

The pH response of near infrared 5,5'-bisulfonic heptamethine indocyanines in water, CTAB solution and metal oxide-based sol under extremely acidic and basic conditions

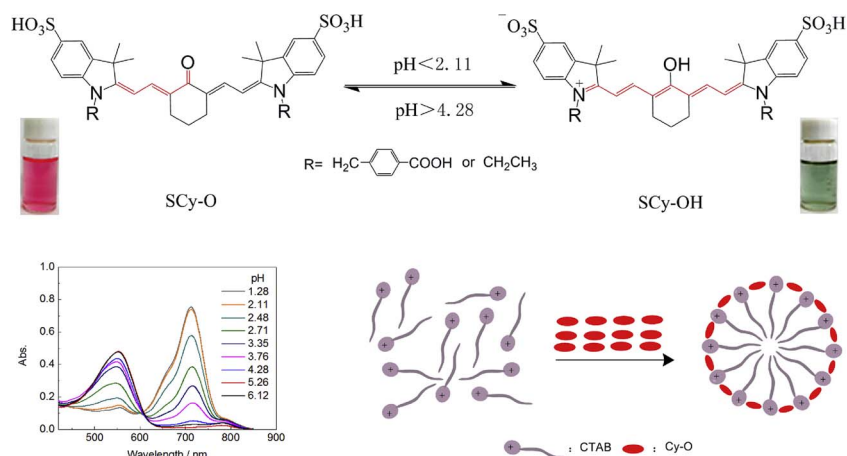


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GRAPHICAL ABSTRACT



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ABSTRACT

In order to detect extreme pH in biosystems, waste water and/or sol/gel formation, six *N*-*p*-carboxybenzyl (or ethyl)-5,5'-bisulfonic heptamethine cyanines (SCy-Cl)s, and their derivatives SCy-Os and SCy-Ns) with spectral absorption and emission in near infrared range were developed, in which the structures of SCy-Os had not been reported before. They all exhibited pH response in water, methanol and/or ethanol, but in different extreme pH conditions. SCy-Os (pKa in 3.02–3.09) reversibly turned to their tautomers (SCy-OHs) at pH 2.11–4.28 accompanying a great change in their maxima absorption and emission wavelengths (from 504–639 nm to 709–762 nm) and the corresponding intensity and in the color of their solutions (from red to green) which made the detection processes recognized by naked eyes. In contrast, SCy-Cl)s and SCy-Ns) took their corresponding tautomerizations at strong basic (pH 9.80–13.90, pKa in 10.41–11.93) conditions rather than acidic condition because of the difference in the meso-atoms (Cl, N, O) and conjugated systems of the cyanine molecules. The interactions between molecules of the cyanines and CTAB in aqueous solutions made not only the absorption and emission wavelengths and intensity of the cyanines vary, but also the pH response turn to more extremely acidic conditions, meanwhile made the CMC of CTAB remarkably decrease. SiO₂ sol and TiO₂ sol also affected the pH

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response due to the interaction of cyanines and the sol particles. So they might have special sensitive pH response in extremely complex acidic and basic environment, and be applied as pH probes in the fields and/or in special materials manufactures.

1. Introduction

Near infrared heptamethine cyanines with meso-chlorine in the conjugated polymethine chain (Cy-Cl)s have been widely used as fluorescence probes in biological imaging and bioanalysis [1–3] for their efficiently avoiding the autofluorescence of biomolecules and tissues. But they usually have small Stokes shift and weak emission intensity and this will affect their detection sensitivity. In order to further improve these spectral properties, various derivatives from Cy-Cl)s by substitution N, O, P or S atoms for the meso-chlorine have been designed and synthesized [4–6], and have more extensive applications in bioimaging, photothermal therapy, dye-sensitized solar cells, and the detection of ions, enzymes, and small molecules [3,7–15].

Recently, pH sensors have been developed more quickly. Nagno et al. [16] explored series ratiometric fluorescence pH aminocyanine probes by the reaction of Cy-Cl with amine compounds like *N,N*-diethyl-*N*'-methylethylenediamine, piperazine, *N*-methylpiperazine or *N*-benzylpiperazine, and made not only the Stokes shifts and strong emission intensity enlarge but also the pKa of the aminocyanine site at pH of 5–9. Strekowski et al. [17–19] developed series of ketone cyanines (Cy-Os) containing carbonyl group (C=O) in the ring of the conjugated polymethine chain, and the Cy-Os showed pH sensitivity at pH 4–7. But most of pH sensors developed are applied in pH 4–9 [20], few for extremely acidic and basic conditions (pH < 4 and pH > 9). They are needed for extreme pH environment, for instance, in some biological environment: helicobacter pylori in human stomach (1.5–3.0) and thiobacillus acidophilus (3.0–3.5); food industry: bacillus pasturii and bacillus calcalophilus (11–12); eutrophic water: cyanobacteria (9–10), and so on. Furthermore, range adjustment of pH response is important for fluorescence probe analysis, self-assembly process [21,22] of supermolecular, surfactant, gel or UV irradiation. Tan et al. [23] developed a type of Cy-O pH probes to detect mitophagy at acidic condition successfully, and found that the pH response range could be adjusted by surfactants.

