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New bis[N-(4-pyridyl)-P-Toluene Sulfonamide] Palladium Dichloride a Novel Fluorophore for Determination of Lysine Amino Acid

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Abstract Here, we are describing the study of the chemiluminescence arising from the reaction of bis (2,4,6-trichlorophenyl) oxalate (TCPO) system with new bis [N-(4-pyridyl)-*p*-toluene sulfonamide] palladium dichloride (BSPC) as a novel luminescent. The optimum concentrations of all reagents such as sodium salicylate (SS) as catalyst, hydrogen peroxide as oxidizing reagent and the relationships between the chemiluminescence intensity and concentrations of TCPO, SS, hydrogen peroxide and BSPC are reported. After optimization the required reagents, the system were used for determination of amino acid lysine, as an effective and selective quencher in the solution functioning in a Stern–Volmer fashion. This resulted in the development of a facile and highly sensitive chemiluminescence detection scheme for the determination of lysine in biological samples. Ultimately, estimating quenching constant K_q of 4.29×10^3 M^{-1} was successfully carried out. Under the optimal conditions, the evaluated lower and upper detection limits of measurable concentration of lysine are 1.17×10^{-7} and 3.18×10^{-4} M, respectively.

Introduction

Chemiluminescence is the generation of electromagnetic radiation as light by the release of energy from a chemical reaction that involves the production of an electronically excited species from a number of reactants which goes on to release light in order to revert to its ground state energy [1]. Chemiluminescence usually occurs when a highly oxidized

molecule, such as peroxide, reacts with another molecule. Chemiluminescence spectroscopy is an important tool in chemical analysis [1–9]. The emissions from excited molecules, either in gas phase or in solution, are measured using a photomultiplier or similar light-sensitive instrument, possibly in combination with a chromatograph. Measurement of the light emitted through chemiluminescence is used to determine the concentration of the excited chemical reagent. The application of chemiluminescence is going to be popular in food [2, 3], pharmaceutical industry [3] and biomedical analyses owing to its simplicity and a need of simple instrumentation without a light source.

Peroxyoxalate chemiluminescence (PO-CL) system is a well-known and powerful method that has been widely utilized in environmental, pharmaceutical and biomedical analyses [7, 8]. 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 [10]. 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 returning to ground state [11]. The advantage of a PO-CL is a wide pH range to carry out the oxidation and stability and high efficiency [12, 13].

Here, we report the study of the chemically-produced light emission of the recently synthesized luminophore Bis [N-(4-pyridyl)-*p*-toluene sulfonamide] palladium dichloride (BSPC, Fig. 1) in the presence of a PO system. Then the luminescence behavior of the system for selective detection of lysine is described in details.

Lysine is one of the 20 most common natural amino acids on Earth and is very important owing to its outstanding role in

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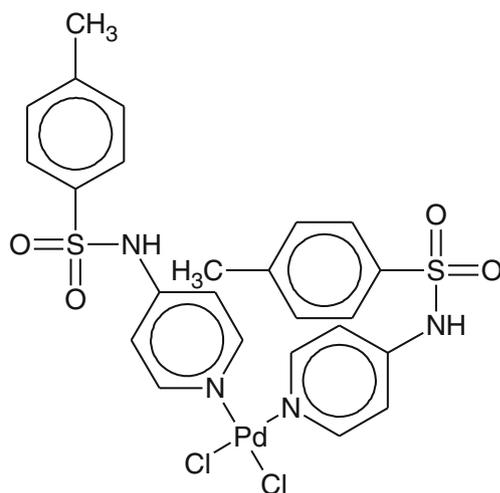e-mail: a.yari@ymail.com

Fig. 1 The chemical structure of bis [N-(4-pyridyl)-p-toluene sulfonamide] palladium dichloride (BSPC)

human health [14]. Lysine aids in building muscle tissue, recovering from injury (or surgery), and absorbing calcium effectively. It also helps the body produce antibodies, enzymes, and hormones [14, 15]. Nutritionally, in humans, lysine is an essential amino acid that has a net positive charge at physiological pH values making it one of the three basic (with respect to charge) amino acids. Lysine cannot be produced by body activities, on the other hand, and its concentration in cereals, an important human and animal food source [16] is low. These facts tell us that any attempt by chemists to determine lysine is valuable. PO-CL system has already been used to investigation the chemiluminescence behavior in the presence of sulfur-containing amino acids [17].

