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Highly optically selective and electrochemically active chemosensor for copper (II) based on triazole-linked glucosyl anthraquinone

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ABSTRACT

A novel triazole-linked acetyl-β-*N*-glucosyl anthraquinone **1** was conveniently synthesized through one-step click chemistry. The functionalized glycoconjugate (**1**) exhibited a remarkable blue shift absorption and quenching fluorescence in the presence of trace amounts of Cu^{2+}, presumably attributable to intramolecular charge transfer (ICT), which also displayed high selectivity over a series of other metal cations tested in acetonitrile. The result yielded by fluorescence spectroscopy titration suggested a 2:1 ligand-to-metal complex which was further demonstrated by NMR spectroscopy titration. Moreover, the addition of Cu^{2+} to **1** also significantly altered its electrochemical behavior which was reflected via differential pulse voltammetry (DPV) measurements. Such optically and electrochemically detectable metal-mediated sugar derivatives could be further used as biosensors for the recognition of multivalent carbohydrate-protein interactions.

1. Introduction

Numerous chemosensors have been designed and synthesized for the detection and recognition of biologically and environmentally significant molecular and ionic species [1–5]. Indeed, fluorescent sensors have distinct advantages over other methods in terms of their sensitivity, selectivity, response time, high spatial resolution, etc. Cupric ion (Cu^{2+}) is not only an environment pollutant when it is in high concentrations [6,7], but also the third most abundant and essential heavy metal ion in human body [8,9]. Accordingly, considerable efforts have been devoted to the development of fluorescent Cu^{2+}-selective chemosensors [10–14].

Bearing densely existed oxygen atoms, carbohydrates are promising chiral scaffolds for the design of cation sensors [15]. In addition, taken its essential merits such as conformational flexibility, high biocompatibility, low toxicity and abundance in nature, carbohydrates are one of the most desired classes of molecular systems to sense metal cations in biological systems [16–18]. However, carbohydrate-containing cation probes [15–21] reported to date are quite limited. More interestingly, carbohydrate–metal complexes have recently been utilized as valuable analytical tools for gaining deeper insight into carbohydrate–protein interactions [22–27].

Anthraquinone derivatives have been described as important dyes for decades [28]. It has also been widely utilized as fluorogenic group in chemosensors [29–32] for metal ions due to its high absorption coefficient and possibility of naked eye detection. Furthermore, since its quinone system shows two successive electron reduction steps forming Q^{1-} and then Q^{2-} [33,34], anthraquinone binding to metal cations can also be detected by its unique electrochemical behavior [29].

We thereby considered the incorporation of a sugar moiety into an anthraquinone scaffold. The Huisgen [2+3] cycloaddition reaction (also known as click reaction) [35,36] was used as the key step for fulfilling such conjugation due to its high compatibility and tolerance toward multiple solvent systems with mild conditions. Additionally, the formed 1,2,3-triazole was envisioned to simultaneously participate in the coordination [37–40] with metal ions. We report here the straightforward synthesis and specific dual optical-electrochemical response of the novel sugar-containing triazoyl anthraquinone sensor **1** toward Cu^{2+} over various other metal cations.

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2. Experimental

2.1. Reagents and instruments

All purchased chemicals and reagents were of high commercially available grade. Solvents were purified by standard procedures. ^{1}H and ^{13}C NMR spectrum were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ or CD_3CN solutions using tetramethylsilane as the internal standard (chemical shifts in departs per million). All reactions were monitored by TLC (thin-layer chromatography) with detection by UV or by spraying with 6 mol/L H_2SO_4 and charring at 300 °C. Optical rotations were measured using a Perkin−Elmer 241 polarimeter at room temperature and a 10-cm 1-mL cell. High resolution mass spectrum (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions (ESI, 70 eV). Azido glucoside **2** and propargyl anthraquinone **3** were synthesized according to the well-known literature procedures [41,42].

