Fluorescent Character of Cu(I/II) Complexes with Bisquinoline-based Ligands and Fluorometric Detection of Reductants

Makoto SAGA,* Tatsuya ANAMUSHI,** Wakayo MIYAHARA,*** Shigeo YAMAZAKI,*** and Keiitsu SAITO*†

*Department of Human Environmental Science, Graduate School of Human Development and Environment, Kobe University, 3-11 Tsurukabuto, Nada, Kobe 657-8501, Japan

**Department of Human Environmental Science, Faculty of Human Development, Kobe University, 3-11 Tsurukabuto, Nada, Kobe 657-8501, Japan

***Department of Applied Science, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita, Okayama 700-0005, Japan

The fluorescence ligands *N,N'*-bis(2-methylquinolyl)dimethylethylenediamine (BQDMEN) and *N,N'*-bis(2-methylquinolyl)dimethyl-1,3-propanediamine (BQDMPN) were synthesized. [Cu(II)(bqdmn)]²⁺ and [Cu(II)(bqdmnp)]²⁺ were prepared, and their reduction to [Cu(I)(bqdmn)]⁺ and [Cu(I)(bqdmnp)]⁺ was confirmed by the observed UV-Vis spectral change. Then, the fluorescence of [Cu(I/II)(bqdmn)]⁺²⁺ and [Cu(I/II)(bqdmnp)]⁺²⁺ in aqueous solution was characterized; [Cu(I)(bqdmn)]⁺ and [Cu(I)(bqdmnp)]⁺ were found to fluoresce in aqueous solution, whereas the fluorescence of [Cu(II)(bqdmn)]²⁺ and [Cu(II)(bqdmnp)]²⁺ was completely quenched. On the basis of these findings, fluorometric detection of reductants with a flow-injection system using a [Cu(II)(bqdmn)]²⁺ or [Cu(II)(bqdmnp)]²⁺ solution as a carrier was explored.

Keywords Fluorescence ligand, copper complex, reductant

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Introduction

The fluorescence of the ligands is not necessarily quenched in a Cu(I) complex because the d¹⁰ electron configuration has no magnetic moment, and many fluorescent Cu(I) complexes have been reported.¹⁻⁴ However, almost all of the reported fluorescent Cu(I) complexes have been in the solid state or in organic solvents. To our knowledge, there have been only a few reports for analytical methods with the fluorescence character of Cu(I) complexes in aqueous media.^{5,6} Therefore, the development of an analytical method based on the fluorescence of Cu(I) complexes in aqueous media has been the topic of our research.

Recently, we found that [Cu(I)(bqdmn)]⁺ (bqdmn = *N,N'*-bis(2-methylquinolyl)dimethylethylenediamine) and [Cu(I)(bqdmnp)]⁺ (bqdmnp = *N,N'*-bis(2-methylquinolyl)dimethyl-1,3-propanediamine) are fluorescent in aqueous solution, whereas the fluorescence of [Cu(II)(bqdmn)]²⁺ and [Cu(II)(bqdmnp)]²⁺ is completely quenched. Although the fluorescence of [Zn(bqdmn)]²⁺ was investigated in detail by Mikata *et al.*,⁷ the fluorescent characters of [Cu(I/II)(bqdmn)]⁺²⁺ and [Cu(I/II)(bqdmnp)]⁺²⁺ were not reported. In the present paper, we report on the synthesis of BQDMEN and BQDMPN, the preparation of [Cu(II)(bqdmn)](NO₃)₂ and [Cu(II)(bqdmnp)](NO₃)₂, the fluorescent characters of [Cu(I/II)(bqdmn)]⁺²⁺ and [Cu(I/II)

(bqdmnp)]⁺²⁺ in aqueous solution, and fluorometric detection of reductants with a flow-injection system based on the fluorescent characters of [Cu(I/II)(bqdmn)]⁺²⁺ and [Cu(I/II)(bqdmnp)]⁺²⁺. The use of an aqueous [Cu(II)(bqdmn)]²⁺ or [Cu(II)(bqdmnp)]²⁺ solution as a carrier for a flow-injection system might enable the detection of water-soluble reductants. Although the detection of metal ions with fluorescent ligands in water or organic solvents has been reported,⁸⁻¹¹ the detection of water-soluble reductants with fluorescence caused by the change of oxidation number of metal ions has not been reported.

