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Novel fluorescent pH sensor based on coumarin with piperazine and imidazole substituents

Na'il Saleh [a,*], Yaseen A. Al-Soud [b], Werner M. Nau [c]

[a] Department of Chemistry, Yarmouk University, 21163 Irbid, Jordan
[b] Department of Chemistry, University of Al al-Bayt, Al-Mafraq, Jordan
[c] School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, D-28759 Bremen, Germany

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Abstract

A new coumarin derivative containing piperazine and imidazole moieties is reported as a fluorophore for hydrogen ions sensing. The fluorescence enhancement of the studied sensor with an increase in hydrogen ions concentration is based on the hindering of photoinduced electron transfer from the piperazinyl amine and the imidazolyl amine to the coumarin fluorophore by protonation. The presented sensor has a novel design of fluorophore-spacer-receptor(1)-receptor(2) format, which is proposed to sense two ranges of pH (from 2.5 to 5.5) and (from 10 to 12) instead of sensing one pH range. A model compound, in which the piperazinyl ring is absent, was synthesized as well to confirm the novel pH sensing of the proposed sensor.

Keywords: Fluorescent multiple pH sensor; Photoinduced electron transfer (PET); Coumarin; Piperazine; Imidazole

1. Introduction

The design of fluorescent molecular sensors is of major importance because of the demand in analytical chemistry, biomedical, biotechnology, nanotechnology, the environment, etc. The success of fluorescent sensors can be explained by the distinct advantages offered by fluorescence detection in terms of sensitivity, selectivity, local observation (e.g. by fluorescence imaging spectroscopy), response time, etc. Numerous chemical and biochemical analytes can be detected by fluorescence methods (e.g. cations [1], anions, neutral molecules [2], gases, etc.). If the analyte is proton, the term fluorescent pH sensor is often used.

The class of fluorescent pH sensor that undergoes photoinduced electron transfer (PET) has gained the interest of scientists in the early 21st century [3]. The pH sensor of this type consists of a fluorophore linked to an amine receptor via a methylene spacer. PET causes fluorescence quenching. When the amino group is protonated, electron transfer (ET) is hindered and a very large enhancement of fluorescence is observed. Several works have reported fluorescent PET sensors that contain coumarin [4] group as the fluorophore and imidazole [5] or piperazine [6,7] moiety as the receptor. In particular, a piperazinyl coumarin derivative was also used as a fluorescent indicator for physiological pH measurement [8].

By taking into consideration, the structural logic of the previously reported PET pH sensors, which has the common format, fluorophore-spacer-receptor, we have thought of designing a pH sensor by connecting a coumarin fluorophore to both a piperazine and an imidazole receptors by a methyl spacer, namely, 4-((4-(1-Benzyl-2-ethyl-4-nitro-1H-imidazol-5-yl)piperazin-1-yl)methyl)-7-methoxy-2H-chromen-2-one (**P-2**), see Fig. 1. It should be said that such new design logic of the pH sensor, fluorophore-spacer-receptor (1)-receptor(2), as compared to other fluorescent sensors designs might enable researchers gaining a better control of pH sensing by extending its dynamic range. The idea of having two receptors that sense different pH ranges has not been previously reported except by the work of de Silva et al. [9] who reported a PET sensor of "fluorophore-spacer-receptor$_i$" format. However, a single compound rather than a mixture of compounds (with an equivalent amount) is reported here to operate the multiple pH sensing. Such design strategy of a single molecule capable of sensing multiple pH ranges might be more practical than

* Corresponding author. Tel.: +962 2 7211111x2793; fax: +962 2 7211117.
E-mail address: nsaleh@yu.edu.jo (N. Saleh).

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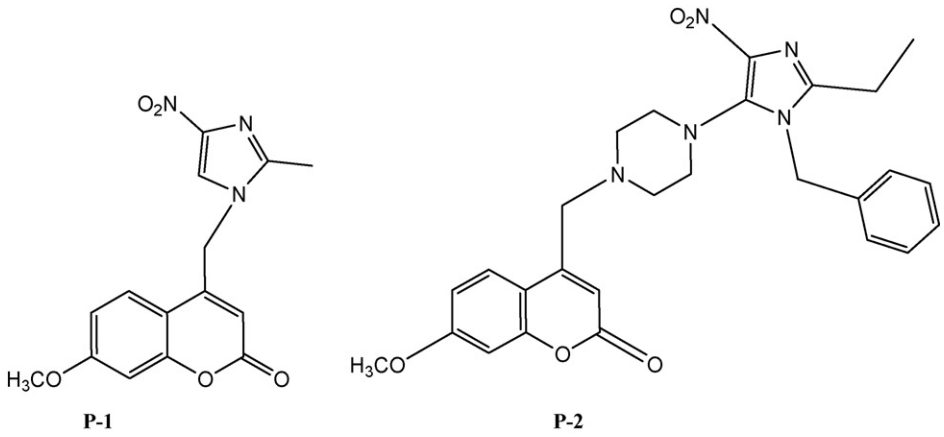

