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Cu(II)-selective fluorescence of a bis-quinolylimine derivative

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ABSTRACT

A new bis-quinolylimine ligand containing an azadiene moiety, 1,4-bis(2-quinolyl)-2,3-diaza-1,3-buthadiene (**1**), was synthesized by one-step facile condensation. This simple ligand, when dissolved in acetonitrile, shows a Cu^{2+}-selective fluorescence enhancement. Coordination of **1** with Cu^{2+} produces two kinds of complexes with 1:1 and 1:2 stoichiometries. The 1:2 complex shows a strong fluorescence ($\Phi_F = 0.37$), while the 1:1 complex does not ($\Phi_F < 0.01$). Ab initio molecular orbital calculation reveals that the 1:1 complex has a distorted structure, while the 1:2 complex has a planar structure. The planar configuration of the 1:2 complex, therefore, allows an extended π-conjugation over the entire molecule and, hence, results in fluorescence enhancement.

1. Introduction

The design and development of fluorescent signaling molecules is an area of intense research activity and of tremendous significance to the field of molecular device fabrication [1]. Various molecular systems whose emission properties can be modulated by external stimuli (temperature, light, redox potential, and pH) have been proposed [2]. Metal cations are often used as external stimuli, which promote fluorescence enhancement or quenching response associated with the coordination with ligand groups [3]. Copper(II) usually behaves as a fluorescence quencher via an energy transfer from the excited state fluorophore to the empty d-orbital [4]; therefore, many of the reported molecular systems show fluorescence quenching response upon addition of Cu^{2+} [5].

Recently, several molecular systems that show Cu^{2+}-selective fluorescence enhancement have been proposed based on several fluorophores such as rhodamine [6], pyrene [7], naphthalimide [8], and coumarin [9]. Quinoline-based molecules have attracted much attention because the quinoline moieties behave as a ligand for metal coordination as well as a fluorophore. A variety of quinoline derivatives has been proposed for selective fluorescence enhancement upon coordination of specific metal cations [10]. There are, however, only three reports of quinoline-based fluorophores showing a fluorescence enhancement response against Cu^{2+} [11].

Here we report a new family of quinoline-based fluorophore, 1,4-bis(2-quinolyl)-2,3-diaza-1,3-butadiene (**1**, Scheme 1), showing Cu^{2+}-selective fluorescence enhancement. This bis-quinolylimine ligand is obtained by one-step facile condensation with a moderate yield (60%), whereas the other quinoline-based ligands require more than two steps with a relatively low yield (11–57%) [11]. The ligand, **1**, shows a bright blue fluorescence upon Cu^{2+} coordination, while showing no fluorescence for other cations. We describe that the Cu^{2+}-selective fluorescence is due to the formation of **1**–Cu^{2+} 1:2 complex with an extended π-electronic structure over the entire molecule.

2. Experimental

2.1. Materials

All of the reagents used were purchased from Wako and Tokyo Kasei and used without further purification. Water was purified by a Milli Q system.

2.1.1. Synthesis of *1*

2-Quinolinecarbaldehyde (0.47 g, 3.0 mmol) and hydrazine hydrate (0.075 g, 1.5 mmol) were refluxed in MeOH (10 ml) for 17 h. The yellow solid formed was recovered by filtration, washed with EtOH, and recrystallized from $CHCl_3$, affording **1** as a yellow solid (0.280 g, 0.90 mmol, yield 60%). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ (ppm) = 8.82 (s, 2H), 8.33 (d, J = 8.6 Hz, 2H), 8.26 (d, J = 8.6 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 7.9 Hz, 2H), 7.77 (t, J = 7.7 Hz, 2H), 7.61 (t, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (ppm) = 161.38, 153.38, 148.24, 136.28, 129.93, 129.73, 128.78, 127.61, 127,59, 118.92. Elemental anal.: Calcd. for $C_{20}H_{14}N_4$: C

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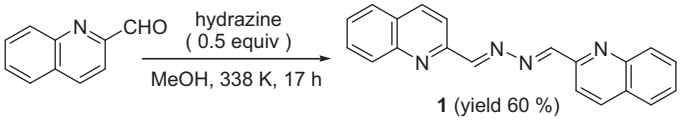


Scheme 1. Synthesis of the ligand **1**.

