J Fluoresc (2010) 20:671–679
DOI 10.1007/s10895-010-0601-9

ORIGINAL PAPER

Studies of New Peroxyoxalate-H_2O_2 Chemiluminescence System Using Quinoxaline Derivatives as Green Fluorophores

Abdolraouf Samadi-Maybodi · Reza Akhoondi · Mohammad Javad Chaichi

Received: 11 October 2009 / Accepted: 29 January 2010 / Published online: 10 March 2010

Abstract Quinoxaline derivatives are a great interest as fluorescent emitters for peroxyoxalate chemiluminescence. Reaction of peroxyoxalates such as bis-(2,4,6-trichlorophenyl) oxalate with H_2O_2 can transfer energy to fluorophore via formation of dioxetanedione intermediate. Two quinoxaline derivatives used as a fluorophore in this study which produce a green light in the chemiluminescence systems. The relationship between the chemiluminescence intensity and concentrations of fluorophore, peroxyoxalate, sodium salicylate and hydrogen peroxide was investigated. Kinetic parameters for the peroxyoxalate-chemiluminescence were also calculated from the computer fitting of the corresponding chemiluminescence intensity/time profiles. It was found that the biphenylquinoxaline can be used as an efficient green fluorescent emitter.

Keywords Quinoxaline derivatives · Hydrogen peroxide · Chemiluminescence · Bis-(2,4,6-trichlorophenyl) oxalate

Introduction

The brilliant emissions resulting from oxidation of certain oxalic acid derivatives, especially in the presence of a variety of fluorophores, are the bases of the most active area of current interest in chemiluminescence. The example of peroxyoxalate chemiluminescence was reported in 1963 by Chandross [1]. The peroxyoxalate-chemiluminescence (PO-CL) system is one of the most regularly used analytical chemiluminescence schemes [2, 3]. PO-CL is based on the reaction of H_2O_2 with peroxyoxalate which result an intermediate [4]. The excited intermediate transfers its energy to an efficient fluorophore [5-9] through the chemically initiated electron exchange luminescence (CIEEL) mechanism [10]. This reaction has been successfully used as a highly sensitive detection technique in several procedures developed for low level determinations of various analytes [11, 12], proteins [13], hydrogen peroxide [14, 15], fluorophore labeled amino acids [16] and prostate specific antigen [17] as well as different quencher species [18, 19].

Quinoxalines are well known fluorescent compounds with high quantum yields and have attracted much attention due to their potential functions for high technology applications [20, 21]. These compounds have been utilized as fluorescence probes in some of elaborated chemosensors. Quinoxalines are, in general, comparatively easy to synthesis, and with numerous derivatives which have been designed for potential use as biologically active materials [22]. The classical synthesis of quinoxalines involves the condensation of 1, 2-diamine with a 1,2-dicarbonyl. The reaction is facile and it is the most widely used method for synthesizing both quinoxaline itself and its derivatives [23]. Quinoxalines have shown broad

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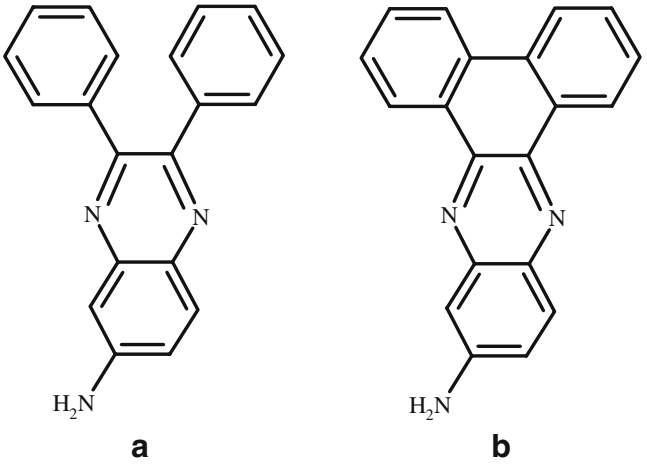


Fig. 1 Molecular structure of 2,3-diphenylquinoxaline **a** and biphenylquinoxaline **b**

biological activities such as in vitro antitumor activity [24], antiviral [25], herbicidal [26] and anti-inflammatory activity [27], hence they are an important class of nitrogen-containing heterocycles and useful intermediates in organic synthesis [28, 29]. Recently some of these types of molecules have been reported as candidates for treatment of cancer and disorders associated with angiogenesis functions [30-33].

One of the most fascinating questions concerning the peroxyoxlate chemiluminescence reaction is the compound capable that generates light which is related the structure of fluorophore. In this paper, we report chemiluminescence system from reaction of bis-(2, 4, 6-trchlorophenyl)oxalate (TCPO) and hydrogen peroxide using quinoxalines derivatives, as an efficient fluorophores. Two quinoxalines derivatives of 2,3-diphenylquinoxaline (A) and biphenylquinoxaline (B) were used (Fig. 1). Tow quinoxalines derivatives are found intense and useful fluoropher compounds containing aromatic functional group with low-energy π→π* transition level (green light emission). Particularly, compound B is favored in molecules that possess rigid structure. However, lack of rigidity in a molecule A causes an enhanced internal conversion rate (internal rotation about phenyl group) and a consequence increase in the likelihood for radiationless deactivation. Kinetic parameters for the peroxyoxalate-chemiluminescence of two quioxalines were calculated from the computer fitting of the corresponding chemiluminescence intensity-time plots.