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 triethylamine as described elsewhere [18]. Luminophore BSPC was synthesized and purified as reported elsewhere [19].

The luminescence spectra were recorded on a JASCO FP 6200 spectrofluorometer (Japan), by which all emission intensities were also measured.

Procedure

At room temperature, 500 μL of stock solutions of TCPO (in ethyl acetate) and 500 μL of sodium salicylate (SS, in

methanol) were added into a 1-cm quartz cell containing 1.0 mL of BSPC (in acetonitrile). The reaction would start after addition of a required amount of hydrogen peroxide, and then the chemiluminescence spectra or emission intensity (a. u.) of the mixture was recorded immediately. All solutions were freshly prepared when they were used for the measurements.

Synthesis of the Luminophore

According to the report in ref. [19], 0.1 g (0.56 mmol) of palladium dichloride was transferred into a 100 mL beaker. Then 30 mL acetone was added to the baker while the mixture being stirred with a magnetic stirrer. 0.28 g (1.1 mmol) N-(4-pyridile)-p-toluensulfonamide was added to the system. The reacting mixture was stirred for 24 h at room temperature. Then the mixture was filtered to gather a pale-yellowish precipitant. The product was washed many times with acetone. In order to extract unbounded palladiums, the resulted precipitant was put under reflux condition for 7 h, after that the product was washed with hot methanol many times in a Bucher funnel filtration system. Finally, the residual was left in a desiccator to drying in ambient atmosphere (mp=359.3 – 359.4ºC). Using ^{13}C-^{1}H-NMR, Raman and IR techniques physical characteristics of the product were confirmed. H-NMR (were taken in a Bruker DPX-300 instrument); δ (ppm): 2.34 (singlet, 6H), 7.09–7.39 (doublet-doublet, 8H), 7.77 – 8.34 (doublet-doublet, 8H) and 11.7 (singlet, 2H); ^{13}C-NMR, δ (ppm): 132 (triplet, 12), 145 (doublet, 10), 12 (singlet, 2); Raman (cm^{-1}): 1320 (sulfonamide), 3070 (C–H, sp^2), 2920 (C–H, sp^3), 268 (Pd–N), 287 (Pd–Cl); IR (ν, cm^{-1}): 3400 (N–H), 3100 (C–H, sp^2), 2950 (C–H, sp^3), 1160 and 1340 (sulfonamide), 840 (aromatic rings).

Results and Discussion

In a primarily experiment, we found that BSPC reacts as a powerful emitter of light when the required reagents for a PO-CL system are provided. So, the luminescence spectra of BSPC (800 μL 3.94×10^{-5} M) was taken in the presence of 500 μL 1.63×10^{-3} M SS, 500 μL 1.3×10^{-3} M TCPO, 80 μL 3.14×10^{-2} M hydrogen peroxide in acetonitrile. As demonstrated in Fig. 2, the luminescence spectra of the system are well shaped and show a clear maximum at 294 nm with a lifetime of approximately 25 s.

In an indirect chemiluminescence fashion, when hydrogen peroxide reacts with oxalate ester (here TCPO), after an intra-molecular displacement, C_2O_4 is formed that will not emit but transfers its energy to a fluorophore (BSPC, in this work) by
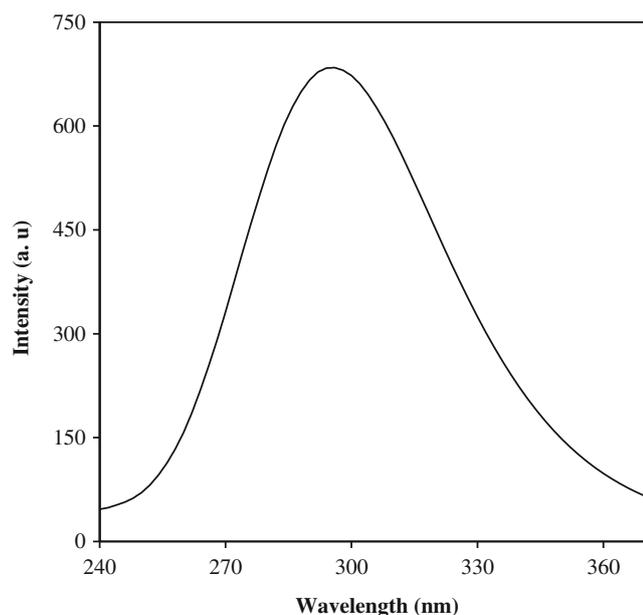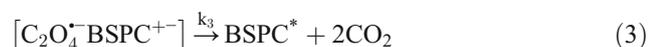
Fig. 2 The luminescence spectra of BSPC (800 μL 3.94×10^{-5} M) was taken in the presence of 500 μL 1.63×10^{-3} M SS, 500 μL 1.3×10^{-3} M TCPO, 80 μL 3.14×10^{-2} M hydrogen peroxide in acetonitrile

