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# Fluorescent ligand design for mononuclear copper(I) complex fluorescence in aqueous solution

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ABSTRACT

The fluorescent ligands 3-(2-methylquinolyl)diethylenetriamine (QDETA) and bis(2-pyridylmethyl)(2-quinolylmethyl)amine (BPQA), and these Cu(II) complexes were synthesized. The fluorescence of $[Cu(I/II)(qdeta)]^{+/2+}$ and $[Cu(I/II)(bpqa)]^{+/2+}$ in aqueous solution was characterized; $[Cu(I)(qdeta)]^{+}$ and $[Cu(I)(bpqa)]^{+}$ were found to fluoresce in aqueous solution, whereas the fluorescence of $[Cu(II)(qdeta)]^{2+}$ and $[Cu(II)(bpqa)]^{2+}$ was almost completely quenched. The chelation enhanced fluorescence effect was observed for both $[Cu(I)(qdeta)]^{+}$ and $[Cu(I)(bpqa)]^{+}$. The pentacoordinated Cu(II) complex, $[Cu(II)(qdeta)(H_2O)]NDSA\cdot 2H_2O$ (NDSA = 1,5-Naphthalenedisulfonate anion) was characterized by single crystal X-ray crystallography. The geometry around the copper center is a distorted square pyramid with four nitrogen atoms from the QDETA and an oxygen atom from the aqua.

## 1. Introduction

Quenching of fluorescent ligands coordinated to transition metal ions has been often reported [1–3]. One of the reasons for the quenching is magnetism caused by the spin of unpaired electrons in transitional metal ions. A Cu(II) ion has an unpaired electron, whereas a Cu(I) ion does not have an unpaired electron. Therefore, the fluorescence of the ligands is not necessarily quenched in Cu(I) complexes. In fact, many fluorescent Cu(I) complexes have been reported [4–6]. As is well known, the structure of copper ion complexes depends on the configuration of d electrons. Cu(I) has a $d^{10}$ electronic configuration with tetrahedral geometry, whereas Cu(II) has a $d^9$ electronic configuration with square planar geometry [7–9]. Cu(I) complexes with 1,10-phenanthroline derivatives are known as typical metal complexes which undergo a large photoinduced structural change [10]. A d electron of the central copper ion is transferred to the ligands with metal-to-ligand charge transfer (MLCT) excitation and the central copper ion is formally oxidized from Cu(I) to Cu(II) which is subject to a Jahn-Teller distortion. Fluorescent properties of Cu(I) complexes with 1,10-phenanthroline derivatives have been reported to depend on difference in energy between the MLCT excited state and the Cu(I) ground state [11–13]. The flattened MLCT state either returns to the Cu(I) ground state via radiative decay pathway or forms a pentacoordinate complex with Lewis basic solvents, resulting in the “exciplex” quenching in this ligated MLCT state [14]. Although many fluorescent Cu(I) complexes have been reported [4–6], 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 fluorescence of Cu(I) complexes in aqueous media [15]. In addition, although fluorescence enhancement of $d^{10}$ complexes containing fluorescent ligands such as Zn(II) and Cd(II) complexes has been reported [16–19], quenching of a fluorescent Cu(I) complex in aqueous media has been reported [20].

From the perspectives described above, it is inferred that quenching of Cu(I) complexes with fluorescent ligands in aqueous media is due to the loss of excitation energy caused by the conformational change from the MLCT excited state to the Cu(I) ground state. Based on this inference, we have explored the fluorescent Cu(I) complexes which are less flattening distortion in the MLCT excited state through the design and synthesis of fluorescent ligands. Recently, we have reported that $[Cu(I)(bqdmen)]^{+}$ (bqdmen = *N,N’*-bis(2-methylquinolyl)dimethylethylenediamine) and $[Cu(I)(bqdmpn)]^{+}$ (bqdmpn = *N,N’*-bis(2-methylquinolyl)dimethyl-1,3-propanediamine) are fluorescent in aqueous

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solution, whereas the fluorescence of $[Cu(II)(bqdmen)]^{2+}$ and $[Cu(II)(bqdmpn)]^{2+}$ is completely quenched [21]. We also reported the coordinate structure of $[Cu(II)(bqdmpn)](NO_3)_2$ which formed a square planar [22]. Furthermore, we found that $[Cu(I)(qdeta)]^+$ (qdeta = 3-(2-methylquinolyl)diethylenetriamine) and $[Cu(I)(bpqa)]^+$ (bpqa = bis(2-pyridylmethyl)(2-quinolylmethyl)amine) are fluorescent in aqueous solution, whereas the fluorescence of $[Cu(II)(qdeta)]^{2+}$ and $[Cu(II)(bpqa)]^{2+}$ is almost completely quenched.

In the present paper, we report the fluorescence behavior of $[Cu(I/II)(qdeta)]^{+/2+}$ and $[Cu(I/II)(bpqa)]^{+/2+}$ in aqueous solution. Additionally, all the Cu(I) complexes were obtained by reacting the reductant with the Cu (II) complexes in aqueous solution, since we have not been able to isolate the Cu(I) complexes. We considered that the reaction of these Cu(II) complexes with reductant are completely achieve based on these constants in the fluorescence intensity and on these disappearances in the d-d transition spectra of these complexes over time. Furthermore, we report the coordination geometry of $[Cu(II)(qdeta)(H_2O)]NDSA$ (NDSA = 1,5-Naphthalenedisulfonate anion) with X-ray structural analysis.

