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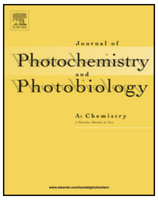

A tetraphenylethylene-based “turn on” fluorescent sensor for the rapid detection of Ag^+ ions with high selectivity

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ABSTRACT

A new fast-responsive “turn on” fluorescent sensor for Ag^+ was successfully developed by taking advantage of the aggregation-induced emission (AIE) property of tetraphenylethylene motif with a detection limit of 8.74×10^{-7} M. The sensor exhibits highly selective and sensitive recognition toward Ag^+ ions over the other 12 metal ions due to the high electrophilic and thiophilic character of Ag^+ ions. The ^1H NMR titration and dynamic light scattering (DLS) spectra conclude that the binding of the sensor with Ag^+ ions forms fluorescent nanoaggregates in aqueous media due to its AIE enhancement. A stoichiometric ratio (1:2) of the sensor and Ag^+ was determined by a Job’s plot.

1. Introduction

Silver is widely used in many industrial fields such as chemistry, pharmacies, photography, and electrical industries [1,2], thus a large amount of silver is discharged into the environment annually from industrial wastes in a variety of chemical forms. As silver ions (Ag^+) can bond with various metabolites such as amine, imidazole and carboxyl groups in enzymes/proteins, it will lead to enzymes/proteins inactivation and bio-accumulation [3,4]. Thus, it is an important research field to develop sensitive and selective methods for detecting and monitoring trace amounts of Ag^+ in various media.

Some traditional methods such as ion-selective electrodes [5], inductively-coupled plasma emission mass spectrometry [6,7], atomic absorption spectrometry [8] and electrochemical method [9] have been employed to detect trace level of Ag^+, but most of them are expensive and time-consuming. Recently, researchers are interested in developing fluorescence probes for Ag^+, which only need simple instruments and are easy to operate. Unlike other transition metal ions such as Cu^{2+} [10] and Fe^{2+}, Ag^+ is spectroscopically and magnetically silent because of its [Kr] $4d^{10}5s^0$ quenching electron configuration [11,12]. As a result, it is a challenge to design a fluorescence “turn on” sensor to discriminate Ag^+ from other chemically similar ions [13].

In recent years, AIE materials have drawn considerable research attention because of their applications in various fields, such as organic light emitting devices and sensors [14–16]. The restricted intramolecular rotation (RIR) is the main mechanism for AIE effect [17]. These materials display excellent fluorescence stability and overcome the drawback of traditional organic dyes [18,19]. Although Liu et al. [20] reported sensors for Ag^+ based on tetraphenylethylene, their applications are limited due to the quenching interference of Hg^{2+}.

Herein, we developed a new fluorescence “turn on” sensor for the detection of Ag^+. The sensor (TPE-4DDC) (Scheme 1) with AIE characteristics shows a strong anti-interference capacity for various metal ions. The selective dimethyldithiocarbamate (DDC) moiety can bind with Ag^+ based on the electrophilic and thiophilic character of Ag^+ [21,22]. As a result, the sensor is non-emissive in solution but becomes strongly emissive after addition of Ag^+.

2. Experimental methods

2.1. Chemicals and instruments

Unless otherwise noted, reagents were purchased from commercial supplies and used without further purification. Solvents and twice-distilled water were purified by standard methods. All metal ions solutions were prepared from their nitrate salts ($AgNO_3$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Cr(NO_3)_3$, $Al(NO_3)_3$, $Fe(NO_3)_3$, $Ba(NO_3)_2$ and $NiNO_3$) in distilled water with a concentration of

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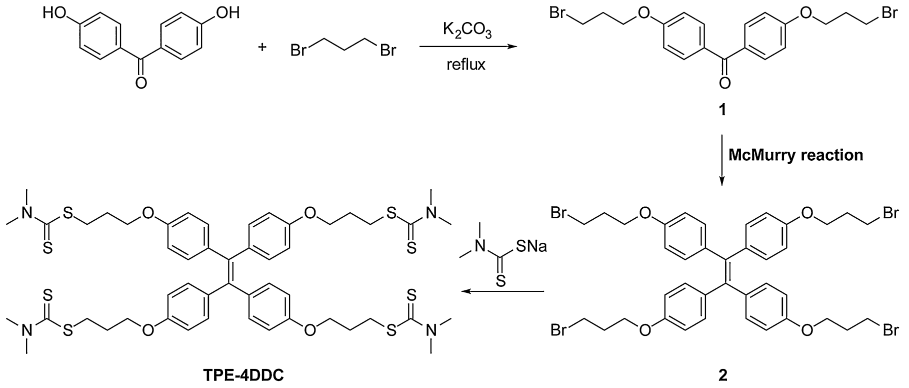

Scheme 1. Synthesis of TPE-4DDC.

10 mM, respectively. The different Ag^+ solutions were prepared from $AgClO_4$, $AgCF_3SO_3$, $AgNO_3$, $AgBF_4$ and AgOAc in distilled water, with a concentration of 10 mM, respectively. All UV–vis absorption and fluorescence spectra were measured in 20 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer solution (pH = 7.0) unless otherwise noted. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (200–300 mesh).

