A quinoline–polyamine conjugate as a fluorescent chemosensor for quantitative detection of Zn(II) in water

Yasuhiro Shiraishi,* Chizuru Ichimura and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

Abstract—A simple ligand (**L1**), a diethylenetriamine bearing two end quinoline fragments, was synthesized. Without metal cations, **L1** shows no fluorescence at pH 2–13; however, Zn^{2+} addition creates strong fluorescence at pH 5–12. The emission intensity exhibits linear and stoichiometrical response to the Zn^{2+} amount. No remarkable emission enhancement was, however, observed for other cations.
© 2007 Elsevier Ltd. All rights reserved.

Design of artificial receptors for monitoring biologically and environmentally important ionic species in aqueous solution is currently of great importance.[1] Zinc(II) is an abundant component in the human body and is known to play many important roles in living organisms. Much effort has therefore been devoted to the design of fluorescent chemosensors for the quantitative detection of Zn^{2+},[2] because they allow simple and rapid detection of Zn^{2+} by a simple fluorescence enhancement without special instrumentation. So far, various fluorescent Zn^{2+} sensors have been proposed; however, most of these lack sufficient solubility in water.[3] Water-soluble fluorescent Zn^{2+} sensors have also been proposed; however, these often suffer from two problems: (i) appearance of background fluorescence even without Zn^{2+};[4] (ii) nonlinear and nonstoichiometrical response to Zn^{2+} amount due to weak binding ability.[4d–f,5] To the best of our knowledge, there are only four reports of the water-soluble fluorescent Zn^{2+} sensor with linear and stoichiometrical response to the Zn^{2+} amount and without background fluorescence.[6]

Herein, we report that a simple-structured ligand (**L1**), a diethylenetriamine bearing two end quinoline (QN) fragments (Scheme 1), is a new member of the water-soluble fluorescent Zn^{2+} sensor capable of showing linear and stoichiometrical response to the Zn^{2+} amount without background fluorescence. It is well-known that most
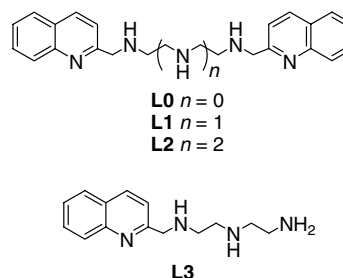
Scheme 1. Structure of quinoline–polyamine conjugates.

of the fluorescent Zn^{2+} sensors show similar fluorescence enhancement against Cd^{2+}, because of the electronic and binding properties of Cd^{2+} similar to that of Zn^{2+}.[4a–d,6a,b,7] We also describe here that the **L1** sensor selectively emits when binding with Zn^{2+}, while showing no remarkable emission enhancement for other cations.

The **L1** ligand is easily synthesized by one-pot reaction in ethanol via condensation of diethylenetriamine and 2-quinolinecarbaldehyde followed by reduction with $NaBH_4$ (81% yield).[8]

As shown in Figure 1a, **L1** dissolved in water (50 μM) shows almost no fluorescence ($\lambda_{ex} = 316$ nm) at pH 2–13 ($\phi < 0.001$). This is due to the photoinduced electron transfer (PET) from the amine nitrogens to the photoexcited QN fragments. As shown in Figure 1b (dotted

* Corresponding author. Tel.: +81 6 6850 6271; fax: +81 6 6850 6273; e-mail: shiraish@cheng.es.osaka-u.ac.jp
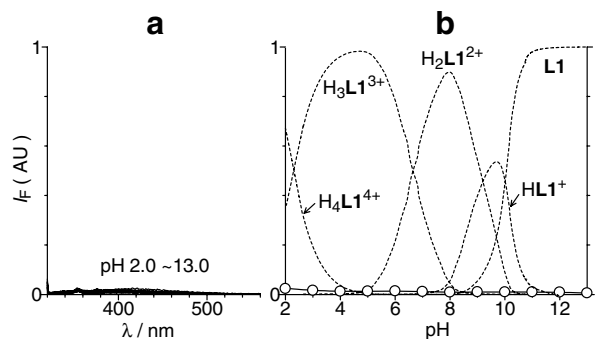
Figure 1. (a) pH-dependent change in fluorescence spectra ($\lambda_{ex} = 316$ nm; 298 K) of **L1** (50 μM) in aqueous NaCl (0.15 M) solution measured without metal cations. (b) pH-dependent change in fluorescence intensity monitored at 410 nm (open symbols) and mole fraction distribution of the species (dotted line).