## 2. Experimental

### 2.1. Materials, chemicals and apparatus

Diethylenetriamine, bis(2-pyridylmethyl)amine, and 2-chlorometylquinoline hydrochloride 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).

The absorption spectra were recorded on a Shimadzu UV-1600 spectrophotometer (Kyoto, 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.

### 2.2. Synthesis

#### 2.2.1. Synthesis of QDETA and $[Cu(II)(NO_3)(qdeta)]NO_3$

1,5-Diphthalimido-3-aza-pentane was synthesized from diethylenetriamine and phthalic anhydride according to a previous paper [23] [Scheme 1 (1)]. 1,5-Diphthalimido-3-aza-pentane (18.17 g; 50 mmol) and 2-(chloromethyl)quinoline hydrochloride (10.70 g; 50 mmol) were dissolved in 150 mL of acetonitrile. To this solution was added anhydrous potassium carbonate (20.73 g; 150 mmol), and the suspension was heated under reflux with vigorous stirring for 3.5 d [Scheme 1 (2)]. The progress of reaction was monitored by thin-layer chromatography (development solvent: hexane/ethyl acetate = 1/1). After cooling to room temperature, potassium carbonate was filtered off. After evaporating acetonitrile under reduced pressure, a yellow oily residue was dissolved in dichloromethane. The organic solution was washed three times with water and dried over anhydrous sodium sulfate. After sodium sulfate was filtered off, the filtrate was evaporated under reduced pressure. The yellow oily residue was dissolved in warmed methanol. A white powder of 3-(2-methylquinolyl)-1,5-diphthalimido-3-aza-pentane appeared in the solution after cooling to room temperature. 3-(2-Methylquinolyl)-1,5-diphthalimido-3-aza-pentane (10.08 g; 20 mmol) was dissolved in 300 mL of ethanol and 10-fold excess of hydrazine hydrate (10.01 g, 200 mmol) was added. The mixture was heated under reflux with stirring for 3 h [Scheme 1 (3)]. The progress of reaction was monitored by thin-layer chromatography (development solvent: hexane/ethyl acetate = 1/1). After cooling to room temperature, white solids were filtered off and washed with cold ethanol. Then, the wash liquid was combined with the filtrate. The ethanol solution was concentrated and cooled until by-products separated out. After the by-products were filtered off, the filtrate was evaporated under highly reduced pressure. QDETA was obtained as yellowish oil.

A solution of copper(II) nitrate trihydrate (2.42 g; 10 mmol) in 50 mL of ethanol was added to a solution of QDETA (2.44 g; 10 mmol) in 200 mL of 50% ethanol. The pH of the mixture was adjusted to 7–8 with a sodium hydroxide solution. The solution was constantly stirred at 50 °C for 60 min. After cooling to room temperature, a green algae-like substance appeared in the reaction solution. The green algae-like substance was filtered off. The dark blue filtrate 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 (GE Healthcare Bio-Sciences AB, Uppsala, Sweden), followed by washing with 1 L of water. The blue band was retained on the resin. A 0.2 M sodium nitrate solution was passed through the column. The dark blue effluent from the column was collected and concentrated with an evaporator under highly reduced pressure at room temperature. Blue needle crystals appeared in the solution after being allowed to stand overnight at room temperature. The confirmation of molecule structure was conducted by the use of X-ray structure analysis (Supplementary information 1 and 2).

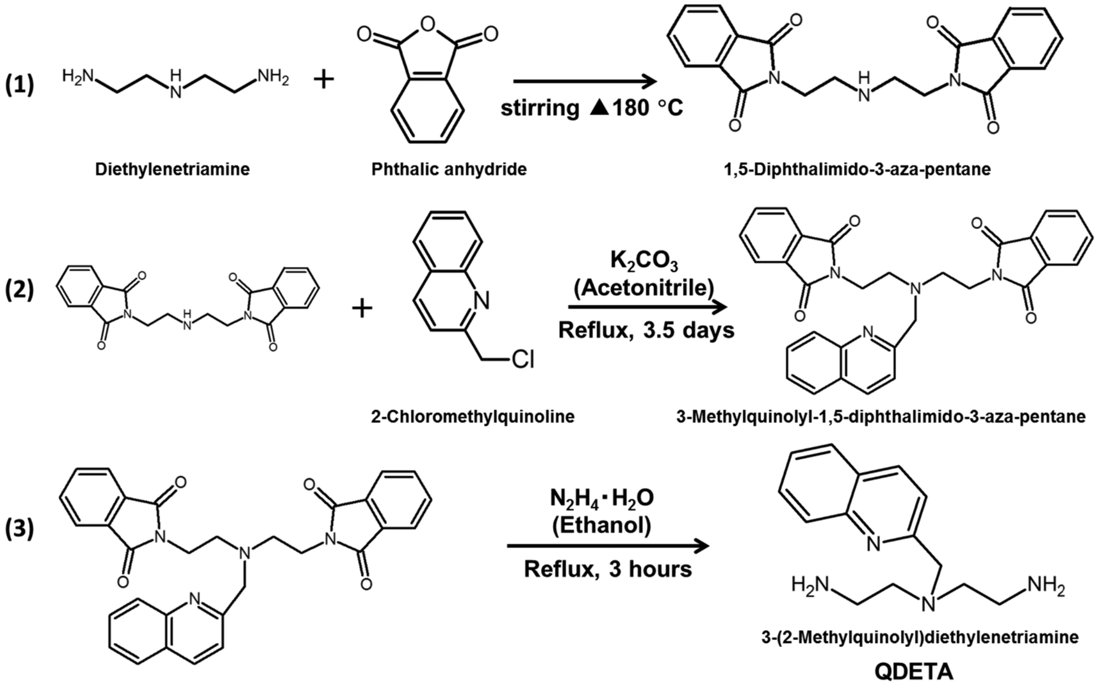
#### 2.2.2. Synthesis of $[Cu(II)(qdeta)(H_2O)]NDSA\cdot 2H_2O$