releasing two CO_2 molecules. Afterward, the resulting sensitized luminophore releases its energy in forms of light or heat through the following steps [20–22].

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

$$C_2O_4 + BSPC \xrightarrow{k_2} \left[C_2O_4^{\bullet-} BSPC^{+-} \right] \qquad (2)$$

$$\left[C_2O_4^{\bullet-} BSPC^{+-} \right] \xrightarrow{k_3} BSPC^* + 2CO_2 \qquad (3)$$

$$BSPC^* \xrightarrow{k_4} BSPC + h\nu \qquad (4)$$

or

$$BSPC^* \xrightarrow{k_5} BSPC + heat \qquad (5)$$

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.

In order to use chemiluminescent reactions effectively for quantitative chemical analysis, the analyst should have an understanding of the key experimental variables affecting luminescence measurements. Therefore, chemiluminescence intensity depends on various factors that are investigated in the following studies.

Choice of a Solvent for PO-CL

Unfortunately, BSPC is slightly soluble in common organic solvents such as chloroform, dimethylformamide, tetrahydrofuran and acetone but somewhat dissolves in acetonitrile. Dimethylsulfoxide can dissolve BSPC considerably but the light emitting activity of the system could be extinguished in the presence of this solvent. So, we were not able to study the effects of different solvents on the chemiluminescence of the system. We found that acetonitrile could serve as the best solvent for the PO-CL system of interest because of low polarity and viscosity, factors that can affect the light emitting ability of the system considerably.

Effect of Reacting Components on PO-CL System

Effect of Sodium Salicylate

In order to study the effect of SS on the PO-CL system, we measured the emission intensities of PO-CL when the fixed concentrations of TCPO (8.5×10^{-3} M), hydrogen peroxide (1.0 M), BSPC (1.0×10^{-3} M) and varying initial concentrations of SS (0.0 to 3.1×10^{-3} M) were used. As can be seen in Fig. 3, the chemiluminescence intensity increases eruptive after addition of SS to the system that confirms the catalytic effect of SS [23] on the reaction. Addition of SS at higher concentrations ($>1.63\times10^{-3}$ M) dramatically decreases the intensity of the emitted light. This is probably due to the quenching effect of the SS at higher concentrations because the decomposition of
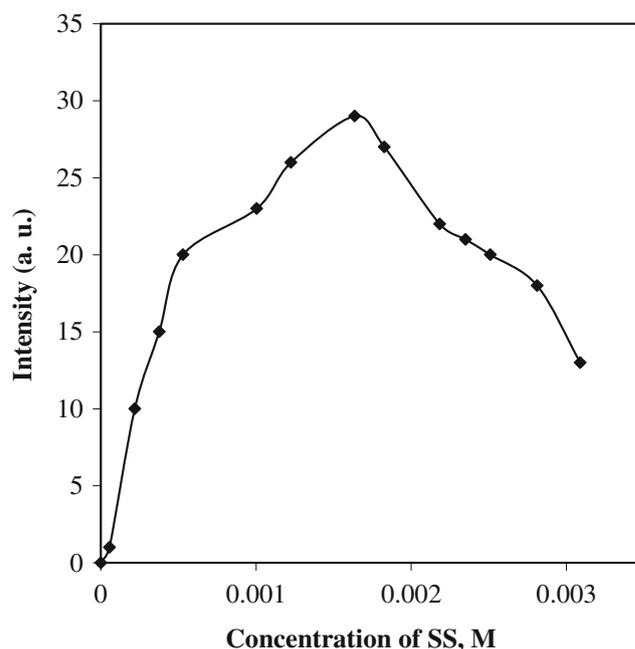