77.4, H 4.55, N 18.05; Found: C 77.18, H 4.34, N 18.07. ^{1}H and ^{13}C NMR charts are shown in Figs. S1 and S2, respectively (Supplementary Material).

2.2. Analysis

Steady-state fluorescence spectra were measured using a 10 mm path length quartz cell on a Hitachi F-4500 fluorescence spectrophotometer at 298 ± 1 K [12]. Absorption spectra were measured on an UV–vis photodiode-array spectrophotometer (Shimadzu; Multispec-1500) at 298 ± 1 K. Fluorescence lifetime was measured on a PTI-3000 apparatus (Photon Technology International) at 298 ± 1 K using a Xe nanoflash lamp filled with N_2 [13]. Fluorescence quantum yield (Φ_F) was determined by comparison of the integrated corrected emission spectrum of standard quinine, which was excited at 366 nm in H_2SO_4 (0.5 M, Φ_F = 0.55) [14]. Perchlorate salts were used as a metal source, and all measurements were carried out in an aerated condition. ^{1}H and ^{13}C NMR spectra were obtained by a JEOL JNM-GSX270 Excalibur. Elemental analysis was performed on a Perkin-Elmer 2400II CHN Elemental Analyzer. The program HYPERQUAD was used for determination of stability constants for Cu^{2+} complexes [15].

2.3. Ab initio calculation

The calculations were performed with the Gaussian 03 program [16]. Geometry optimization was carried out with the density functional theory (DFT) using the B3LYP function. Metal-free compounds were calculated using the 6-31G* basis set. Cu^{2+} complexes were calculated using the 6-31G* basis set for all atoms except for Cu, for which LANL2DZ basis set with effective core potential was used. Hg^{2+} complex was calculated using the 6-31G* basis set for all atoms except for Hg, for which the Stuttgart Relativistic Small-Core basis set with effective core potential was used.

3. Results and discussion

3.1. Synthesis and properties of the ligand

The bis-quinolylimine ligand, **1**, was synthesized by condensation of 2-quinolinecarboxyaldehyde and hydrazine with 60% yield (Scheme 1). Fig. 1a shows the fluorescence spectra (λ_{ex} = 369 nm) of **1** (20 μM) measured in MeCN with and without metal cation (3 equiv). Without cation, **1** shows almost no fluorescence with the fluorescence quantum yield (Φ_F) <0.004. Addition of Cu^{2+} to the solution, however, creates a strong fluorescence at 380–520 nm. As shown in Fig. 2, a bright blue fluorescence is observed upon Cu^{2+} addition. In contrast, addition of other metal cations (Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, and Hg^{2+}) to the solution shows almost no fluorescence (Fig. 1b). This suggests that **1** shows selective fluorescence enhancement against Cu^{2+}. It is noted that, as shown in Fig. S3 (Supplementary Material), the fluorescence enhancement upon Cu^{2+} addition occurs very slowly; 15 h stirring is required for saturation of the fluorescence intensity.

Fig. 3 shows the fluorescence excitation spectra of **1** monitored at 430 nm with and without metal cation. With Cu^{2+}, a vibrational excitation band appears at 350–410 nm. Addition of Hg^{2+} or Fe^{3+} also exhibits excitation band, but their wavelengths are much

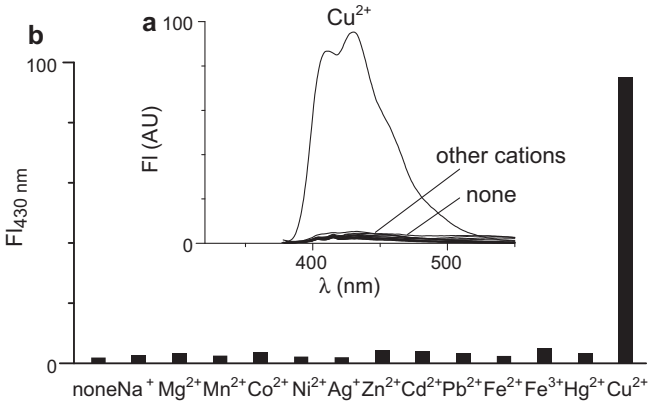


Fig. 1. (a) Fluorescence spectra (λ_{ex} = 369 nm) of **1** (20 μM) measured in MeCN with and without respective metal cation (3 equiv). (b) Fluorescence intensity of **1** at 430 nm. The spectra were measured after stirring the solution containing **1** and each metal cation for 24 h at 298 K.

