



Research paper

A hydroxyquinoline-base nanoprobe for fluorescent sensing of Hg²⁺ ion in aqueous solutionLi-Na Liu¹, Lu He¹, Yun Qu, Nong Lu, Qian-Yong Cao^{*}, Zhaohua Yan^{*}

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ABSTRACT

A new amphiphilic probe **Q-16** bearing a hydroxyquinoline ring and a long hydrophobic cetyl chain has been synthesized and characterized. In aqueous solution, this probe can self-assemble fluorescent nanostructure aggregation, which is confirmed by the tyndall scattering experiment, dynamic light scattering (DLS) and transmission electron microscopy (TEM) techniques. Upon the addition of Hg²⁺, this probe shows a fluorescence quenching effect without interference from other metal ions. The detection limit of **Q-16** to Hg²⁺ is 4.42 nM. ¹H NMR titrations and DFT calculation results reveal that the triazole ring, the quinoline ring and the ether O atom of **Q-16** play an important role for binding with the Hg²⁺ center. However, probe **Q-16** shows sensing of Hg²⁺, Cd²⁺, Ni²⁺, Cu²⁺ and Al³⁺ in CH₃CN solution. Importantly, sensitivity and selectivity of **Q-16** toward Hg²⁺ in aqueous solution is higher than that in CH₃CN solution for aggregation.

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1. Introduction

Fluorescent organic nanoparticles have attracted much attention for their diversity in molecular structure, unique optical properties, low-cost and good biocompatibility [1–4]. Recently research has witnessed that the fluorescent organic nanoparticles are also good candidates for detecting important analytes in environmental and biological systems [5–8]. Compared with the small organic probes, the nanoprobe shows unique advantages including good water soluble, more sensitivity and selectively, and better biocompatibility. The nanoprobe for detecting metal ions, anions, and biomolecules have been reported [9–16]. Until now, different methods such as emulsification evaporation, emulsification diffusion, laser ablation and reprecipitation method [17–22], have been developed for preparing fluorescent organic nanoparticles. Among them, the reprecipitation method of self-assembling amphiphilic compounds has achieved particular attention for its simplicity and easily controlling. The amphiphilic compounds have a hydrophilic head and a hydrophobic tail, and can easily assemble micellar-like nanoparticles when the concentration is higher than their critical micelle concentration.

As one of high toxic heavy metal ions, Hg(II) intake and bioaccumulation has serious impact to human health such as kidney failure, Minamata disease, and neural disorders [23,24]. Thus, the

development of Hg(II) chemosensors with high sensitivity and selective functions is greatly desired [24–26]. Some traditional method such as atomic spectroscopy, electrochemical analysis have established for detection environmental Hg(II) [27–29]. Importantly, fluorescence method based on small organic molecules was also well established for its high selectivity and sensitivity, and easily carrying out on-site testing. Many fluorescent chemosensors have been reported for sensing and detection of Hg(II) [30–40]. Owing to the poor solubility of the organic compounds, most of these probes work only in organic and/or semi-aqueous solutions, examples for working in pure aqueous solution are still rare.

Herein, we design and synthesize a fluorescent chemical sensor **Q-16** (Scheme 1) by triazole linked a hydroxyquinoline ring and a hydrophobic cetyl chain. Hydroxyquinoline was selected for its high fluorescence and good metal ions binding ability [41–46]. We found probe **Q-16** can self assemble nanoaggregation, and shows exclusive fluorescence quenching sensing of Hg²⁺ over other metal ions. For comparison, the metal ions sensing ability in organic CH₃CN solution was also investigated.

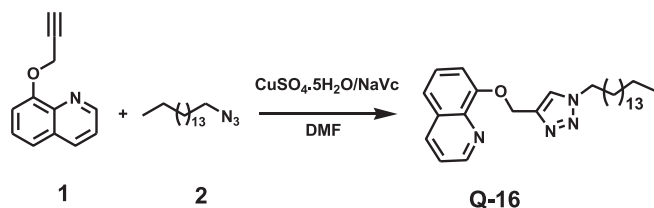
2. Experiment

2.1. Materials and characterization

All of the chemicals were commercially available and used without further purification. The two precursors 8-(2-propyn-1-yloxy)-quinoline (**1**) and 1-azido-hexadecane (**2**) were prepared

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Scheme 1. The synthesis route of target compound **Q-16**.

according to the literature method [47,48]. The solvents used for UV-vis and emission measurements were purified by standard procedures.

