

An intramolecular charge transfer fluorescent probe: Synthesis and selective fluorescent sensing of Ag^+

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Abstract

An intramolecular charge transfer (ICT) fluorescent probe, in which the thiourea derivative moiety is linked to the fluorescent 4-(dimethylamino)benzamide, has been designed and synthesized. The ions-selective signaling behaviors of the probe were investigated. Upon the addition of Ag^+ , an overall emission enhancement of 14-fold was observed. Compound **1** displayed highly selective chelation enhanced fluorescence (CHEF) effect with Ag^+ over alkali, alkali earth metal ions and some transition metal ions in aqueous methanol solutions. The prominent selective and efficient fluorescent enhancing behavior could be utilized as a new chemosensing probe for the analysis of Ag^+ ion in aqueous environment.

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1. Introduction

Fluorescent probes capable of selectively recognizing guest species are of particular interest in supramolecular chemistry because of their high selectivity, sensitivity, and simplicity [1]. Especially, fluorescent sensing of heavy and transition metal (HTM) ions have received increasing attention due to their importance in many biological processes and environmental relevancy [2]. In the previous literatures, a number of fluorescent probes for HTM ions have been reported [3]. Most of them display fluorescence intensity changes, but relatively few of them result in fluorescence enhancing with HTM analytes, such as Hg (II), Pb (II), Ag (I), and Cu (II), since these ions generally act as quenchers via the electron transfer or facilitated intersystem crossing (isc) processes.

It is generally believed that sensors with a fluorescence enhancement signal when interacting with analytes are much more efficient. Whereas, the examples of Ag^+ -selective fluorescence enhancement probes have been still scarce [4]. Therefore the development of new fluorescent Ag^+ sensors, especially those that exhibit selective Ag^+ -amplified emission, is still a challenge.

The intramolecular charge transfer (ICT) mechanism has been widely exploited for metal ions sensing [2a,b,5]. In most cases, the ionophore is the electron-donor or electron-deficient substituent of the fluorophore and coordination of a metal ion leads to a pronounced blue or red shift of the intramolecular charge transfer absorption band but often to change in fluorescence intensity [6]. It is known that the excited-state intramolecular charge transfer and the accompanied dual fluorescence of the electron donor/acceptor substituted benzenes such as 4-(dimethylamino)benzonitrile (DMABN) and 4-(dimethylamino)benzamide (DMABA). The generally favored concept to explain the anomalous, long wavelength fluorescence is a TICT state [7]. The dual fluorescent behavior depends sensitively on the nature of the electron donor/acceptor [8], therefore it is possible to design fluorescent sensors for metal ions sensing. In this paper we report an intramolecular charge transfer (ICT) fluorescent probe, in which the thiourea derivative moiety is linked to the fluorescent 4-(dimethylamino)benzamide, and its Ag^+ ion-selective signaling behaviors. The fluorophore in this fluorescent probe is a strong “push–pull” π -electron system, with an aniline nitrogen atom as an electron donor and a carbonyl as an electron acceptor. Based on the principle of hard and soft acids and bases, the S atom in the thiourea moiety tends to coordinate the Ag^+ [9]. Therefore, we can expect that the complexation of Ag^+ ion will have a dramatic influence

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upon the emission of fluorophore and transmit the signal of recognition.

2. Experimental

2.1. Reagents and apparatus

Absorption spectra were determined on a UV-2550 UV–visible spectrophotometer. Fluorescence spectra were determined on a F-4500 fluorescence spectrophotometer. Melting points were determined on a X-6 micro-melting point apparatus and were uncorrected. IR spectra were obtained on a Nicolet 170SX FT-IR or a Shimadzu FT-IR 8000 spectrophotometer. NMR spectra were recorded on Varian Mercury VX300 FT-NMR spectrometer with $(\text{CH}_3)_4\text{Si}$ as internal reference. Elemental analyses were determined on a Perkin-Elmer 204B elemental auto analysis apparatus. Twice-distilled water was used throughout the experiments. All the materials for synthesis and test were purchased from Shanghai Chemicals (Shanghai, China) and used as received. Except specified, other chemicals were analytical reagent grade and used without further purification. The solutions of metal ions were prepared from their acetate salts, except for Pb^{2+} , Ag^+ from nitrate and Fe^{2+} from sulfate, respectively.

^1H NMR studies were recorded after adding two equivalents Ag^+ into probe (20 mM) in $\text{DMSO}-d_6$. The effect of the metal ions upon the absorption and fluorescence intensity was examined by adding a few microliters of stock solution of the metal cations to a known volume of the solution (2 mL). The addition was limited to 0.1 mL, so that dilution remained insignificant. Association constants (1:2) of **1** with Ag^+ are calculated by followed equation [10] and linearly fitted in origin 7.0:

$$\log \left[\frac{(X - X_0)}{(X_\infty - X)} \right] = n \log[G] + \log K_d$$

X_0 : fluorescent intensity of host without guest; X_∞ : fluorescent intensity reaching a limitation by adding excessive guest; n : the stoichiometric ratio of host and guest; $[G]$: concentrations of guest.

2.2. Synthesis of **1** and **2**

The synthetic route of **1** and **2** is shown in Scheme 1. 4-(dimethylamino)benzoic acid [11](5). 3.2 g(0.019 mol) AgNO_3 was dissolved into a 60 mL potassium hydroxide aqueous solution (7%) and 1.5 g(0.01 mol) 4-(dimethylamino)-benzaldehyde was added into this solution. The mixture was stirred at 60°C for 24 h, then cooled to room temperature, and filtered. After the solution was acidified with concentration hydrochloric acid, the product precipitated gradually. The solid was filtrated and then recrystallized from ethanol to give white needle product **5** in 89% yields: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.98(\text{d}, J = 8.1 \text{ Hz}, 2\text{H}), 6.68(\text{d}, J = 8.1 \text{ Hz}, 2\text{H}), 3.06(\text{s}, 6\text{H})$.