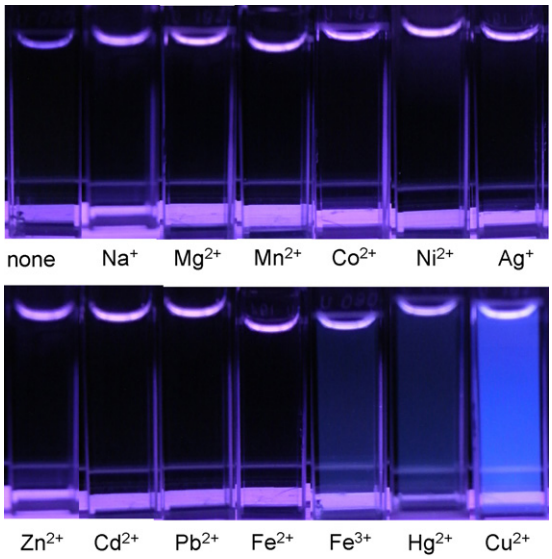


Fig. 2. Change in fluorescence emission color of MeCN solutions containing **1** and each metal cation.

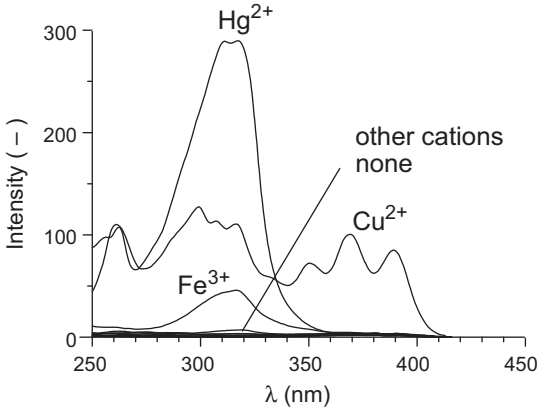


Fig. 3. Fluorescence excitation spectra (λ_{em} = 430 nm) of **1** (20 μM) measured in MeCN with and without respective metal cation (3 equiv). The spectra were measured after stirring the solution containing **1** and each metal cation for 24 h at 298 K.

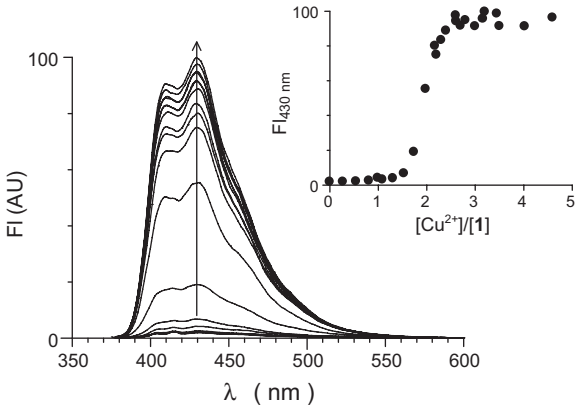


Fig. 4. Fluorescence spectra (λ_{ex} = 369 nm) of **1** (20 μM) measured in MeCN with different amount of Cu^{2+}. (Inset) Fluorescence intensity monitored at 430 nm. The spectra were measured after stirring the solution containing **1** and different amount of Cu^{2+} for 24 h at 298 K.