Figure 2. (a) pH-dependent change in fluorescent spectra ($\lambda_{ex} = 316$ nm) of **L1** (50 μM) in aqueous NaCl (0.15 M) solution measured with 1 equiv of $ZnCl_2$. (b) pH-dependent change in the emission intensity monitored at 410 nm (closed symbols) and mole fraction distribution of the species (dotted line).

line), mole fraction distribution of the species, which is calculated from the protonation constants determined potentiometrically,[9] reveals that, at pH > 6, amine nitrogens of **L1** are partially or fully deprotonated ($H_2\mathbf{L1}^{2+}$, $H\mathbf{L1}^+$, and **L1** species form). These species, therefore, undergo PET to the photoexcited QN fragments, leading to emission quenching.[3b,10] This is confirmed by ab initio calculation[11] using time-dependent density functional theory (TDDFT) with the B3LYP/6-31+G(d) basis (Tables S1 and S4[12]). Electron density of HOMO orbital of the fully deprotonated **L1** species is located on the polyamine chain, while π-orbital of the QN fragments is located at the lower energy level than HOMO,[3b] indicating that PET actually quenches the **L1** fluorescence. As shown in Figure 1b, at 2 < pH < 6, $H_3\mathbf{L1}^{3+}$ and $H_4\mathbf{L1}^{4+}$ species exist, where all three amine nitrogens of both species are protonated and one QN fragment of the latter species is also protonated;[13] however, both species still show no fluorescence. This is due to the photoinduced proton transfer (PPT) from the amine nitrogen to the excited-state of the unprotonated QN fragment.[14] This leads to subsequent PET from the resulting deprotonated amine nitrogen to the photoexcited QN fragment, resulting in emission quenching at 2 < pH < 6. As a result of this, background fluorescence of **L1** does not appear at pH 2–13 (Fig. 1).[15]

Zn^{2+} addition to a solution containing **L1** allows an appearance of distinctive QN fluorescence at 320–560 nm (Fig. 2a). Figure 2b shows pH-dependent change in the emission intensity of **L1** (monitored at 410 nm) obtained with 1 equiv of Zn^{2+}, where dotted lines in the figure denote the mole fraction distribution of the species, which is calculated from the protonation and stability constants determined potentiometrically.[9] The emission intensity is almost zero at pH < 4, where Zn^{2+}-free $H_4\mathbf{L1}^{4+}$ and $H_3\mathbf{L1}^{3+}$ species exist. In contrast, at pH > 4, the intensity drastically increases with a pH increase, which is in accordance with the formation of Zn^{2+}–**L1** complexes ($HZn\mathbf{L1}^{3+}$ and $Zn\mathbf{L1}^{2+}$ species).[16] The emission appearance upon the coordination of Zn^{2+} with **L1** is due to the decrease in electron density of the amine nitrogens[17] of **L1**, leading to the suppression of PET from the unprotonated amine nitrogens to
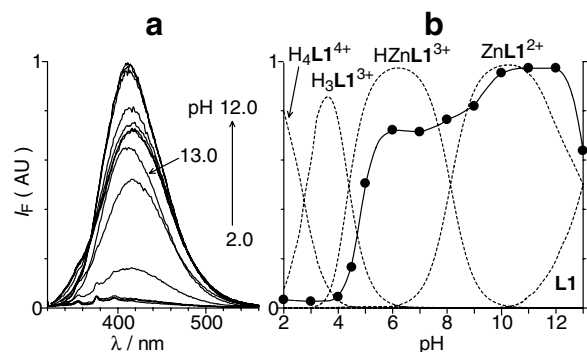
the excited QN fragment. TDDFT calculation of $Zn\mathbf{L1}^{2+}$ complex with the B3LYP/LANL2DZ basis (Tables S2 and S4[12]) reveals that the lowest singlet electron transition of the complex is ππ* and the electron density located on the polyamine chain, observed for the free **L1** (Tables S1 and S4[12]), is neither observed on HOMO nor on the lower energy level orbitals (HOMO−1, −2, and −3). This finding clearly suggests that the PET suppression by the coordination with Zn^{2+} allows the appearance of the **L1** emission.

