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Short Communication

Convenient and selective “off–on” detection nitric oxide in solution and thin film with quinoline based fluorescence sensor

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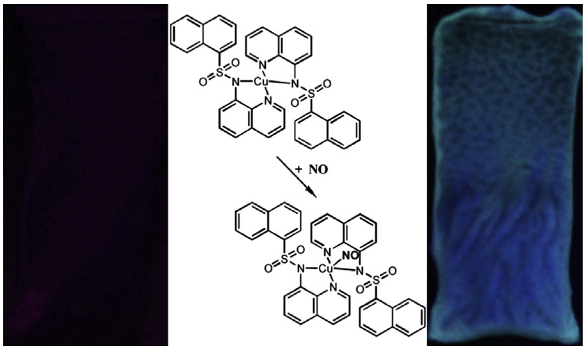
HIGHLIGHTS

- A naphthalene-sulfonamino-quinoline based copper(II) complex has been synthesized to effective probe nitric oxide (NO) in solution and thin film.
- The complex has potential application to meet the detection requirements of a NO assay.

GRAPHICAL ABSTRACT

A naphthalene-sulfonamino-quinoline based copper(II) complex has been synthesized to effective probe nitric oxide (NO) in solution and thin film. The complex has potential application to meet the detection requirements of a NO assay.



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ABSTRACT

Quinoline based fluorescence sensor (**1**) was synthesized and characterized with mass spectra (MS), ^{1}H nuclear magnetic resonance (^{1}H NMR) spectrometer, elemental analyses, and infrared (IR) spectra. Following fluorescence experiments demonstrate **1** can coordinate with copper ions, and lead to fluorescence completely quenched. The **1**-copper complex was used as a “turn-on” fluorescence biosensor to convenient and highly effective detect nitric oxide (NO) over other radicals in solution and PCL-based thin film. The finding would enable the quinoline based fluorescence probe to be an “off–on” convenient NO fluorescence probe.

Introduction

Nitric oxide (NO), a reactive free radical, is produced by inducible and constitutive nitric oxide synthases. NO can act as an important biological mediator of some biological processes in plants and animals [1–6], and modulate the activities of proteins [7], or exert cytotoxic effects on a variety of pathogens, a requirement for understanding fully the details of its biological roles [8]. Due to its significance to human health and disease, development of a convenient and effective detecting method for NO is a challenge for scientists [9]. Possessing high sensitivity and simple manipulation, fluorescence sensing method has been widely regarded as the best tool for tracking NO [10–15].

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Herein, a quinoline derivative (**1**) was synthesized. Its spectral property has been investigated. The experimental results indicated that it can coordinate with copper ions, and lead to fluorescence completely quenched. Significantly, the copper complex (**2**) exhibited the specific fluorescence "turn-on" sensing ability for NO in either solution or the polycaprolactone (PCL)-based thin film. The results enable the quinoline derivative as a convenient and highly efficient fluorescence "off–on" sensor for NO detection.

Experimental

Materials and methods

All chemicals used in this report were reagent grade unless noted. Polycaprolactone (PCL, M_n 4.5 × 10^4) was purchased from Sigma–Aldrich Co., Ltd. and used as a polymer matrices. DMF (chromatographically pure), 4-aminobenzenesulfonic acid (SULF), N-(1-naphthyl) ethylenediamine dihydrochloride (NNED), and sodium nitrite were purchased from Aladdin reagent Co., Ltd. Pyridine was dried over CaH_2 for 2–3 days and then distilled prior to use.

Naphthalene-sulfonaminoquinoline (NSQ, 1) was synthesized according to the method of literature. [16] The copper complex (Cu·$(NSQ)_2$) was synthesized by a one-step reaction and characterized (Scheme 1).

Synthesis of naphthalene-sulfonaminoquinoline (NSQ, ***1****)*

2-Naphene sulfonate chloride (4.7 g, 0.021 mol) has been added to the 25 mL pyridine solution of 8-amino quinoline (3 g, 0.021 mol) under ice bath. This solution has been stirred under 0 °C for 2 h, and then 60 °C for 5 h. After that, the mixture poured into 200 mL ice water. The precipitate has been collected, and recrystallized with chloroform as slight yellow solid as product (6.2 g, yield 88.4%). MS (ESI): *m*/*z* 333.1 ($[M–H]^-$), (334.1 calcd for $C_{19}H_{14}N_2O_2S$); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.364 (m, 3H), 7.504 (m, 2H), 7.679 (m, 2H), 7.968 (d, *J* = 6.3, 1H), 8.026 (m, 2H), 8.373(d, *J* = 5.7, 1H), 8.701(d, *J* = 3, 1H), 8.837(d, *J* = 6.3, 1H), 9.554(s, 1H). Anal. Calcd for $C_{19}H_{14}N_2O_2S$: C, 68.24; H, 4.22; N, 8.38; S, 9.59%. Found: C, 68.16; H, 4.33; N, 8.52; S, 9.31%.

