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Switchable fluorescence behaviors of pyronine Y at different pH values upon complexation with biquinolino-bridged bis(β-cyclodextrin)

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Abstract

An xanthene dye, pyronine Y, was found to exhibit opposite fluorescence behaviors at different pH values in the presence of *N*,*N*′-bis(2-aminoethyl)-2,2′-biquinoline-4,4′-dicarboxamide-bridged bis(β-cyclodextrin) (**2**). That is, pyronine Y showed the quenched fluorescence in an acidic (pH 2.0) or a neutral (pH 7.2) environment, while the enhanced fluorescence in a basic environment (pH 12.0), with the addition of **2**. Further studies by fluorescence titrations and 2D NMR indicated that different binding modes of positively charged and neutral PY molecules upon complexation with bis(β-cyclodextrin) **2** should be responsible for opposite fluorescence behaviors. This result may enable the biquinolino-bridged bis(β-cyclodextrin) as an efficient chemical sensor for the protonation and deprotonation of xanthene dyes.

Keywords: Spectrophotometric titration; Cyclodextrin; Pyronine Y; Fluorescence sensing; Photoinduced electron transfer

1. Introduction

Water-soluble xanthene dyes, such as pyronines, acridines and rhodamines, are very sensitive to the local microenvironment. Therefore, they have been widely applied in the labeling of proteins and cell organelles [1–4], the loading of gels [5], the doping of organic thin films [6], and depositing on a p-type silicon surface to construct diodes [7,8], etc. For all these applications, it is vital to understand their photophysical behavior in organized media [9,10] and to know the role of interactions between the substrate and the medium. On the other hand, as excellent model acceptors, cyclodextrins (CDs) can bind various substrates, including dye guests, to form host-guest supramolecular complexes due to the hydrophobicity of the CD cavity [11–15]. Recently, Novo et al. investigated the inclusion complexation of pyronine Y (PY) and pyronine B (PB) with native β-CD in different solvents, and characterized the photophysical properties of these included pyronines by using fluorescence measurements [16]. As compared with native CDs and simply modified CDs, bridged bis(CD)s generally exhibit higher binding abilities and molecular selectivities toward model substrates due to a multiple recognition mechanism [17–38]. In preliminary works, we have reported that biquinolino-bridged bis(β-CD)s can form more stable inclusion complexes with both fluorescent dyes [39] and steroids [40,41] than their monomeric analogues through the cooperative binding of one guest by two CD cavities in a single molecule. In this context, we wish to report pH-dependent fluorescence behaviors of PY upon complexation with *N*,*N*′-bis(2-aminoethyl)-2,2′-biquinoline-4,4′-dicarboxamide-bridged bis(β-CD) (**2**) (Plate 1). The aim of this work is to investigate how the nature of the media affects binding behaviors of bis(β-CD)s with model substrates. We are also particularly interested in examining the protonation/deprotonation of model substrates in the presence of bis(β-CD) through a fluorescence-sensing mechanism. This approach will serve our further understanding of this significant, but little investigated, area in the field of CD chemistry.

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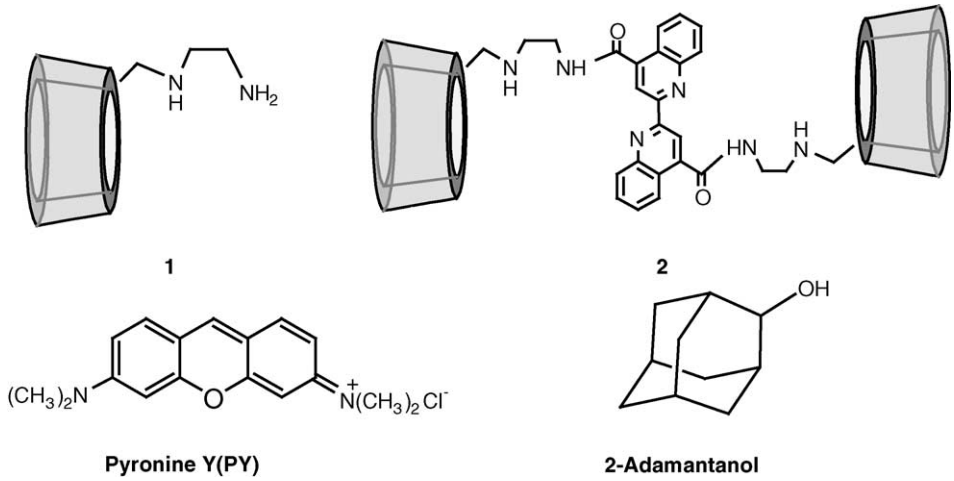

Plate 1. Structures of hosts and guests.