$[Cu(II)(NO_3)(qdeta)]NO_3$ (4.32 g; 10 mmol) was dissolved in 100 mL of water. Then, 10 mL of 0.2 M disodium 1,5-Naphthalenedisulfonate solution was added dropwise. Blue precipitate appeared in the solution after being allowed to stand overnight at room temperature. After filtration, the blue precipitates were recrystallized from water. Blue prismatic crystals were obtained. Yield: 1.29 g (20%). Found: C, 44.2; H, 5.1; N, 8.7; S, 9.9%. Calcd for $C_{24}H_{32}CuN_4O_9S_2$: C, 44.5; H, 5.0; N, 8.6; S, 9.9%.

#### 2.2.3. Synthesis of BPQA and $[Cu(II)(NO_3)(bpqa)]NO_3\cdot 2.5H_2O$

Although the synthesis of BPQA has already been reported [24], in the present study, BPQA was prepared using a different method. Bis(2-pyridylmethyl)amine (2.02 g; 10 mmol) and 2-(chloromethyl)quinoline (2.14 g; 10 mmol) were dissolved in 200 mL of ethanol. To this solution was added anhydrous potassium carbonate (6.91 g; 50 mmol), and the suspension was heated under reflux with vigorous stirring for 5 d (Scheme 2). After cooling to room temperature, potassium carbonate was filtered off. A yellow oily residue remained after evaporating ethanol under reduced pressure. The residue was dissolved in dichloromethane. The organic solution was washed several times with water and dried over anhydrous sodium sulfate. After sodium sulfate was filtered off, the filtrate was evaporated under reduced pressure. The yellow oily residue was dissolved in 200 mL of warmed hexane. A pale yellow powder appeared in the solution after being allowed to stand overnight at room temperature.

A solution of copper(II) nitrate trihydrate (2.42 g; 10 mmol) in 20 mL of ethanol was added to a solution of BPQA (3.40 g; 10 mmol) in 100 mL of ethanol. The solution was constantly stirred for 45 min at 50 °C. After cooling to room temperature, the reaction mixture was allowed to stand for a while. A precipitate appeared in the solution was filtered off. A light blue powder was obtained by drying. The light blue powder was dissolved in 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 green band was retained on the resin. A 0.2 M sodium nitrate solution was passed through the column. The blue effluent from the column was collected and concentrated with an evaporator under highly reduced pressure at room temperature. Blue plate crystals appeared in the solution after being allowed to stand overnight at room temperature. Yield: 1.54 g (27%). Found: C, 45.9; H, 4.1; N, 14.7%. Calcd for $C_{22}H_{25}CuN_6O_{8.5}$: C, 46.1; H, 4.4; N, 14.7%. The confirmation of coordination structure was conducted by the use of X-ray structure analysis (Supplementary information 1 and 3).



**Scheme 1.** Synthesis of QDETA.

### 2.3. X-ray crystallography

Crystals of [Cu(II)(qdeta)($H_2O$)]NDSA·$2H_2O$ suitable for X-ray analysis were obtained by slow recrystallization from water. The X-ray diffraction data for [Cu(II)(qdeta)($H_2O$)]NDSA·$2H_2O$ was collected at 93 K on a Rigaku VariMax Saturn724 diffractometer (Tokyo, Japan) using multi-layer mirror monochromated Mo-$K_\alpha$ with a radiation wavelength of 0.71075 Å. Data were processed using CrystalClear (Rigaku) [25]. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The entire refinement procedure was based on 6133 observed reflections and 361 variable parameters, which converged with unweighted and weighted agreement factors of $R_1$ [$I > 2\sigma(I)$] = 0.0281 and w$R_2$ (all data) = 0.0804, respectively.

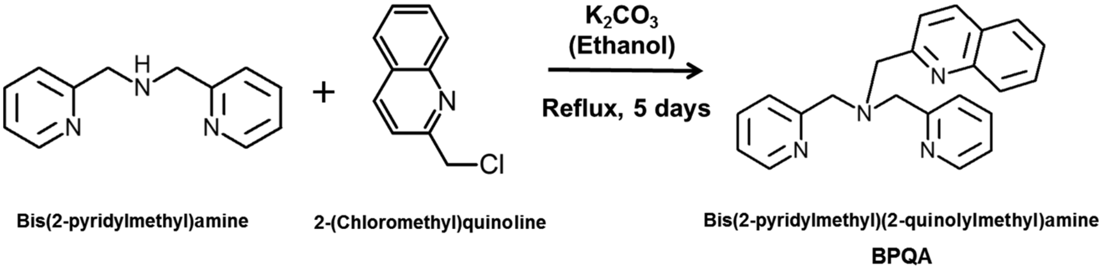
Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 [26]. All calculations were performed using the CrystalStructure (Rigaku) [27] crystallographic software package except for refinement, which was performed using SHELXL Version 2018/3 [28]. Details concerning collection and analysis are included in Table 1. Full structural data (atom coordinates, interatomic distances and bond angles) have been deposited with the Cambridge Crystallographic Data Centre: Deposit number CCDC-1917067.