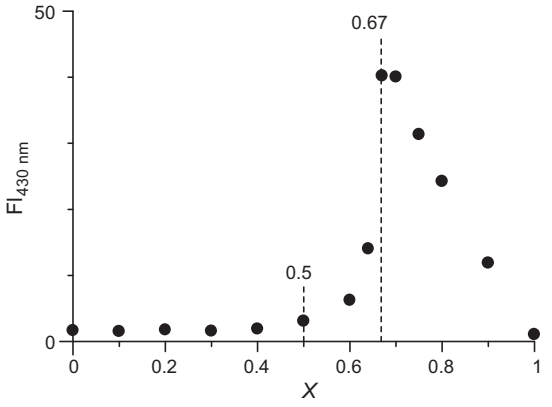


Fig. 5. Fluorescence-based Job's plot of **1** with Cu^{2+} (X = [Cu^{2+}]/([Cu^{2+}] + [**1**]) measured at λ_{ex} = 369 nm and λ_{em} = 430 nm. The total concentration of **1** and Cu^{2+} is set 20 μM.

shorter (<350 nm). This suggests that the interaction between **1** and Cu^{2+} produces an emitting species that is photoexcited at a longer wavelength. The photoexcitation at λ > 350 nm (Fig. 1) therefore allows selective fluorescence enhancement against Cu^{2+}. It must be noted that the Cu^{2+} sample, when left for 30 days (exposed to interior lighting at room temperature under aerated condition) does not show fluorescence decrease (Fig. S3, Supplementary Material). This indicates that the formed emitting species is chemically stable. It is also noted that the fluorescence response of **1** to Cu^{2+} is unaffected by many cations. As shown in Fig. S4 (Supplementary Material), addition of other metal cation (Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, or Fe^{3+}) to the solution containing **1** and Cu^{2+} scarcely affects the fluorescence intensity, although addition of Hg^{2+} leads to an intensity decrease. These indicate that **1** detects Cu^{2+} selectively even in the presence of many other cations.

3.2. Stoichiometry for Cu^{2+} coordination

Fig. 4 shows the fluorescence spectra of **1** measured at different Cu^{2+} concentration. With <1.5 equiv of Cu^{2+}, only a weak fluorescence enhancement is observed (Φ_F < 0.01), indicating that, at this concentration range, a nonfluorescent species is produced via the interaction with Cu^{2+}. Addition of >1.7 equiv of Cu^{2+}, however, leads to a strong fluorescence enhancement, where the intensity is saturated upon addition of >2.5 equiv of Cu^{2+} (Φ_F = 0.37). These imply that two kinds of **1**–Cu^{2+} complexes are produced in response to Cu^{2+} concentration. Fluorescence-based Job's plot analysis was performed to clarify the stoichiometry for association of **1** with Cu^{2+}. As shown in Fig. 5, two inflection points are observed at X (=[Cu^{2+}]/([Cu^{2+}] + [**1**])) = 0.5 and 0.67, suggesting that two kinds of **1**–Cu^{2+} complexes with 1:1 and 1:2 stoichiometries are produced. The apparent stability constants for the 1:1 and 1:2 complexes were determined by the Hyperquad program [15] to be log K(Cu**1**/Cu·**1**) = 8.9 and log K(Cu_2**1**/2Cu·**1**) = 14.5, respectively.

Fig. 6 shows the absorption spectra of **1** obtained at different Cu^{2+} concentration. Without cation, **1** exhibits a strong absorption band centered at 325 nm (ε = 37 940 M^{-1} cm^{-1}), which is assigned to the imine moiety (Ar–CH=N) [17]. Addition of <1.5 equiv of Cu^{2+} leads to a decrease in the 325 nm band, suggesting that the imine nitrogens are involved in Cu^{2+} coordination. Fig. 7 shows the fluorescence excitation spectra of **1** obtained at different Cu^{2+} concentration. Addition of <1.5 equiv of Cu^{2+} leads to a formation of excitation band at 270–350 nm, but the long wavelength band (350–410 nm) does not appear. The result is consistent with the flu-