As shown in Figure 2b, the emission intensity of the $Zn\mathbf{L1}^{2+}$ complex ($\phi = 0.042$ at pH 10.5) is 1.3-fold higher than that of the $HZn\mathbf{L1}^{3+}$ complex ($\phi = 0.027$ at pH 7.0). This indicates that Zn^{2+} coordination with all of the amine nitrogens of **L1** produces stronger emitting species. In addition, nanosecond time-resolved emission decay measurement reveals that the $Zn\mathbf{L1}^{2+}$ emission has a decay time (14.2 ns) longer than that of $HZn\mathbf{L1}^{3+}$ (9.2 ns) (Fig. S4[12]). As shown in Figure 2b, the emission intensity decreases at pH > 12. This is due to the removal of Zn^{2+} from the **L1** ligand by a Zn hydroxide formation.

It is notable that **L0**, **L2**, and **L3** ligands (Scheme 1; see: Synthesis[12]), comprised of one QN fragment or different lengths of polyamine chains, show much weaker emission intensity (less than half of that of **L1**) in the presence of 1 equiv of Zn^{2+}, although background fluorescence of these ligands is almost zero (Fig. S5[12]). This implies that the coordination geometry of the amine and the QN nitrogens to Zn^{2+} strongly affect the QN emission intensity.

A notable feature of the **L1** emission is the linear and stoichiometrical response to the Zn^{2+} amount. As shown in Figure 3, stepwise Zn^{2+} additions to **L1** both at pH 7.0 and 10.5 clearly demonstrate the linear increase in the emission intensity, and the increase is precisely saturated upon the addition of 1 equiv of Zn^{2+}. This indicates that the Zn^{2+} coordination with **L1** (formation of $HZn\mathbf{L1}^{3+}$ and $Zn\mathbf{L1}^{2+}$ complexes) is quite strong. This is consistent with the high stability constants for the respective $HZn\mathbf{L1}^{3+}$ ($\log K(HZn\mathbf{L1}/$
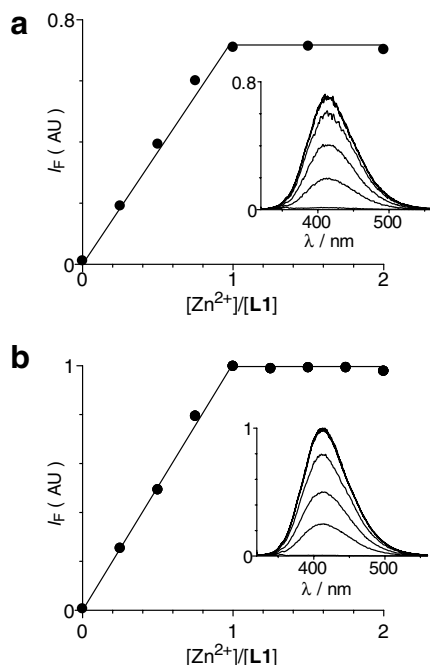
Figure 3. Change in fluorescence intensity of **L1** (50 μM) monitored at 410 nm with the amount of Zn^{2+} added at pH (a) 7.0 (KH_2PO_4–NaOH buffered solution) and (b) 10.5.

HL1·Zn) = 11.48) and $ZnL1^{2+}$ (log K(ZnL1/Zn·L1) = 13.14) complexes. **L1** and therefore has a potential as a fluorescent chemosensor for quantitative detection of Zn^{2+} in aqueous solution of neutral–basic media (pH 5–12).

Another notable feature of **L1** is the high emission selectivity to Zn^{2+}. As shown in Figure 4, other metal cations show no remarkable emission enhancement both at pH 7.0 and 10.5. Absorption spectra of **L1** scarcely change upon the addition of Li^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, and Al^{3+} (Fig. S6[12]). This is because, as is also observed for related polyamine ligands,[17d,e] **L1** scarcely coordinate with these cations. Other metal cations coordinate with **L1**. Co^{2+}, Ni^{2+}, Cu^{2+}, and Mn^{2+}, however, lead to an energy transfer from the photoexcited QN fragment to their empty d-orbital,[17] thus resulting in emission quenching. Hg^{2+}, Pb^{2+}, and Ag^+ accelerate the intersystem crossing (ISC) of singlet excited-state (S_1) QN to its triplet (nonfluorescent) excited-state (T_n) via a spin–orbital coupling,[17c–e,18] thus also resulting in emission quenching.

A noteworthy feature of **L1** is the very low response to Cd^{2+} (Fig. 4). As reported,[4a–d,6a,b,7] diamagnetic Cd^{2+} usually shows coordination behavior and emission response similar to the diamagnetic Zn^{2+}; the ratio of the fluorescence intensity obtained with Zn^{2+} in relation to that obtained with the same amount of Cd^{2+} is less than 5, with few exceptions.[19] However, the intensity ratio of the present **L1** sensor is about 7 (Fig. 4). Potentiometrical[9] and fluorescence titration measurements (Figs. S7 and S8[12]) reveal that Cd^{2+} strongly coordinates with **L1** and forms 1:1 complex (HCdL1[3+] and CdL1[2+] species form), as is also the case for Zn^{2+}, although the sta-
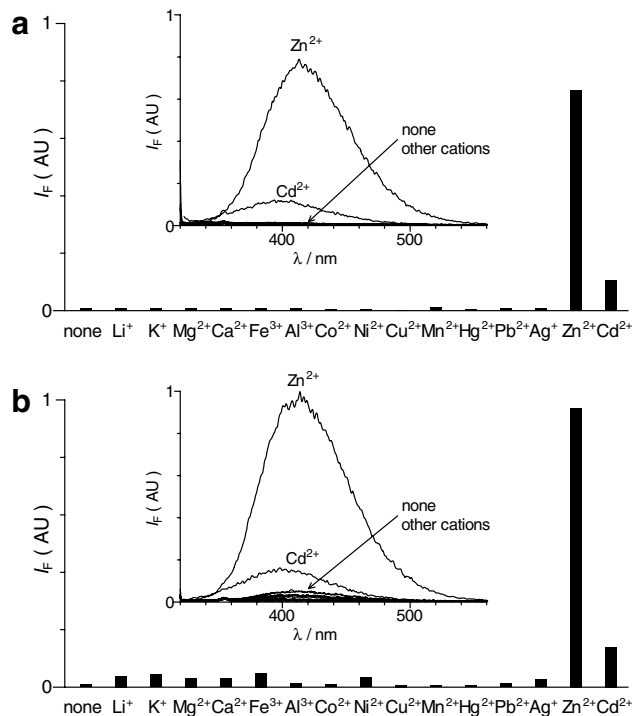

Figure 4. Fluorescence spectra and intensity (monitored at 410 nm) of **L1** (50 μM) measured with respective metal cations (1 equiv) at pH (a) 7.0 (KH_2PO_4–NaOH buffered solution) and (b) 10.5.