Fig. 3 The effect of SS concentration on the PO-CL system, when the fixed concentrations of TCPO (8.5×10^{-3} M), hydrogen peroxide (1.0 M), BSPC (1.0×10^{-3} M) and varying initial concentrations of SS (0.0 to 3.1×10^{-3} M) were used

the reactive intermediate 1,2-dioxetanedione [22]. Thus, a 1.6×10^{-3} M of SS was used as the optimal concentration in subsequent studies.

Effect of Hydrogen Peroxide

To investigate the effect of hydrogen peroxide concentration on PO-CL, the results showed that the chemiluminescence intensity of the system increases in the presence of hydrogen peroxide. This fact is indicative the oxidant role of this reagent [24]. The intensity of the light raises until the added hydrogen peroxide concentration reaches to 0.019 M, after which the intensity of the emitted light is almost constant, as demonstrated in Fig. 4. For this case, constant concentrations of other reactants (1.0×10^{-3} M of BSPC, 8.5×10^{-3} M of TCPO and the optimal concentration 1.6×10^{-3} M of SS) were used and then the emission intensities of PO-CL were measured from the solutions with different concentrations of hydrogen peroxide (0.0 to 2.8×10^{-2} M). We selected 1.9×10^{-2} M as an optimal concentration of hydrogen peroxide for next reaction mixtures.

Effect of TCPO

To find the relationship between the concentrations of TCPO and intensities of the emitted chemiluminescence from the tested system [25], the chemiluminescence of the system were plotted against the concentrations of TCPO in the solution. Figure 5 shows a typical response curves for the PO-CL system in the presence of the constant amount of
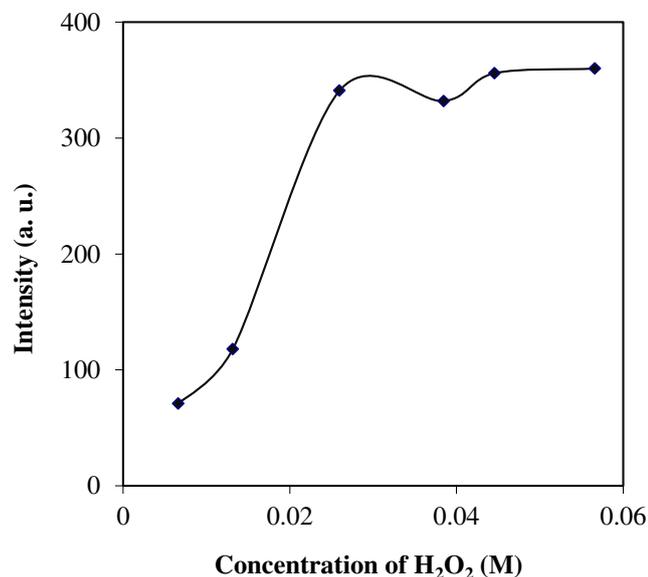

Fig. 5 Chemiluminescence of PO-CL system in the presence of the constant amount of BSPC (1.0×10^{-3} M) and optimal concentrations of SS (1.6×10^{-3} M), hydrogen peroxide (1.9×10^{-2} M) and various initial concentrations of TCPO (1.2×10^{-4} to 5.5×10^{-3} M)

BSPC (1.0×10^{-3} M) and optimal concentrations of SS (1.6×10^{-3} M), hydrogen peroxide (1.9×10^{-2} M) and various initial concentrations of TCPO (1.2×10^{-4} to 5.5×10^{-3} M). As shown in this figure, there is a linear relationship (7.3×10^{-4} to 2.3×10^{-3} M) between the chemiluminescence intensities and the TCPO concentrations. Choosing 1.3×10^{-3} M of TCPO, as an optimal concentration of this reagent, resulted in reasonable consequences.