Emission spectra were recorded on a Hitach F-4500 spectrophotometer. The excitation and emission slit width for checking are 5 nm. UV-vis spectra were recorded on a Hitach UV-3010 spectrophotometer. NMR spectra were recorded using a Varian instrument (400 MHz). HR MS were recorded using a LC/MSD TRAP XCT Plus (1200 Agilent) instrument.

2.2. Preparation of the nanoprobe **Q-16** and emission titrations

The high concentration (4.0×10^{-3} M) of **Q-16** in CH_3CN was first prepared. Then 10 μL of this stock solution was dropped to 2 mL of distilled water with strong stirring to obtain the nano-aggregation, which the concentration of **Q-16** is 2.0×10^{-5} M in aqueous solution. The stock solutions (4.0×10^{-3} M) of respective metal ions (Hg^{2+} , Ag^+ , Cu^{2+} , Mg^{2+} , Ni^{2+} , Cr^{3+} , Na^+ , Co^{2+} , Ba^{2+} , Cd^{2+} , Zn^{2+} , Al^{3+} , Pb^{2+} , Fe^{3+}) in their perchlorate salts were prepared in distilled water. Then different equivalents of metal ions were added into the aqueous solution of **Q-16** using a micro injector. The volume of metal ion solution added is negligible compared to that of **Q-16**. The whole volume of the final system can be considered constant.

The binding constants between **Q-16** and Hg^{2+} were obtained according to the fluorescence titration data by the Benesi-Hildebrand method [49]. The equation for a 1:1 host:guest complex is given below:

$$\frac{1}{I - I_0} - \frac{1}{I' - I_0} = \frac{1}{K(I' - I_0)[\text{Hg}^{2+}]}$$

In the equation, I_0 is the fluorescence intensity of **Q-16** without metal ions, I is the intensity with a particular concentration of metal ions, I' is the intensity of the fully complexed form at the highest concentration of metal ions, and K is the binding constant.

2.3. DFT calculations

The optimized structures of **Q-16** and **Q-16** Hg^{2+} complex were obtained by the Gaussian 09 program. A 6-31G (d, p) basis set was used for C, H, O and N, and a LANL2DZ ECP was selected for Hg atom. No imaginary frequencies were available after vibration analysis of the optimized structures, which implied that the optimized structure was at the real minimum on the potential energy surfaces (PES).

2.4. Synthesis of **Q-16**

A mixture of 8-(2-propyn-1-yloxy)-quinoline (**1**, 570.7 mg, 1.64 mmol), 1-azidoheptadecane (**2**, 300 mg, 1.64 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (112.2 mg, 0.45 mmol) and sodium ascorbate (158.2 mg, 0.8 mmol) were dissolved in 4 mL DMF solution. The mixture was stirred at room temperature for 4 h under nitrogen atmosphere. Then 30 mL H_2O was added to get the precipitate. The solid was filtered, and purified by silica gel column chromatography using CH_2Cl_2 :

CH_3OH (95:5, v/v) as the eluent to get **Q-16** as a yellow powder (700 mg, yield 80%). ^1H NMR (400 MHz, CDCl_3 , δ ppm): 8.94 (s, 1H), 8.14 (d, $J = 7.8$ Hz, 1H), 7.72 (s, 1H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 6.9$ Hz, 1H), 5.58 (s, 2H), 4.31 (t, $J = 7.3$ Hz, 1H), 1.88 (d, $J = 13.1$, 7.1 Hz, 1H), 1.25 (t, $J = 10.3$ Hz, 15H). ^{13}C NMR (101 MHz, DMSO, δ ppm): 149.3, 136.2, 127.1, 125.1, 120.5, 110.5, 62.4, 49.8, 40.0, 31.7, 30.2, 29.5, 29.5, 29.4, 29.3, 29.2, 28.8, 26.3, 22.5, 14.4. HR-MS (APCI) m/z : Calcd. for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}$: 450.3359; Found 451.3436 ($M + 1$).