2.2. Synthesis of 1,8-bis((1-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1H-1,2,3-triazol-4-yl)methoxy) anthracene-9,10-dione (1)

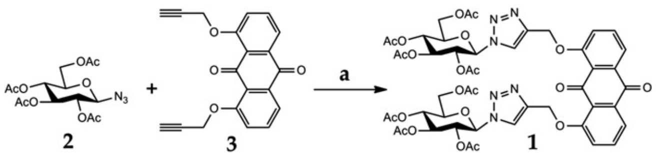
To a solution of propargyl anthraquinone **3** (158.1 mg, 0.5 mmol) and azido glucoside **2** (373.2 mg, 1.0 mmol) in DMF (2 mL), CH_2Cl_2 (5 mL) and H_2O (2 mL), sodium ascorbate (594.3 mg, 3.0 mmol) and $CuSO_4 \cdot 5H_2O$ (499.3 mg, 2.0 mmol) were added. After stirring for 16 h at room temperature, the mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, filtered and concentrated. Column chromatography (petroleum ether/EtOAc = 2:3) afforded **1** as a yellow solid (316.7 mg, 59.6%). TLC: $R_f = 0.54$ (petroleum ether/EtOAc = 1:3); $[\alpha]_D = -4.1$ ($c = 0.1$, CH_3CN); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.23$ (s, 2H), 7.90 (d, $J = 7.6$ Hz, 2H), 7.65 (t, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 6.13 (d, $J = 9.2$ Hz, 2H), 5.60 (t, $J = 9.4$ Hz, 2H), 5.50 (t, $J = 9.4$ Hz, 2H), 5.45 (s, 4H), 5.31 (t, $J = 9.7$ Hz, 2H), 4.29 (dd, $J = 12.7$, 5.1 Hz, 2H), 4.18-4.10 (m, 4H), 2.08 (s, 6H), 2.04 (s, 6H), 2.02 (s, 6H), 1.80 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 183.8$, 182.8, 170.8, 170.4, 169.7, 169.0, 158.0, 144.8, 135.2, 134.3, 125.4, 123.2, 121.7, 120.6, 85.8, 75.2, 73.2, 70.6, 68.1, 64.3, 62.0, 30.0, 21.0, 20.9, 20.4; HRMS (ESI): calcd for $[C_{48}H_{50}N_6O_{22} + Na]^+$: 1085.2876; found: m/z 1085.2871.

2.3. General UV−Vis and fluorescence spectrum measurements

All UV−Vis absorption and fluorescence emission spectrum were recorded with Ocean Optics USB2000+ and HORIBAJOBIN YVON FluoroMAX-4 spectrophotometer, respectively. Excitation was carried out at 378 nm with excitation and emission slit widths at 1 and 0.35 nm, respectively. Solutions of **1** and various concentrations of metal nitrates were prepared in CH_3CN.

2.4. Differential pulse voltammetry (DPV) measurements

Differential pulse voltammetry were measured with a CHI 830 electrochemical workstation (CHEN HUA Instrumental Co., Shanghai) using a conventional three-electrode cell. The surface of a glassy carbon working electrode was polished with alumina and then rinsed with deionized water. Residual alumina particles were thoroughly removed by sonicating the working electrode. The electrode was then rinsed successively with deionized water and CH_3CN, and blown dry with a N_2 stream. A Pt wire and an Ag/Ag^+ (10.0 mmol/L $AgNO_3$) electrode were used as a counter and reference electrode, respectively. The experiments were run at room temperature under a dry N_2 atmosphere using a 0.1 mol/L TBAP electrolyte solution (with 0.04 V increment, 100 mV pulse amplitude and 0.5 s pulse period).



Scheme 1. Synthesis of **1** via click chemistry, reagents and conditions: (a) Sodium ascorbate (6 equiv), $CuSO_4 \cdot 5H_2O$ (4 equiv) in DMF/CH_2Cl_2/H_2O, 16 h.