Experimental

Reagents and chemicals

N,N'-Dimethylethylenediamine (DMEN), *N,N'*-dimethyl-1,3-propanediamine (DMPN), and 2-chloromethylquinoline hydrochloride (CMQ) were obtained from Tokyo Chemical Industry (Tokyo, Japan). Copper(II) nitrate trihydrate was purchased from Sigma Aldrich Japan (Tokyo, Japan). Other chemicals used were purchased from Wako Pure Chemical Industries (Osaka, Japan).

Synthesis of BQDMEN and [Cu(II)(bqdmn)](NO₃)₂

Although the synthesis of BQDMEN and its Zn(II), Co(II), Fe(II), Mn(II), Cr(0), and Cu(II) complexes have already been reported,¹²⁻¹⁴ in the present study, BQDMEN and [Cu(II)(bqdmn)](NO₃)₂ were prepared using a different method.

† To whom correspondence should be addressed.
E-mail: keisaito@kobe-u.ac.jp

Fig. 1 Synthesis of (a) BQDMEN and (b) BQDMPN.

CMQ (6.42 g; 0.03 mol) and DMEN (1.32 g; 0.015 mol) were dissolved in 75% ethanol containing NaOH (2.4 g; 0.06 mol). The pH of the reaction mixture was kept at 10 by adding an NaOH solution dropwise to the constantly stirred solution at 50°C. After about 3 h, the pH did not decrease. The reaction was considered to be at its end point (Fig. 1a). The reaction solution was diluted with 1 L of water. After the pH of the solution was adjusted to 2 with HNO₃, the solution was passed through a column (3 cm i.d. × 20 cm length) packed with SP-Sephadex C-25 (GE Healthcare Bio-Sciences AB, Uppsala, Sweden), followed by washing with 1 L of water. A suspension consisting of water and the resin was prepared in a beaker with a pH meter. After the pH of the suspension was adjusted to 4 with a concentrated NaOH solution, an excess Cu(NO₃)₂ solution was added to the suspension. The color of the resin changed to green immediately, suggesting that the desired [Cu(II)(bqdmn)]²⁺ was formed. The green resin was packed in a column, followed by washing with 1 L of dilute acetic acid. A 1 M NaNO₃ solution was passed through the column. The blue effluent from the column was collected and concentrated with an evaporator below 50°C. Blue plate crystals appeared in the solution after being allowed to stand overnight in a refrigerator. After filtration, the blue crystals were recrystallized twice from high-diluted acetic acid. Found: C, 49.15; H, 4.66; N, 14.23%. Calcd for [CuC₂₄H₂₆N₄](N₂O₆)·1.5H₂O: C, 49.27; H, 5.00; N, 14.36%.

Synthesis of BQDMPN and [Cu(II)(bqdmnpn)](NO₃)₂

CMQ (4.28 g; 0.02 mol) and DMPN (1.02 g; 0.01 mol) were dissolved in 200 mL of ethanol. To this solution was added 5 g of K₂CO₃, and the suspension was heated under reflux with vigorous stirring for 6 d (Fig. 1b). After cooling to room temperature, K₂CO₃ was filtered off. A brown oily residue remained after evaporating the solvent under reduced pressure. The residue was dissolved in 200 mL of petroleum ether. Colorless crystals appeared in the solution after being allowed to stand overnight at room temperature. Found: C, 77.82; H, 6.97; N, 14.46%. Calcd for C₂₅H₂₈N₄: C, 78.07; H, 7.35; N, 14.57%.

