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Pyrazoline derived new “off-on-off” fluorescent pH sensors

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ABSTRACT

Pyrazolines are reported with a broad range of bioactivities, excellent fluorescence properties and easy synthesis. But unfortunately, there is no or very limited information available about their pH sensor application. Additionally, there is a little information about “off-on-off” type of pH sensors in literature. To fulfill the gap in literature and try to find out new possible “off-on-off” pH sensor, in this study it was planned to investigate the changes in the photo-physical properties of four pyrazolines **D1–D4**, 4-(5-(3,4-dimethoxyphenyl)-3-(4-substitutedphenyl)-4,5-dihydro-1H-pyrazol-1-yl)benzene sulfonamide, in water and different pH (2, 4, 6, 8, 9, 10, 12) in which on phenyl was H (**D1**), F (**D2**), Cl (**D3**) and Br (**D4**). The compound **D1** exhibited excellent fluorescence properties and high fluorescence quantum yields in water. When the compounds **D2–D4** which have electron-withdrawing substituents F, Cl and Br in **D2–D4**, respectively, were considered, it was observed that fluorescence quenching occurred in the molecules in question due to increased intersystem crossing probability while **D1** did not show fluorescence quenching. However, the photo-physical properties of the compounds **D1–D4** displayed important changes as a function of pH. It follows from these important changes that the compounds **D1–D4** have “off-on-off” type of fluorescent pH sensor properties based on intramolecular charge transfer (ICT). These results indicated that these pyrazoline derivatives would be able to act as an efficient “off-on-off” fluorescent pH sensor in biological, environmental and medical etc. areas.

1. Introduction

Design of new optical pH sensors is a remarkable field of research due to its important functions in many areas such as environmental, biochemical, electrochemical and analytical [1,2]. Fluorescent pH sensors have superior properties such as high sensitivity, high selectivity, fast response and low cost compared to other methods such as acid–base indicator titration [3] and potentiometric titration [4]. Fluorescence pH sensors respond to pH changes either “on-off (or off-on)” or “off-on-off (or on-off-on)”. While “on-off (or off-on)” fluorescence sensors are quite common [5–8], “off-on-off (or on-off-on)” sensors are limited since to develop “off-on-off (or on-off-on)” sensors requires complex molecular designs to meet the structural and electronic properties. Therefore, designing “off-on-off (or on-off-on)” pH sensors is very important work area to fulfill the gap in literature.

Generally, fluorescence pH sensors are designed based on basic principles including photoinduced electron transfer (PET), intramolecular charge transfer system (ICT) and electron transfer (ET). ICT fluorophores are conjugated systems that have both electron donor and electron acceptor groups. When ICT fluorophore is excited, intramolecular charge transfer takes place between the electron donor and acceptor groups. This charge transfer is very sensitive to environmental conditions (polarity, pH etc.). So, the ICT systems have an important place in the pH sensor studies [9,10].

Pyrazoline derivatives, typical intramolecular charge transfer (ICT) compounds, are often used many areas such as light emitting diode design [11,12], ion sensor [13], labeling [14] due to their high fluorescence quantum yields and strong fluorescence properties. Although there are many studies on pyrazoline derivatives focusing on their synthesis and/or several bioactivities, unfortunately, there are very limited number studies on the pH sensor application of pyrazoline derivatives [15]. Indeed, pyrazolines have several advantageous over the other sensor candidates since they can be synthesized easily and have excellent fluorescence property. Therefore, new pyrazoline derivatives which subject to this investigation can provide very valuable information to the researcher working on the development on pH sensors.

In this study, new “off-on-off” type fluorescence pH sensors which has pyrazoline structure were designed (Scheme 1). Pyrazolines studied here have the chemical structure of 4-(5-(3,4-dimethoxyphenyl)-3-(4-substitutedphenyl)-4,5-dihydro-1H-pyrazol-1-yl)benzene sulfonamide

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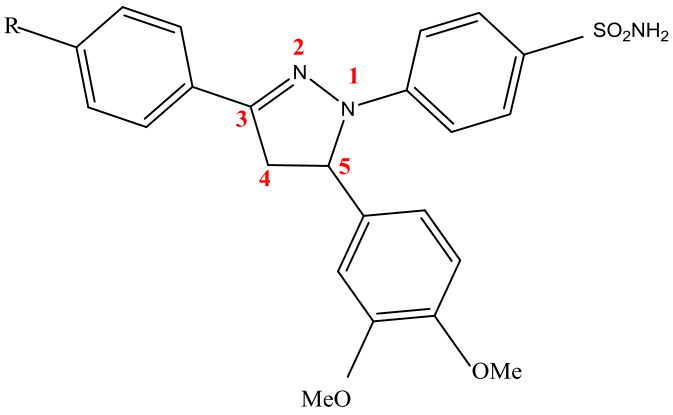

Scheme 1. Structure of the pyrazoline derivatives **D1–D4**.

in which R was H (**D1**), F (**D2**), Cl (**D3**) and Br (**D4**). It was aimed to investigate the effect of pH on the optical properties of the pyrazolines **D1–D4** considering them as new "off-on-off" type fluorescence pH sensors candidates. For this purpose, it was planned to take UV–Vis. absorption and fluorescence measurements of the compounds **D1–D4** and to calculate their photo-physical parameters. The information to be obtained by this study will be useful to the people who are working on the development "off-on-off" type fluorescence pH sensor on which very limited information is available. In addition, it will be very contributory to the uses of pyrazolines as pH sensors since there are very limited studies related to uses of pyrazoline as pH sensor.