Experimental

Reagents

All chemical compounds were reagent-grade and purchased from Fluka chemical company (CH-9470, Buchs, Switzerland) and used as received without further purification. Quinoxaline derivatives were prepared from the reaction of 4-Nitro-O-phenylen diamine with benzyl and 9,10-phenanthroquinone in glacial acetic acid as a solvent and then were reduced by hydrazine monohydrate as described elsewhere [23, 34].

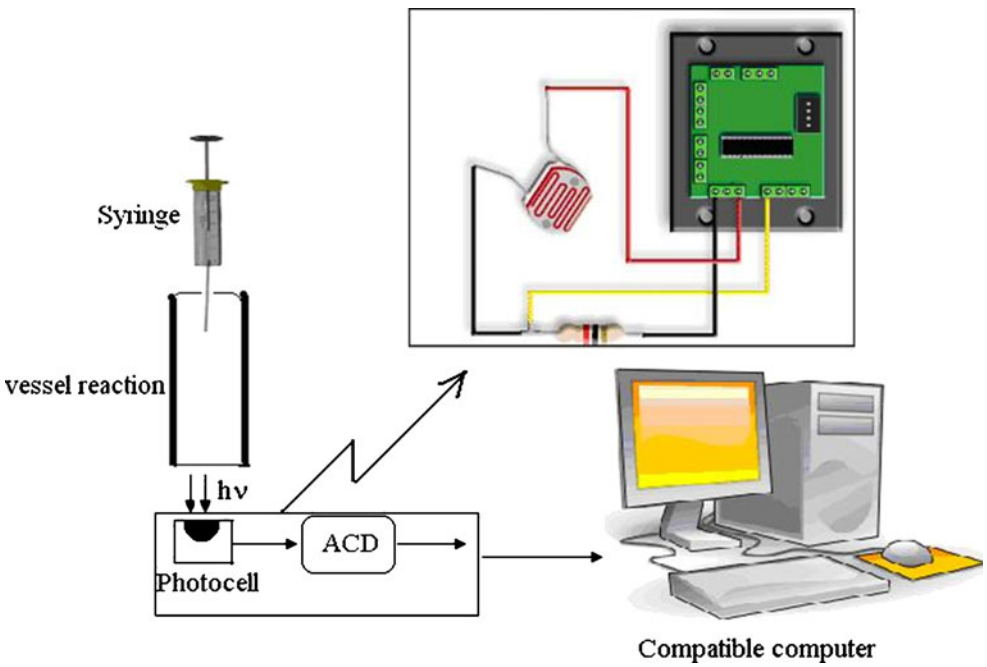


Fig. 2 Shematic representation of batch system for measuring visible chemiluminescence

Apparatus

Chemiluminescence detection was performed with a homemade apparatus equipped with a Model BPY47 photocell (Leybold, Huerth, Germany). The apparatus was connected to a personal computer via a suitable interface (Micropars, Tehran, Iran) as shown in Fig. 2. Experiments were carried out with magnetic stirring (500 rpm) in a light-tight flat-bottom glass cell of 15 mm diameter at 25 °C. Chemiluminescence intensity was recorded as a function of time, the time resolution of the apparatus was 0.6 s.

Steady-state fluorescence spectra were recorded on a Perkin Elmer, Ls-3B spectrofluorimeter instrument. The excitation monochromators were set at 390 and 440 nm for compounds 2,3-diphenylquinoxaline (A) and biphenylquinoxaline (B), respectively. Spectral bandwidth of 3 nm was used.

Procedures

Solution *I* was made with mixing 1.0 mL of TCPO (0.01 M) and 0.5 mL of quinoxaline derivatives (various concentrations in ethyl acetate). Solution *II* contained 2 mL of hydrogen peroxide (3.2 M) and 1.0 mL of catalyst (0.1 M) in methanol. Solution *I* was transferred into glass cell using polypropene syringes. Then 100 μL of solution *II* was injected in the glass cell, chemiluminescence spectrum was recorded soon after mixing of solutions. The fluorescence spectra were carried out using freshly prepared solutions containing 3.3×10^{-5} M of fluorophores in ethyl acetate, using a 3-cm quartz cuvette.