## 3. Result and discussion

Under the conception that quenching of Cu(I) complexes with fluorescent ligands in aqueous media is due to the loss of excitation energy caused by the conformational change from the MLCT excited state to the Cu(I) ground state, we have explored the fluorescent Cu(I) complexes which are less flattening distortion in the MLCT excited state through the design and synthesis of fluorescent ligands. The QDETA and BPQA were designed and synthesized as the fluorescent ligands which are hard to form square planar geometry in Cu(II) complexes having $d^9$ electronic configuration. The spectral characteristics of the Cu(I/II) complexes with these ligands were investigated in aqueous media. In addition, the coordination geometries of [Cu(II)(qdeta)($H_2O$)]NDSA·$2H_2O$ was confirmed with X-ray crystallography.

### 3.1. Absorption spectra of Cu(I/II) complexes

The absorption spectra of $[\mathrm{Cu(I/II)(qdeta)}]^{+/2+}$ and $[\mathrm{Cu(I/II)(bpqa)}]^{+/2+}$ at pH 8 (borate buffer) are shown in Figs. 1 and 2, respectively. The Cu(I) complex solutions were prepared by reducing corresponding Cu(II) complex solutions with excess hydrazinium hydrogensulfate in a 100 mM borate buffer solution (pH 8) at 70 °C for 30 h. After cooling at room temperature, the absorption spectra were measured.



**Scheme 2.** Synthesis of BPQA.

**Table 1**
Crystal data and structure refinement for [Cu(II)(qdeta)($H_2O$)]NDSA·$2H_2O$.

| Complex | [Cu(II)(qdeta)($H_2O$)]NDSA·$2H_2O$ |
|---|---|
| Empirical formula | $C_{24}H_{32}CuN_4O_9S_2$ |
| Formula weight | 648.20 |
| Color | blue |
| Temperature (K) | 93 |
| Crystal System | monoclinic |
| Space Group | $P2_1/n$ (#14) |
| Crystal size (mm) | 0.300 × 0.200 × 0.150 |
| Lattice Type | Primitive |
| Lattice Parameters | |
| $a$ (Å) | 12.2756(19) |
| $b$ (Å) | 14.275(2) |
| $c$ (Å) | 16.108(3) |
| β (°) | 105.3814(16) |
| $V$ (Å$^3$) | 2721.7(7) |
| $Z$ | 4 |
| $D_{calc.}$ (g/cm$^3$) | 1.582 |
| Radiation (Å) | 0.71075 |
| $\mu$(Mo $K_\alpha$) (cm$^{-1}$) | 10.156 |
| $F$ (0 0 0) | 1348.00 |
| No. of reflections collected | 40,622 |
| No. of independent reflections | 6133 |
| $R_{int}$ | 0.0253 |
| $2\theta_{max}$ (°) | 55.0 |
| Goodness-of-fit on $F^2$ | 1.097 |
| $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0281$ |
| $R$ indices (all data) | $R = 0.0295$ |
| | $wR_2 = 0.0804$ |
| CCDC deposition number | 1,917,067 |

Fig. 1 shows the absorption spectra of Cu(II) complexes. The absorption maxima of [Cu(II)(qdeta)]$^{2+}$ and [Cu(II)(bpqa)]$^{2+}$ in the visible region were observed at 650 and 848 nm, respectively. The molar absorption coefficients of [Cu(II)(qdeta)]$^{2+}$ and [Cu(II)(bpqa)]$^{2+}$ were 90 and 180 cm$^{-1}$ M$^{-1}$ at the maximal absorption wavelengths, respectively. These weak absorption bands are assignable to d-d transition of metal center because of the small molar absorption coefficients. The absorption maximum and molar absorption coefficient of [Cu(II)(qdeta)]$^{2+}$ and [Cu(II)(bpqa)]$^{2+}$ in the ultraviolet region are shown in Table 2, respectively.

Fig. 2 shows the spectra of Cu(I) complexes. These absorbance of [Cu(I)(qdeta)]$^+$ and [Cu(I)(bpqa)]$^+$ increased as the wavelength became shorter. The absorption shoulder band and absorption maxima of [Cu(I)(qdeta)]$^+$ and [Cu(I)(bpqa)]$^+$ were observed at 248–252 and 258 nm, respectively. The molar absorption coefficients of [Cu(I)(qdeta)]$^+$ and [Cu(I)(bpqa)]$^+$ were 11,000 and 17000 cm$^{-1}$ M$^{-1}$ at the shoulder and maximal absorption wavelengths, respectively.

### 3.2. Fluorescence spectra of QDETA and BPQA

Since QDETA could not be isolated as a solid state, the fluorescence spectra of QDETA were measured by using a ligand substitution reaction. [Cu(II)($NO_3$)(qdeta)]$NO_3$ was dissolved in a 100 mM borate buffer (pH 8) to give a 10 μM solution, and then disodium dihydrogen ethylenediaminetetraacetate dihydrate was added to the solution to give a 1 mM solution. After the mixture was shaken and allowed to stand for 1 d, the excitation and fluorescence spectra were measured. Fig. 3(a) shows the excitation and fluorescence spectra of QDETA at pH 8. The fluorescence spectrum was measured with excitation at 313 nm because the excitation maximum was observed at 313 nm. The fluorescence maximum of QDETA was observed at 390 nm.

Since BPQA was insoluble in water, a 10 μM BPQA solution was prepared in ethanol/100 mM borate buffer solution (pH 8) = 1/1 (v/v). Fig. 3(b) shows the excitation and fluorescence spectra of BPQA at pH 8. The excitation maxima of BPQA were observed at 280 and 340 nm. The fluorescence spectrum of BPQA was acquired with excitation at 280 nm. The fluorescence maximum of BPQA was observed at 425 nm.