bility constants for these complexes (log K(HCdL1/Cd·HL1) = 10.64; (CdL1/Cd·L1) = 11.01) are relatively lower than that of the Zn complexes (log K > 11.4).[9] These indicate that the low fluorescence response to Cd^{2+} (Fig. 4) is due to the photophysical properties of the Cd^{2+}–**L1** complexes. TDDFT calculation of the CdL1[2+] complex reveals that the lowest singlet electronic transition is $\pi\pi^*$ (Tables S3 and S4[12]), as is also the case for ZnL1[2+]. However, phosphorescence intensity of the CdL1[2+] complex, when measured in methanol/water glass (4/1 v/v; pH 10.5) at 77 K,[20] is larger than twice that of the ZnL1[2+] complex (Fig. S9[12]). This suggests that ISC of the S_1 state QN is much accelerated within the CdL1[2+] complex and is definitely the reason for the low fluorescence response to Cd^{2+}. As reported, the ISC efficiency depends strongly on (i) the energy gap between S_1 and T_n lying just below the S_1 state (ΔE_{ST})[21] and (ii) the spin–orbital coupling effect.[17,18] TDDFT calculation (Tables S2 and S3[12]) reveals that ΔE_{ST} $(S_1 \rightarrow T_4)$ of the CdL1[2+] complex (0.4104 eV) is larger than ΔE_{ST} $(S_1 \rightarrow T_4)$ of the ZnL1[2+] complex (0.1883 eV). As reported,[21] ISC occurs efficiently within the system with a smaller ΔE_{ST} value. These findings indicate that the ISC enhancement of the S_1 state QN fragment driven by the spin–orbital coupling with Cd^{2+} results in the low fluorescence intensity of the Cd^{2+}–**L1** complexes (Fig. 4).

In conclusion, we have synthesized a new water-soluble fluorescent Zn^{2+} sensor, **L1**, which shows linear and stoichiometrical fluorescence response to Zn^{2+} at pH 5–12 without the appearance of background fluorescence. **L1** may be applicable as one of the fluorescent chemosen-

sors for quantitative detection of Zn^{2+} in aqueous solution. The emission enhancement of **L1** is responsive for Zn^{2+}, while other cations, especially for Cd^{2+}, show no remarkable emission enhancement. This unusual low response to Cd^{2+} is due to the enhanced ISC of the S_1 state QN fragment by the Cd^{2+} coordination. The obtained findings indicate that the ligand design using a quinoline moiety may open the way toward the development of water-soluble fluorescent chemosensor for selective Zn^{2+} detection.

Acknowledgements

Supplementary data

Supplementary data (Synthesis, experimental procedure, Figs. S1–S12, Tables S1–S4, and Cartesian Coordinates for free **L1** ligand and $ZnL1^{2+}$ and $CdL1^{2+}$ complexes). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet. 2007.09.032.

References and notes

1. (a) *Fluorescent Chemosensors of Ion and Molecule Recognition*; Czarnik, A. W., Ed.; American Chemical Society: Washington DC, 1993; (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566; (c) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3–40; (d) Rurack, K.; Resch-Genger, U. *Chem. Soc. Rev.* **2002**, *31*, 116–127; (e) Amendola, V.; Fabbrizzi, L.; Licchelli, M.; Mangano, C.; Pallavicini, P.; Parodi, L.; Poggi, A. *Coord. Chem. Rev.* **1999**, *190–192*, 649–669; (f) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59–83; (g) Rurak, K. *Spectrochim. Acta A* **2001**, *57*, 2161–2195.

2. (a) Kimura, E.; Aoki, S. *Biometals* **2001**, *14*, 191–204; (b) Jiang, P.; Guo, Z. *Coord. Chem. Rev.* **2004**, *248*, 205–229.

3. For example: (a) Wu, J.-S.; Liu, W.-M.; Zhuang, X.-Q.; Wang, F.; Wang, P.-F.; Tao, S.-L.; Zhang, X.-H.; Wu, S.-K.; Lee, S.-T. *Org. Lett.* **2007**, *9*, 33–36; (b) Salman, H.; Tai, S.; Chuvilov, Y.; Solovey, O.; Abraham, Y.; Kapon, M.; Suwinska, K.; Eichen, Y. *Inorg. Chem.* **2006**, *45*, 5315–5320; (c) Wu, D.-Y.; Xie, L.-X.; Zhang, C.-L.; Duan, C.-Y.; Zhao, Y.-G.; Guo, Z.-J. *Dalton Trans.* **2006**, 3528–3533; (d) Fahrni, C. J.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 11448–11458; (e) Xu, Z.; Qian, X.; Cui, J.; Zhang, R. *Tetrahedron* **2006**, *62*, 10117–10122; (f) Zhang, G.; Yang, G.; Wang, S.; Chen, Q.; Ma, J. S. *Chem. Eur. J.* **2007**, *13*, 3630–3635; (g) Zhang, L.; Dong, S.; Zhu, L. *Chem. Commun.* **2007**, 1891–1893; (h) Zepata, F.; Caballo, A.; Espinosa, A.; Tárraga, A.; Morina, P. *Org. Lett.* **2007**, *9*, 2385–2388; (i) Dessingou, J.; Joseph, R.; Rao, C. *Tetrahedron Lett.* **2005**, *46*, 7967–7971; (j) Mikata, Y.; Wakamatsu, M.; Kawamura, A.; Yamanaka, N.; Yano, S.; Odani, A.; Morihiro, K.; Tamotsu, S. *Inorg.*