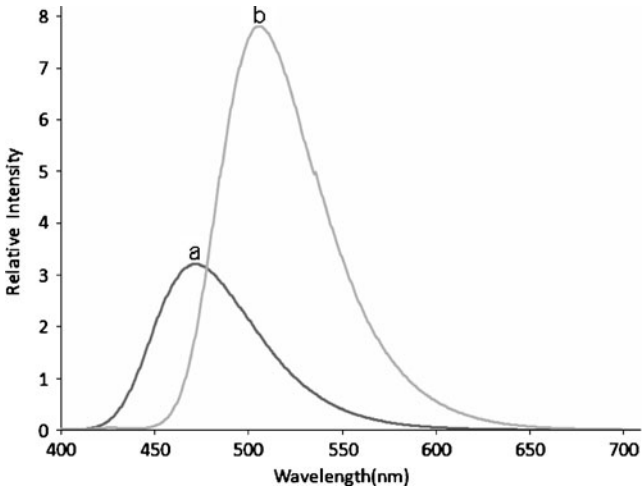


Fig. 3 The fluorescence emission spectra of (**a**): 3.3×10^{-5} M of 2,3-diphenylquinoxaline with λ_{ex}=390 nm, and (**b**) 3.3×10^{-5} M of biphenylquinoxaline with λ_{ex}=430 nm in ethyl acetate

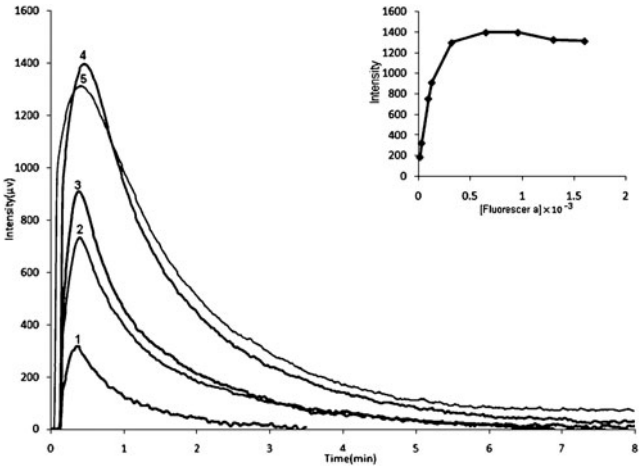


Fig. 4 Chemiluminescence emission intensity as a function of time for the bis-(2, 4, 6-trchlorophenyl) oxalate (TCPO)-H_2O_2-quinoxaline derivatives and sodium salysilate system with constant concentration of TCPO (3.2×10^{-3} M), H_2O_2 (6.8×10^{-2} M), sodium salicylate (1.0×10^{-3} M), and varying concentrations of 2,3-diphenylquinoxaline: (1) 3.2×10^{-5}, (2) 6.5×10^{-5}, (3) 1.3×10^{-4}, (4) 6.5×10^{-4} and (5) 1.6×10^{-3} M. Corner of right hand side: The correlation diagram for the chemiluminescence emission with 2,3-diphenylquinoxaline concentrations

Results and discussion

Peroxyoxalate-chemiluminescence (PO-CL) is well-known as one of the most efficient non-biological light producing systems (Scheme 1). Like many chemiluminescence reactions, the PO-CL reaction can be presented in following steps [35-40].

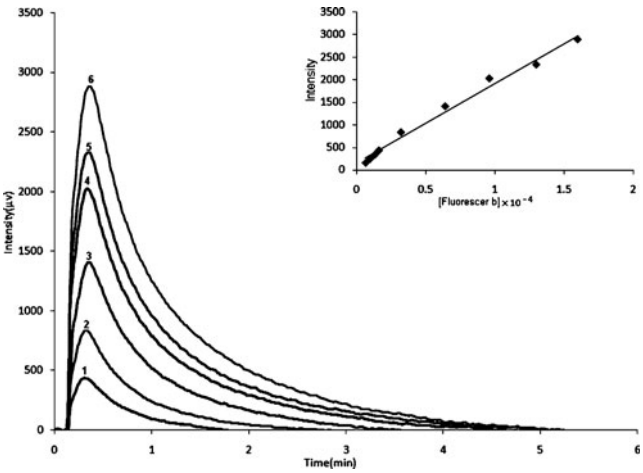
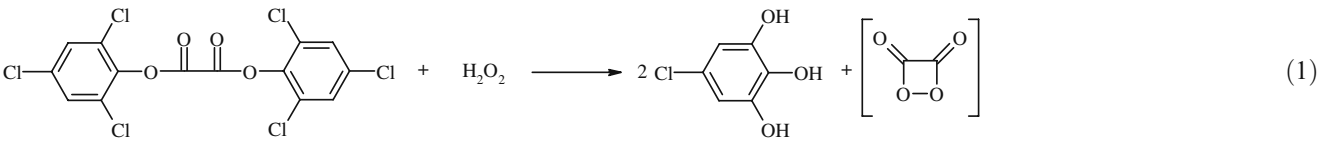


Fig. 5 Chemiluminescence emission intensity as a function of time for the bis-(2, 4, 6-trchlorophenyl) oxalate (TCPO)- H_2O_2-quinoxaline derivatives and sodium salysilate system with constant concentration of TCPO (3.2×10^{-3} M), H_2O_2 (6.8×10^{-2} M), sodium salicylate (1.0×10^{-3} M), and varying concentrations of biphenylquinoxaline: (1) 1.6×10^{-5}, (2) 3.2×10^{-5}, (3) 6.4×10^{-5}, (4) 9.6×10^{-5}, (5) 1.3×10^{-4}, and 1.6×10^{-4} M. Corner of right hand side: correlation diagram for the chemiluminescence emission with biphenylquinoxaline concentrations

