Dyes and Pigments 136 (2017) 175–181

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Dipyridylphenylamine-based chemodosimeter for sulfite with optimizing ratiometric signals via synchronous fluorescence spectroscopy

Jianwei Wu, Yi Qu*, Linlin Wang, Liliang Huang, Yichuan Rui, Jian Cao**, Jingli Xu

College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, 333 Longteng Road, Shanghai, 201620, PR China

ARTICLE INFO

Article history:
Received 9 July 2016
Received in revised form
16 August 2016
Accepted 22 August 2016
Available online 24 August 2016

Keywords:
Dipyridyltriphenylamine
Synchronous fluorescence spectroscopy
Sulfite ion
Large Stokes shift

ABSTRACT

A dipyridyltriphenylamine derivative, (*E*)-4-(2-nitrovinyl)-*N*,*N*-bis(4-(pyridin-4-yl)-phenyl)aniline, was synthesized as a fluorescent probe for sulfite ion, which can be used in detecting excessive addition of sulfite in the food industry. The chemodosimeter can output far-red to near-infrared emission under both aqueous and solid state conditions exhibiting potential applications in the field of luminescent functional materials. Based on synchronous fluorescence spectroscopy, a ratiometric method was developed for determination of sulfite ion with small overlap in the emission spectrum, whose emission band is narrower than that observed in normal emission spectrum.

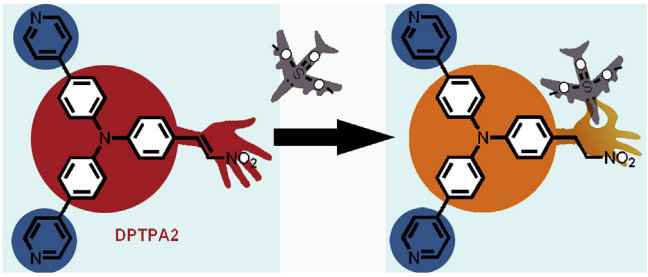
1. Introduction

In recent years, the process in the design and synthesis of small molecular fluorescent probes for different analytes has attracted considerable attention in the field of optical function materials, as anions, metal ions and small molecular markers have shown immense importance in human health and environmental issues [1–6]. Among these species, the sulfite ion, a common substance that naturally occurred in some foods and the human body [7,8], acts as the antimicrobial additive widely used in food, pharmaceutical drugs, paints, biological samples and cosmetics to prevent decomposition by microbial growth or undesirable chemical changes [9]. Therefore, a powerful detection method for the sulfite ion is of great significance [10–13].

With high sensitivity, fast response and multi-wavelength output signals, fluorescent sensors have raised widespread interest within the field of analyst chemistry [14–18]. Nowadays, some researchers attempted to design and use this tool for on-line detection of different biological markers and additives [19–23]. Compared to both “turn on” and “turn off” type sensors, the ratiometric fluorescent sensor has received widespread attention, which can enable the measurement of fluorescent intensities at dual wavelengths and provide a built-in correction in real sample conditions [24–28]. One of the biggest challenges in developing such ratiometric fluorescent probes is that spectral multiplexing of ratiometric mode, which could disturb the fluorescent signals. A common resolving strategy was reported by D. Chiu's group, who fabricated a series of narrow-emission conjugated polymer materials [29]. However, the large amount of organic small molecule probes that can be designed as the ratiometric probe is still limited due to overlapping emission spectra. Therefore, there is an extraordinary need to develop a new protocol that can minimize the overlap area of different emission bands with a narrow spectral width [30]. Herein, we introduced synchronous fluorescence spectroscopy (SFS) in this case which was systematically tuned to obtain narrow emissive signals to distinguish the two emission bands of a ratiometric fluorescent probe [31]. To evidence the feasibility of this strategy, we designed a ratiometric fluorescent probe (**DPTPA2**) containing dipyridyltripenylamine (**DPTPA**) as a signal unit, which showed far red emission with the large Stokes shift under aqueous and solid state conditions [32]. The 2-nitrovinyl group attached on **DPTPA** offered an active site for detecting sulfite ion which is a nucleophilic species (Scheme 1). The difference of intramolecular charge transfer (ICT) states between **DPTPA2** and its sulphite-adduct induced two distinguishable synchronous signals. Fluorescent assays are carried out to explore the

* Corresponding author.
** Corresponding author.
E-mail addresses: quyi@fudan.edu.cn (Y. Qu), caoj@sues.edu.cn (J. Cao).

http://dx.doi.org/10.1016/j.dyepig.2016.08.052
0143-7208/



Scheme 1. The descript of **DPTPA2** and its recognition mechanism towards sulfite.

sensing actions of **DPTPA2** in synchronous fluorescence spectroscopy (SFS) method. ^{1}H and ^{13}C NMR spectra are used to determine the sensing mechanism of our probe.

2. Experimental

2.1. Materials and instruments

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AM-400 spectrometer with tetramethylsilane (TMS) as the internal standard and deuterated chloroform was used as the solvent. Mass spectra were measured on a SHIMADZU LCMS-IT-TOF spectrometer. The melting point was recorded on a Shenguang Melting Point System (WRS-1B). Absorption spectrum was measured on a SHIMADZU UV-3600 spectrophotometer. Fluorescence measurements were performed on a FS-5 spectrophotometer (Edinburgh, Britain) and the slit width was set at 1 nm for excitation and emission, respectively. The relative quantum yield of the chemodosimeter was measured via comparison of the integrated emission intensity and absorbance with those of Cy 5.5 dye (in PBS buffer, $\Phi = 0.28$). Different from normal fluorescence measurements, the Synchronous Fluorescence Spectra were recorded in $\lambda_{ex.}$-intensity relationship (X-Y axis). SEM images were obtained from a SU-8010 scanning electron microscope. TLC analysis was performed on silica gel plates and Silica gel (100–200 meshes) was used for column chromatography. In both absorption or fluorescence measurements, compounds were dissolved in DMSO to obtain stock solutions (0.01 M). The stock solutions were diluted with deionised water or buffer solutions to the desired concentration.

