Available online at www.sciencedirect.com
ScienceDirect
Journal of Luminescence 124 (2007) 365–369
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Synthesis and fluorescence study of sodium-2-(4′-dimethyl-aminocinnamicacyl)-3,3-(1′,3′-alkylenedithio) acrylate

Zhenjun Si, Yun Shao*, Chunxia Li, Qun Liu

School of Chemistry, Northeast Normal University, Changchun 130024, PR China

Received 9 January 2006; received in revised form 5 April 2006; accepted 14 April 2006
Available online 5 June 2006

Abstract

We synthesized two new compounds: Sodium 2-(4′-dimethyl-aminocinnamicacyl)-3,3-(1′,3′- ethyl- enedithio) acrylate (STAA-1) and Sodium 2-(4′-dimethyl-aminocinnamicacyl)-3, 3-(1′,3′-propylenedithio) acrylate (STAA-2). The maximum absorption of these compounds ranges from 460 to 520 nm with different molecular structures in different solvents. Meanwhile, the emission peak of these compounds arranges from yellow (510 nm) to red (605 nm). The emission spectra show red shift according to the strength of the hydrogen bonding property of the solvent. But the absorption spectra do not show clearly relationship with the strength of the hydrogen bonding property of the solvent. The Stoke shift of the compounds ranges from 42 to 102 nm. It changes in the following order, EtOH > H_2O > DMF, and STAA-1 > STAA-2 in the same solvent. The fluorescent quantum yield of STAA-1 was measured to be 7.12% with quinine sulphate as the standard compound in ethanol. Furthermore, the relationship of the fluorescence of STAA-1 with pH (ranges form 4 to 14) in water ($c = \sim 10^{-4}$) was studied to make sure that these compounds could be used as proton sensors.

PACS: 07.07.Df; 78.55.−m; 81.20.−n

Keywords: Proton sensor; Fluorescence quantum yield; Synthesis

1. Introduction

π-Conjugated organic compounds have emerged in the past two decades as a promising class of materials for potential applications in photonics and optoelectronics. Lots of active materials used in these fields are the derivatives of aniline. These materials are used in non-linear optics [1], photovoltaic cell [2], light emitting devices [3], and optically pumped lasers [4]. The photo-physical properties of the aromatic amino acids depend on the status of the amino and carboxyl groups although they are separated form chromophore by some methylene groups [5,6] or other groups [7,8], the quenching efficiency is controlled by the orientation of the quenching groups and the process is distance dependent. The rotamer model of fluorescence decays of aromatic amino acids has been supported by some investigations [9–11] that included studies of constrained tryptophan [12,13], tryptophan in protein crystals [14] and tryptophan in peptides with defined secondary structure [15].

For several decades, fluorescence spectroscopy has been widely used for the detection and analysis of different analytes [16,17]. Wavelength-ratiometric [18,19], fluorescence lifetime-based sensing [20,21] and polarization assays [22] are some techniques available for the detection and analysis of analytes by fluorescence spectroscopy. Fluorescence techniques for pH sensor have been used most of the time with enzymes and proteins [23]. Despite some promising results, enzymes and proteins show some stability problems against organic solvents and heat. In contrast, synthetic organic probes show high stability and flexibility due to the versatility of the organic synthesis. Modification of the affinity for the analyte, of the wavelength of emission of the probes and of the immobilization of the probes is in support for the building of a sensor.

*Corresponding author. Tel.: +86 0431 5099667.
E-mail address: shaoy834@nenu.edu.cn (Y. Shao).

0022-2313/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2006.04.005

In this essay, we introduce two compounds we synthesized, present photo-physical properties of STAA-1 and STAA-2 in different solvents in order to study the solvent polarity effects on the photo-physical property, furthermore we present the photo-physical property of STAA-1 in water at different pH value. Up to now, the latest report is about the fluorescent molecular, which contains dithioacetals as we know.

2. Experiment

2.1. Materials

Ethanol (EtOH), *N*,*N*-dimethylformamide (DMF), carbon bisulphide (CS_2), acetic acid ethyl ester, potassium carbonate (K_2CO_3), 1,2-dibromoethane, 1,3-dibromopropane were used as supplied, but only after checking the purity fluorometrically in the wavelength region of interest. The solvent, water, was distilled twice in vacuum and tested for the absence of any emission in the wavelength regions studied.