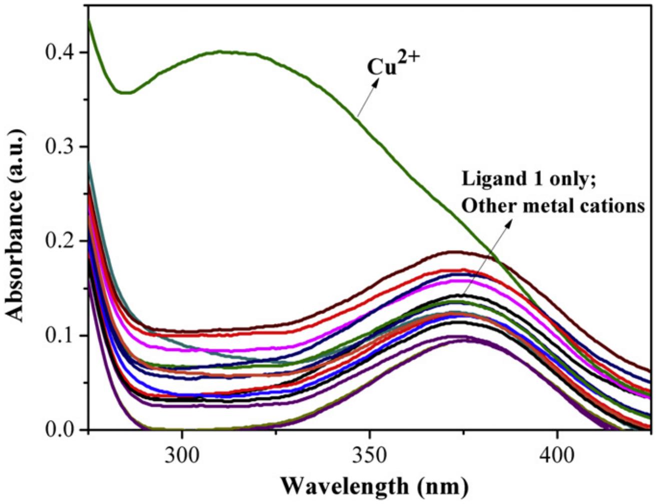


Fig. 1. UV−Vis absorption spectrum of **1** in CH_3CN (25 μmol/L) upon addition of the nitrate salts of: Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Co^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Al^{3+} and Cu^{2+} (250 μmol/L).

3. Results and discussion

Glucosyl-triazoyl anthraquinone **1** was readily prepared via click reaction from azido glucoside **2** and propargyl anthraquinone **3** (Scheme 1) under the promotion of sodium ascorbate and $CuSO_4 \cdot 5H_2O$. The moderate yield of **1** (59.6%) could be explained by the low solubility of propargyl material **3** in the commixed solvent system of DMF/CH_2Cl_2/H_2O.

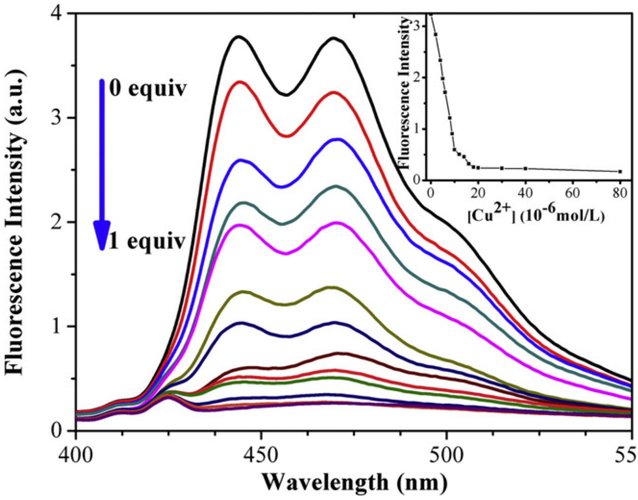


Fig. 2. Fluorescence spectrum of **1** (20 μmol/L) in CH_3CN upon the gradual addition of Cu^{2+} (0, 2, 4, 5, 6, 8, 9, 10, 12, 14, 16, 18, 20 μmol/L) with an excitation at 378 nm. Inset: titration curve of the fluorescence intensity as a function of Cu^{2+} concentration.

