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Ratiometric glyco-probe for transient determination of thiophenol in full aqueous solution and river water

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ABSTRACT

Although being widely used in organic synthesis, thiophenol (Tp) is toxic to the human body. We report here the preparation of a ratiometric fluorescence probe for the selective, transient determination of Tp in full aqueous solution. The probe was synthesized by a click reaction coupling between an alkynyl naphthalimide-dansyl dyad and an azido galactoside which increases the water solubility. Fluorescence spectroscopic analyses showed that the probe had a specific ratiometric response to Tp transiently in a full aqueous solution, over a range of other species. The probe has also proven suitable for the quantification of Tp in environmental water samples, and possesses superior properties to previous Tp fluorescence probes in terms of water solubility and sensitivity.

1. Introduction

Thiophenol (Tp) is a crucial reaction intermediate for organic syntheses, and can be used for the construction of a variety of drugs, catalysts and fuels [1,2]. However, Tp is also a highly toxic pollutant with the median lethal dose (LC_{50}) ranging from 0.01 to 0.4 mM for fish. Exposure to Tp can lead to a series of deleterious effects including central nervous system damage, muscle weakness, increased respiratory, hind limb paralysis, coma and, even death [3–5]. Meanwhile, Tp is explosive in case of the improper control of fire, high temperature and oxidant. Therefore, monitoring of Tp in environmental samples using simple, rapid and sensitive techniques is of great importance. The traditional approach for detection of Tp mainly depends on the employment of GC-MS and HPLC. Despite their accuracy and repeatability, these techniques have some substantial limitations such as high detection cost, long detection time and onerous conducting procedures.

Small-molecule fluorescence (FL) probes, because of their high sensitivity, concise detection procedure and easy-to-manipulate detection facility, have become the agent of choice for measuring environmental pollutants [6–16]. Recently, a number of FL probes for Tp have been developed [17–24]. The design rationale of the majority of the probes lies in the covalent coupling of the strong electron-withdrawing 2,4-dinitrobenzene group with a fluorophore (to quench the FL of the fluorophore due to photoinduced electron transfer (PET)) via a linkage cleavable by Tp. On the basis of this rationale, Wang et al. [18] reported the first reaction-based "off-on" Tp probe which can selectively react with Tp in a phosphate buffer with a limit of detection (LOD) of 2.0 μM. Since then, a number of similar probes have been developed [19–24]. Alternatively, Zhao et al. [25] prepared a ratiometric Tp probe based on a boron-dipyrromethene (BODIPY) scaffold with a LOD of 34 nM. Although this probe gives a more specific ratiometric detection signal (that avoids the interference caused by variation of detection environment, facility, probe concentration, etc.), the detection requires the presence of 50% ethanol as co-solvent because of the limited water solubility. Collectively, previous Tp FL probes developed suffer from potentially inaccurate detection signal (fluorimetric), long reaction time (generally >10 min) and, especially unsatisfactory water solubility.

The naphthalimide structure has found application in many fields of chemistry due to its unique optical features. Both the naphthalene and the *N*-imide site can be easily modified to tune the phytophysical properties of naphthalimide. As a consequence, the 1,8-naphthalimide structure has been extensively employed for the development of chemosensors [26]. Considering that the dansyl

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moiety has been widely used for the construction of thiol-reactive molecular probes [27–29], here we report the simple construction of a ratiometric Tp probe based on a glycosyl naphthalimide-dansyl dyad for the transient detection of Tp in full aqueous solution with nanomolar LOD (Fig. 1). The probe has also proven suitable for monitoring trace Tp in environmental river water samples.

2. Materials and methods

2.1. General

All purchased chemicals and reagents are of analytical grade. Solvents were purified by standard procedures. Reactions were monitored by TLC (thin-layer chromatography) using E-Merck aluminum precoated plates of Silica Gel. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer using tetramethylsilane (TMS) as the internal standard (chemical shifts in parts per million). High resolution mass spectra were recorded on a Waters LCT Premier XE spectrometer using standard conditions (ESI, 70 eV). Analytical HPLC was measured using Agilent 1100 Series equipment.

2.2. Synthesis of **2**

To a solution of **1** (500 mg, 1.50 mmol) in anhydrous dichloromethane (20 mL) under nitrogen atmosphere was added Et_3N (226 mg, 2.20 mmol). After stirring for 10 min, a dichloromethane (10 mL) solution of dansyl chloride (402 mg, 1.50 mmol) was added dropwise at 0 °C. The mixture was stirred for another 4 h at room temperature, followed by removal of solvent under reduced pressure. The resulting residue was purified by column chromatography on silica gel (DCM/MeOH = 10:1, v/v) to afford **2** (218 mg, 82%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.86 (s, 6H), 3.13 (t, J = 1.2 Hz, 1H), 3.27 (t, J = 4.0 Hz, 4H), 3.47 (t, J = 4.0 Hz, 4H), 4.75 (s, 2H), 7.31 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.71–7.79 (m, 2H), 8.23 (d, J = 4.0 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.41–8.44 (m, 2H), 8.49 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 28.9, 45.1, 45.4, 52.2, 72.8, 79.4, 115.4, 115.6, 115.7, 119.0, 122.0, 123.8, 125.3, 126.3, 128.3, 128.9, 129.7, 130.2, 130.9, 131.0, 132.3, 132.7, 151.4, 155.2, 162.1, 162.7. HR-ESI-MS m/z: $[M + H]^+$ calcd. for 533.1910, found 533.1902. HPLC: t_R = 6.7 min over 20 min of eluent (methanol), purity 97%.