4-(dimethylamino)benzoic acid ethyl ester [12] (4). In a 100 mL round-bottomed flask was placed 3.0 g(0.018 mol) 4-(dimethylamino)benzoic acid with 50 mL alcohol. Then 2 mL concentrated sulfuric acid was added dropwise under vigorous

stirring. The solution was allowed to reflux for 6 h and cooled to room temperature. Saturated aqueous sodium carbonate was added with stirring until pH was 7–8. The precipitated product was filtered and recrystallized from ethanol and water (1:1) to give white crystals **4** in 71% yields: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.93(\text{d}, J = 8.7 \text{ Hz}, 2\text{H}), 6.66(\text{d}, J = 8.7 \text{ Hz}, 2\text{H}), 4.33(\text{q}, J = 7.2 \text{ Hz}, 2\text{H}), 3.03(\text{s}, 6\text{H}), 1.36(\text{t}, J = 7.2 \text{ Hz}, 3\text{H})$.

4-(dimethylamino)benzoic acid hydrazide (3). In a 100 mL round-bottomed flask was placed 1.0 g(0.005 mol) 4-(dimethylamino)benzoic acid ethyl ester with 50 mL alcohol. Then 5 g hydrazine hydrate (85%) was dropped into under stirring. The solution was allowed to reflux for 2 days. The reaction mixture was allowed to cool to room temperature and evaporated under reduced pressure to give a solid. The solid recrystallized from ethanol to give white product **3** in 75% yields: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.68(\text{d}, J = 8.7 \text{ Hz}, 2\text{H}), 7.29(\text{s}, 1\text{H}), 6.68(\text{d}, J = 8.7 \text{ Hz}, 2\text{H}), 4.06(\text{s}, 2\text{H}), 3.02(\text{s}, 6\text{H})$.

N-4-(dimethylamino)benzamido-*N'*-1-naphthylthiourea (1). A mixture of 0.72 g (0.004 mol) **3** and 0.74 g(0.004 mol) 1-naphthyl isothiocyanate were stirred to dissolve in 50 mL ethylene glycol monomethyl ether. The mixture was then stirred at room temperature for 8 h and filtered. The solid was washed with ethanol ($3 \times 50 \text{ mL}$) and further dried under a vacuum pump to afford 0.88 g white powder product **1** in 67% yield: ^1H NMR (300 MHz, $\text{DMSO}-d_6$): $\delta = 10.31(\text{s}, 1\text{H}), 9.96(\text{s}, 1\text{H}), 9.65(\text{s}, 1\text{H}), 7.97\text{--}7.90(\text{m}, 2\text{H}), 7.85\text{--}7.81(\text{m}, 3\text{H}), 7.50\text{--}7.46(\text{m}, 3\text{H}), 7.32(\text{d}, J = 9.0 \text{ Hz}, 1\text{H}), 6.71(\text{d}, J = 9.0 \text{ Hz}, 2\text{H}), 2.95(\text{s}, 6\text{H})$. ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): $\delta = 183.4, 166.8, 153.1, 136.6, 134.3, 131.5, 130.1, 128.4, 127.4, 127.1, 126.6, 126.4, 126.0, 124.6, 119.6, 111.2$; IR (KBr): ν/cm^{-1} 3336.6, 3298.0, 3261.0, 1649.9, 1603.3, 1501.0, 1464.1, 1295.1, 1203.0, 769.1; EI MS found: $m/z = 364.2$ (M^+); Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{OS}$: C 65.91, H 5.53, N 15.37; found: C 65.76, H 5.55, N 15.34.

N-4-(dimethylamino) benzamido-*N'*-1-naphthylurea (2). A mixture of 0.72 g(0.004 mol) **3** and 0.70 g(0.004 mol) 1-naphthyl isothiocyanate were stirred to dissolve in 50 mL ethylene glycol monomethyl ether. The mixture was then stirred at room temperature for 12 h and filtered. The solid was washed with ethanol ($3 \times 50 \text{ mL}$) and further dried under a vacuum pump to afford 0.94 g white powder product **2** in 55% yield: ^1H NMR (300 MHz, $\text{DMSO}-d_6$): $\delta = 10.07(\text{s}, 1\text{H}), 8.89(\text{s}, 1\text{H}), 8.34(\text{s}, 1\text{H}), 8.1(\text{d}, J = 9.0 \text{ Hz}, 1\text{H}), 7.92(\text{d}, J = 9.0 \text{ Hz}, 1\text{H}), 7.82(\text{d}, J = 9.0 \text{ Hz}, 3\text{H}), 7.65(\text{d}, J = 9.0 \text{ Hz}, 1\text{H}), 7.59\text{--}7.43(\text{m}, 3\text{H}), 6.73(\text{d}, J = 9.0 \text{ Hz}, 2\text{H}), 2.98(\text{s}, 6\text{H})$; ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): $\delta = 167.1, 157.2, 153.1, 135.1, 134.4, 129.6, 128.9, 126.5, 126.4, 126.3, 124.1, 122.6, 119.6, 111.4$; IR(KBr): ν/cm^{-1} 3277.7, 1650.1, 1598.7, 1552.1, 1485.5, 1205.6, 765.8; EI MS found: $m/z = 347.9$ (M^+); Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2$: C 68.95, H 5.79, N 16.08; found: C 69.03, H 5.80, N 16.03.

3. Results and discussion

The metal ion binding properties of compound **1** were investigated by UV–vis absorption and fluorescence spectroscopy. The titration experiments were carried out in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ sys-

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