### 3.3. Fluorescence spectra of Cu(I/II) complexes

The fluorescence spectra of [Cu(I)(qdeta)]$^+$ and [Cu(I)(bpqa)]$^+$ shown in Fig. 4 were considered as fluorescence from Cu(I) complexes for the following reason. The emission maximal wavelengths of fluorescent spectra band from the reaction products of the Cu(II) complexes with reductive reagent differed from those of the free ligands, additionally the fluorescence intensities of [Cu(I)(qdeta)]$^+$ and [Cu(I)(bpqa)]$^+$ at the maximal emission wavelengths are stronger than those of QDETA and BPQA, respectively. Furthermore, we also confirmed that the fluorescence spectrum of a mixed solution containing fluorescent ligand, reducing agent, and borate buffer after heated for sufficient time was rarely different from the fluorescence ligand at pH 8. These experimental facts suggest that the fluorescence of the Cu (II) complex reduced product in aqueous solution is fluorescence from the Cu (I) complex.

Fig. 4(a) shows the excitation and fluorescence spectra of 10 μM [Cu(I/II)(qdeta)]$^{+/2+}$ solutions at pH 8. The [Cu(I)(qdeta)]$^+$ solution was prepared by reducing [Cu(II)(qdeta)]$^{2+}$ with excess hydrazinium hydrogensulfate in a 100 mM borate buffer solution (pH 8) at 70 °C for 27 h. After $N_2$ bubbling and cooling at room temperature, the excitation and fluorescence spectra were measured. The excitation maxima of [Cu(I)(qdeta)]$^+$ were observed at 256, 308, and 340 nm. The fluorescence spectra of [Cu(I/II)(qdeta)]$^{+/2+}$ were acquired with excitation at 340 nm. The emission maximum of [Cu(I)(qdeta)]$^+$ was observed at 450 nm. The emission maximum of [Cu(I)(qdeta)]$^+$ was shifted to longer wavelengths by comparison with that of the free ligand.

Fig. 4(b) shows the excitation and fluorescence spectra of 10 μM [Cu(I/II)(bpqa)]$^{+/2+}$ solutions at pH 8. The [Cu(I)(bpqa)]$^+$ solution was prepared by reducing [Cu(II)(bpqa)]$^{2+}$ with excess hydrazinium hydrogensulfate in a 100 mM borate buffer solution (pH 8) at 70 °C for 30 h. After $N_2$ bubbling and cooling at room temperature, the excitation

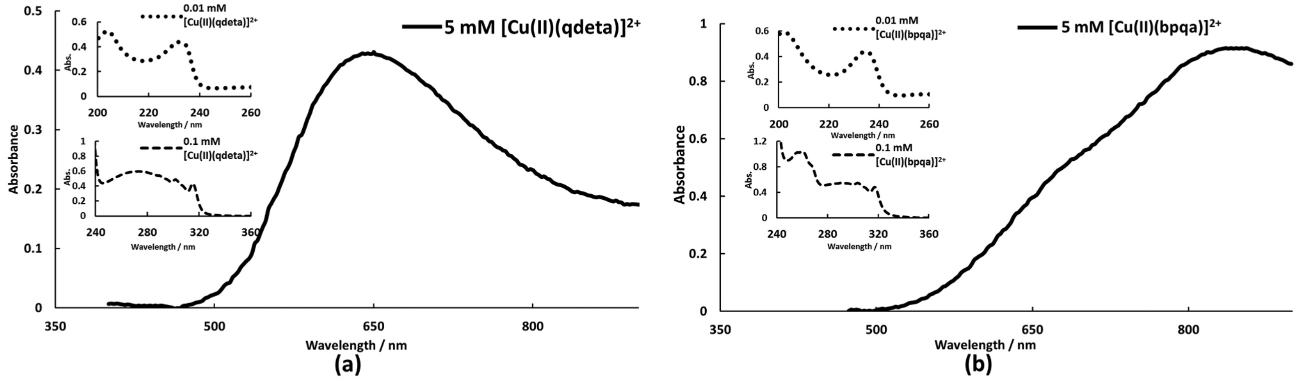


**Fig. 1.** Absorption spectra of (a) [Cu(II)(qdeta)]$^{2+}$ and (b) [Cu(II)(bpqa)]$^{2+}$ at pH 8 (borate buffer solution).