2.2. Synthesis of ratiometric probe DPTPA2

2.2.1. Synthesis of compound DPTPA-CHO

4-[Bis-(4-iodophenyl)amino]benzaldehyde **1** (525 mg, 1 mmol), 4-pyridinylboronic acid (370 mg, 3 mmol), Cs_2CO_3 (650 mg, 2 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.054 mmol) were added in toluene (10 mL). The mixture was stirred at 100 °C under Ar for 4 h. Then the mixture was cooled to room temperature and poured into water and the organic layer was separated and the aqueous phase was extracted with dichloromethane (DCM). The combined organic phases were washed with brine and dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified on column chromatography using DCM/EtOH (70/1, v/v) as eluent to give yellow solid **DPTPA-CHO** (242 mg, 56.7%). m.p.: 128.6–141.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: (ppm) 7.20 (d, $J = 8.0$ Hz, 2 H), 7.30 (d, $J = 8.0$ Hz, 4 H), 7.51–7.52 (m, 4 H), 7.65 (d, $J = 12$ Hz, 4 H), 7.78 (d, $J = 8.0$ Hz, 2 H), 8.66–8.68 (m, 4 H), 9.89 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: (ppm) 121.45, 126.10, 128.37, 130.54, 131.42, 134.37, 145.55, 146.99, 147.22, 150.33, 150.67, 152.44, 190.51. HRMS (*m*/*z*): calcd. for $[M+H]^+$ ($C_{29}H_{21}N_3O$): 427.1685; found: 428.1772.

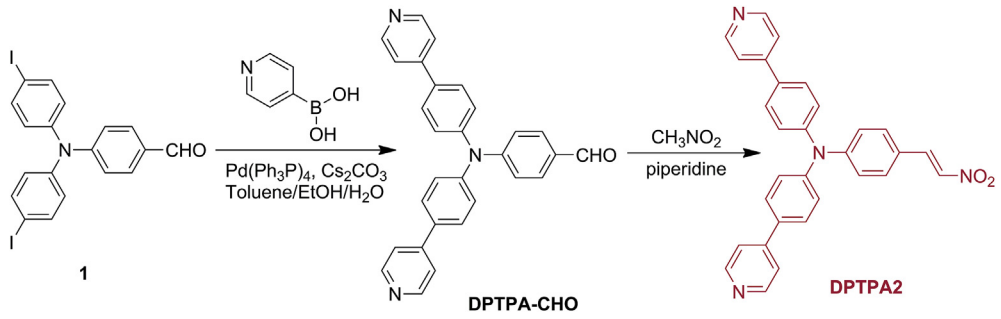
2.2.2. Synthesis of ratiometric probe DPTPA2

DPTPA2 was synthesized according to the literature report without modification. **DPTPA-CHO** (700 mg, 1.64 mmol), nitromethane (126.7 μL, 1.97 mmol), piperidine (233.4 μL, 1.97 mmol) were dissolved in EtOH (5 mL) in a flask. The reaction mixture was stirred overnight at 70 °C and then the solvent was removed under reduced pressure and the residue was purified by column chromatography using acetate/methanol (15/1, v/v) afforded the red solid **DPTPA2** (463 mg, yield 60%). m.p.: 204.5–205.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: (ppm) 8.69 (d, $J = 6.02$ Hz, 4 H), 8.00 (d, $J = 13.55$ Hz, 1 H), 7.66 (d, $J = 8.53$ Hz, 4 H), 7.54–7.58 (m, 1 H), 7.53 (d, $J = 6.27$ Hz, 4 H), 7.48 (m, $J = 8.78$ Hz, 2 H), 7.30 (d, $J = 8.53$ Hz, 4 H), 7.18 (m, $J = 8.78$ Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: (ppm) 150.7, 150.6, 150.3, 147.2, 147.0, 138.6, 135.2, 134.2, 130.8, 128.3, 126.1, 125.8, 123.8, 122.5, 121.4, 121.2. HRMS (*m*/*z*): calcd. for $[M+H]^+$ ($C_{30}H_{22}N_4O_2$): 470.1743; found: 471.1819.

3. Results and discussion

3.1. Design, synthesis and characteristic

Because of the deep tissue penetration of light of long wavelength, the fluorophores with long wave emission in far-red to near-infrared region were important in modern research in biosensing and bioimaging [33]. The strategy we used to design and synthesize the SFS probe for sulfite ion as depicted in Scheme 1 and Scheme 2. **DPTPA2** was synthesized from triphenylamine derivative (1). Two pyridine moieties were introduced into triphenylamine core by typical Suzuki coupling reaction. The nitro group ($-NO_2$), a strong acceptor, was designed to end-cap the vinyl group with **DPTPA**-CHO and nitromethane as substrates through Knoevenagel condensation reaction. The dipyridyltriphenylamine with a π-extended vinyl active site was developed by our group. The direct



Scheme 2. Synthesis routine of probe **DPTPA2**.