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NOTE

A Highly pH-Sensitive Fluorescent Membrane Based on Two Dyes Dione and Porphyrine with Close Excitation Peaks

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A fluorescence pH sensing membrane based on immobilization of two dyes 1-allyloxy-4-hydroxyanthrance-9,10-dione/5-(4-aminophenyl)-10,15,20-triphenylporphyrine with close excitation peaks is prepared and its application for pH sensor are described. Compared to pH 2-4, both dyes showed that presented membrane is highly sensitive to pH variation, with a linear response working range from pH 2 to pH 13.5. The response of sensor is reversible and reproducible.

Keywords: Fluorescent pH assay, 1-Allyloxy-4-hydroxyanthrance-9,10-dione.

Porphyrins and their derivatives represent an important class of macro-heterocycles with unique fluorescence properties. Though several reports have described the successful use of potentiometric and fiber optic sensors for pH based on an electropolymerized cobalt porphyrin[1], the porphyrin itself is not sensitive to pH, which limits the wide usage and application of this excellent fluorescein. Optical pH sensors are based on pH dependent change of the absorbance or luminescence of certain carrier molecules[2-5]. The pH sensors based on the change of fluorescent intensity attracted attention due to their relatively high sensitivity[6]. Generally, the response of the optode is governed by sample diffusion to the membrane phase and is typically limited to a narrow pH range[2-5], We synthesized an unsymmetrically compound, 5-(4-aminophenyl)-10,15,20-triphenylporphyrine (ATPP). The excitation peak of ATPP (λ_{ex} = 423 nm) is close to that of the solvatchromic dye 1-allyloxy-4-hydroxyanthracene-9,10-dione (AHD) (λ_{ex} = 434 nm). 1-Allyloxy-4-hydroxyan-thracene-9,10-dione with double bonds could be photocopoly-merized under UV radiation[10,11], the polymer formed embedded in PVC membrane adhered on the glass plate shows strong fluorescence, which is sensitive to change of solution pH[7,8].

High molecular weight poly(vinyl chloride) (PVC) and *bis*(2-ethylhexyl) sebacate (BOS) were obtained from Shanghai Chemicals (Shanghai, China). For measurement of pH, a series Britton-Robinson buffer solutions were prepared using 0.2 M acetic acid, phosphate and borate, mixed with 0.2 mol L^{-1} NaOH. 1-Allyloxy-4-hydroxyanthracene-9,10-dione (Fig. 1a) and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (Fig. 1b) were synthesized exactly as reported[9]. The glass slides were made hydrophobic by silanization as described in the literature[10].

The sensing membrane adhered on the plate was mounted in a cell tightly matching light source. The sample solution was driven through syringing. The sensing membrane was equilibrated with the sample solution for obtaining a stable fluorescence signal. The fluorescence emission spectra (450-750 nm) of the sensing membrane containing two dyes (1-allyloxy-4-hydroxyanthracene-9,10-dione and 5-(4-amino-phenyl)-10,15,20- triphenylporphyrine) were recorded with excitation wavelengths fixed of 423 nm. After each measurement, the sensing membrane was washed by syringing the blank solution through the cell until the fluorescence intensity of the optode reached the original blank value.

Fig. 2 shows the fluorescence spectra of 1-allyloxy-4-hydroxyanthracene-9,10-dione and 5-(4-aminophenyl)-10,15,20- triphenylporphyrine in 50 % ethanol solution, which are recorded at maximal excitation wavelength λ_{ex} = 434 nm and maximal emission wavelength λ_{em} = 576 nm of 1-allyloxy-4-hydroxyanthracene-9,10-dione and at λ_{ex} = 423 nm, λ_{em} = 654 nm of 5-(4-aminophenyl)-10,15,20-triphenylporphyrine.

From Fig. 2, it is obvious that 1-allyloxy-4-hydroxyan-thracene-9,10-dione and 5-(4-aminophenyl)-10,15,20-tri-phenylporphyrine have the overlapped excitation wavelength region, which makes it possible to use an excitation wave length fixed at 423 nm for the membrane to produce the double fluorescence emission spectra. The assay reported in this article was based on the pH-dependent response of such a two-dye

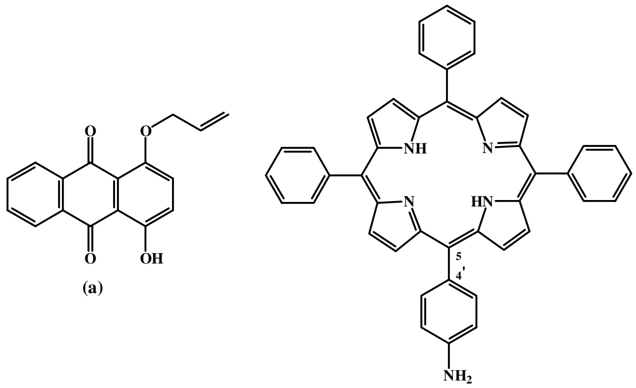

Fig. 1. Chemical structures of (a) 1-allyloxy-4-hydroxyanthracene-9,10-dione (AHD) and (b) 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrine (ATPP)