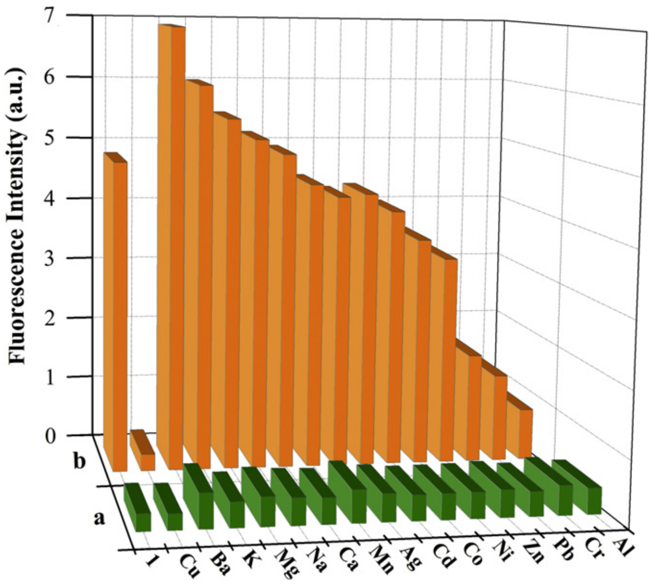


Fig. 3. Fluorescence intensity change profiles of **1** at 455 nm in CH_3CN (25 μmol/L) with selected cations (250 μmol/L) in the absence (b) or presence (a) of Cu^{2+} (25 μmol/L). $\lambda_{ex} = 378$ nm.

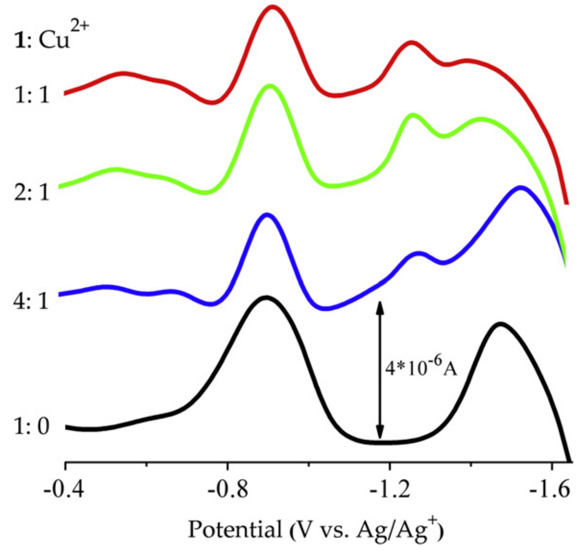


Fig. 5. Differential pulse voltammograms of 0.2 mmol/L **1** in the absence or presence of Cu^{2+}. Electrolyte: 0.1 mol/L TBAP/CH_3CN. Pulse amplitude: 100 mV; Pulse period: 0.5 s. The molar ratio of **1** to Cu^{2+} varied from 1:0 to 1:1.

The photophysical properties of **1** were investigated with absorption and fluorescence studies upon addition of the nitrate salts of various metal cations in CH_3CN, including Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Co^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Pb^{2+} and Cu^{2+}. As shown in Fig. 1 and Fig. S3 (see supporting information), the UV–Vis absorption spectrum of **1** contained a wavelength maximum at 378 nm. Upon the addition of Cu^{2+}, a marked absorption blue shift ($\Delta\lambda = 70$ nm) and intensity enhancement (2.7 fold) were observed. In contrast, other metal cations gave almost no change either in wavelength or in absorption intensity, suggesting **1** could be a selective chemosensor for Cu^{2+}.

Interestingly, Cu^{2+} quenched fluorescence intensity of **1** distinctively (95.0%, Fig. 2). When solutions containing 20 μmol/L **1** were gradually added with Cu^{2+} (0–20 μmol/L) in CH_3CN, the resulting fluorescence emission (excited at 378 nm) peaked at 444 nm and 469 nm precipitously dropped with the increase of Cu^{2+} before reaching its quenching plateau (>15 μmol/L Cu^{2+}, Fig. 3, Inset).

Job's plot [43] (Fig. S4 in supporting information) indicated that **1**-Cu^{2+} complex exhibited a 1:2 metal-to-ligand ratio and the association constant (log K_a) [44] of **1** for Cu^{2+} was calculated to be 5.64. The fluorescence quenching of **1** on addition of Cu^{2+} could be attributed to anthraquinone → Cu^{2+} π-cation interactions [45], paramagnetic effect of Cu^{2+} [46,47] and the absorption blue shift of **1**.