Chem. **2006**, *45*, 9262–9268; (k) Wang, J.; Xiao, Y.; Zhang, Z.; Qian, X.; Yang, Y.; Xu, Q. *J. Mater. Chem.* **2005**, *15*, 2836–2839; (l) Lu, C.; Xu, Z.; Cui, J.; Zhang, R.; Qian, X. *J. Org. Chem.* **2007**, *72*, 3554–3557.

4. For example: (a) Koike, T.; Watanabe, T.; Aoki, S.; Kimura, E.; Shiro, M. *J. Am. Chem. Soc.* **1996**, *118*, 12696–12703; (b) Royzen, M.; Durandin, A.; Young, Y. G., Jr.; Geacintov, N. E.; Canary, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 3854–3855; (c) Nolan, E. M.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 8310–8317; (d) Nolan, E. M.; Burdette, S. C.; Hervey, J. H.; Hilderbrand, S. A.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 2624–2635; (e) Burdette, S. C.; Frederickson, C. J.; Bu, W.; Lippard, S. J. *J. Am Chem. Soc.* **2003**, *125*, 1778–1787; (f) Chang, C. J.; Nolan, E. M.; Jaworski, J.; Burdette, S. C.; Sheng, M.; Lippard, S. J. *Chem. Biol.* **2004**, *11*, 203–210; (g) Yin, Q.; Zhang, Z.; Zhao, Y.-F. *J. Chem. Res.* **2006**, 160–162; (h) Wooddroofe, C. C.; Won, A. C.; Lippard, S. J. *Inorg. Chem.* **2005**, *44*, 3112–3120; (i) Sclafani, J. A.; Maranto, M. T.; Sisk, T. M.; Van Arman, S. A. *Tetrahedron Lett.* **1996**, *37*, 2193–2196.

5. For example: (a) Komatsu, K.; Kikuchi, K.; Kojima, H.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2005**, *127*, 10197–10204; (b) Fabbrizzi, L.; Licchelli, M.; Mancin, F.; Pizzeghello, M.; Rabaioli, G.; Taglietti, A.; Tecilla, P.; Tonellato, U. *Chem. Eur. J.* **2002**, *8*, 94–101; (c) Chang, C. J.; Nolan, E. M.; Jaworski, J.; Okamoto, K.-I.; Hayashi, Y.; Sheng, M.; Lippard, S. J. *Inorg. Chem.* **2004**, *43*, 6774–6779.

6. (a) Aoki, S.; Sakurama, K.; Matsuo, N.; Yamada, Y.; Takasaka, R.; Tanuma, S.-i.; Shiro, M.; Takeda, K.; Kimura, E. *Chem. Eur. J.* **2006**, *12*, 9066–9080; (b) Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590–3593; (c) de Silva, S. A.; Zavaleta, A.; Baron, D. E. *Tetrahedron Lett.* **1997**, *38*, 2237–2240; (d) Castagnetto, J. M.; Canary, J. W. *Chem. Commun.* **1998**, 203–204.