Absorption and emission spectra were recorded on Shimadzu Model 3100 spectrometer and Hitachi Spectrophotometer model F-4500, respectively. Spectrum correction has been performed in order to measure a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromators or detectors. For all measurements, the sample concentration was restricted at $\sim 10^{-5}$ mol/L in order to avoid the aggregation problems such as self-quenching. The cut-off filter was used to prevent scattering of excitation beam. The relative fluorescent quantum yield of STAA-1 was measured with quinine sulphate as the standard compound in sulphuric acid according to the following equation [24]:

$$\phi_{fx} = n_x^2 \cdot F_x \cdot \phi_{fstd} / n_{std}^2 \cdot F_{std}. \quad (1)$$

2.2. Preparation of materials (Scheme 1)

2.2.1. 3-(1′, 3′)-Dithiolan-2-ylidene-pentane-2, 4-dione Ia

Anhydrous K_2CO_3 (13.8 g) and 6.25 mL acetic acid ethyl ester were added to 100 mL DMF in 250 mL flask, the mixture was stirred 0.5 h and cooled to 0–5 °C, 3.5 mL CS_2 was added, the stirring was continued for another 0.5 h, then 4.75 mL 1,2-Dibromo-ethane was added to the mixture. The mixture was poured into a 400 mL flask with 200 g ice after it was stirred overnight. The deposition was filtrated, the yield of Ia was 98%. (The data of characterization is in Refs. [25,26].)

2.2.2. Sodium-2-(4′-dimethyl aminocinnamicacyl)-3,3-(1′,3′-propylenedithio) acrylate STAA-1

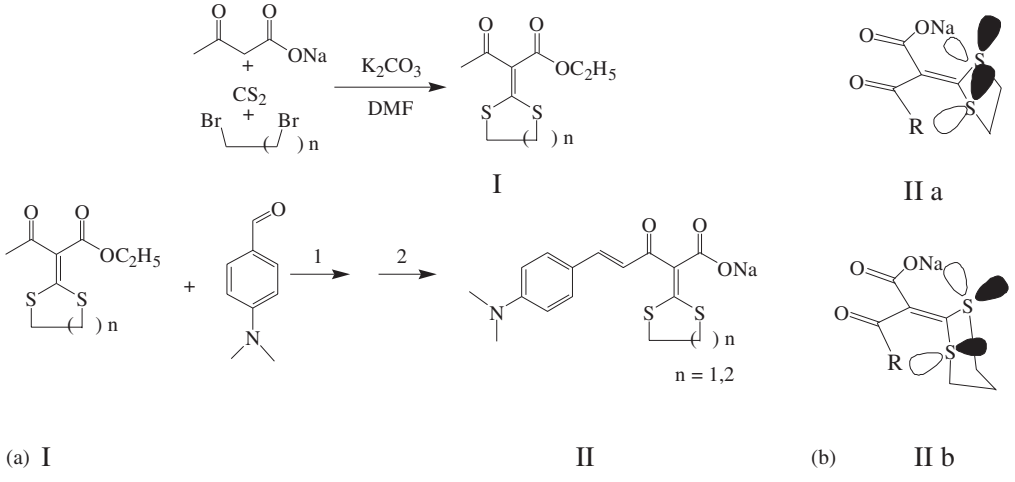
2.2 mmol 4-Dimethylamino-benzaldehyde and 2.0 mmol compound Ia were added into 10 mL EtOH in a 25 mL flask, then 2.0 mmol EtONa was dropped into the flask, then stirred at 70 °C, detected with TLC until the completion of the reaction. Then the yellow solid was filtrated and collected after the mixture was cooled to room temperature. The yield was 70%.

The synthesis of Ib and STAA-2 is similar to that of Ia and STAA-1, respectively.

2.3. Characterization of compounds STAA-1 and STAA-2

STAA-1: Yellow solid, yield: 85%, m.p. 210–211 °C ^{1}HNMR: 7.370 (2 H, d, $J = 21$ ArH), 7.234 (2H, d, $J = 3.8$, ═H), 6.670(2H, d, $J = 3.8$, ═H), 6.549 (1H, d, $J = 21$, ArH), 3.36 (4H, tri, $J = 6$, –SCH_2–), 2.945 (6H, s, –NC_2H_6); IR ν (cm^{-1}) 1579, 1524, 1348, 1182, 3425.

STAA-2: Green-yellow solid, yield: 83%, m.p. 207–208.5 °C ^{1}HNMR 7.407(2H, d, $J = 22$ ArH), 7.301(1H, d, $J = 4$, ═H), 6.797(1H, d, $J = 4$, ═H), 6.718 (2H, d, $J = 22$, ArH), 2.965 (6H, s, –NC_2H_6),



Scheme 1. (a) Synthesis of compounds STAA-1 and STAA-2 and (b) the configurations of compounds STAA-1 and STAA-2.