ORGANIC LETTERS

2007
Vol. 9, No. 16
3125−3128

Hg(II)-Selective Excimer Emission of a Bisnaphthyl Azadiene Derivative

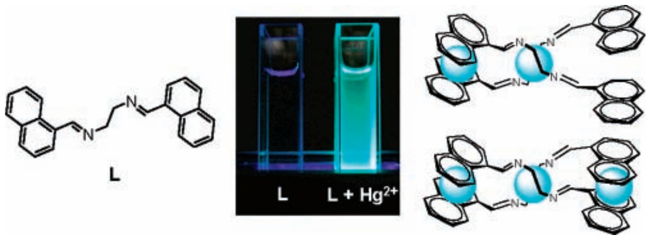
Yasuhiro Shiraishi,* Hajime Maehara, Katsutake Ishizumi, and Takayuki Hirai

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

shiraish@cheng.es.osaka-u.ac.jp

Received June 4, 2007

ABSTRACT



A bisnaphthyl azadiene derivative (L) demonstrates Hg^{2+}-selective intermolecular excimer emission. This emission is responsive to the number of coordinated Hg^{2+} atoms, where 2:2 and 2:3 L–Hg^{2+} complexes are the strongly emissive components, whereas the 2:1 complex is nonemissive.

Design and development of fluorescent signaling devices is an area of intense research activity and of tremendous significance to the field of molecular device fabrication.[1] So far, 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 emission enhancement (turn-on) or quenching (turn-off), associated with the coordination with ligand groups.[3] Mercury(II) usually acts as a fluorescence quencher via a spin-orbital coupling effect;[4] therefore, most of the already reported molecular systems show turn-off response upon Hg^{2+} input.[5] