

A Highly Efficient Turn-On Fluorescent Sensor for Determination of Water in Organic Solvents

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Abstract 2, 3 biphenyl quinoxaline 6-amine is a fluorescent compound in some organic solvents with an excitation wavelength at 435 nm and a fluorescence emission at 518 nm. The fluorescence intensity of 2, 3 biphenyl quinoxaline 6-amine is significantly reduced in the presence of bis-(2, 4, 6-trichlorophenyl) oxalate (TCPO) and Zn^{2+} due to the nonfluorescent complex formation. The low stability of the complex in presence of trace amount of water results in decomposing complex, thereby recovering the photoluminescence of 2, 3 biphenyl quinoxaline 6-amine. Based on this fact, a turn-on fluorescence photoluminescence sensor for determination of water content in organic solvents was introduced for the first time.

The fluorescence intensity of 2, 3 biphenyl quinoxaline 6-amine as a function of water concentration was used as a simple, sensitive and rapid method for determining trace amount of water in some organic solvents such as ethanol and methanol. The obtained results showed a good linear relationship between fluorescence intensity and the water content with a dynamic range of 0.0094–1(v/v%), related coefficient of 0.9922 and limit of detection of 0.0026(v/v%).

Keywords Determination of water · 2,3 biphenyl 6-amine-bis-(2,4,6-trichlorophenyl) oxalate · Zn^{2+} ion · Fluorimetry technique

Introduction

Determination of trace amounts of water as impurities in organic solvents is of utmost importance in several fields of chemistry and industry. It also makes a decisive influence on productions, yield and selectivity of reactions. Generally, Karl Fischer titration [1] is the most reliable and accurate method for determination of trace amount of water in solvents, but it still has some disadvantages such as low precision and low sensitivity. In addition, it is time consuming and harmful to operator's health [2, 3]. Besides the Karl Fischer titration, other types of methods such as gas chromatography [4], liquid chromatography, and infrared spectroscopy [5] and fluorescence spectroscopy [6] have been employed for monitoring water content in the organic solvents. Fluorescence spectroscopy as an attractive method was used for determining water content. [7–9]. In this method, different fluorescent dyes such as merocyanine dyes [10], flavone derivatives [11, 12], luminescent nanospheres [13] and 8-hydroxyquinoxaline [14] have been used. Quinoxalines are well known fluorescent compounds with high quantum yields and have attracted much attention due to their potential functions for high technology applications [15, 16]. Quinoxalines are, in general, comparatively easy to synthesize, and have numerous derivatives which have been designed for potential use as biologically active materials [17]. The classical synthesis of quinoxalines involves the condensation of 1, 2-diamine with a 1,2-dicarbonyl. The reaction is facile and it is commonly used for synthesizing both quinoxaline itself and its derivatives [18].

It was recently reported that the quinoxaline derivatives react with mixture of $ZnEt_2$ and $HOR(R=2,6\text{-diisopropyl})$

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phenyl) to obtain new phenolate-zinc complexes containing one or two phenolate ligands. 2,3 biphenyl nonaqueous 6-amine is one of the quinoxaline derivatives that exhibits a broad emission spectrum centered at 518 nm and this compound has been recently introduced as a fluorophore in peroxyoxalae chemiluminescence reaction [19]. Due to these observation we introduced a system in which the presence of Zn^{2+} ion in the mixture of 2,3 biphenyl nonaqueous 6-amine and TCPO induces a strong fluorescence quenching of 2,3 biphenyl nonaqueous 6-amine due to the complexation process. The obtained results indicated that the addition of a trace amount of water leads to an increment in the intensity of fluorescence emission.

Most fluorescence methods reported for determination of water content generally undergo fluorescence quenching which is less sensitive than a fluorescence enhancement response [20, 21] because the fluorescence intensity of fluorescer may be quenched by polarity of solvent and impurities as well as water. It is worth mentioning that the outstanding result of the present work is measuring water using a fluorescent turn-on sensor. The sensor is based on water-induced modulation of the quenching effect of Zn^{2+} on the photoluminescence (PL) of 2,3 biphenyl quinoxaline 6-amine in the presence of TCPO. The PL is firstly quenched by Zn^{2+} in the presence of TCPO, and then surprisingly recovered by trace amount of water owing to decomposing complex and consequently releasing 2, 3 biphenyl quinoxaline 6-amine. Based on this unique phenomenon, a new strategy was proposed for determination of trace amounts of water in nonaqueous solvents. The aim of this work is to introduce a new method as a sensor for determining the trace amount of water in nonaqueous solvents.

Experimental

All chemical compounds were reagent-grade and purchased from Fluka (CH-9470, Buchs, Switzerland) and used as received without further purification. 2,3 biphenyl nonaqueous 6-amine was prepared from the reaction of 4-Nitro-O-phenylen diamine with benzyl and 9,10-phenanthroquinone in the glacial acetic acid solvent and then was reduced by hydrazine monohydrate as described elsewhere [19]. Methanol and ethanol used in the experiments were HPLC grade.

Apparatus

Fluorescence and UV-vis spectra were recorded on LS-3B fluorescence (Perkin-Elmer) and CE 5501 UV-vis spectrophotometers (5000series, England), respectively.

Procedure

Stock solutions of 2, 3 biphenyl nonaqueous 6-amine (0.001 M) and TCPO (0.01 M) were prepared by dissolving an appropriate amount of the reagent in ethyl acetate. Stock solution of zinc perchlorate (0.01 M) was prepared in methanol. Fluorescence spectra of 2, 3 biphenyl nonaqueous 6-amine were recorded in the presence and absent of the mixture of Zn^{2+} and TCPO with similar experimental conditions. The concentration of each reactant was optimized by varying the concentration of each reactant whilst holding constant the concentrations of the others.

Analytical Procedures for Determination of Water in Ethanol and Methanol

50 μ L of 2,3 biphenyl 6-amine (0.001 M), 0.8 mL of TCPO (0.01 M) and 20 μ L of zinc perchlorate (0.01 M) were added in a 1-cm quartz cell and well mixed. Then, it was diluted to 2 mL with anhydrous ethyl acetate and mixed well. The fluorescence intensity was measured at the maximum wavelength ($\lambda_{max}=518$ nm) with excitation at 435 nm in a 1 cm quartz cell. Ultimately, various trace amounts of water were added to the organic solvent and then fluorescence spectra were recorded. The difference in fluorescence intensity in the presence and absence ($\Delta F=F-F_0$) of trace amount of water was considered as the analytical signal.

Results and Discussion

The fluorescence spectrum of 2,3 biphenyl quinoxaline 6-amine shows an excitation band centered at 435 nm and an emission maximum at 518 nm [19]. The obtained results from our experiments specified that the addition of Zn^{2+} ion (5.0×10^{-4} M) to the solution containing 2,3 biphenyl quinoxaline 6-amine (2.5×10^{-5} M) and TCPO (4.0×10^{-3} M) leads to a change in the solution color from green to red. Interestingly, we observed that adding a trace amount of water to the solution restored the color of the solution back to green. It is worth to be mentioned that this phenomenon is observed by naked eye.

Fluorescence spectrum of the solution containing 2,3 biphenyl quinoxaline 6-amine and TCPO in ethyl acetate shows a broad band centered at 518 nm (Fig. 1a). The signal intensity significantly decreases in the presence of Zn^{2+} (Fig. 1b). It is assumed that a complex is formed by reaction of Zn^{2+} ion, 2,3 biphenyl quinoxaline 6-amine and TCPO. As mentioned above, addition of a small amount of water leads to enhance the intensity of fluorescence signal and consequently the color of the solution is restored back to the initial one. To obtain optimal conditions of quenching effect,

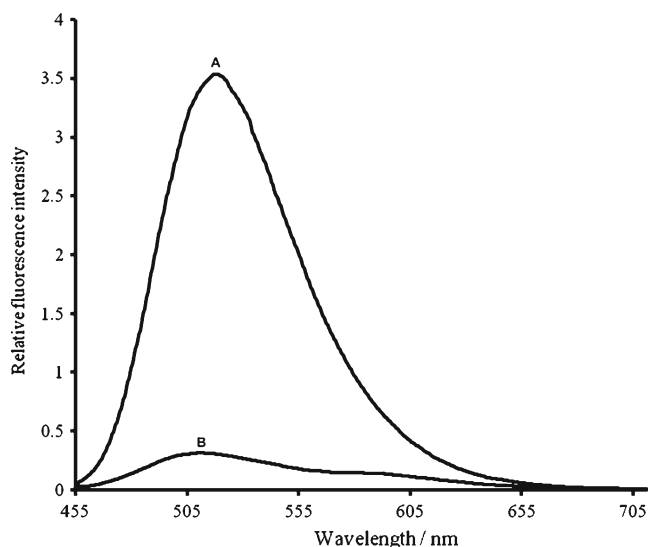
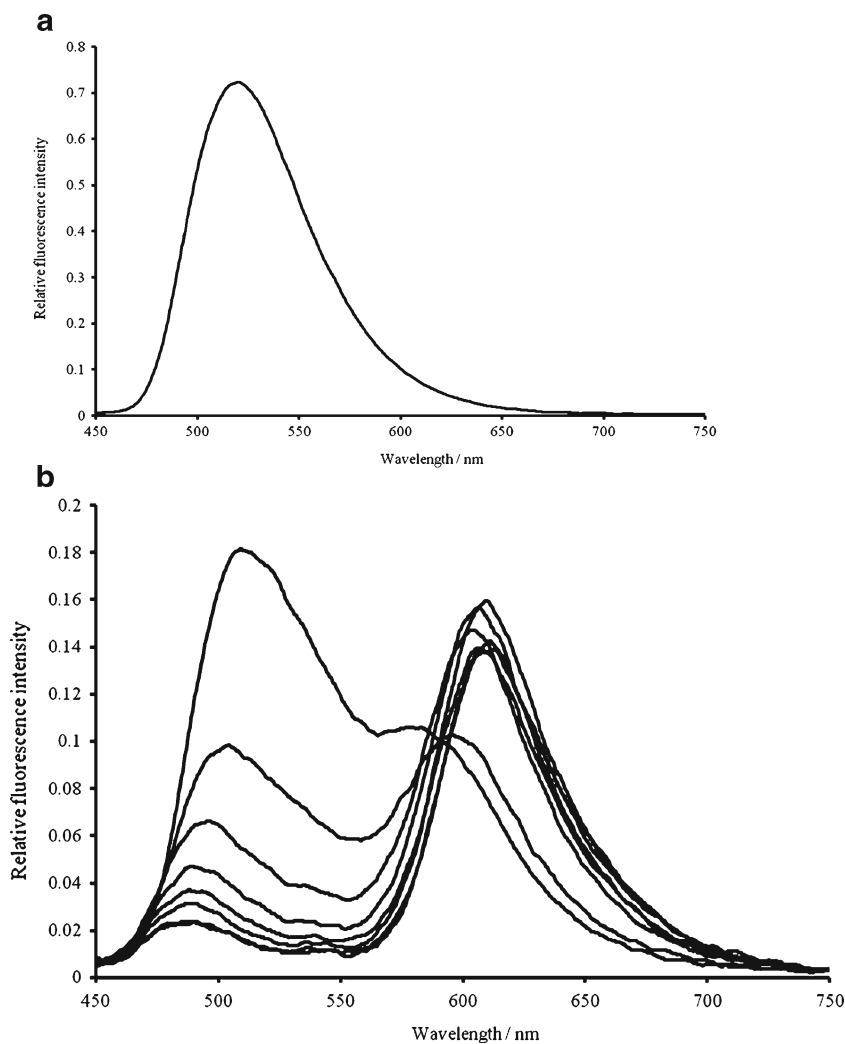


Fig. 1 Fluorescence spectra of **a**) 2, 3 biphenyl quinoxaline 6-amine (2.5×10^{-5} M) and TCPO (4.0×10^{-3}); **b**) 2, 3 biphenyl quinoxaline 6-amine (2.5×10^{-5} M) and TCPO (4.0×10^{-3} M) in the presence of Zn^{2+} (5.0×10^{-4} M)

Fig. 2 Fluorescence spectra of the 2, 3 biphenyl quinoxaline 6-amine (2.5×10^{-4} M), **a** without and **b** with Zn^{2+} (5.0×10^{-4} M) with various concentrations of TCPO from top to bottom: 5.0×10^{-4} , 1.0×10^{-3} , 1.5×10^{-3} , 2.0×10^{-3} , 2.5×10^{-3} , 3.0×10^{-3} , 3.5×10^{-3} , 4.0×10^{-3} , 4.5×10^{-3} M)



the concentration of three compounds (i.e., bis-(2, 4, 6-trichlorophenyl) oxalate (TCPO), 2, 3 biphenyl quinoxaline 6-amine and Zn^{2+}) was changed one at a time as follows.

Concentration of bis-(2, 4, 6-trichlorophenyl) Oxalate (TCPO)

Series of experiments were performed with different concentrations of TCPO in two separate solutions (i) 2,3 biphenyl quinoxaline 6-amine (2.5×10^{-4} mol/L) in the absence of Zn^{2+} ion and (ii) 2,3 biphenyl quinoxaline 6-amine in the presence of Zn^{2+} ion (5.0×10^{-4} mol/L). Fluorescence spectra of the corresponding solutions were recorded in the same experimental conditions (i.e., temperature, pH and excitation wavelength 435 nm). Results revealed that the fluorescence spectra for all solutions in the absence of Zn^{2+} ion are the same and all bands appeared at the same position with the maximum wavelength (λ_{max}) centered at 518 nm (Fig. 2a). Nevertheless, the fluorescence

spectra of the solutions in the presence of Zn^{2+} are significantly changed by variation of TCPO concentration (Fig. 2b). Figure 2b indicates that by increasing concentration of TCPO, the intensity of the band ($\lambda_{\text{max}}=518 \text{ nm}$) is decreased. It should be noted that the band appeared at 608 nm is ascribed to the complex. According to the obtained results, the optimal concentration of TCPO is 0.004 M.

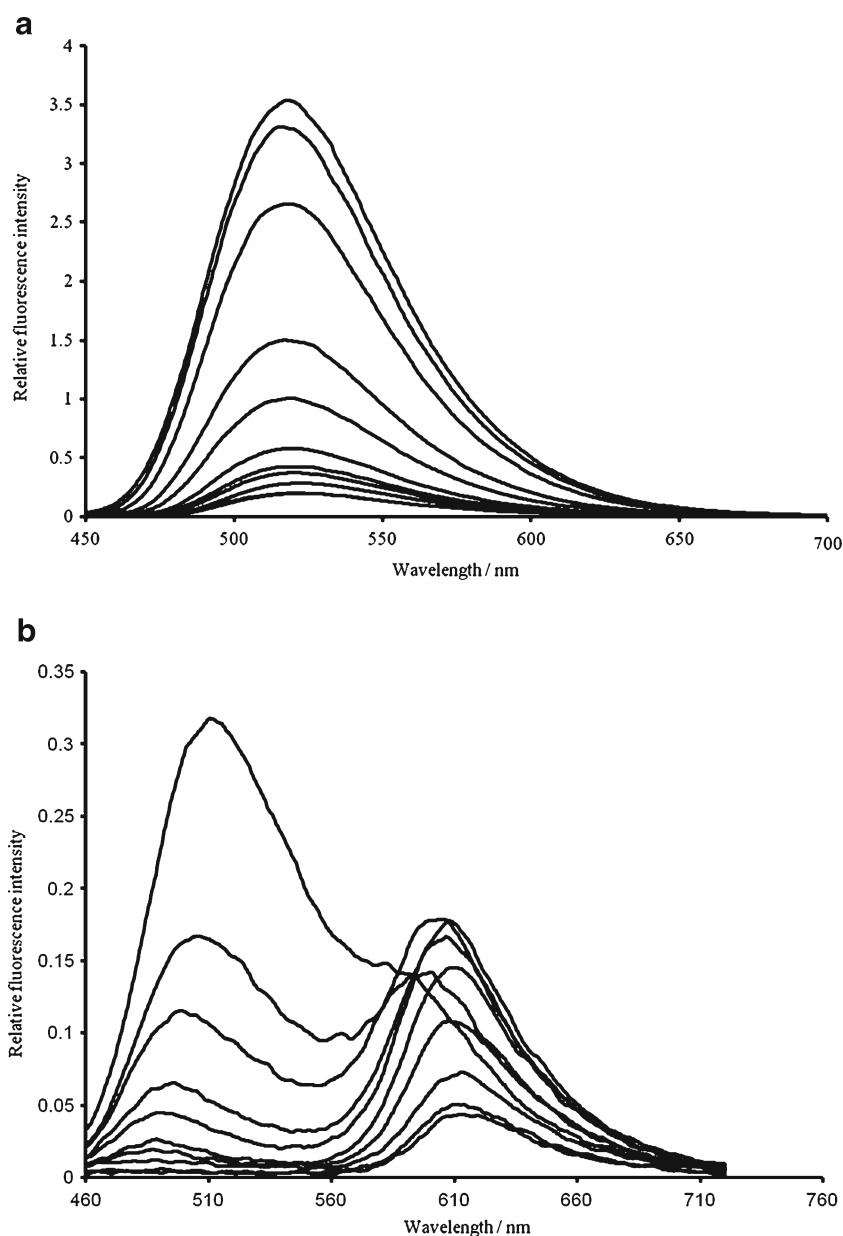
Concentration of 2, 3 Biphenyl Quinoxaline 6-amine