Effect of BSPC

Finally, the obtained results shown in Fig. 6 reveals that a linear correlation between the chemiluminescence intensities of the system and amount of the luminophore (BSPC), from 2.0×10^{-5} to 3.9×10^{-5} M, is established beyond which the intensity of the emitted light did not change linearly with regard to concentration additions. 3.8×10^{-5} M of BSPC was used in subsequent reactions as a proper concentration.

So far, we have realized that BSPC can be used as a useful chemiluminescence probe and determined the optimal concentrations of all reaction components required to produce the PO-CL system of interest as TCPO, SS, BSPC and hydrogen peroxide 1.3×10^{-3}, 1.6×10^{-3}, 3.8×10^{-5} and 1.9×10^{-2} M, respectively.

Effect of Temperature

The effect of temperature on the intensity of the emitted light is a very important factor that the analyst should investigate it during the study of the chemiluminescence

Fig. 4 The effect of hydrogen peroxide concentration, constant concentrations of other reactants (1.0×10^{-3} M of BSPC, 8.5×10^{-3} M of TCPO and the optimal concentration 1.6×10^{-3} M of SS) were used with different concentrations of hydrogen peroxide (0.0 to 2.8×10^{-2} M)
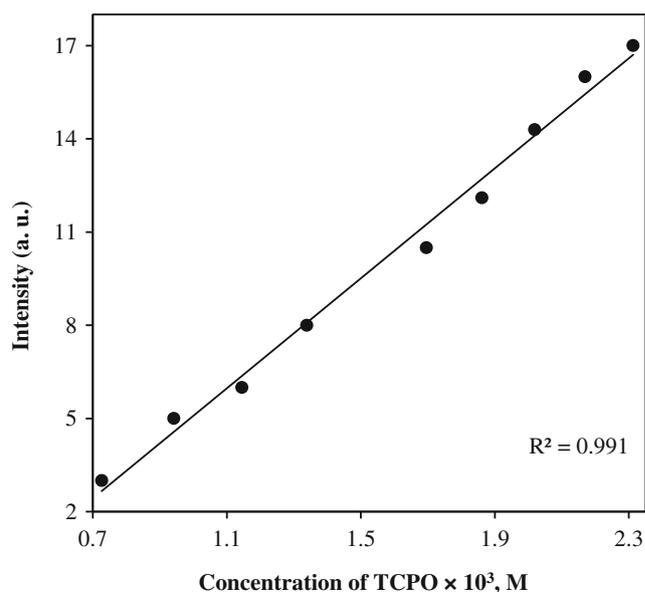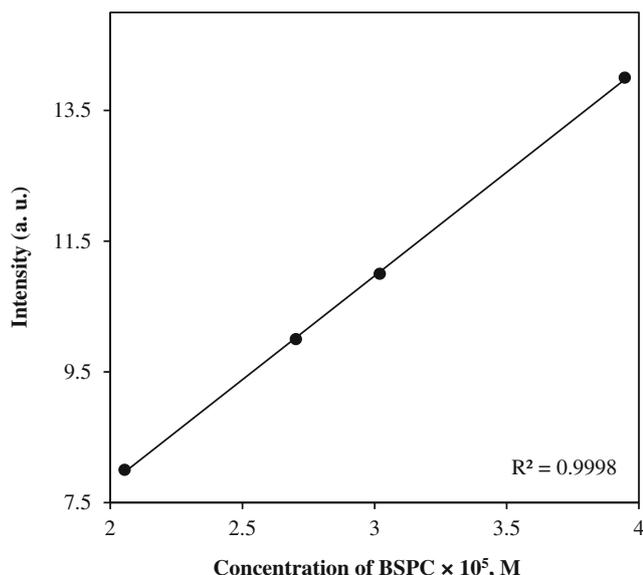
Fig. 6 The effect of BSPC concentration (from 2.0×10^{-5} to 3.9×10^{-5} M) on the chemiluminescence intensity of BSPC/PO-CL system in the presence of the optimal concentrations of TCPO, SS, and hydrogen peroxide 1.3×10^{-3}, 1.6×10^{-3}, and 1.9×10^{-2} M, respectively

of a system. The method for such study has already been introduced by Eyring's transition-state theory [26, 27]. We will be considering the bimolecular reaction of A with B to form C, as shown below:

$$A + B \xrightarrow{k} C \tag{6}$$

k is the bimolecular rate constant for conversion of A and B to C. According to the transition state model, the reactants are getting over into an unsteady intermediate state (AB^*) on the reaction pathway:

$$A + B \underset{k_r}{\overset{k_f}{\longleftrightarrow}} AB^* \xrightarrow{k^*} C \tag{7}$$