Table 1 CL parameters calculated from computer fitting of the CL intensity–time plots for TCPO–H_2O_2–2,3-diphenylquinoxaline–sodium salicylate system

Parameter changed	Concentration (M)	k_r (min^{-1})	k_f (min^{-1})	M	J	T_{exp} (min)	T_{max} (min)	Y	I
H_2O_2	3.4×10^{-2}	3.40±0.09	0.55±0.01	864±11	608	0.50	0.63	1,570	602
	5.1×10^{-2}	3.28±0.09	0.72±0.01	1368±20	893	0.53	0.59	1,894	910
	6.8×10^{-2}	3.54±0.12	0.89±0.02	1992±37	1,252	0.46	0.52	2,236	1,358
	8.5×10^{-2}	2.97±0.12	0.90±0.03	2192±56	1,304	0.52	0.57	2,433	1,454
TCPO	3.2×10^{-4}	3.56±0.11	0.55±0.01	374±6	253	0.52	0.57	546	257
	6.0×10^{-4}	3.32±0.10	0.68±0.01	702±11	467	0.47	0.59	1,029	469
	1.2×10^{-3}	3.43±0.11	0.72±0.02	1040±16	687	0.58	0.57	1,443	711
	1.9×10^{-3}	3.36±0.10	0.53±0.01	1381±21	911	0.56	0.58	1,941	642
	2.5×10^{-3}	3.53±0.11	0.75±0.02	1740±27	1,145	0.51	0.55	2,308	1,214
Sodium salycilate	2.0×10^{-4}	3.29±0.13	0.69±0.02	1424±30	942	0.50	0.60	2,070	1,138
	4.0×10^{-4}	3.39±0.14	0.85±0.03	2038±49	1,282	0.47	0.54	2,381	1,561
	6.0×10^{-4}	3.58±0.13	0.81±0.02	1 998±40	1,292	0.45	0.53	2,456	1,494
	8.0×10^{-4}	3.94±0.13	0.82±0.02	1,976±32	1,309	0.45	0.50	2,420	1,462
	1.0×10^{-3}	3.90±0.12	0.80±0.02	1,911±32	1,269	0.48	0.51	2,375	1,391
2,3-diphenyl quinoxaline 6-amine	1.6×10^{-5}	1.32±0.05	4.28±0.22	778±47	142	0.34	0.39	181	185
	3.2×10^{-5}	1.70±0.09	3.49±0.22	1,011±73	248	0.37	0.40	289	321
	9.6×10^{-5}	4.22±0.18	1.06±0.03	944±24	593	0.37	0.43	882	753
	1.3×10^{-4}	4.24±0.17	1.01±0.03	1,156±27	737	0.38	0.44	1,137	910
	3.2×10^{-4}	4.17±0.14	0.92±0.02	1,736±32	1,129	0.41	0.46	1,870	1,298
	6.5×10^{-4}	3.79±0.13	0.89±0.02	1,987±35	1,275	0.46	0.49	2,235	1,397

Statistical parameters R^2 =0.981 F=875.069 correlation is significant at the 0.01 level



(1)

(2)

$$F^* \longrightarrow F + hv \quad (3)$$

where, F is fluorophore.

In the first step, an aryl oxalate ester like TCPO reacts with H_2O_2 to produce a key chemical intermediate of 1,2-dioxetandione (C_2O_4) as an excitation source. The second step, excited cyclic C_2O_4 intermediate transfers its energy to fluorophore (here quinoxaline derivatives were used as fluorophore). The final step is the emission of light energy by returning the excited fluorophore molecule to the ground state. The florescence spectra of compounds A and B are shown in Fig. 3. By comparison fluorescence spectra A and B, it can be deduced that spectrum B is more intense than that A (hyperchromic effect) and also the maximum wavelength (λ_{max}) of spectrum B is shifted to longer wavelength (bathochrom shift). Typically, in chemiluminescence system, soon after mixing of ingredients (e.g., 2,3-Diphenylquinoxaline, bis-(2, 4, 6-trchlorophenyl) oxalate, H_2O_2 and sodium salysilate) the intensity of emitted light is risen rapidly and then exponential decay of light intensity follows. Figures 4 and 5 show chemiluminescence intensity as a function of time (intensity/time emission profile) for the PO-CL system in the presence of varying concentrations of quinoxaline derivatives A and B, respec-

Table 2 CL parameters evaluated from computer fitting of the CL intensity–time plots for TCPO–H_2O_2–2,3-biphenylquinoxaline 6-amine – sodium salicylate system system