7. For example: (a) Aoki, S.; Kagata, D.; Shiro, M.; Takeda, K.; Kimura, E. *J. Am. Chem. Soc.* **2004**, *126*, 13377–13390; (b) Lim, N. C.; Schuster, J. V.; Porto, M. C.; Tanudra, M. A.; Yao, L.; Freake, H. C.; Brückner, C. *Inorg. Chem.* **2005**, *44*, 2018–2030; (c) Lim, N. C.; Brückner, C. *Chem. Commun.* **2004**, *43*, 1094–1095; (d) Parkesh, R.; Lee, T. C.; Gunnlaugsson, T. *Org. Biomol. Chem.* **2007**, *5*, 310–317; (e) Taki, M.; Wolford, J. L.; O'Halloran, T. V. *J. Am. Chem. Soc.* **2004**, *126*, 712–713; (f) Maruyama, S.; Kikuchi, K.; Hirano, T.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2002**, *124*, 10650–10651.

8. Compound **L1**. 2-Quinolinecarbaldehyde (0.47 g, 3.0 mmol) and diethylenetriamine (0.16 g, 1.5 mmol) were dissolved in ethanol (50 mL) and stirred at 298 K for 17 h under dry N_2. $NaBH_4$ (1.03 g, 27 mmol) was carefully added to the solution and stirred for 4 h at 323 K. The solvent was removed by evaporation. Water (30 mL) and CH_2Cl_2 (90 mL) were added to the residue, and the resulting organic layer was dried over Na_2SO_4 and concentrated by evaporation. The semisolid residue was dissolved in ethanol and precipitated by an addition of concentrated aqueous HCl solution, affording a flesh-colored powder of **L1** as its HCl salt (0.60 g, yield: 81%). ^{1}H NMR (270 MHz, DMSO-d_6, TMS): δ (ppm) = 3.56 (s, 8H, CH_2 of polyamine), 4.65 (s, 4H, ArCH_2), 7.64–8.50 (m, 12H, ArH). ^{13}C NMR (270 MHz, DMSO-d_6, TMS): δ (ppm) = 152.24, 146.07, 137.14, 129.98, 128.01, 127.79, 126.94, 126.76, 120.12, 50.55, 42.79, 42.59. Anal. Calcd for $C_{24}H_{27}N_5$: 385.23. FAB-MS: m/z 386.2 (M+H$^+$). ^{1}H, ^{13}C NMR, and FAB-MS spectra of **L1**: see Figures S10–S12.

9. Potentiometric titration was carried out in an aqueous NaCl (0.15 M) solution at 298 K. The program HYPER-

QUAD (Sabatini, A.; Vacca, A.; Gans, P. *Coord. Chem. Rev.* **1992**, *120*, 389–405.) was employed for the determination of the protonation and stability constants, where K_w (=[H$^+$][OH$^-$]) value used was $10^{-14.00}$ (298 K). The stepwise protonation constants of **L1**: $\log K$(H**L1**/H·**L1**) = 9.91, (H$_2$**L1**/H·H**L1**) = 9.17, (H$_3$**L1**/H·H$_2$**L1**) = 6.66, (H$_4$**L1**/H·H$_3$**L1**) = 2.54. The stability constants for coordination between **L1** and 1 equiv of Zn^{2+}: $\log K$(Zn**L1**/Zn·**L1**) = 13.14, (HZn**L1**/Zn·H**L1**) = 11.48; between **L1** and 1 equiv of Cd^{2+}: $\log K$(Cd**L1**/Cd·**L1**) = 11.01, (HCd**L1**/Cd·H**L1**) = 10.64.

10. (a) Shiraishi, Y.; Tokitoh, Y.; Nishimura, G.; Hirai, T. *Org. Lett.* **2005**, *7*, 2611–2614; (b) Shiraishi, Y.; Tokitoh, Y.; Hirai, T. *Org. Lett.* **2006**, *8*, 3841–3844; (c) Shiraishi, Y.; Tokitoh, Y.; Nishimura, G.; Hirai, T. *J. Phys. Chem. B* **2007**, *111*, 5090–5100.

11. GAUSSIAN 03, Revision B.05, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitano, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 2003.

12. See Supplementary data.

13. Increase in absorbance at >325 nm, ascribed to the protonation of QN nitrogen, takes place at pH < 5 (Fig. S1[12]): Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 373–379.