To examine the influence of concentration of 2,3 biphenyl quinoxaline 6-amine on the fluorescence intensity, series of

experiments were performed with different concentrations of 2,3 biphenyl quinoxaline 6-amine (i.e., 2.5×10^{-5} – $5 \times 10^{-4} \text{ mol/L}$) containing TCPO (0.004 M) without and with Zn^{2+} ion ($5.0 \times 10^{-4} \text{ mol/L}$). Fluorescence spectra of the corresponding solutions were recorded with the same spectral conditions and presented in Fig. 3a and 3b, respectively. According to Fig. 4a, increasing concentration of 2, 3 biphenylquinoxaline 6-amine leads to a gradual decrease in the fluorescence intensity which can be related to the self absorption effect.

Comparison of Fig. 3a and 3b reveals that the fluorescence intensity at $\lambda_{\text{max}}=518 \text{ nm}$ is significantly lower for the solution containing Zn^{2+} ion than for the one without Zn^{2+} .

Fig. 3 Fluorescence spectra of the 2, 3 biphenyl quinoxaline 6-amine, **a** without and **b** with Zn^{2+} ($5.0 \times 10^{-4} \text{ M}$) in the presence of TCPO ($4.0 \times 10^{-3} \text{ M}$) with different concentrations of 2, 3 biphenyl quinoxaline 6-amine, from top to bottom: 2.5×10^{-5} , 5.0×10^{-5} , 1.0×10^{-4} , 1.5×10^{-4} , 2.0×10^{-4} , 2.5×10^{-4} , 3.0×10^{-4} , 3.5×10^{-4} , 4.0×10^{-4} , 4.5×10^{-4} , 5.0×10^{-4}



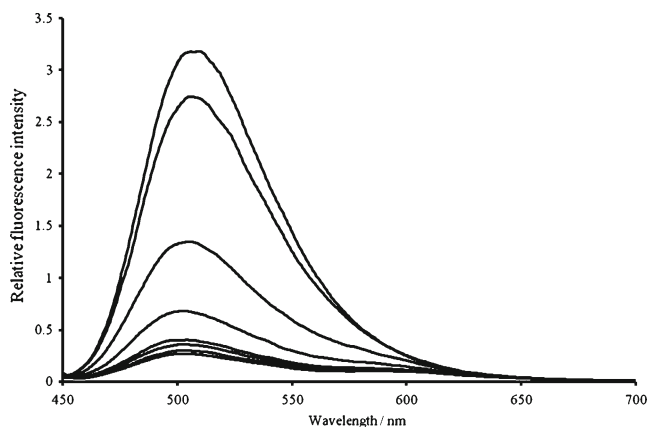


Fig. 4 Fluorescence emission spectra of the 2, 3 biphenyl quinoxaline 6-amine (2.5×10^{-5} M) in the presence of TCPO (4.0×10^{-3} M) with the various molar concentrations of Zn^{2+} from top to bottom: 1.5×10^{-5} , 2.5×10^{-5} , 3.5×10^{-5} , 5.0×10^{-5} , 6.0×10^{-5} , 7.5×10^{-5} , 9.0×10^{-5}

In order to prevent self-quenching effects, the lowest concentration of 2.5×10^{-5} M was selected for 2,3 biphenyl quinoxaline 6-amine.

Concentration of Zn^{2+} Ion

As discussed above, the intensity of fluorescence emission in the solution containing 2,3 biphenyl quinoxaline 6-amine and TCPO is significantly reduced by increasing the Zn^{2+} concentration. The influence of Zn^{2+} concentration on the fluorescence intensity was investigated and the obtained results are presented in Fig. 4. As can be seen in Fig. 4, the fluorescence intensity at $\lambda_{max}=518$ was reduced by increasing the Zn^{2+} concentration up to 9×10^{-5} M. Nevertheless further

increasing concentration of Zn^{2+} ion has no more effect on the fluorescence intensity.