A solution of Cu(NO₃)₂·3H₂O (2.42 g; 0.01 mol) in 30 mL of

Fig. 2 Schematic diagram of the flow-injection fluorescence system. P1, P2 = pump; T = mixing tee; I = injector (20 µL); WB = water bath; RC = reaction coil; FL = fluorescence detector; DP = data processor; W = waste.

ethanol was added to a solution of BQDMPN (3.84 g; 0.01 mol) in 150 mL of 50% ethanol. The pH of the mixture was adjusted to 6 with an NaOH solution. The solution was constantly stirred at 50°C. After about 30 min, the reaction solution was diluted with 1 L of water, and then passed through a column (3 cm i.d. × 20 cm length) packed with SP-Sephadex C-25, followed by washing with 1 L of water. The blue band was retained on the resin. A 0.2 M NaNO₃ solution was passed through the column. The blue effluent from the column was collected and concentrated with an evaporator below 50°C. Dark-blue needle crystals appeared in the solution after being allowed to stand overnight in a refrigerator. Found: C, 52.20; H, 4.58; N, 14.53%. Calcd for [CuC₂₅H₂₈N₄](N₂O₆): C, 52.48; H, 4.94; N, 14.69%.

Apparatus

The absorption spectra were recorded on a Jasco V-550 spectrophotometer (Tokyo, Japan). The fluorescence and excitation spectra were recorded on a Shimadzu RF-5300 spectrofluorometer (Kyoto, Japan) with a quartz cell (1 cm × 1 cm cross-section) equipped with a xenon lamp and dual monochromators. For all experiments, the bandwidths for both excitation and emission were set at 5 nm.

Fluorometric detection of reductant with a flow-injection system

A schematic diagram of a flow-injection system used for fluorometric detection of reductants is shown in Fig. 2. A GL Sciences PU611 pump (GL Sciences, Tokyo, Japan) was used to

Fig. 3 Absorption spectra of (a) $[\text{Cu(I/II)(bqdmn)}]^{+/2+}$ and (b) $[\text{Cu(I/II)(bqdmnp)}]^{+/2+}$.

Fig. 4 Excitation spectra of (a) $[\text{Cu(I)(bqdmn)}]^+$ (λ_{em} , 403 nm) and (b) $[\text{Cu(I)(bqdmnp)}]^+$ (λ_{em} , 453 nm).

deliver the solutions. A Cu(II) complex solution and a buffer solution were delivered to a mixing tea. The mixed carrier solution was delivered to an FP 2020 fluorescence detector (Jasco, Tokyo, Japan) through a Rheodyne 7125 sample injector (Rheodyne, Cotati, CA) equipped with a 20 μL injector loop and a reaction coil in a thermostated water bath. The reaction coil and all connecting PTFE tubing were of 0.5 mm i.d. The resulting peak profiles were recorded on a PC.

Sample preparation of spring-water

Two spring-water samples were collected at the Hirota shrine, Nishinomiya, Hyogo, Japan (Water 1) and Nagatecho, Nada, Hyogo, Kobe, Japan (Water 2), and were filtered through a 0.45 μm membrane filter. The spiked spring-water samples were prepared by the addition of appropriate amounts of the standard solution of hydrazinium hydrogensulfate.

Results and Discussion

Absorption spectra of Cu(I/II) complexes

The absorption spectra of $[\text{Cu(I/II)(bqdmn)}]^{+/2+}$ and $[\text{Cu(I/II)(bqdmnp)}]^{+/2+}$ are shown in Figs. 3a and 3b, respectively. The Cu(I) complex solutions were prepared by reducing the corresponding Cu(II) complex solutions with excess ascorbic

acid in a 10 mM acetate buffer solution (pH 5.5) at 70°C for 5 min.