2. Experimental

2.1. Measurements

Fluorescence spectra were measured in a conventional rectangular quartz cell (10 mm × 10 mm × 45 mm) at 25 °C on a JASCO FP-750 spectrometer equipped with a constant-temperature water bath, with the excitation and emission slits width of 5 nm, and the excitation wavelength was 493 nm. A 2D NMR spectrum was obtained on a Varian INVOA 300 spectrometer at 25 ± 1 °C.

In spectral measurements, disodium hydrogen phosphate dodecahydrate (25.79 g) and sodium dihydrogen phosphate dihydrate (4.37 g) were dissolved in 1000 mL of deionized water to make a 0.10 M aqueous phosphate buffer solution of pH 7.2. Whereas 20 mM potassium chloride was adjusted to pH 2.0 with 1 M hydrochloric acid to give an acidic buffer solution or was adjusted to pH 12.0 with 1 M sodium hydroxide to give a basic buffer solution, which were used as solvent for all measurements.

2.2. Materials and sample preparation

6-(2-Aminoethylamino)-6-deoxy-β-CD (**1**) [42] and *N*,*N*′-bis(2-aminoethyl)-2,2′-biquinoline-4,4′-dicarboxamide-bridged bis(β-CD) (**2**) [40] were prepared according to our previous reports. 2-Adamentanol was purchased from Aldrich, and pyronine Y was purchased from Chroma. All other chemicals were commercially available and used without further purification, except noted otherwise.

Aqueous solutions of PY for measurements were freshly prepared by dissolving the commercial product in buffer solutions with concentrations in the range of 1.5 to 5.0 × 10^{-6} mol dm^{-3} for fluorescence titrations. These concentrations were low enough to avoid the aggregation of dyes in aqueous solution, while concentrations of **1** and **2** were varied from 0 to 100 times correspondingly in each titration experiment.

3. Results and discussion

3.1. Fluorescence titration

Fluorescence titrations of **1** and **2** with PY in different buffer solutions (pH 2.0, 7.2 and 12.0) were performed at 25 °C to quantitatively assess binding behaviors between hosts and guests. In spectral titration experiments, the concentration of PY was kept constant, while concentrations of **1** and **2** were varied from 0 to 100 times as high as that of PY correspondingly. The spectral changes depended critically on the formation of new species, i.e., host-guest inclusion complex, showing the spectral enhancement or quenching. As shown in Fig. 1, the fluorescence intensity of PY gradually decreased in buffer solutions of pH 2.0 and pH 7.2 upon the addition of bis(β-CD) **2**. In sharp contrast, in a basic buffer solution of pH 12.0, the fluorescence intensity of PY gradually increased with the addition of **2**.

Validating the 1:1 inclusion complexation stoichiometry between CD hosts and PY by Job's experiments, complex stability constants (K_S) could be calculated by analyzing sequential changes in fluorescence intensities (ΔI_f) of dyes that occurred with changes in host concentrations. This analysis was carried out by using a nonlinear least squares curve-fitting method [43]. For each dye guest examined, the plot of ΔI_f as a function of $[H]_0$ gave an excellent fit. In repeated measurements, K_S values were reproducible within an error of ±5%. Complex stability constants (K_S) obtained for all of host-guest combinations were listed in Table 1, along with free energy changes ($-\Delta G^\circ$) as well as fluorescence intensity changes of guest dye upon addition of hosts **1** and **2**.

3.2. Unique fluorescence behaviors of PY

As shown in Fig. 1, fluorescence behaviors of PY in the presence of bis(β-CD) **2** were largely dependent on the solution's pH value, i.e., the fluorescence intensity of PY gradully