In order to develop more novel pH probes with better properties, especially for extremely acidic and basic conditions, this paper designed and synthesized two novel ketone cyanines (SCy-Os) with *N-p*-carboxybenzyl and *N*-ethyl from 5,5'-bisulfonic heptamethine cyanines with meso-chlorine cyanines (SCy-Cl)s (Scheme 1). They showed the maxima UV-vis absorption and fluorescence wavelengths in 548–560 nm and 632–639 nm in water and pH response in 2.11–4.28 (pKa in 3.02–3.09), and color of the solutions absolutely turned from red to green. We also detected the pH response of their parents SCy-Cl)s and SCy-Ns (the other derivatives from SCy-Cl)s developed by us before), and found that they exhibited the pH sensitivity at strong basic (pH 9.80–13.90, pKa in

10.41–11.93) conditions rather than the extremely acidic condition. CTAB aqueous solution, TiO₂ sol and SiO₂ sol might regulate the pH response to more extremely acidic conditions. So the six *N-p*-carboxybenzyl (or ethyl)-5,5'-bisulfonic heptamethine cyanines could be used as pH probes, and be applied in extreme pH environment and special materials manufactures.

2. Experimental

2.1. Materials and instruments

Mass spectrometry (ESI-MS) were performed on an Agilent 6460 triple quadrupole mass spectrometer and ¹H NMR spectra were obtained on Bruker-600 MHz NMR spectrometer. Absorption spectra and emission spectra were recorded on a SHIMADZU UV-2550 spectrophotometer and a Hitachi F-7000 FL spectrophotometer, respectively.

2.2. Syntheses of SCy-Cl)s and SCy-Ns

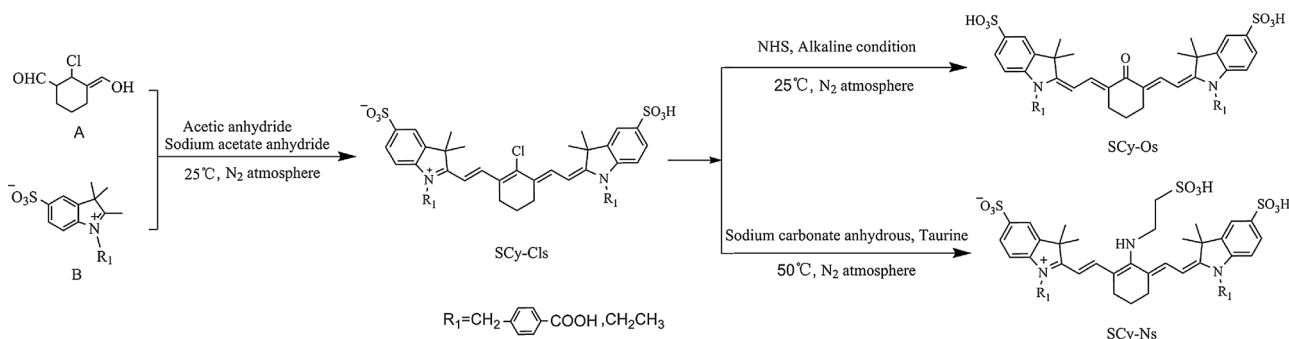
SCy1-Cl and SCy2-Cl were obtained by a condensation of bisaldehyde compound (A) with 1-*p*-carboxybenzyl-5-sulfonic benzoindole (B1) or 1-ethyl-5-sulfonic benzoindole (B2) at a mild condition (Scheme 1), and their corresponding aminoderivatives SCy1-N and SCy2-N were synthesized by substitution of the meso-chlorine of SCy1-Cl and SCy2-Cl by taurine [24].

2.3. Syntheses of SCy-Os

A mixture of 0.2 mmol SCy-Cl (SCy1-Cl 176.6 mg or SCy2-Cl 134.2 mg), 0.6 mmol *N*-hydroxysuccinimide (69 mg), 0.6 mmol alkali (49.6 mg sodium acetate anhydrous or 0.8 ml triethylamine) in 10 ml DMF were stirred at 25 °C for 3 h under nitrogen atmosphere. After addition of ethyl acetate (60 ml) to the mixtures, crude products (SCy1-O and SCy2-O) were obtained by filtration, respectively. The crude products were purified by SiO₂ column chromatography (CH₂Cl₂:CH₃OH = 1:1).

2.3.1. SCy1-O

R_f = 0.22; Yield: 79%; ¹H NMR (600 MHz, MeOD) δ: 8.08 (d, *J* = 13.2 Hz, 2H), 8.00 (s, 2H), 7.93 (d, *J* = 8.1 Hz, 4H), 7.74 (m, 4H), 7.25 (d, *J* = 8.2 Hz, 4H), 5.58 (d, *J* = 13.2 Hz, 2H), 5.08 (s, 4H), 2.37 (m, 4H), 1.73 (s, 12H), 1.36 (m, 2H). ESI-MS: *m/z* calcd for [M–2H]^{2–} = 431.12, [M–3H]^{3–} = 287.08, Found: [M–2H]^{2–} = 431.20, [M–3H]^{3–} = 287.20.



Scheme 1. Synthetic route to SCy-Cl)s, SCy-Os and SCy-Ns.

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