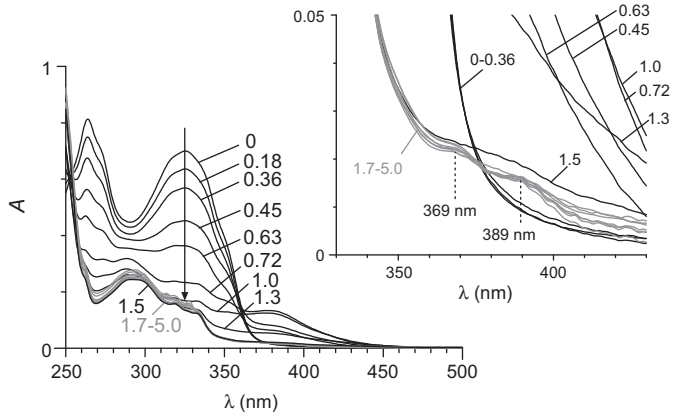


Fig. 6. Absorption spectra of **1** (20 μM) measured in MeCN at different Cu^{2+} concentration. The numbers in the Fig. denote the equivalents of Cu^{2+} added (0, 0.18, 0.36, 0.45, 0.63, 0.72, 1.0, 1.3, 1.5, 1.7, 2.0, 2.1, 2.3, 3, 3.75, and 5 equiv). The grey lines are the spectra obtained with 1.7–5.0 equiv of Cu^{2+}. The spectra were measured after stirring the solution containing **1** and different amount of Cu^{2+} for 24 h at 298 K.

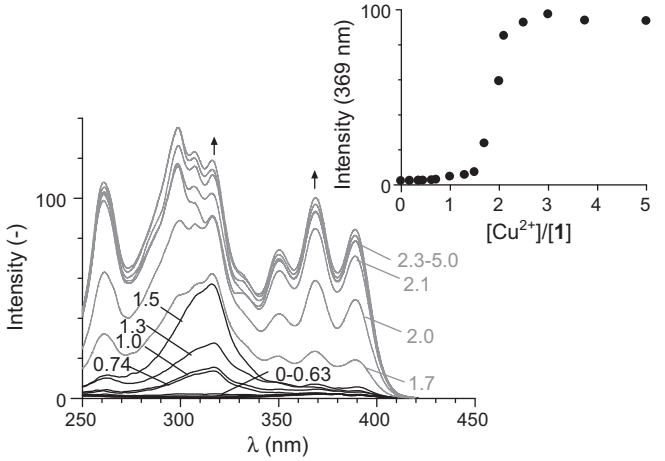


Fig. 7. Fluorescence excitation spectra (λ_{em} = 430 nm) of **1** (20 μM) measured in MeCN at different Cu^{2+} concentration. The numbers in the Fig. denote the equivalents of Cu^{2+} added (0, 0.18, 0.36, 0.45, 0.63, 0.72, 1.0, 1.3, 1.5, 1.7, 2.0, 2.1, 2.3, 3, 3.75, and 5 equiv). The grey lines are the spectra obtained with 1.7–5.0 equiv of Cu^{2+}. (Inset) Intensity monitored at 369 nm. The spectra were measured after stirring the solution containing **1** and different amount of Cu^{2+} for 24 h at 298 K.

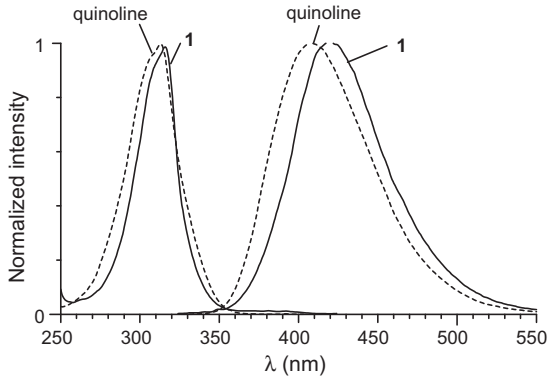
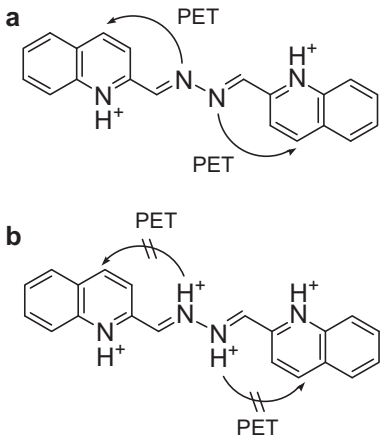


Fig. 8. Fluorescence (λ_{ex} = 316 nm) and excitation (λ_{em} = 410 nm) spectra of (dotted line) quinoline (40 μM) and (solid line) **1** (20 μM) measured in MeCN with 1 mM $HClO_4$.