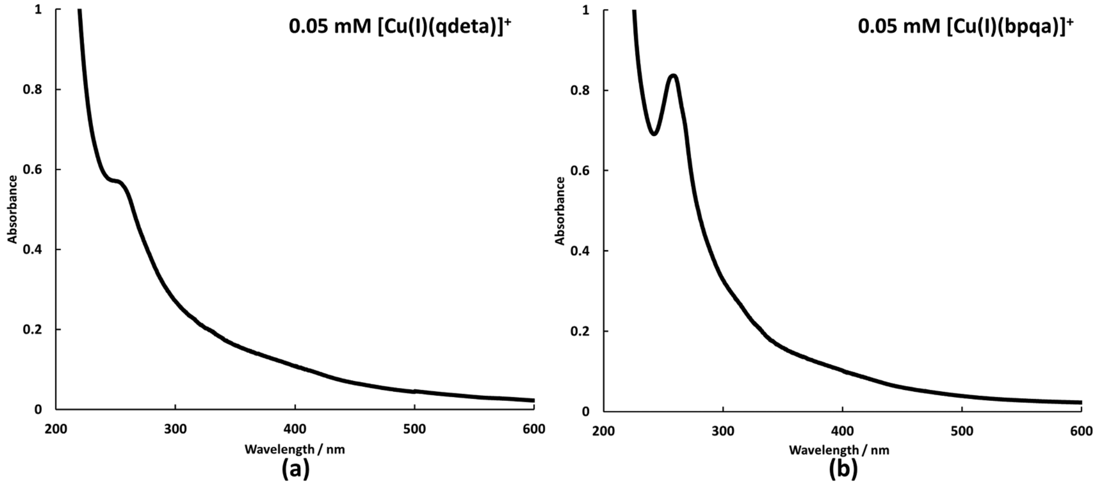


**Fig. 2.** Absorption spectra of (a) $[Cu(I)(qdeta)]^+$ and (b) $[Cu(I)(bpqa)]^+$ at pH 8 (borate buffer solution).

**Table 2**
Absorption data of $[Cu(I/II)(qdeta)]^{+/2+}$ and $[Cu(I/II)(bpqa)]^{+/2+}$.

| Complex | $\lambda_{abs}$/nm | $\varepsilon$/cm$^{-1}$ M$^{-1}$ | Solvent (pH) | Temperature |
|---|---|---|---|---|
| $[Cu(II)(qdeta)]^{2+}$ | 204 | 52,000 | Water (8.0) | r.t. |
| | 231 | 44,000 | | |
| | 273 | 6000 | | |
| | 301 | 4900 | | |
| | 315 | 4300 | | |
| | 650 | 90 | | |
| $[Cu(II)(bpqa)]^{2+}$ | 202 | 59,000 | Water (8.0) | r.t. |
| | 234 | 44,000 | | |
| | 260 | 10,000 | | |
| | 292 | 5500 | | |
| | 317 | 4800 | | |
| | 848 | 180 | | |
| $[Cu(I)(qdeta)]^+$ | 248–252* | 11,000 | Water (8.0) | r.t. |
| $[Cu(I)(bpqa)]^+$ | 258 | 17,000 | Water (8.0) | r.t. |

* Shoulder.

and fluorescence spectra were measured. The excitation maxima of $[Cu(I)(bpqa)]^+$ were observed at 244 and 317 nm. The fluorescence spectra of $[Cu(I/II)(bpqa)]^{+/2+}$ were acquired with excitation at 317 nm. The emission maximum of $[Cu(I)(bpqa)]^+$ was observed at 397 nm. The emission maximum of $[Cu(I)(bpqa)]^+$ was shifted to shorter wavelengths by comparison with that of the free ligand.

Fig. 4 shows that the fluorescence of $[Cu(II)(qdeta)]^{2+}$ and $[Cu(II)(bpqa)]^{2+}$ was almost completely quenched, whereas $[Cu(I)(qdeta)]^+$ and $[Cu(I)(bpqa)]^+$ are fluorescent in aqueous media. Fluorescence intensities of $[Cu(I)(qdeta)]^+$ and $[Cu(I)(bpqa)]^+$ at the maximal emission wavelengths are 21 and 14 times stronger than those of QDETA and BPQA, respectively, suggesting that Cu(I) ions induce fluorescence enhancement. These fluorescence quantum yields ($\phi$) were calculated using follow equation:

$$\phi s = \phi R\left(\frac{F_s}{F_R}\right)\left(\frac{\varepsilon_R C_R}{\varepsilon_s C_s}\right)$$

*F* is area of fluorescence spectrum. $\varepsilon$ is molar absorbance coefficient in excitation wavelength. *C* is molar concentration. The subscript $_R$ refers to the reference (quinine sulfate) fluorophore of known fluorescence quantum yield. The subscript $_S$ refer to the Sample solutions ($[Cu(I)(qdeta)]^+$ or $[Cu(I)(bpqa)]^+$). The emission quantum yields of $[Cu(I)(qdeta)]^+$ and $[Cu(I)(bpqa)]^+$ in aqueous solution at room temperature were 0.037 and 0.022, respectively (Table 3). Compared with previous study [21], the fluorescence intensity of Cu(I) complex in aqueous solution were almost same or upper than the copper complex containing bisquinoline-based ligand. As a result, we succeeded to design and synthesize the fluorescent ligands which are low the loss of excitation energy caused by the conformational change from the MLCT excited state to the Cu(I) ground state than previous ligand.