The fluorescence intensity of **1** (25 μmol/L) was not significantly affected by a representative selection of 10 equiv of alkali metal ions (Na^+, K^+), alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Ba^{2+}) and transition-metal ions (Ag^+, Co^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}) (Fig. 3). Cr^{3+}, Pb^{2+}, Al^{3+} quenched the emission intensity more than other metal ions examined, but fortunately the quenching ability of Cu^{2+} was still much stronger (Upon addition of 10 equiv of different salts, the fluorescence intensity of **1** with Cu^{2+} was one-fifth as that with Cr^{3+}, one-sixth as that with Pb^{2+} and one-third as that with Al^{3+}). The selectivity toward Cu^{2+} was further ascertained by the competition experiment, where the emission of **1** with 10 equiv of various metal ions was almost totally quenched by only 1 equiv of

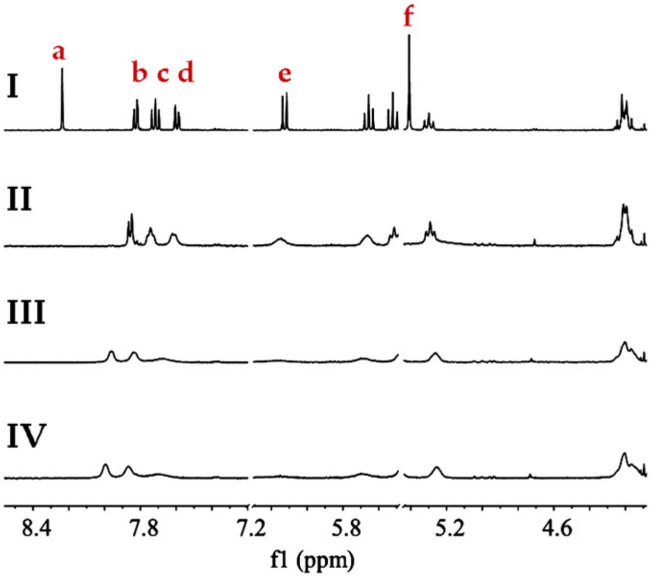
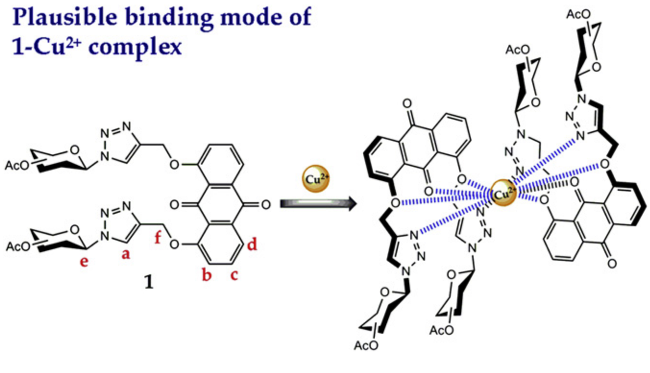


Fig. 4. Binding mode of **1**-Cu^{2+} and ^1H NMR spectrum of **1** with $Cu(NO_3)_2$ in CD_3CN. (I) **1**, (II) **1** with 0.1 equiv of Cu^{2+}, (III) **1** with 0.5 equiv of Cu^{2+} and (IV) **1** with 1.0 equiv of Cu^{2+}.



Plausible binding mode of 1-Cu^{2+} complex.

Cu^{2+}. Thus **1** could be utilized as a highly effective Cu^{2+} selective fluorescent sensor.

To determine the complex mode between **1** and Cu^{2+}, ^1H NMR spectrum of **1** on addition of various concentrations of Cu^{2+} in CD_3CN were recorded (Fig. 4). The signals of H blurred because of the paramagnetic effect [46,47] of Cu^{2+}. The peaks of H_a and H_f completely disappeared as soon as 0.1 equiv of Cu^{2+} was added. On addition of 0.5 equiv of Cu^{2+} to **1**, peaks corresponding to the anthraquinone ring (H_b, H_c and H_d) underwent an overall downfield shift of 0.12 ppm and the anomeric proton of glucoside (H_e) was downfield shifted by 0.03 ppm. The results suggested 1,2,3-triazole and the ether oxygen on anthraquinone were directly involved in coordinating with Cu^{2+}. There was no appreciable change in the signal positions on addition of another 0.5 equiv of Cu^{2+} to **1**, confirming a 2:1 binding stoichiometry for **1** and Cu^{2+}.