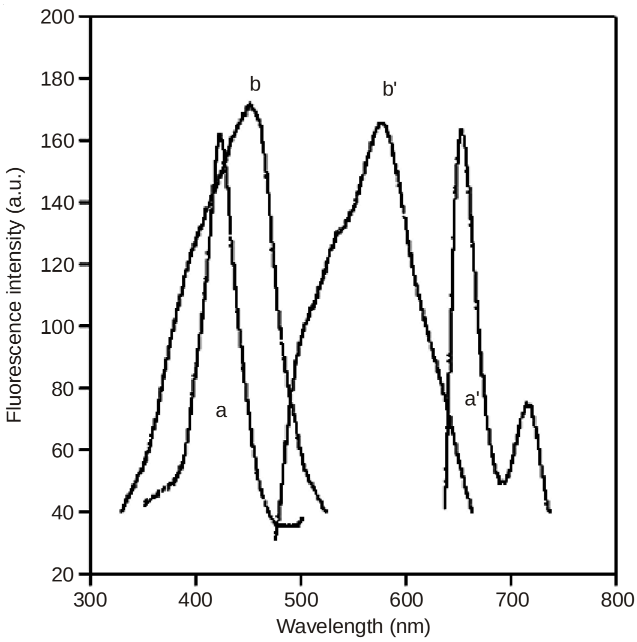

Fig. 2. Excitation and emission spectra of 1-allyloxy-4-hydroxyanthracene-9,10-dione (AHD) (a, a') and 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrine (ATPP) (b,b')

sensor. Fig. 3 shows the fluorescence spectra (450-750 nm) of the sensing membrane with the maximum emission wavelength of 1-allyloxy-4-hydroxyanthracene-9,10-dione at 576 nm of 1-allyloxy-4-hydroxyanthracene-9,10-dione and those of 5-(4-aminophenyl)-10,15,20- triphenyl-porphyrine at 654 and 715 nm recorded at different solution pH.

The hydroxy group in 1-allyloxy-4-hydroxyanthracene-9,10-dione and the amino group in 5-(4-aminophenyl)-10,15,20-triphenyl-porphyrine are capable to protonation, which is the source of the pH-dependent fluorescence emission of the sensor. The spectral characteristics of the mixed membrane exactly reflect the properties of the two individual dyes. The sensing membrane based on two dyes shows sensitive response to solution pH.

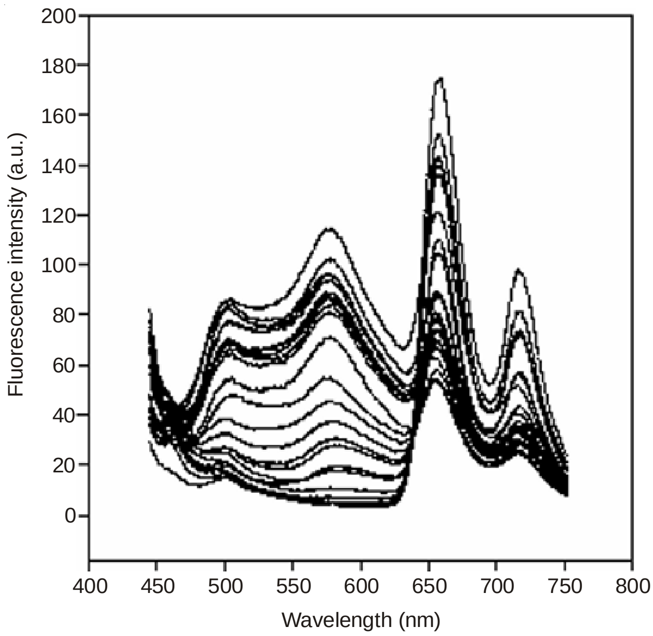

Fig. 3. Fluorescence spectra of optode contacting with solutions of different pH. From top to bottom at 576 nm: pH of 2.0-13.5

Conclusion

The application of a mixture of two fluorophores, (1-allyloxy-4-hydroxyanthrance-9,10-dione (AHD) and 5-(4-aminophenyl)-10,15,20-triphenylporphyrine (ATPP) with close excitation peaks immobilized on a glass slice can offer a suitable pH sensor for wide range pH measurements. The sensing membrane based on two dyes shows wide dynamic pH range, high stability, good reversibility, short response time and excellent spectral characteristics.

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