*Synthesis of Cu·(NSQ)$_2$ (**2**)*

1 (33.4 mg, 0.1 mmol) and sodium hydroxyl (4 mg, 0.1 mmol) were dissolved in the mixture of dichloromethane (4.5 mL) and methanol (4.5 mL) to obtain a light brown solution. After $CuSO_4$·$5H_2O$ (25 mg, 0.1 mmol) has been added, the solution become dark brown. After stirred overnight under RT, the obtained precipitate was filter out as final product. MS (ESI): *m*/*z* 752.2 ($[M + Na]^+$), (729.1 calcd for $C_{38}H_{26}CuN_4O_4S_2$); 1482.6 ($[2 M + Na]^+$), (1482.1 calcd for $NaC_{76}H_{52}Cu_2N_8O_8S_4$); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.29–7.55 (m, 5H), 7.72–7.88 (m, 3H), 7.92–8.12 (m, 3H), 8.80–8.94 (m, 2H); IR (KBr pellet): ν (cm^{-1}): 3455, 1632, 1580, 1505, 1467, 1383, 1321, 1300, 1267, 1132, 1115, 953, 879, 829, 794, 767, 677, 638, 596, 581. UV–vis (DMF): λ_{mas} (ε) 371 nm (20 M^{-1} cm^{-1}), 318 nm (2.6 × 10^2 M^{-1} cm^{-1}), 294 nm (3.9 × 10^2 - M^{-1} cm^{-1}). Anal. Calcd for $C_{38}H_{26}CuN_4O_4S_2$·$2H_2O$: C, 59.56; H, 3.95; N, 7.31. Found: C, 60.12; H, 4.11; N, 6.97.

Analysis

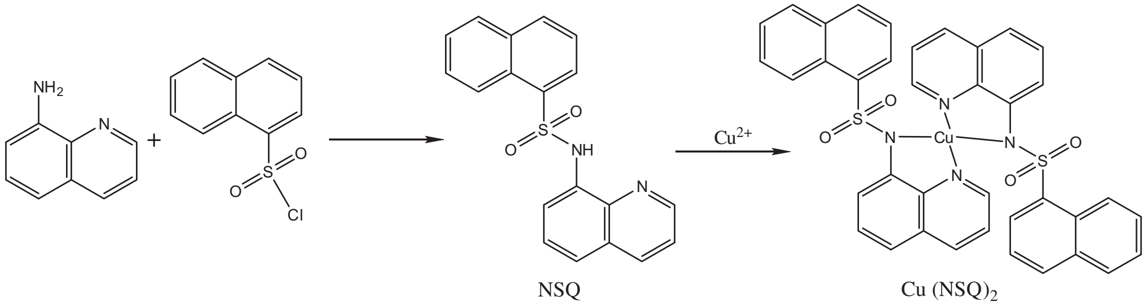
Elemental analyses were performed on a Perkin–Elmer-2400C instrument. Mass spectra were performed on an IonSpec QFT-ESI MS. FT-IR spectra were obtained in KBr pellets with a Bruker Tensor 27 FT-IR instrument. Thermogravimetric (TG) and differential thermal analysis (DTA) were recorded with a Rigaku Standard TG-DTA type. Samples were heated at 10 °C min^{-1} from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL min^{-1}). Ultraviolet/visible (UV/vis) spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary 100 UV–visible spectrophotometer equipped with temperature controller to keep the temperature at 25 °C. Fluorescence spectra were recorded in a conventional quartz cell (10 × 10 × 45 mm) at 25 °C on a Shimadzu RF-5301PC spectrofluorophotometer (xenon lamp photosource) equipped with a single cell Peltier temperature controller accessory to keep the temperature at 25 °C. Fluorescence images were performed on a ZF-7B three-used ultraviolet analysis instrument (Shanghai Kanghua Biochemistry instrument Co., Ltd.) and a Kodak Z885 zoom digital camera (Eastman Kodak Company) for photo collection. Tri-distill water and N, N-dimethyl formamide (DMF, chromatographically pure) was used as solvent in all spectral measurements without special mentioned.

Results and discussion

The absorption and emission spectral property of **1** has been investigated. The typical UV–vis curves of **1** with the gradual addition of Cu^{2+} has shown in Fig. 1. In Fig. 1a, intensity of absorbance peak at 370 nm gradually increased in the UV–vis spectrum of **1** with the stepwise addition of Cu^{2+}. This absorbance was expected to correspond to the formation of a five-membered chelate ring between two nitrogen atoms in **1** and Cu^{2+}, which extended the conjugated system and thus resulted in the increase of the absorbance at 370 nm. The phenomenon illustrated that the Cu^{2+} was coordinated to **1**.

The IR spectrum displayed the bands of N–H stretching vibration at 3299 cm^{-1} **1** in Fig. 2a have dissappeared in Fig. 2b, which indicated the coordinate complex formed between **1** and Cu^{2+} with N–Cu bond formation.

Therefore, the quinoline based copper complex **2** have been synthesized and characterized with MS (Fig. S3), ^{1}H NMR



Scheme 1. The synthesis process of Cu$(NSQ)_2$ (**2**).