Determination of Trace Water in Ethanol and Methanol

Different amounts of water were mixed with 50 μ L of 2,3 biphenyl quinoxaline 6-amine (0.001 M), 0.8 mL of TCPO (0.01 M) and 20 μ L of Zn^{2+} (0.01 M) in a test-tube. The fluorescence spectra shown in Fig. 5 were recorded with excitation wavelength at 435 nm in a 1 cm quartz cell. According to the obtained calibration curve (i.e., fluorescence intensity against concentration of water) shown in top of right hand side of Fig. 5, the regression equation is $\Delta F = 2.875 C + 0.1734$. Where F and C are the fluorescence intensity and the concentration of water (v/v%), respectively. The Figures of merit are as follows: correlation coefficient (r^2) of 0.9922, the linear range of 0.0094 - 1(v/v %) and LOD of 0.0026(v/v%).

The proposed method was applied for the determination of water content in methanol and ethanol and results are presented in Table 1. The results obtained from this method were in good agreement with those of Karl Fisher method.

Conclusion

A new method for determination of trace water in methanol and ethanol was successfully introduced. This method is based on the enhancement of fluorescence intensity by addition of water in the luminescence system of 2,3

Fig. 5 Changes in fluorescence spectra of the 2, 3 biphenyl quinoxaline 6-amine as a function of water content (v/v%) from bottom to top respectively: 0.05, 0.15, 0.25, 0.35, 0.5, 0.75, 0.9 and 1. The excitation wavelength is 435 nm and the concentrations of 2,3 biphenyl quinoxaline 6-amine, TCPO and Zn^{2+} are 2.5×10^{-5} , 4.0×10^{-3} and 9.0×10^{-5} M, respectively. Inset: The plot of relative fluorescence intensity as a function of water content (v/v%)

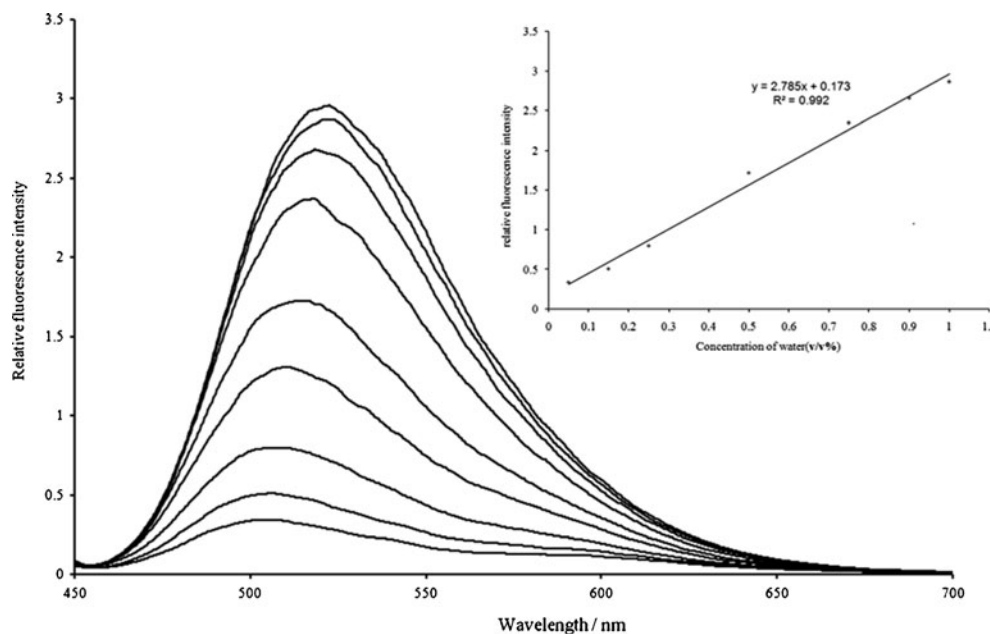


Table 1 Determination of water in methanol and ethanol

Sample ^a	Labeled value of water (v/v %)	Karl fisher method	This method ^b
Methanol (Merk)	2 %	-	1.96±0.08 %
Ethanol	unknown	3.40±0.03 %	3.45±0.26 %

^a samples were diluted down to dynamic linear range of the method

^b ±Standard deviation ($n=5$)

biphenyl quinoxaline 6-amine, bis-(2, 4, 6-trichlorophenyl) oxalate (TCPO) and Zn^{2+} . This paper describes enhancement of fluorescence intensity by addition of water in the above luminescence system. This method is simple and sensitive for determination of trace water in organic solvents.

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