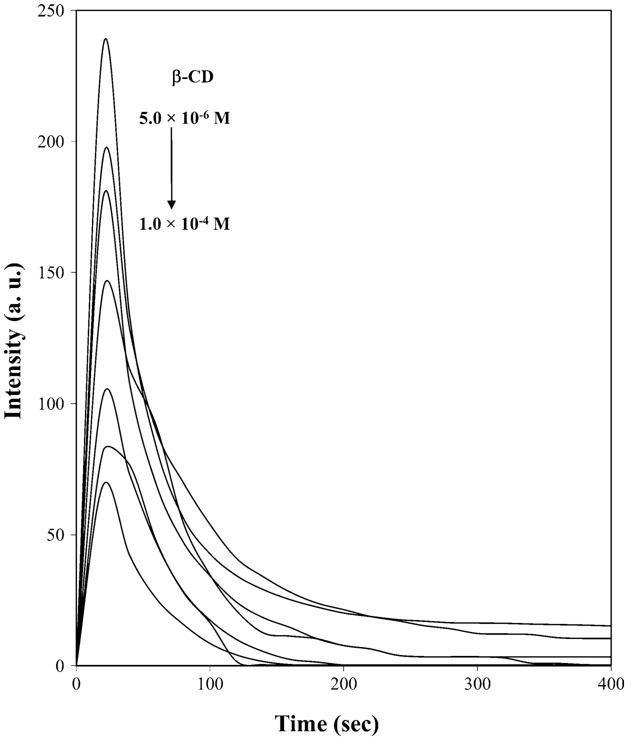

Fig. 9 Intensity-time spectra plot for the linear portion of quenching effect of β-CD concentration (5.0×10^{-6} M to 1.0×10^{-4} M) on the DMT/PO-CL intensity at the optimized concentrations of the chemiluminescence reactants

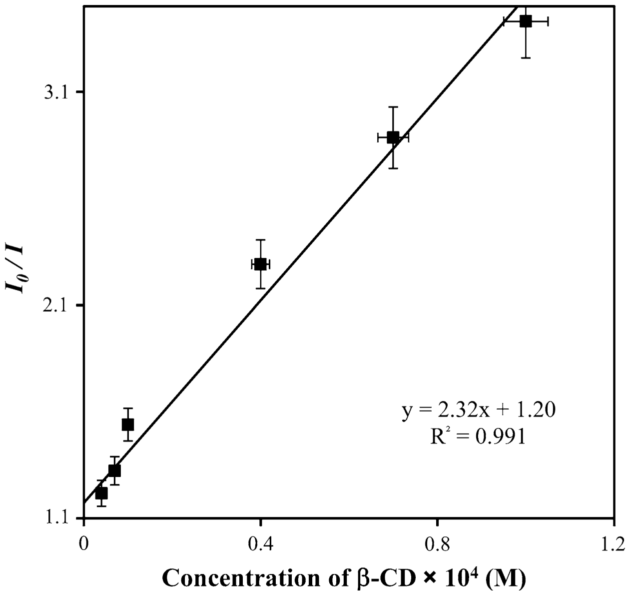

Fig. 10 Stern-Volmer plot for the DMT/PO-CL system, from the data shown in Fig. 9, influenced by the quenching effect of β-CD. The percentage bars display the error bars for the selected data with 5% value

intensities vs. the luminophore C (here, DMT) concentrations gives a linear regression equation, from which k^* value (radiation constant) for a proposed PO-CL system could be evaluated.

The Stern–Volmer quenching constant K_q ($=k_q/k_{nr}$), which is the result of rationing Eqs. 6 and 7, is expressed as by Eq. 8.

$$\frac{I_0}{I} = 1 + K_q[Q] \tag{8}$$

A plot of the I_0/I ratio vs. [Q] (here, [β-CD]) should yield a straight line, from which the Stern–Volmer quenching constant (K_q) can be determined. A linear regression (LR) with intercept = 1, on the experimental data from linear portion of the curve given in Fig. 9, gave $(2.32 \pm 0.01) \times 10^4$ M^{-1} for K_q. This so high value for K_q is indicative the establishment of strong inclusion forces between the host and guest. The regression plot and the corresponding LR-equation, $I_0/I = 1.2 + 2.32[Q]$ ($R^2 = 0.991$ for intercept = 1) are shown in Fig. 10. The response behavior of the system was nonlinear at out of the above-mentioned concentration range of β-CD. So the lowest and the highest detection limits, measureable concentrations of β-CD, were evaluated as $(5.0 \pm 0.1) \times 10^{-6}$ and $(1.0 \pm 0.1) \times 10^{-4}$ M, respectively.

There are so many methods for determination of β-CD in the literature but none of them has reported the measurement of the concentration of β-CD quantitavely so we were not able to do any comparison between our own work and others.

Conclusions

From the results obtained in this work, we found that 1,4-DMT emits an intense light with relatively high lifetime (about 20 s) when it is sensitized in a peroxyoxalate (PO) reaction so it can be used as a strong luminophore. Thus, DMT, which is an important compound in biological and industrial fields, could successfully be traced under the evaluated optimal condition. In addition, we demonstrated that DMT/PO-CL could be influenced by β-Cyclodextrin (β-CD) quenching effect, from which trace amounts of β-CD are detectable by using the inherently sensitive chemiluminescence method.

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