Parameter changed	Concentration (M)	k_r (min^{-1})	k_f (min^{-1})	M	J	T_{exp}(min)	$_{Tmax}$ (min)	Y	I
H_2O_2	1.7×10^{-2}	2.86±0.09	0.40±0.01	811±12	578	0.94	0.78	1,850	562
	3.4×10^{-2}	2.99±0.09	0.79±0.02	1,986±33	1,228	0.61	0.60	2,482	1,290
	5.1×10^{-2}	3.63±0.13	0.91±0.02	2,796±57	1,761	0.48	0.50	3,077	2,005
	6.8×10^{-2}	4.31±0.18	1.03±0.03	3,527±81	2,251	0.38	0.43	3,426	2,720
	8.5×10^{-2}	4.51±0.18	1.03±0.03	3,773±85	2,436	0.38	0.42	3,654	2,972
TCPO	3.2×10^{-4}	3.52±12	1.18±0.04	498±12	287	0.41	0.46	420	2,99
	6.0×10^{-4}	3.96±0.17	1.27±0.04	953±24	556	0.38	0.42	747	606
	1.2×10^{-3}	4.27±0.17	1.24±0.04	1,592±37	960	0.40	0.41	1,281	1,091
	1.9×10^{-3}	4.13±0.19	1.24±0.04	2,320±63	1,385	0.39	0.41	1,871	1,652
	2.5×10^{-3}	4.26±0.19	1.26±0.05	3,150±88	1,860	0.36	0.40	2,453	2,292
	3.2×10^{-3}	4.56±0.18	1.14±0.03	3,383±79	2,132	0.36	0.40	2,966	2,595
Sodium salycilate	2.0×10^{-4}	2.31±0.09	0.81±0.03	2,634±74	1,496	0.64	0.69	3,250	1,692
	4.0×10^{-4}	3.59±0.16	0.95±0.04	3,457±90	2,147	0.45	0.50	3,661	2,735
	6.0×10^{-4}	4.24±0.18	1.00±0.03	3,670±70	2,347	0.39	0.44	3,656	2,991
	8.0×10^{-4}	4.34±0.18	1.02±0.03	3,659±76	2,349	0.39	0.43	3,603	2,924
	1.0×10^{-3}	4.34±0.17	0.98±0.03	3,236±67	2,094	0.41	0.44	3,282	2,497
2,3 biphenyl quinoxaline 6-amine	6.4×10^{-6}	3.20±0.21	3.20±0.21	333±22	123	0.33	0.31	104	161
	9.6×10^{-6}	3.11±0.22	3.11±0.22	530±38	195	0.32	0.32	170	250
	1.3×10^{-5}	1.47±0.07	4.64±0.27	1,338±94	249	0.33	0.36	288	338
	1.6×10^{-5}	3.18±0.22	3.18±0.22	885±62	326	0.31	0.32	278	436
	3.2×10^{-5}	2.86±0.24	2.86±0.24	1,707±144	628	0.32	0.34	595	836
	6.4×10^{-5}	3.16±.31	1.93±0.17	2,333±190	1,077	0.35	0.40	1,206	1,410
	9.6×10^{-5}	1.46±0.06	4.17±0.22	7,914±485	1,576	0.34	0.39	1,895	2,024
	1.3×10^{-4}	4.22±0.21	1.38±0.05	3,165±101	1,838	0.35	0.39	2,286	2,331
	1.6×10^{-4}	4.12±.20	1.30±0.05	3,887±121	2,284	0.36	0.40	2,985	2,884

Statistical Parameters R^2 =0.992 F=2933.591 Correlation is significant at the 0.01 level

tively. Plot of chemiluminescence intensity as a function of fluorophore concentration (compounds A and B) is inserted on top of right hand side of Figs. 4 and 5 respectively. Correlation between the CL intensity and the TCPO concentration for both fluorophore is listed in Tables 1 and 2. The influence of H_2O_2 concentration on the PO-CL for both compounds A and B was studied at constant concentrations of other reagents and presented in Tables 1 and 2. Results revealed that there is a direct linear relationship between concentration of H_2O_2 (i.e., 0.017–0.085) and PO-CL intensity (Fig 6a and b). It is pertinent to mention that further increase in H_2O_2 concentration has no more effect on the PO-CL intensity. The intensity/time emission profile of both quinoxaline derivatives under the optimal constant concentrations of TCPO, H_2O_2 and fluorophore indicated that the emmison intensity is significantly enhanced by addition of sodium salicylate. This confirms a key role of catalyst in the PO-CL system [41]. In order to investigate the optimal concentration of sodium salicylate, the CL response of the H_2O_2-TCPO-quioxalines systems was measured against the varying concentrations of the base, results are shown in Tables 1 and 2. The PO-CL intensity dramatically increased with increasing concentration of sodium salicylate until a concentration of 6.0×10^{-4} M is reached. However, further addition of sodium salicylate causes to decrease the CL intensity (Fig 7a and b). This, probably due to the quenching effect of the base at higher concentrations, which possibly it leads to decompose the intermediate, dioxetane dione, and hence reduces the PO-CL light [42].