From all spectroscopic data, it could be speculated that the intramolecular charge transfer (ICT) mechanism [1–3] was the basis for optical selectivity of **1** toward Cu^{2+}. When a fluorophore contains an electron-rich terminal (e.g., an oxygen atom) conjugated to an electron-withdrawing group (e.g., an aromatic system), it undergoes ICT from the donor to the acceptor upon excitation by light. If the electron-donating group of the fluorophore interacts with a cation, a partial positive charge is photoinduced adjacent to the cation, and then an abosorption blue shift of the fluorophore is expected with an ICT excited state. The blue shift in the absorption band of **1** could be attributed to the Cu^{2+} binding to ether oxygen (electron-donor) on anthraquinone ring (electron-acceptor) by ICT (Fig. 4). Though electron-withdrawing carbonyl oxygen of anthraquinone also interacted with Cu^{2+} (ascertained by the electrochemical behavior of **1**-Cu^{2+} complex discussed below), it had less impact on the absorption wavelength compared with the ether oxygen. Besides ICT, anthraquinone → Cu^{2+} π-cation interactions and paramagnetic effect of Cu^{2+} could also lead to optical changes of **1**.

The differential pulse voltammograms (DPV) for **1** in CH_3CN are displayed in Fig. 5 as a function of added $Cu(NO_3)_2$. The voltammogram of free **1** exhibited quasi-reversible waves at −0.9 and −1.7 V, corresponding to the two successive electron-transfer processes [48] leading to the formation of the dianionic anthraquinone. Addition of successive amounts of Cu^{2+} ($[\mathbf{1}]:[Cu^{2+}] = 4:1$, 2:1 and 1:1) resulted in an additional three reduction waves, one (near −1.3 V) corresponding to the first reduction of free **1** and two waves (−0.5 and −0.7 V) corresponding to the successive reductions of the **1**-Cu^{2+} 2:1 ligand-to metal complex. New reduction peaks were positioned at more positive potentials compared with free **1**, suggesting Cu^{2+} strongly interacted with **1** and this interaction strengthened upon reduction of the ligand [49]. The original wave at −1.7 V gradually weakened with the growth of new reduction peak at 1.3 V, reflecting the decreasing amount of free **1**. Only one carbonyl oxygen atom on the anthraquinone ring bound to Cu^{2+} (Fig. 4) for the invariant intensity of the peak at 0.9 V. The distinct voltammetric responses of **1** in the presence of Cu^{2+} indicated high electrochemical activity of this novel Cu^{2+}-selective chemosensor.

4. Conclusion

A novel optical selective and electrochemical active chemosensor for Cu^{2+} was well-designed and achieved through mild straightforward click chemistry. The **1**-Cu^{2+} complex displayed a 2:1 ligand-to-metal stoichiometry with high binding strength. The absorption blue shift could be ascribed by an ICT process on the anthraquinone ring induced by Cu^{2+}, while the fluorescence of **1** was quenched by anthraquinone → Cu^{2+} π-cation interactions, paramagnetic effect of Cu^{2+} and the absorption blue shift of **1**. The anthraquinone oxygen and triazole ring served as cation binding sites. Furthermore, unique successive quinone reductions of free **1** and **1**-Cu^{2+} complex were observed by DPV measurement.

In addition, since it is reported that glycoside hyper-branched dendrimers accessed by metal-associated self-assembly could reinforce carbohydrate-protein interactions [22–27], we sought to employ this strategy to further study the interactions between deacetylated **1**-Cu^{2+} complex and sugar-recognizable proteins in aqueous biological environment and such investigation would be reported in due course.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2010.08.010.

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