Scheme 2. Effect of protonation of **1** on the intramolecular PET mechanism.

orescence data (Fig. 4). These indicate that the addition of <1.5 equiv of Cu^{2+} produces the 1:1 complex, which has no excitation band at 350–410 nm and shows almost no fluorescence upon excitation at >350 nm.

As shown in Fig. 6 (gray lines), addition of >1.7 equiv of Cu^{2+} leads to a minor absorption change, where weak absorption bands appear at 369 and 389 nm (inset). As shown in Fig. 7 (gray lines), addition of >1.7 equiv of Cu^{2+} leads to a formation of long wavelength excitation band at 350–410 nm. The band maxima at 350, 369, and 389 nm agree with the absorption band maxima (Fig. 6, inset). The inset of Fig. 7 shows the change in intensity of 369 nm band with the Cu^{2+} amount. The profile is similar to the fluorescence intensity profile (Fig. 4, inset). These clearly suggest that the addition of >1.7 equiv of Cu^{2+} produces the 1:2 complex, which has an excitation band at 350–410 nm and shows fluorescence upon excitation at >350 nm.

3.3. Coordination and fluorescence properties of the ligand

It is well known that a quinoline molecule is nonfluorescent because of its *n*, π* transition [18]. Protonation or metal coordination of quinoline nitrogen, however, converts the transition to π, π* and results in fluorescence enhancement. To clarify the fluorescence enhancement mechanism for the **1**–Cu^{2+} 1:2 complex, effects of proton on the fluorescence properties of quinoline and **1** were studied. Fluorescence titration of quinoline was performed in MeCN with $HClO_4$ (Fig. S5, Supplementary Material). The absence of H^+ shows no fluorescence, but H^+ addition (<0.05 mM) shows a strong fluorescence centered at ca. 410 nm, along with a formation of excitation band at 270–350 nm [19], as shown in Fig. 8 (dotted line). In contrast, **1** shows different fluorescence behaviors upon H^+ titration (Fig. S5, Supplementary Material). Addition of H^+ (<0.05 mM) does not show fluorescence, although the quinoline nitrogens of **1** are fully protonated. This is because, as shown in Scheme 2a, the photoinduced electron transfer (PET) from the imine nitrogens to the excited state quinoline moieties quenches the fluorescence [20]. However, as shown in Fig. 8 (solid line), further H^+ addition (>0.05 mM) promotes a fluorescence enhancement along with a formation of excitation band at 270–350 nm. This is because, as shown in Scheme 2b, protonation of imine nitrogens suppresses PET [20]. These indicate that the protonation (or metal coordination) of both quinoline and imine nitrogens of **1** is necessary for fluorescence enhancement. However, as shown in Fig. 8, the excitation spectrum of **1** measured with H^+ does not show longer wavelength excitation band at 350–410 nm, which is observed in the presence of Cu^{2+} (Fig. 7). This indicates that Cu^{2+} coordination is necessary for the formation of a longer wavelength excitation band.

The properties of fluorescence obtained upon excitation of the 1:2 complex at longer wavelength must be clarified. As shown in Fig. 9 (solid line), the excitation spectrum consists of two major bands at 270–350 nm and 350–410 nm, respectively. The former is similar to the band for the protonated quinoline and **1** (Fig. 8). Fig. 9 (dotted line) shows the fluorescence spectrum of 1:2 complex obtained upon excitation at 316 nm. A broad fluorescence centered at 410 nm appears, which is similar to the spectra for the protonated quinoline and **1** (Fig. 8). In contrast, as shown in Fig. 9 (dashed line), the excitation at 369 nm shows a red-shifted fluorescence centered at 430 nm, indicating that the longer wavelength excitation produces a different emitting species. Time-resolved emission decay analysis of the 1:2 complex (Fig. S6, Supplementary Material) reveals that the fluorescence obtained upon longer wavelength excitation has 3.3 ns lifetime, whereas that obtained upon shorter wavelength excitation has a much longer lifetime (30.1 ns). The fluorescence of the protonated quinoline (35.6 ns) and **1** (31.4 ns) also has a longer lifetime (Fig. S7, Supplementary material). This indicates that the fluorescence obtained upon shorter wavelength excitation of the 1:2 complex is due to the π, π* transition of the quinoline moieties [21], and that obtained upon longer wavelength excitation is due to the different emitting species.