Results revealed that the concentration of TCPO and sodium salicylate have no significant influence on the chemiluminescence system, i.e., the rise (k_r) and fall (k_f) rates constant in different concentrations of TCPO and sodium salicylate have nearly the same values. Nonetheless, the kinetics parameters of the chemiluminescence system are moderately influenced by both concentrations of H_2O_2 and fluorophore. In the former case, by increasing

concentration of H_2O_2, the values of fall rates constant (k_f) become larger, on the other hand, enhancing concentration of fluorophore caused to decrease of k_f .

In order to evaluate the kinetic data for the PO-CL system, a pooled-intermediate model was used [36, 43, 44]. According to this model, the CL reaction is simplified as:

$$\mathrm{A} \xrightarrow{K_r} \mathrm{B} \xrightarrow{K_f} \mathrm{C} \tag{4}$$

where A, B and C represent pools of reactants, intermediates and products, respectively, and both reaction steps designated by the rate constants k_r and k_f are irreversible first order reactions. The integrated rate equation for the CL intensity versus time is:

$$I_t = \left[\frac{Mk_r}{k_f - k_r}\right]\left[\exp(-k_r t) - \exp\left(-k_f t\right)\right] \tag{5}$$

Where, I_t is the CL intensity at time t, M is a theoretical maximum level of intensity if the reactants were entirely converted to a CL-generating material, k_r and k_f are, respectively, the first order rate constants for the rise and fall of the burst of CL. A further advantage of this model is that it not only allows the determination of parameters M, k_r and k_f, but also it permits an estimate of the intensity at maximum level (J), the time of maximum intensity (T_{max}) and the total light yield (Y), as follows:

$$J = M\left(\frac{k_f}{k_r}\right)^{\left[k_f/\left(k_f - k_r\right)\right]} \tag{6}$$

$$\tau_{\max} = \frac{\ln\left(k_f/k_r\right)}{k_f - k_r} \tag{7}$$

$$Y = \int_0^\infty I_t\, dt = \frac{M}{k_f} \tag{8}$$

In this work, a non-linear least-squares curve fitting program KINFIT [45] was used to evaluate the M, k_r and k_f values from the corresponding CL intensity-time plots. A

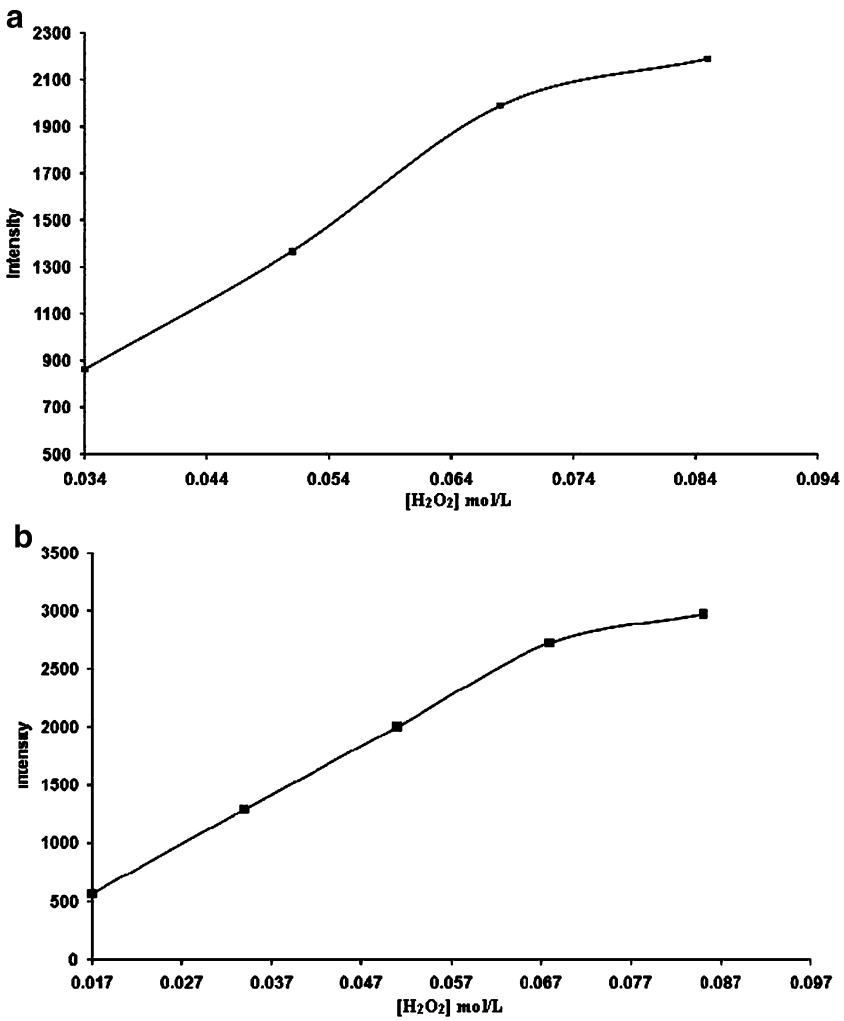


Fig. 6 Dependence of the H_2O_2 concentration **a** on the CL intensity of TCPO–H_2O_2–2, 3-diphenylquinoxaline—sodium salicylate system, **b** on the CL intensity of TCPO-H_2O_2–biphenylquinoxaline–sodium salicylate system