14. (a) Kyrychenko, A.; Waluk, J. *J. Phys. Chem. A* **2006**, *110*, 11958–11967; (b) Bardez, E.; Devol, I.; Larrey, B.; Valeur, B. *J. Phys. Chem. B* **1997**, *101*, 7786–7793; (c) Schulman, S. G.; Sanders, L. B. *Anal. Chim. Acta* **1971**, *56*, 83–89; (d) Liu, Y.; Zhang, N.; Chen, Y.; Wang, L.-H. *Org. Lett.* **2007**, *9*, 315–318.

15. H$_5$**L1**$^{5+}$ species with protonated two QN fragments appear in strongly acidic media (pH < 1). This is confirmed by fluorescence enhancement at pH < 1 (Fig. S2[12]).

16. Excitation spectra of the **L1** emission collected at 410 nm are similar to the absorption spectra (Fig. S3[12]), indicating that the **L1** emission is due to the photoexcited monomer QN fragment.

17. (a) Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1305–1314; (b) Alves, S.; Pina, F.; Albelda, M. T.; García-España, E.; Soriano, C.; Luis, S. V. *Eur. J. Inorg. Chem.* **2001**, 405–412; (c) Shiraishi, Y.; Tokitoh, Y.; Hirai, T. *Chem. Commun.* **2005**, 5316–5318; (d) Shiraishi, Y.; Kohno, Y.; Hirai, T. *J. Phys. Chem. B* **2005**, *109*, 19139–19147; (e) Nishimura, G.; Ishizumi, K.; Shiraishi, Y.; Hirai, T. *J. Phys. Chem. B* **2006**, *110*, 21596–21602.

18. (a) Vaidya, B.; Zak, J.; Bastiaans, G. J.; Porter, M. C.; Hallman, J. L.; Nabulsi, N. A. R.; Utterback, M. D.; Strzelbicka, B.; Bartsch, R. A. *Anal. Chem.* **1995**, *67*, 4101–4111; (b) Kim, S. K.; Lee, S. H.; Lee, J. Y.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499–16506; (c) Chidawanyika, W.; Ogunsipe, A.; Nyokong, T. *New J. Chem.* **2007**, *31*, 377–384; (d) Saito, T.; Yasoshima, S.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1978**, *59*, 193–196; (e) Nosaka, Y.; Kira, A.; Imamura, M. *J. Phys. Chem.* **1981**, *85*, 1353–1358; (f) Nakamura, T.; Kira, A.; Imamura, M. *J. Phys. Chem.* **1982**, *86*, 3359–3363.

19. (a) Hirano, T.; Kikuchi, K.; Urano, Y.; Higuchi, T.; Nagano, T. *J. Am. Chem. Soc.* **2000**, *122*, 12399–12400 (intensity ratio: 10.4); (b) Roy, P.; Chara, K.; Manassero, M.; Ratha, J.; Banerjee, P. *Inorg. Chem.* **2007**, *46*, 6405–6412 (intensity ratio: 19.0); (c) Nolan, E. M.; Jaworski, J.; Okamoto, K.-i.; Hayashi, Y.; Sheng, M.; Lippard, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 16812–16823 (intensity ratio: 7.5); (d) Meng, X.; Zhu, M.-Z.; Liu, Lei.; Guo, Q.-X. *Tetrahedron Lett.* **2006**, *47*, 1559–1562 (intensity ratio: 8.6).

20. Komura, A.; Uchida, K.; Yagi, M.; Higuchi, J. *J. Photochem. Photobiol. A* **1988**, *42*, 293–300.

21. (a) Cheng, Y.-M.; Yeh, Y.-S.; Ho, M.-L.; Chou, P.-T.; Chen, P.-S.; Chi, Y. *Inorg. Chem.* **2005**, *44*, 4594–4603; (b) Miyamoto, R.; Kawakami, J.; Takahashi, S.; Ito, S.; Nagaki, M.; Kitahara, H. *J. Comput. Chem. Jpn.* **2006**, *5*, 19–22.