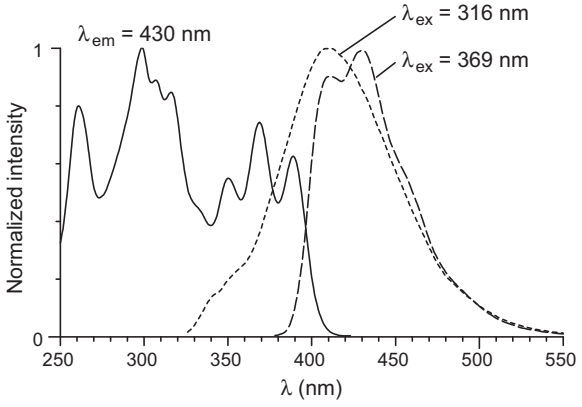


Fig. 9. Fluorescence spectra of **1** (20 μM) measured in MeCN with 3 equiv of Cu^{2+}, when excited at (dotted line) 316 nm and (dashed line) 369 nm. (Solid line) Fluorescence excitation spectrum monitored at 430 nm. The spectra were measured after stirring the solution containing **1** and Cu^{2+} for 24 h at 298 K.

Table 1
Geometry optimized structures of (a) **1**, (b) fully protonated form of **1**, (c) **1**–Cu^{2+} 1:1 complex, (d) **1**–Cu^{2+} 1:2 complex, and (e) **1**–Hg^{2+} 1:2 complex determined by ab initio calculation.[a]

Top view	Side view
(a) **1**	
(b) fully protonated form of **1**	
(c) **1**–Cu^{2+} 1:1 complex [**1**·Cu(MeCN)]$^{2+}$[b]	
(d) **1**–Cu^{2+} 1:2 complex [**1**·Cu_2(MeCN)$_2$]$^{4+}$[b]	
(e) **1**–Hg^{2+} 1:2 complex [**1**·Hg_2(MeCN)$_2$]$^{4+}$	

[a] The gray, blue, orange, black, and white atoms denote C, N, Cu, Hg, and H atoms, respectively.
[b] Counter anions of the complexes were omitted for clarity.

3.4. Emission mechanism for 1:2 complex

The longer wavelength excitation band for 1:2 complex is formed by extended π-conjugation over the entire molecule due to the planar configuration of the complex, as observed for related alkyne- or imine-containing molecules [22]. This is confirmed by coordination geometry of the complex, calculated with the Gaussian 03 program at the DFT level [16]. Table 1 shows the optimized geometry of the molecules. As shown in Table 1a, **1** has a planar structure, where the dihedral angle between two quinoline moieties is 0.0°. As shown in Fig. 8, the protonated form of **1** does not show longer wavelength excitation band, while showing π, π* band. As shown in Table 1b, the protonated **1** has a distorted structure with dihedral angle 72.2°. This may be due to the electrostatic repulsion of the positive charges. This probably leads to a disconnection of the π-conjugation over the entire molecule and results in the absence of long wavelength excitation band. In the case of **1**–Cu^{2+} 1:1 complex (Table 1c), all four nitrogens of **1** coordinate with Cu^{2+}, forming a (*E*,*Z*)-configuration. The complex also has a distorted structure with dihedral angle 59.5°. This may also suppress the π-conjugational extension, resulting in no formation of longer wavelength band. In contrast, for **1**–Cu^{2+} 1:2 complex (Table 1d), two Cu^{2+} are coordinated with each set of adjacent quinoline and imine nitrogens, forming a (*E*,*E*)-configuration. The dihedral angle of the complex is 5.2°, suggesting that the complex has a planar structure with a sp^2 hybridized bridging unit [22]. The 1:2 complex therefore allows an extended π-conjugation over the entire molecule and, hence, shows longer wavelength excitation band at 350–410 nm.