2. Experimental

2.1. Material

pH buffer solutions (Fluka), quinine sulfate (Fluka) and H_2SO_4 (Sigma) were purchased and used without further purification. The stock solutions of all compounds were prepared in ethanol. A certain amount of fresh probe samples in different solution was obtained from this stock solution by evaporating the solvent. For all measurements, the concentrations of compounds were 1 μM. All the experiments were performed at room temperature.

2.2. Equipment

The UV–Vis absorption and fluorescence spectra of the samples were recorded with Perkin Elmer Lambda 35 UV/VIS spectrophotometer and Shimadzu RF-5301 P C spectrofluorophotometer, respectively. Fluorescence and absorption measurements were taken for all compounds at room temperature. For the steady-state fluorescence measurements, all the samples were excited at 350 nm and fluorescence intensity were recorded between 360 nm and 650 nm. The fluorescence lifetime measurements were carried out with a LaserStrobe model TM3 spectrofluorophotometer from Photon Technology International (PTI). The excitation source combined a pulsed nitrogen laser/tunable dye laser. The samples were excited at 366 nm. The decay curves were collected over 200 channels using a nonlinear time scale with the time increment increasing according to arithmetic progression. The fluorescence decays were analyzed with the lifetime distribution analysis software from the instrument supplying company. The quality of fits was assessed by χ^2 values and weighed residuals [16].

The fluorescence quantum yields of all compounds were calculated through the Parker-Rees equation:

$$\varnothing_s = \varnothing_r\left(\frac{D_S}{D_r}\right)\left(\frac{\eta_s^2}{\eta_r^2}\right)\left(\frac{1-10^{-OD_r}}{1-10^{-OD_s}}\right) \quad (1)$$

where D is the integrated area under the corrected fluorescence spectrum, n is the refractive index of the solution, and O_D is the optical density at the excitation wavelength (λ_{ex} = 350 nm). The subscripts s and r refer to the sample and reference solutions, respectively. Quinine sulfate in 0.5 M H_2SO_4 solution was used as the reference. The fluorescence quantum yield of quinine sulfate was 0.55 in 0.5 M H_2SO_4 solution [17].

The rate constants of the radiative (k_r) and non-radiative (k_{nr}) deactivation were calculated by using the following equations.

$$k_r = \frac{\Phi}{\tau_{av}} \quad (2)$$

$$\frac{1}{\tau_{av}} = k_r + k_{nr} \quad (3)$$

where Φ is fluorescence quantum yield and τ_{av} is average fluorescence lifetime of samples [18].

2.3. Synthesis of pyrazoline derivatives

The compounds were synthesized as presented in Scheme 2 and characterized by ^{1}H NMR, ^{13}C NMR and HRMS [19]. ^{1}H NMR, ^{13}C NMR and HRMS data for compound **D1–D4** can be found in the supplementary file.

3. Results and discussion

3.1. Optical properties of pyrazoline derivatives

Absorption and fluorescence measurements were taken by UV–vis. spectrophotometer and spectrofluorophotometer to determine the optical properties of the pyrazoline derivatives **D1–D4** (1 μM) in water. As shown in Fig. 1, the non-substituted compound (**D1**) has an absorption band at 358 nm. When electron-withdrawing substituents F, Cl and Br were attached to 4-position of phenyl ring in compounds **D2–D4**, bathochromic shifts were seen and peak intensities decreased in the absorption spectrum of the compounds **D2–D4** (Fig. 1). Generally, the presence of electron-donating substituents shifts the absorption band maximum to red region [20]. But, the size of red shift is greater compared to the effect of only single substituent in the presence of both electron-withdrawing and electron-donating substituents (As seen in Scheme 1, the electron-withdrawing group in the 3-position and the electron-donating groups in the 5-position of pyrazole ring) [21]. Furthermore, the compounds **D1–D4** exhibited large Stokes shifts and high molar absorptivities (ε) in water (Table S1). However, while compound **D1** (1 μM) had a high intensity fluorescence peak at about 452 nm in water, a significant decrease was observed in the fluorescence intensity of **D2–D4** spectra comparing with **D1**'s since the hydrogen in **D1** was replaced by a halogen substituent in **D2–D4** (Fig. 2). Halogens (e.g., Br, I) have internal heavy atomic effect on the fluorescence properties of