Fig. 1. Molecular structures of **P-1** and **P-2**. Notice the absence of piperazine group in the structure of **P-1**.

having a sensor with similar functions but made of a mixture of molecules as suggested by de Silva group. To confirm the PET process and the pH sensing mechanism, the newly designed pH indicator was prepared together with a model compound, 7-Methoxy-4-((2-methyl-4-nitro-1H-imidazol-1-yl)methyl)-2H-chromen-2-one (**P-1**), see Fig. 1, in which the piperazine substituent was removed. This article focused on the absorption and fluorescence properties of **P-1** and **P-2** compounds, as well as their solvent dependence as a function of pH.

2. Experimental

The synthesis of compounds **P-1** and **P-2** was reported elsewhere by Al-Soud et al. [10]. The absorption spectra were collected using Unicam UV–vis spectrophotometer, while the fluorescence spectra were collected using Edinburgh FS-900CDT fluorometer with excitation and emission slit width of 4 ± 0.5 nm. The absorption of each chromophore was checked to be about 0.05 absorbance unit at the excitation wavelength ($\lambda_{excitation} = 321$ nm) (see S-1 and S-2). The quantum yields (ϕ_f) were measured using anthracene in ethanol as a standard ($\phi_f = 0.27$) [11]. The pH of water was adjusted by adding small aliquots of aqueous solutions of strong acid HCl or strong base NaOH to achieve the desired ionic states. The pH values of the solutions were measured using a pH-meter model WTW 330i equipped with a WTW SenTix Mic glass electrode.

3. Results

The photophysical properties of **P-1** and **P-2** are listed in Tables 1 and 2, respectively, together with the most common solvent properties that represent polarity and viscosity. The first observation of these tables indicated that both solvent polarity and solvent viscosity have negligible influence on the position of absorption and fluorescence peaks. Solvent viscosity, however, affects the fluorescence quantum yields obtained for **P-1** and **P-2**. For example, in glycerol the emissions of **P-1** and **P-2** become equal and increased by a factor of two and four, respectively, in comparison to the emissions in ethanol as shown in S-3 and S-4. It should be said that the viscosity of glycerol is almost 1000 times that of ethanol in centipoises at room temperature.

An enhancement of emission was observed for **P-1** and **P-2** in protonated media as observed from the pH-dependence of the fluorescence spectra at room temperature in Figs. 2 and 3. Fig. 2 shows the plot of fluorescence intensity at the maximum peak (415 nm) as a function of pH in the range from 1.85 to 12.2 for both **P-1** and **P-2** molecules. As the surrounding media become more acidic, fluorescence enhanced and red-shifted (see S-5 and S-6). For **P-1** the fluorescence enhancement occurs by one step, while for **P-2** it occurs via two steps.

In Fig. 3, the evolution of fluorescence spectra with pH in the range from 2 to 8 is analyzed by the following equation:

$$\mathrm{pH} - \mathrm{p}K_a = \log\left(\frac{F_{max} - F}{F - F_{min}}\right) \tag{3.1}$$

Table 1
Absorption and fluorescence maxima, quantum yields (ϕ_f), and stokes shifts ($\nu_A - \nu_F$) of **P-1** in solvents with different properties at 25 °C[a]

No.	Solvent	ε	η	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	ϕ_f	$\nu_A - \nu_F$ (cm^{-1})
1.	Benzene	2.3	0.65	321	11,624	397	0.008	5964
2.	Ethyl acetate	6.0	0.44	321	14,175	395	0.050	5836
3.	Ethanol	24.6	1.10	322	16,985	400	0.050	6056
4.	Ethylene glycol	37.7	16	321	16,263	398	0.050	6027
5.	Dimethylformamide (DMF)	38.3	0.85	319	19,124	401	0.018	6410
6.	Glycerol	46.5	934	325	12,397	399	0.087	5707
7.	Dimethyl sulfoxide (DMSO)	46.5	2.14	322	17,526	400	0.016	6056
8.	Water (pH 7)	78.3	0.89	322	14,179	405	0.050	6365

[a] ε = solvent dielectric constants and η = solvent viscosities in centipoises at 25 °C.