Figure 3 shows that Cu(II) complexes were reduced to corresponding Cu(I) complexes. The absorption maxima in the visible region of $[\text{Cu(II)(bqdmn)}]^{2+}$ and $[\text{Cu(II)(bqdmnp)}]^{2+}$ were observed at 642 and 694 nm, respectively. The molar absorption coefficients of $[\text{Cu(II)(bqdmn)}]^{2+}$ and $[\text{Cu(II)(bqdmnp)}]^{2+}$ were 160 and 130 $\text{cm}^{-1} \text{M}^{-1}$ at the maximal absorption wavelengths, respectively. These weak absorption bands are assignable to the d-d transition of the metal center because of the small molar absorption coefficients. The absorption maxima of $[\text{Cu(I)(bqdmn)}]^+$ and $[\text{Cu(I)(bqdmnp)}]^+$ were observed at 387 and 417 nm, respectively. The molar absorption coefficients of $[\text{Cu(I)(bqdmn)}]^+$ and $[\text{Cu(I)(bqdmnp)}]^+$ were 2100 and 2900 $\text{cm}^{-1} \text{M}^{-1}$ at the maximal absorption wavelengths, respectively. These absorption bands should be assignable to a metal-to-ligand charge-transfer transition.

Fluorescence spectra of Cu(I/II) complexes

Figure 4 shows the excitation spectra of $[\text{Cu(I)(bqdmn)}]^+$ and $[\text{Cu(I)(bqdmnp)}]^+$. The excitation maxima of $[\text{Cu(I)(bqdmn)}]^+$ and $[\text{Cu(I)(bqdmnp)}]^+$ were observed at 317 and 343 nm, respectively.

Figure 5a shows the fluorescence spectra of $[\text{Cu(I/II)}$

Fig. 5 Fluorescence spectra of (a) $[\text{Cu(I/II)}(\text{bqdmn})]^{+/2+}$ and BQDMEN, and (b) $[\text{Cu(I/II)}(\text{bqdmnp})]^{+/2+}$ and BQDMPN.

(bqdmn)] $^{+/2+}$ and BQDMEN acquired with excitation at 317 and 313 nm, respectively. The $[\text{Cu(I)}(\text{bqdmn})]^+$ solution was prepared by reducing $[\text{Cu(II)}(\text{bqdmn})]^{2+}$ with excess ascorbic acid at 70°C for 5 min. The BQDMEN solution was prepared in 50% ethanol. The emission maxima of $[\text{Cu(I)}(\text{bqdmn})]^+$ and BQDMEN were observed at 403 and 388 nm, respectively.

The fluorescence spectra of $[\text{Cu(I/II)}(\text{bqdmnp})]^{+/2+}$ and BQDMPN acquired with excitation at 343 and 271 nm, respectively, are shown in Fig. 5b. The $[\text{Cu(I)}(\text{bqdmnp})]^+$ solution was prepared by reducing $[\text{Cu(II)}(\text{bqdmnp})]^{2+}$ with excess ascorbic acid at 70°C for 5 min. The BQDMPN solution was prepared in 20% 1-propanol. The emission maxima of $[\text{Cu(I)}(\text{bqdmnp})]^+$ and BQDMPN were observed at 453 and 388 nm, respectively.

It has been reported that upon changing the metal ion and/or ligand the emission maxima of the metal complexes are altered. For example, the emission maximum of the Zn(II) complex with *N,N'*-bis(6-methoxy-2-quinolylmethyl)-*N,N'*-dimethylethylenediamine (6-MeOBQDMEN) was shifted to longer wavelengths by comparison with that of the free ligand, whereas the emission maximum of $[\text{Zn(II)}(\text{bqdmn})]^{2+}$ was slightly shifted to shorter wavelengths in comparison with that of the free ligand;⁷ the emission maxima of the metal complexes with 8-methoxyquinoline based ligands were shifted to longer wavelengths in comparison with those of the free ligands.¹⁵ The emission maxima of $[\text{Cu(I)}(\text{bqdmn})]^+$ and $[\text{Cu(I)}(\text{bqdmnp})]^+$ were shifted to longer wavelengths in comparison with those of the free ligands, as well as the Zn(II) complex with 6-MeOBQDMEN⁷ and the metal complexes with 8-methoxyquinoline-based ligands.¹⁵