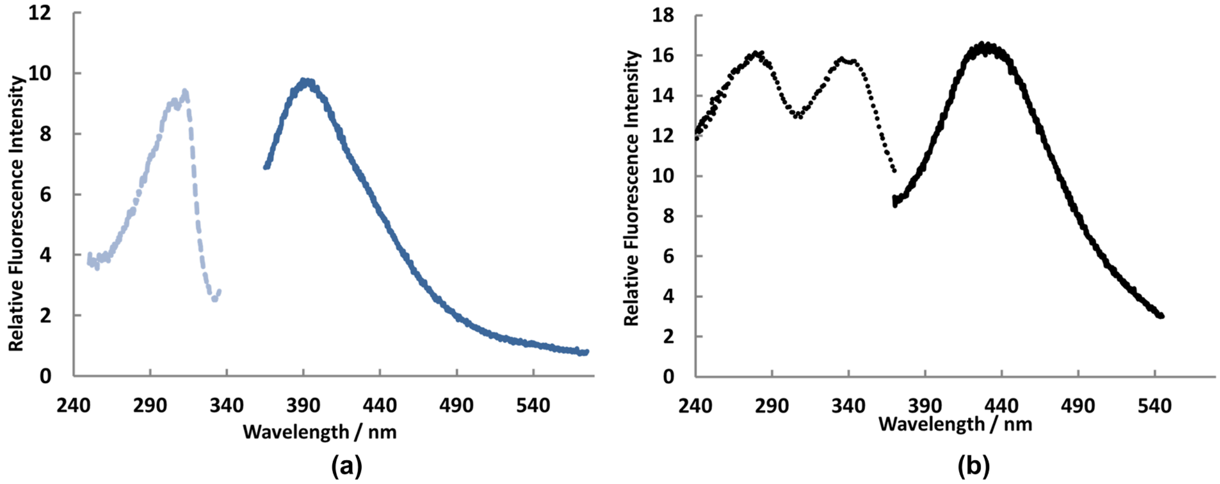


**Fig. 3.** Excitation and fluorescence spectra of fluorescent ligands at pH 8 (borate buffer solution); (a) 10 μM QDETA and (b) 10 μM BPQA.

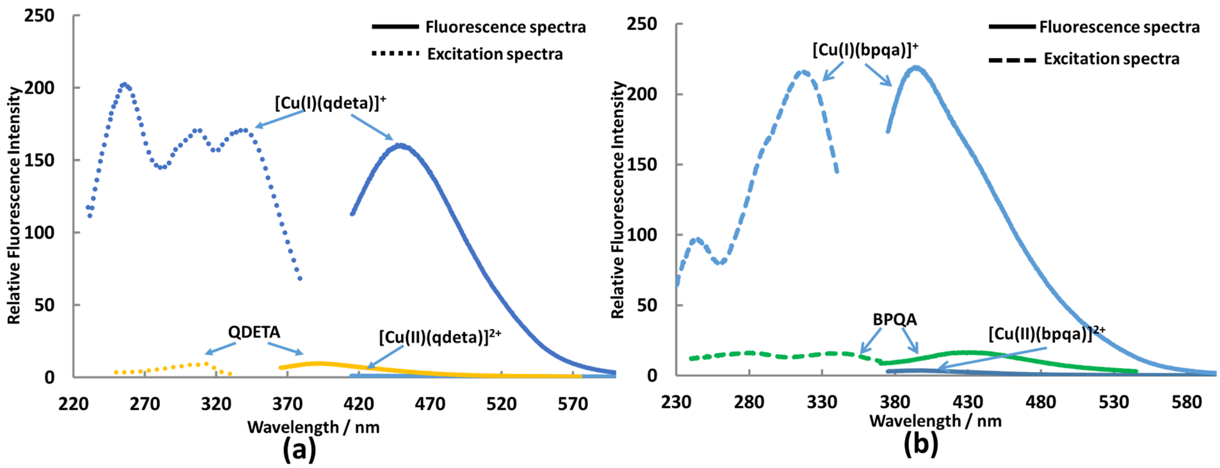


**Fig. 4.** Excitation and fluorescence spectra of Cu(I/II) complexes at pH 8 (borate buffer solution); (a) 10 µM $[Cu(I/II)(qdeta)]^{+/2+}$ and (b) 10 µM $[Cu(I/II)(bpqa)]^{+/2+}$.

**Table 3**
Fluorescence behavior data of $[Cu(I)(qdeta)]^+$ and $[Cu(I)(bpqa)]^+$.

| Complex | $\lambda_{ex}$/nm ($\varepsilon$/cm$^{-1}$ M$^{-1}$) | $\lambda_{em}$/nm | $\phi$ | Solvent (pH) | Temperature |
|---|---|---|---|---|---|
| $[Cu(I)(qdeta)]^+$ | 340* (3500), 308, 256 | 450 | 0.037 | Water (8.0) | r.t. |
| $[Cu(I)(bpqa)]^+$ | 317* (5100), 244 | 397 | 0.022 | Water (8.0) | r.t. |

*Used excitation wavelength.

### 3.4. *Coordination structure of $[Cu(II)(qdeta)(H_2O)]NDSA\cdot 2H_2O$*

The X-ray structural characterization of $[Cu(II)(qdeta)(H_2O)]NDSA\cdot 2H_2O$ revealed a discrete complex cation $[Cu(II)(qdeta)(H_2O)]^{2+}$ and a 1,5-naphthalenedisulfonate anion. The ORTEP view of $[Cu(II)(qdeta)(H_2O)]^{2+}$ is shown in Fig. 5(a) [29]. The geometry around the copper center is a distorted square pyramidal with QDETA and an aqua ligand. The copper atom is coordinated with four nitrogen atoms and one oxygen atom (Fig. 5(b) [30]), namely the tertiary amine-nitrogen N1, primary amine-nitrogen N2 and N3, quinolyl-nitrogen N4 atoms of QDETA, and the aqua ligand-oxygen atom O1. Relevant interatomic bond lengths and angles are presented in Table 4. The deviation from ideal square pyramidal geometry is manifested by the deviation of basal bond angles from 90°, that is, the bond angles of N1–Cu1–N2, N1–Cu1–N3, O1–Cu1–N2, and O1–Cu1–N3 are 85.40(4)°, 85.89(4)°, 92.21(4)°, and 92.55(4)°, respectively. Furthermore, on the basis of the coordinates shown in Table S6 (Supporting Information 4), the shortest distance from the O1 to a plane N2N1N3 is calculated to be about 0.44 Å, indicating that the O1 atom is not located in the plane N2N1N3. The shortest distance from the Cu1 to the plane N2N1N3 is calculated to be about 0.41 Å, indicating that the Cu1 atom also, is not located in the plane N2N1N3. The dihedral angle formed between the plane N1Cu1N3 and the plane O1Cu1N2 is calculated to be about 158.7°, indicating that the five atoms (N1, N2, N3, Cu1, O1) are not substantially coplanar. The bond angles of N4–Cu1–N1, N4–Cu1–N2,