In this equation, k^* is the unimolecular rate constant for decomposition of the activated complex AB^* to form C, k_f and k_r are rate constants for the forward and the backward reactions, respectively. The high-energy complex represents an unstable molecular arrangement, in which bonds break and form to generate the product C or to degenerate back to the reactants A and B. The linear form of Eyring's equation is finally found as follows:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^*}{R} \cdot \frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R} \tag{8}$$

$k = k^* \cdot k_B \cdot T/h$, where k_B is the Boltzmann's constant (1.381×10^{-23} J.K.$^{-1}$), h is Palnk constant (6.626×10^{-34} J.s), ΔH^* and ΔS^* are activation enthalpy and entropy changes, respectively. T is absolute temperature (in degrees Kelvin) and

R is universal gas constant (8.3144 J.mol^{-1}.K^{-1}). Clearly, a plot of ln (k/T) versus 1/T produces a straight line that ΔH^* can be calculated from the slope of this line. A precise determination of the activation enthalpy (and the other activation parameters) requires at least three different rate constants. This means three kinetic runs at different temperatures are carried out.

The influences of different temperatures of the reaction solution 293, 298 and 303 K, on the chemiluminescence of the system were studied under the optimized condition (Fig. 7 points). This figure shows that the intensity of the system increases when the temperature of the solution rises. From Eyring's transition-state theory, the corresponding response curves were constructed theoretically (Fig. 7 solid lines) by using a computerized curve fitting program KINFIT [28]. As shown in this figure, the experimental data fits the theoretically predicted values very good that is indicative the proposed rate mechanism steps are governed by a bimolecular fashion. The theoretically predicted activation parameters thus were determined as listed in Table 1.

In addition, using the plot of ln (k/T) versus 1/T, the activation parameters ΔH^* and ΔS^* of the system were evaluated from the slope and intercept of the linear regression plot of ln (k/T) versus 1/T (inset in Fig. 7). Gibb's free energy change (ΔG^*) and activation energy (E_a) were also evaluated. Thus, they were determined as follows: ΔH^* (5.44 kJ mol^{-1}), ΔS^* (1.04 kJ mol^{-1} K^{-1}), $\Delta G^* = 5.44 - 1.04$ T (r=0.997) and $E_a = 5.44 + 0.008$ T (r=0.999).
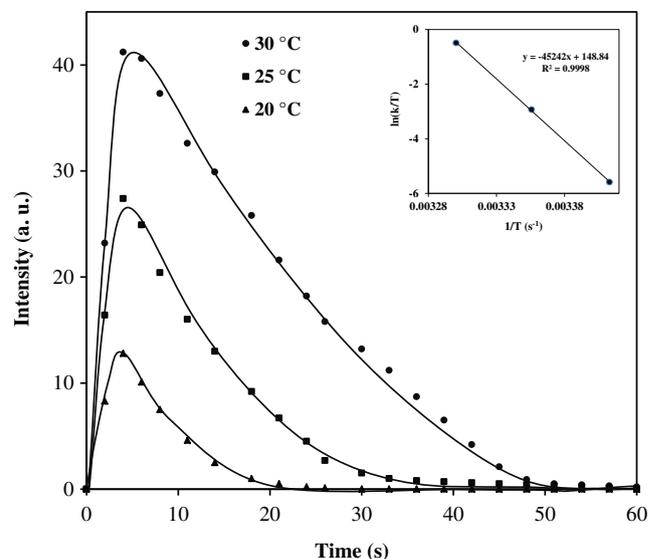

Fig. 7 The influences of different temperatures of the reaction solution 293, 298 and 303 K, on the chemiluminescence of the system under the optimized condition (points). The corresponding theoretical response curves (solid lines) predicted by the computerized curve fitting program KINFIT. The inset shows the linear regression plot of ln (k/T) versus 1/T to evaluate the activation parameters ΔH^* and ΔS^* of the system