The melting points were measured on an YRT-3 (Tianjin Xintian Optical Analytical Instruments Co., Ltd.) melting point apparatus without calibration. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 300 MHz or 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts were reported relative to Me_4Si for ^1H and ^{13}CNMR spectra. Mass spectra were obtained from DSQ (Thermo) and LCMS-2010A (Shimadzu). High-resolution mass spectrometry (HRMS) was performed on MAT95XP (Thermo). FT-IR spectra were recorded as KBr pellets on an IR-Nicolet Avatrar 330 spectrometer at room temperature. UV–vis absorption spectra were characterized by a UV-3150 spectrophotometer (Shimadzu) at room temperature. Fluorescence emission spectra were investigated by a RF-5301 (Shimadzu) at room temperature. Quantum yields were measured by a photoluminescence spectrometer (FLS-980, Edinburgh Instruments Ltd) at room temperature.

2.2. Synthesis

2.2.1. Synthesis of compound 1

A mixture of 4,4′-dihydroxybenzophenone (5.00 g, 23.3 mmol), 1,3-dibromopropane (14.20 g, 70.0 mmol) and K_2CO_3 (9.50 g, 70.0 mmol) in dry DMF (50 mL) was stirred under Ar atmosphere at room temperature for 24 h. After reaction, the resulting mixture was extracted with ethyl acetate (3 × 20 mL). Then the organic phase was washed with saturated brine (20 mL) and dried over Na_2SO_4. After removing solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using petroleum ether (60–90 °C) and EtOAc (v/v, 10/1) as eluent. A white powder of compound **1** was obtained in a yield of 26.0% (2.36 g). mp = 62.4–63.7 °C; ^1H NMR (300 MHz, $CDCl_3$), δ: 7.76 (d, *J* = 8.7 Hz, 4H), 6.94 (d, *J* = 8.7 Hz, 4H), 4.18 (t, *J* = 5.8 Hz, 4H), 3.61 (t, *J* = 6.3 Hz, 4H), 2.39–2.31 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 194.74, 161.73, 132.06, 130.79, 113.87, 65.52, 32.23, 29.74. MS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{20}Br_2O_3Na$: 479.0; Found: 478.7.

2.2.2. Synthesis of compound 2

A suspension of $TiCl_4$ (0.78 mL, 7.0 mmol) and Zn powder (0.92 g, 14.0 mmol) in 35 mL of dry THF was refluxed under Ar atmosphere for 2 h. A solution of compound **1** (1.60 g, 3.50 mmol) in dry THF (15 mL) was added to the suspension of the titanium reagent and the reaction was refluxed for 10 h at 80 °C. The reaction mixture was cooled to room temperature and a 10% aqueous K_2CO_3 solution (50 mL) was added. The dispersed insoluble material was removed by vacuum filtration using a celite pad after vigorous stirring for 5 min. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). Then the combined organic phase was dried over Na_2SO_4 and concentrated in vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether (60–90 °C)/EtOAc/CH_2Cl_2 (v/v/v, 10/1/1) as eluent. The product was obtained as white powder in a yield of 57.0% (0.88 g). mp = 118.2–120.1 °C. ^1H NMR (400 MHz, $CDCl_3$), *δ*: 6.91 (d, *J* = 8.8 Hz, 8H), 6.62 (d, *J* = 8.8 Hz, 8H), 4.01 (t, *J* = 5.8 Hz, 8H), 3.56 (t, *J* = 6.4 Hz, 8H), 2.29–2.23 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$), *δ*: 156.84, 138.29, 136.98, 132.48, 113.57, 65.05, 32.40, 30.05. MS (EI) *m*/*z*: $[M]^+$ Calcd for $C_{38}H_{40}Br_4O_4$: 880; Found: 880. HRMS (EI) *m*/*z*: $[M]^+$ Calcd for $C_{38}H_{40}Br_4O_4$: 879.9614; Found: 879.9627.

2.2.3. Synthesis of TPE-4DDC

A mixture of compound **2** (0.41 g, 3.50 mmol), sodium dimethyldithiocarbamate (0.40 g, 14.00 mmol) and KI (0.14 g, 1.4 mmol) in acetone (15 mL) was refluxed for 20 h under Ar atmosphere. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using petroleum ether (60–90 °C)/EtOAc (v/v, 5/1) as eluent. A white powder of TPE-4DDC was obtained in a yield of 41% (0.18 g). mp = 134.4–136.4 °C. ^1H NMR (300 MHz, DMSO-d_6), *δ*: 6.82 (d, *J* = 8.1 Hz, 8H), 6.67 (d, *J* = 8.1 Hz, 8H), 3.96–3.92 (m, 8H), 3.44 (s, 12H), 3.33–3.28 (m, 20H), 2.05–2.01 (m, 8H). ^{13}C NMR (75 MHz, DMSO-d_6), *δ*: 194.80, 156.45, 137.82, 136.15, 131.81, 113.60, 65.94, 44.85, 41.24, 33.35, 28.13. IR (cm^{-1}): 3428.51, 2921.74, 1605.09, 1506.30, 1374.29, 1290.23, 1242.17, 1172.56, 1143.28, 1038.79, 983.32. MS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{50}H_{65}N_4O_4S_8$: 1041.2; Found: 1041.0. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{50}H_{65}N_4O_4S_8$: 1041.27660; Found: 1041.27691.

3. Results and discussion

3.1. AIE studies

The AIE properties of TPE-4DDC were examined by studying the fluorescence behavior of its diluted solution in H_2O/THF under different H_2O fractions (Fig. 1). TPE-4DDC has four phenyl rings with intramolecular rotations that quench its emission, however, when it turns into an aggregated form, the intramolecular coordinations occur. Accordingly, the intramolecular rotations are restricted and the non-radiative decay channels are hindered. As a result, TPE-4DDC