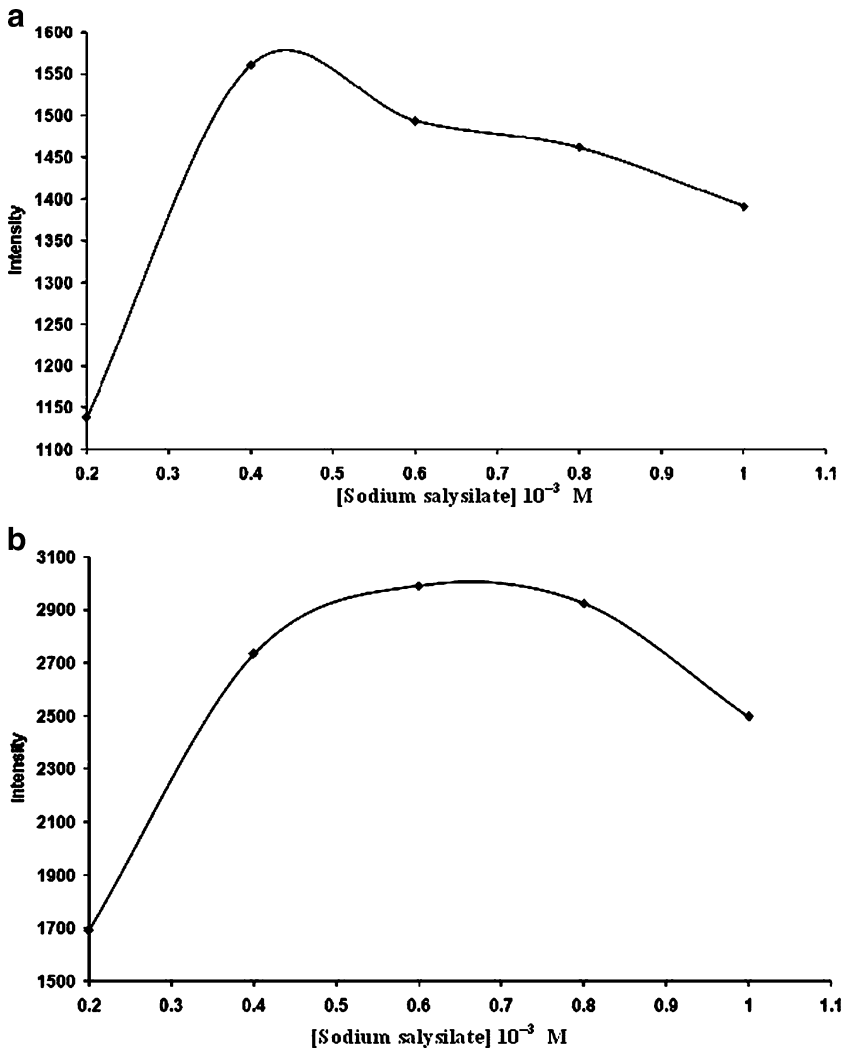


Fig. 7 Influence of sodium salicylate concentration **a** on the CL intensity of TCPO–H_2O_2–2,3-diphenylquinoxaline—sodium salicylate system, **b** on the CL intensity of TCPO–H_2O_2–biphenylquinoxaline–sodium salicylate system