Table 1 The activation parameters evaluated by computer fitting of the chemiluminescence intensity-time plots for the system at various temperatures

Temperatures (K)	k (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (kJ mol^{-1} K^{-1})	$-\Delta G^*$ (kJ mol^{-1})
303	185.7±3.2	2.3±0.8	2.1±0.1	634.0±4.3
298	15.9±1.1	5.1±1.0	1.3±0.1	382.3±2.2
293	1.1±0.1	8.3±1.2	0.8±0.1	226.1±1.2

As seen, a positive value for entropy of activation indicates that the transition state is highly disordered compared to the ground state. Degrees of freedom are 'liberated' in going from the ground state to the transition state, which, in turn, increase the rate of the reaction. The existence of a bimolecular interaction between the intermediate 1,2-dioxetanedione (C_2O_4) and BSPC, which is in agreement with the CIEEL mechanism in the chemi-excitation step and excludes the BSPC excitation by an electronic energy transfer [10], proved the proposed theoretical models.

The Quenching Effect of Lysine

Now, as an extension of our research on the chemiluminescence of BSPC/PO-CL system, we are interested in reporting the results of using the proposed PO-CL system on the study of interaction of amino acid lysine with BSPC. There are many reports on determination of lysine in the literature. They are electrochemical [29] or mostly chromatographic methods [30] such as HPLC, which are multi-stage and time consumer.
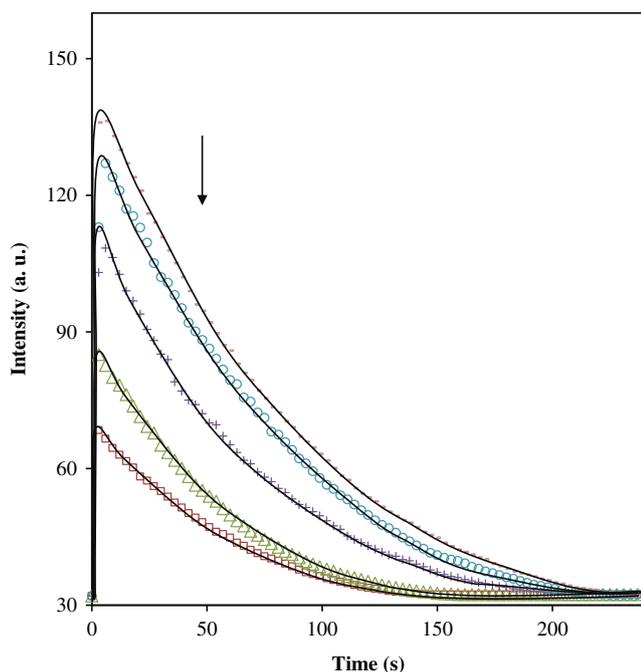
The proposed method which is a simple and rapid way to relatively accurate determination of lysine could be used anywhere that no need to highly expertized analyst or any sophisticated devices.

Here, effects of the different amino acids on the proposed PO-CL system were examined. We couldn't find any considerable change in the intensity of emitted light after addition of glycine, tryptophan, cysteine, alanine and arginine. But, we found that the emitted light to be quenched considerably in the presence one of the best essential amino acids, lysine. This fact could be attributed to the interaction of the amino or carboxylic functional groups on lysine towards palladium atom in BSPC. Figure 8 shows the intensity-time spectra curves for the quenching effects of different concentrations of lysine (5.0×10^{-5} M to 1.0×10^{-4} M) in the solution on the BSPC/PO-CL intensity at the optimized concentrations of the chemiluminescent reactants.