2.3. Synthesis of ***KB5***

To a solution of **2** (200 mg, 0.36 mmol) and **3** (74 mg, 0.36 mmol) in CH_2Cl_2/H_2O (5 mL/5 mL) were added sodium ascorbate (280 mg, 1.40 mmol) and $CuSO_4 \cdot 5H_2O$ (265 mg, 1.07 mmol). The resulting mixture was stirred over night at room temperature, and was directly purified by column chromatography on silica gel (DCM/MeOH = 30:1, v/v) to afford **KB5** (218 mg, 80%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.86 (s, 6H), 3.26 (t, J = 4.0 Hz, 4H), 3.44–3.48 (m, 7H), 3.63–3.69 (m, 2H), 3.90–3.96 (m, 1H), 4.54 (d, J = 4.0 Hz, 1H), 4.68 (t, J = 8.0 Hz, 1H), 4.95 (d, J = 8.0 Hz, 1H), 5.15 (d, J = 4.0 Hz, 1H), 5.29 (s, 2H), 5.45 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 12.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.71–7.78 (m, 2H), 8.12 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.40–8.43 (m, 2H), 8.48 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 35.2, 45.1, 45.4, 52.2, 60.4, 68.4, 69.2, 73.6, 78.4, 88.0, 115.4, 115.7, 116.2, 118.9, 121.7, 122.4, 123.8, 125.4, 126.3, 128.3, 129.1, 129.2, 129.7, 130.2, 130.5, 130.7, 130.9, 132.2, 132.7, 143.3, 151.5, 155.1, 162.7, 163.3. HR-ESI-MS m/z: $[M + H]^+$ calcd. for 758.2608, found 758.2601. HPLC: t_R = 3.3 min over 20 min of eluent (methanol), purity 99%.

2.4. Spectroscopic measurements

Stock solution of **KB5** (5 mM) was prepared in DMSO. Stock solutions of 0.1 M of PhOH, $PhNH_2$, $CH_3(CH_2)_{11}SH$, CH_3CH_2SH, $PhCH_2SH$, thiophenol, *p*-nitro-thiophenol and *p*-amino-thiophenol were prepared in DMSO and those of GSH, Cys and glycine were prepared in deionized water. The fluorescence measurements were carried out with a path length of 10 mm and an excitation wavelength at 260 nm by scanning the spectra between 270 nm and 750 nm. The bandwidth for both excitation and emission spectra was 10 nm. Unless otherwise mentioned, all the spectra were recorded in aqueous solution at 25 °C. The limit of detection was calculated with the following equation:

$$\mathrm{LOD} = 3\sigma/k \quad (1)$$

where σ is the standard deviation of blank measurement and k the linear correlation slope of ratio I_{414}/I_{534} vs. the concentrations of Tp.

2.5. Quantification of Tp in river water

Water samples were collected from Huang-Pu River of Shanghai and Qing-Chun River of East China University of Science and

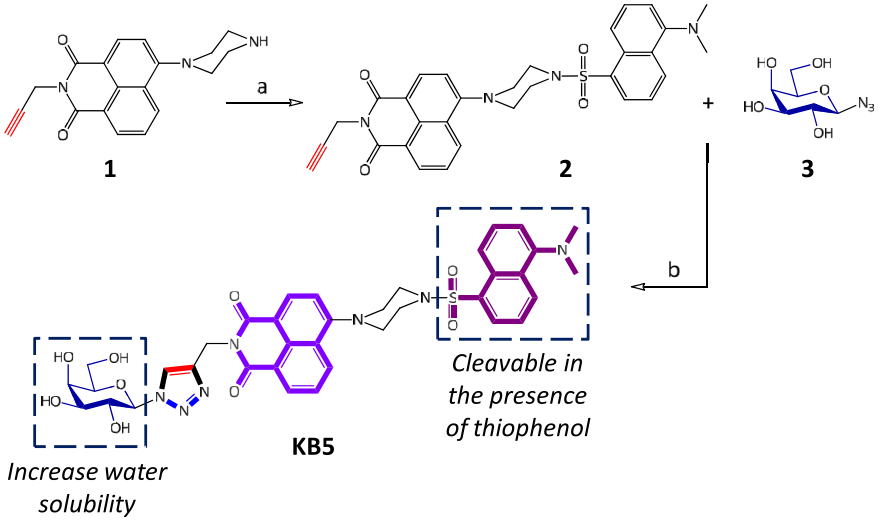

Fig. 1. Reagents and conditions: (a) Et_3N, CH_2Cl_2; (b) $CuSO_4 \cdot 5H_2O$, sodium ascorbate in CH_2Cl_2/H_2O (1:1, v/v).