Figure 5 shows that the fluorescence of $[\text{Cu(II)}(\text{bqdmn})]^{2+}$ and $[\text{Cu(II)}(\text{bqdmnp})]^{2+}$ are completely quenched, whereas $[\text{Cu(I)}(\text{bqdmn})]^+$ and $[\text{Cu(I)}(\text{bqdmnp})]^+$ are fluorescent in aqueous solution. The fluorescence intensities of $[\text{Cu(I)}(\text{bqdmn})]^+$ and $[\text{Cu(I)}(\text{bqdmnp})]^+$ at the maximal emission wavelengths are 5.2 and 1.7-times stronger than those of BQDMEN and BQDMPN, respectively, suggesting that the Cu(I) ions somewhat induce fluorescence enhancement. Fluorescent ligands that have a high degree of flexibility will tend to have lower fluorescence, which means that more rigid structures have more fluorescence potential.¹⁶ Since the ethylenediamine and 1,3-propanediamine moieties in BQDMEN

Fig. 6 Peak profiles of (1) sodium dithionite, (2) ascorbic acid, (3) hydrazinium hydrogensulfate, (4) hydroxylammonium chloride, and (5) sodium sulfite obtained with $[\text{Cu(I/II)}(\text{bqdmn})]^{+/2+}$ system. Sample solution: 20 μM . Conditions: Cu(II) complex solution, 0.16 mM $[\text{Cu(II)}(\text{bqdmnp})]^{2+}$ in 10 mM acetate buffer solution (pH 5.5)/ethanol = 4/1 (v/v); buffer solution, 30 mM borate buffer solution (pH 9)/ethanol = 4/1 (v/v); flow rate of a Cu(II) complex solution, 0.3 mL/min; flow rate of the buffer solution, 0.3 mL/min; reaction temperature, 65°C; reaction time, 3 min; λ_{ex} , 317 nm; λ_{em} , 411 nm.

and BQDMPN are rather flexible, the intensities of the fluorescence from $[\text{Cu(I)}(\text{bqdmn})]^+$ and $[\text{Cu(I)}(\text{bqdmnp})]^+$ are somewhat weak.

Fluorometric detection of reductant with flow injection system

The detection of eight compounds with a $[\text{Cu(I/II)}(\text{bqdmn})]^{+/2+}$ system was examined: sodium dithionite, ascorbic acid, hydrazinium hydrogensulfate, hydroxylammonium chloride, sodium sulfite, thiourea, oxalic acid, and sodium pyruvate. We used 0.16 mM $[\text{Cu(II)}(\text{bqdmn})]^{2+}$ in a 10 mM acetate buffer solution (pH 5.5)/ethanol = 4/1 (v/v) and a 30 mM borate buffer solution (pH 9)/ethanol = 4/1 (v/v) as a Cu(II) complex and buffer solutions (Fig. 2), respectively. The flow rates of the $[\text{Cu(II)}(\text{bqdmn})]^{2+}$ solution and the buffer solution were of 0.3 mL/min. The sample solution injected into the mixed carrier solution was delivered to the fluorescence detector (λ_{ex} = 317 nm, λ_{em} = 411 nm) through a reaction coil (3 min) in the water bath (65°C). Figure 6 shows the obtained results. Thiourea,

Fig. 7 Peak profiles of (1) sodium dithionite, (2) ascorbic acid, (3) hydrazinium hydrogensulfate, (4) hydroxylammonium chloride, and (5) sodium sulfite obtained with $[\text{Cu}(\text{I/II})(\text{bqdmnpn})]^{+/2+}$ system. Sample solution: 1 mM. Conditions: Cu(II) complex solution, 0.2 mM $[\text{Cu}(\text{II})(\text{bqdmnpn})]^{2+}$ in 10 mM acetate buffer solution (pH 5.5)/1-propanol = 4/1 (v/v); buffer solution, 40 mM borate buffer solution (pH 9)/1-propanol = 4/1 (v/v); flow rate of a Cu(II) complex solution, 0.3 mL/min; flow rate of the buffer solution, 0.3 mL/min; reaction temperature, 70°C; reaction time, 3 min; λ_{ex} , 343 nm; λ_{em} , 453 nm.

oxalic acid, and sodium pyruvate were not detected. The calibration curve for sodium dithionite, which is used as a food additive, was linear in the range of 6 to 20 μM (correlation coefficient, 0.9967), and the detection limit was 4 μM (signal-to-noise ratio 3).