3. Results and discussion

The synthesis route of probe **Q-16** is shown in Scheme 1. With 8-hydroxyquinoline as the starting material, 8-(2-propyn-1-yloxy)-quinoline was first prepared by the literature method. Click reaction 8-(2-propyn-1-yloxy)-quinoline with 1-azidoheptadecane gets the pale yellow powder **Q-16** in high yield. The chemical structure of **Q-16** was fully characterized by ^1H NMR, ^{13}C NMR and ESI-MS spectra.

The fluorescence spectra of the **Q-16** toward various metal ions (Hg^{2+} , Ag^+ , Cu^{2+} , Mg^{2+} , Ni^{2+} , Cr^{3+} , Na^+ , Co^{2+} , Ba^{2+} , Cd^{2+} , Zn^{2+} , Al^{3+} , Pb^{2+} , Fe^{3+}) in aqueous solution was investigated by absorption and emission spectra. The probe shows a low energy broad band absorption at about 330 nm, and a blue emission at 400 nm with excitation at 325 nm, which can be attributed to the π - π^* transition of the quinoline ring. Upon addition various metal ions, the absorption of **Q-16** gives barely change (Fig. S1). In contrast, probe **Q-16** shows exclusive fluorescence response toward Hg^{2+} . As shown in Fig. 1, when 1.0 equivalence of Hg^{2+} was added, almost 80% fluorescence of **Q-16** was quenched. Hg^{2+} is a well-known quenching ion for heavy atom effect and/or photo-induced electron transfer mechanism [50]. The addition of other metal ions leads little emission changes. Thus, probe **Q-16** can be used as a fluorescence sensor for detection Hg^{2+} in aqueous solution. Some hydroxyquinoline-based chemosensors for particular sensing of Hg^{2+} over some interference metal ions (Ag^+ , Cu^{2+} and Cd^{2+}) in competitive aqueous solution have been reported, which may be attributed to the difference of the size or softness of these metal ions in this condition [51,52].

Fig. 2 shows the emission changes of **Q-16** upon addition of various amount of Hg^{2+} . With increasing the concentration of Hg^{2+} , the fluorescence intensity of **Q-16** at 400 nm was gradually decreased and saturated at about 1.0 equivalent. The binding constant between **Q-16** and Hg^{2+} was obtained according to the emission titration data. A 1:1 stoichiometry **Q-16**- Hg^{2+} complex was obtained by the fluorescence Job's plot (Fig. S2). The complex constant K was calculated to be $6.34 \times 10^5 \text{ M}^{-1}$ (Fig. S3) by the Benesi-Hildebrand equation. In addition, the detection limit (LOD) of **Q-16** for Hg^{2+} was calculated to be 4.42 nM (Fig. S3) in aqueous solution, based on the $3\sigma/k$ ($\sigma = 1.12$, $k = 7.6 \times 10^8$) method. The detection limit value is lower than the maximum allowable level (10 nM, 2 ppb) of Hg^{2+} in drinking water by EPA [53], indicating that probe **Q-16** exhibit high sensitive toward Hg^{2+} .

In addition, we compared probe **Q-16** with those previously reported fluorescence probes for determination of Hg^{2+} (Table 1) [28–32,46,54]. As can be seen, the proposed sensor results seem good with respect to the binding constants, the limit of detection (LOD) and working medium.

In probe **Q-16**, the quinoline ring N atom, the ether O atom and the triazole N atom are the potential donors for binding with Hg^{2+} ion (See Fig. 3). To confirm this assumption, the ^1H NMR signal changes of **Q-16** upon addition of Hg^{2+} in CDCl_3 - CD_3OD (9:1, v/v) was carried out. When 1.0 equivalence of Hg^{2+} was added to the solution of **Q-16**, a large down field shift was found in the triazole proton Ha (from 7.72 ppm to 8.30 ppm) and methyl proton Hb

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