The above π-conjugation mechanism is further confirmed by the configuration of a **1**–Hg^{2+} 1:2 complex. As shown in Fig. 3, addition of Hg^{2+} to a solution containing **1** leads to a formation of π, π* transition band at 270–350 nm, but does not show longer wavelength band. As shown in Fig. S8 (Supplementary Material), Job's plot analysis indicates that **1** coordinates with Hg^{2+} in a 1:2 stoichiometry, as is the case for Cu^{2+}. However, as shown in Table 1e, the **1**–Hg^{2+} 1:2 complex has a distorted structure with dihedral angle 47.5°. The average distance of Hg–quinoline nitrogen is 2.16 Å, which is shorter than that of Hg–imine nitrogen (2.61 Å). In contrast, the distance of Cu–quinoline nitrogen (2.23 Å) of the **1**–Cu^{2+} 1:2 complex is longer than that of Cu–imine nitrogen (2.09 Å). The different distances for coordination of Hg^{2+} and Cu^{2+} are probably due to the stronger affinity of quinoline nitrogen with Hg^{2+} than Cu^{2+} [23]. The different coordination distance around Hg^{2+} probably leads to a distortion of the **1**–Hg^{2+} 1:2 complex (Table 1e). The above results again suggest that the π-conjugational extension of the **1**–Cu^{2+} 1:2 complex is due to the planar configuration of the complex.

3.5. Effect of other factors on fluorescence properties of 1:2 complex

The above results suggest that the coordination geometry of the **1**–Cu^{2+} 1:2 complex is crucial for fluorescence enhancement. It is well known that coordination of imine ligands with metal cations depends on several factors such as solvents and counter anions [24]. The fluorescence properties of the 1:2 complex are also affected by these factors: (i) the fluorescence intensity depends strongly on solvents. As shown in Fig. S9 (Supplementary Material), cyanide solvents such as MeCN and butylonitrile show strong fluorescence, while other common solvents such as alcohols show very weak fluorescence. This is probably because the cyanide molecules behave as a ligand for Cu^{2+} center (Table 1) [25]. (ii) Addition of water leads to a decrease in fluorescence intensity. As shown in Fig. S10 (Supplementary Material), the fluorescence intensity of the 1:2 complex in MeCN is not affected by the addition of 0.05% water, but 0.2% and 1% additions lead to 54% and 93% intensity decrease. (iii) Counter anion of Cu^{2+} also strongly affects the intensity. As shown in Fig. S11 (Supplementary Material), addition of $Cu(ClO_4)_2$ or $Cu(OTf)_2$ to **1** shows strong fluorescence, while $CuCl_2$ or $Cu(NO_3)_2$ does not. These findings suggest that application of this ligand for fluorescence sensing of Cu^{2+} in real environmental samples is difficult at present. However, the mechanism for Cu^{2+}-selective fluorescence enhancement based on the structure change upon Cu^{2+} coordination may contribute to the development of new Cu^{2+}-selective fluorescent ligands.

4. Conclusion

We found that a bis-quinolylimine ligand, **1**, shows a selective fluorescence enhancement against Cu^{2+}. Coordination of **1** with two Cu^{2+} (1:2 complex formation) creates a new emitting species that is photoexcited at 350–410 nm, while the addition of other metal cations does not create such species. The **1**–Cu^{2+} 1:2 complex has a planar structure and, hence, promotes an extension of π-electrons over the entire molecule. This thus allows fluorescence enhancement upon photoexcitation at 350–410 nm. The fluorescence properties of the 1:2 complex depend strongly on several factors such as solvents and counter anions. Although further investigation on the extended π-conjugation mechanism for fluorescence enhancement is still required, the simple mechanism driven by Cu^{2+}-induced structure change would be effective for creation of new Cu^{2+}-selective fluorescent ligands.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.10.018.

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