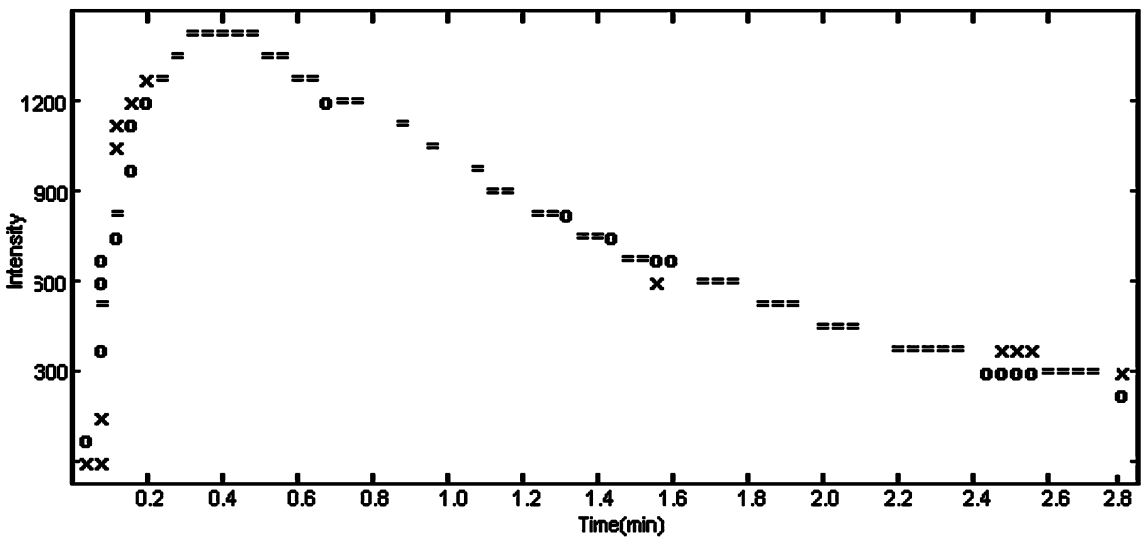


Fig. 8 A typical computer fitting of the CL intensity–time plot for TCPO–H_2O_2–2,3-diphenylquinoxaline–sodium salicylate system. ([H_2O_2]=0.068 M, [sodium salicylate]=1.0×10^{-3} M, [2,3-diphenylquinoxaline]=1.6×10^{-3} M) and [TCPO]=3.2×10^{-3} M.): (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot

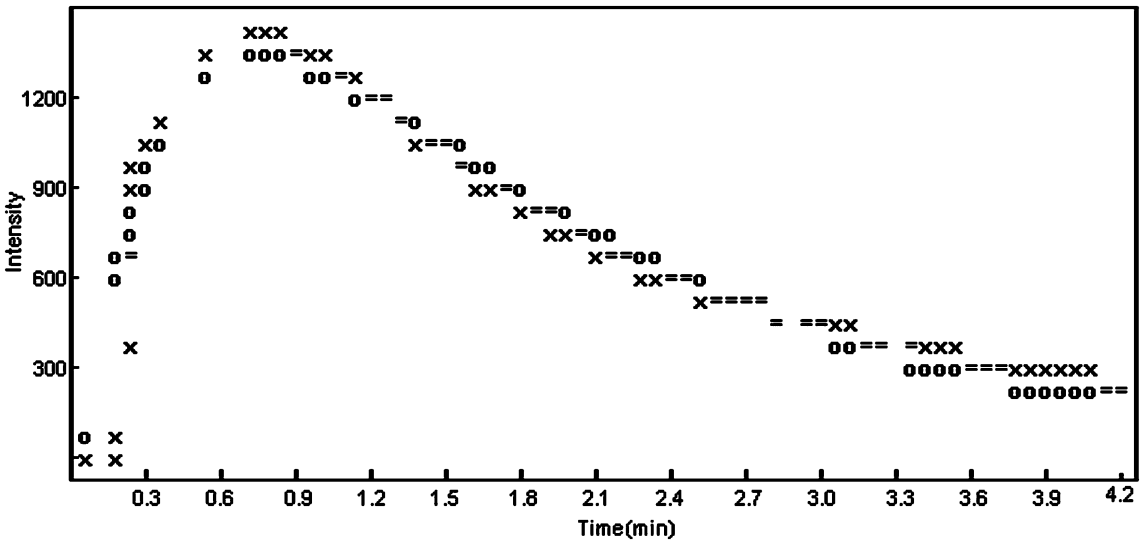


Fig. 9 A typical computer fit of the CL intensity–time plot for TCPO–H_2O_2–2,3-biphenylquinoxaline 6-amine –sodium salicylate system ([H_2O_2]=0.068 M, [sodium salicylate]=1.0×10^{-3}, [biphenylquinoxaline]=1.6×10^{-4} M) and [TCPO]=3.2×10^{-3} M.): (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot

typical computer fitting of the CL intensity time plots is shown in Figs. 8 and 9. The theoretical values of maximum intensity (J), and corresponding time (T_{max}) and Y can be calculated by Eqs. 6, 7 and 8 using parameters of k_f, k_r and M which were determined from the resulting CL intensity-time plots. All kinetic parameters are listed in Tables 1 and 2. The experimental values of maximum intensity (I_{max}) and T_{max} were extracted from CL intensity-time plots (Figs. 4 and 5)). The statistical results (R^2 and F) obtained by application of SPSS indicate that, there is a satisfactory agreement between the calculated (J) and experimental (I_{max}) values of the intensity at the maximum CL (Tables 1 and 2).

Conclusion

The present study describes a new chemiluminesecence system of H_2O_2- bis-(2,4,6-trichlorophenyl) oxalate (TCPO) using quioxalines derivatives as fluorophore. In this system a green light is produced in the present of quinoxaline derivatives. The results indicated that how concentrations of the components involved in CL influence on the light emission. Results showed that concentrations of H_2O_2 TCPO and quioxalines have direction relationship on the light intensity. Kinetic parameters for the peroxyoxalate-chemiluminescence of two quioxalines were calculated from the corresponding chemiluminescence intensity-time plots. A non-linear least-squares curve fitting program KINFIT was used to evaluate the theoretical maximum level of intensity (M), the first order rate constants for the rise k_r and fall k_f of the burst of CL. Tow quinoxalines derivatives are found intense and useful fluoropher compounds which produce green light emission. Particularly, compound B is favored in molecules that possess rigid structure.

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