**Table 4**
Selected bond distances (Å) and angles (°) for $[Cu(II)(qdeta)(H_2O)]NDSA\cdot 2H_2O$.

| Atom | Atom | Distance(Å) | Atom | Atom | Distance(Å) |
|---|---|---|---|---|---|
| Cu1 | N1 | 2.0646(10) | Cu1 | N4 | 2.2134(14) |
| Cu1 | N2 | 2.0176(12) | Cu1 | O1 | 1.9914(9) |
| Cu1 | N3 | 2.0047(12) | | | |

| Atom | Atom | Atom | Angle(°) | Atom | Atom | Atom | Angle(°) |
|---|---|---|---|---|---|---|---|
| N1 | Cu1 | N2 | 85.40(4) | N3 | Cu1 | N4 | 100.69(5) |
| N1 | Cu1 | N3 | 85.89(4) | O1 | Cu1 | N1 | 169.72(5) |
| N1 | Cu1 | N4 | 81.31(5) | O1 | Cu1 | N2 | 92.21(4) |
| N2 | Cu1 | N3 | 156.77(5) | O1 | Cu1 | N3 | 92.55(4) |
| N2 | Cu1 | N4 | 99.22(5) | O1 | Cu1 | N4 | 108.95(5) |

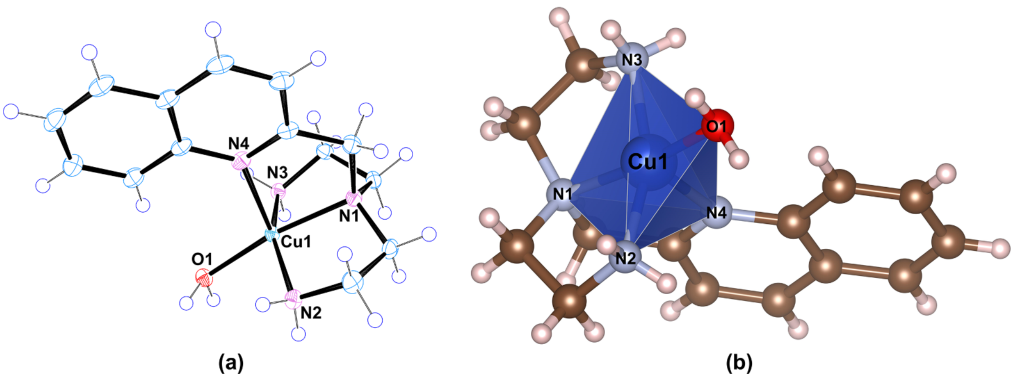


**Fig. 5.** (a) ORTEP view of $[Cu(II)(qdeta)(H_2O)]^{2+}$. Thermal ellipsoids are shown at the 50% probability level. (b) Coordinate structure of $[Cu(II)(qdeta)(H_2O)]^{2+}$.

N4–Cu1–N3, and N4–Cu1–O1 are 81.31(5)°, 99.22(5)°, 100.69(5)°, and 108.95(5)°, respectively, showing that the N4 atom occupies the apical position of distorted square pyramid. The Cu1–N4 distance (2.2134(14) Å) is somewhat longer than the Cu1–N1, Cu1–N2, Cu1–N3, and Cu1–O1 distances (1.9914(9)-2.0646(10) Å), showing that the quinolyl-nitrogen atom is bonded to the copper atom somewhat more weakly.

## 4. Conclusion

In order to create the Cu(I) complex that fluoresces in aqueous solution, we designed and synthesized the fluorescent ligands (QDETA and BPQA) which reduce the excited-state distortions in Cu(I) complexes. In addition, the coordinate structure of $[Cu(II)(qdeta)(H_2O)]^{2+}$ was a distorted square pyramidal.

In previous studies, bisquinolyl-type fluorescent ligands (BQDMPN) with two fluorescent sites were used, however the fluorescence intensity of $[Cu(I)(bqdmpn)]^+$ was weaker than Cu(I) complex containing the monoquinolyl-type of this study. The coordinate structure of $[Cu(II)(bqdmpn)]^{2+}$ was a square planer.

Assuming that the coordinate structure of $d^{10*}$ and $d^9$ state are the same, the coordinate structure of $[Cu(I)(bqdmpn)]^+$ form a square planar in the excited state ($d^{10*}$). Therefore, more excitation energy is consumed for conformation change when $[Cu(I)(bqdmpn)]^+$ in excited state ($d^{10*}$) return to the ground state ($d^{10}$). On the other hand, the coordinate structure of $[Cu(II)(qdeta)(H_2O)]^{2+}$ cannot form a square planar in the $d^9$ state. The coordinate structure of $[Cu(II)(qdeta)(H_2O)]^{2+}$ which is similar to a tetrahedral, has little distortion with the $d^{10}$ state. Therefore, the excitation energy consumed for conformation change is less and the fluorescence intensity is strong. The above explanation is suggested by the results of this study.

Based on the above, if the fluorescence ligand is designed to less distortion of copper complex in the $d^{10}$ state, the fluorescence enhancement of Cu(I) complex can be expected even in aqueous solution.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

CCDC 1917067 contain the supplementary crystallographic data for [Cu(II)(qdeta)(H2O)]NDSA·2H2O. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary material associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2019.119368.

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