The detection of five compounds with a $[\text{Cu}(\text{I/II})(\text{bqdmnpn})]^{+/2+}$ system was examined: sodium dithionite, ascorbic acid, hydrazinium hydrogensulfate, hydroxylammonium chloride, and sodium sulfite, which were detected with the $[\text{Cu}(\text{I/II})(\text{bqdmnpn})]^{+/2+}$ system. We used 0.2 mM $[\text{Cu}(\text{II})(\text{bqdmnpn})]^{2+}$ in a 10 mM acetate buffer solution (pH 5.5)/1-propanol = 4/1 (v/v) and 40 mM borate buffer solution (pH 9)/1-propanol = 4/1 (v/v) as the Cu(II) complex solution and buffer solution, respectively. The temperature of the water bath, λ_{ex} , and λ_{em} were set at 70°C, 343 nm, and 453 nm, respectively. Figure 7 shows the obtained results. Hydrazinium hydrogensulfate was selectively detected in comparison with the $[\text{Cu}(\text{I/II})(\text{bqdmnpn})]^{+/2+}$ system.

The fluorescence spectra of $[\text{Cu}(\text{I})(\text{bqdmnpn})]^+$ and $[\text{Cu}(\text{I})(\text{bqdmnpn})]^+$ obtained by reducing the corresponding Cu(II) complex solutions with a large excess of sodium sulfite were almost the same as those shown in Fig. 5. The differences in the peak height of each reductant are therefore presumed to be due to the differences in the reduction efficiency.

Hydrazine and its derivatives have been used in various fields, such as rocket fuel, synthetic raw material of agricultural, an oxygen scavenger and a resin curing agent. Hydrazine is poisonous, and is classified as Group 2B by the International Agency for Research on Cancer. Therefore, in order to increase the sensitivity for the detection of hydrazinium hydrogensulfate, the effects of the pH, flow rate, temperature, and $[\text{Cu}(\text{II})(\text{bqdmnpn})]^{2+}$ concentration on the signal-to-noise ratio were examined. The conditions determined as optimum for detecting hydrazinium hydrogensulfate were pH 9 (buffer solution), 0.1 mL/min (both $[\text{Cu}(\text{II})(\text{bqdmnpn})]^{2+}$ solution and buffer solution), 70°C, and 0.2 mM $[\text{Cu}(\text{II})(\text{bqdmnpn})]^{2+}$, respectively. The calibration curve under the optimal conditions was linear in the range of 0.05 to 1 mM (correlation coefficient, 0.9994) and the detection limit was 15 μM (signal-to-noise ratio 3). Spring-

Table 1 Analytical results for hydrazine in spiked spring-water samples

Sample	Added/ μM	Found/ μM	Recovery ^a , %
Water 1	100	110 $\pm$ 2	110 $\pm$ 2
	300	329 $\pm$ 4	109 $\pm$ 1
	600	676 $\pm$ 8	113 $\pm$ 1
Water 2	100	100 $\pm$ 4	100 $\pm$ 4
	300	371 $\pm$ 4	124 $\pm$ 1
	600	677 $\pm$ 12	113 $\pm$ 2

a. Values are means for three determination $\pm$ standard deviation.

water was analyzed to check the applicability of the proposed method. Non-spiked samples were first analyzed, but these samples did not show the presence of hydrazine. Therefore, subsequent samples were spiked with different quantities of hydrazinium hydrogensulfate. Table 1 gives the obtained results. The recoveries were 100 – 124%.

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