From the literatures, 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
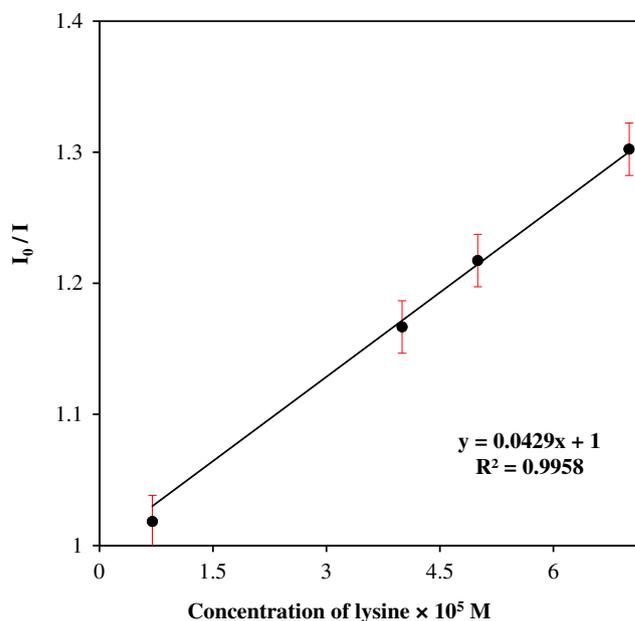

Fig. 8 The intensity-time spectra of the quenching effects of different concentrations of lysine (5.0×10^{-5} M to 1.0×10^{-4} M) in the solution on the BSPC/PO-CL intensity at the optimized concentrations of the chemiluminescent reactants

Fig. 9 A linear regression Stern-Volmer plot (with intercept=1) for the BSPC/PO-CL system, from the experimental data shown in Fig. 8, influenced by the quenching effect of lysine. The corresponding equation is $I_0/I = 1.0 + 4.29\times10^3$ [Q] ($R^2 = 0.996$)

of interest [31, 32]. This method allows determining the quencher concentration in the solution successfully.

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 Equations (9) and (10), respectively:

$$I_0 = \frac{k^\circ}{k_{nr}} [C] \qquad (9)$$

$$I = \frac{k^\circ [C]}{k_{nr} + k_q[Q]} \qquad (10)$$

where k_{nr} describes the k value for nonradiative deactivation processes, k_q is the quenching rate constant and Q denotes the quencher lysine. A plot of chemiluminescence intensities vs. the luminophore C (here, BSPC) concentrations gives a linear regression equation, from which k^o value (radiation constant) for the proposed PO–CL system could be evaluated.

The Stern-Volmer quenching constant K_q ($=k_q/k_{nr}$), which is the result of ratioing Equations (9) and (10), is expressed as by Equation 11.

$$\frac{I_0}{I} = 1 + K_q[Q] \qquad (11)$$

A plot of the I_0/I ratio vs. [Q] (here, [lysine]) 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 function of the curve given in Fig. 8, gave 4.29×10^3 M^{-1} for K_q. This so high value for K_q is indicative the establishment of strong interaction forces between the luminophore and quencher. The regression plot and the corresponding LR-equation, $I_0/I = 1.0 + 4.29 \times 10^3$ [Q] ($R^2 = 0.996$ for intercept=1.0) are shown in Fig. 9. The evaluated lower and upper detection limits of measurable concentration of lysine are 1.17×10^{-7} and 3.18×10^{-4} M, respectively.

Lysine Content Determination in Protein Supplements

In order to prepare a test sample, 0.5 g of a protein supplements (10.9 % lysine, from DOOBIS Company, www.dabi.ir) was weighted and dissolved in proper volume of methanol and filtered on a paper-filter for any impurities. The solution transferred into a flask (100 mL) then diluted to the mark by the solvent. After addition the optimal concentrations of the reactants, 200 μL of the sample solution was added to the mixture in the measuring cell. The initial intensity of the emitted light (I_0) was recorded (91.1 a.u.) and the testing was repeated four times, 50.1, 49.9, 50.0 and 49.8 after addition the lysine solution. The lysine (molar mass 146. 19 g mol^{-1}) content of the sample was evaluated as 11.24± 0.06 % from the Stern-Volmer plot.

Conclusions

From the results obtained in this work, we found that new bis [N-(4-pyridyl)-*p*-toluene sulfonamide] palladium dichloride (BSPC) emits an intense light with relatively high lifetime (about 20 s, at 25ºC) when it is sensitized in a peroxyoxalate (PO) reaction so can be used as a strong luminophore. In addition, we demonstrated that BSPC/PO–CL could be influenced by lysine quenching effect, from which trace amounts of lysine are detectable by using the inherently sensitive chemiluminescence method. Thus, lysine, which is an important compound in biological field and food industries, could successfully be traced under the evaluated optimal condition.

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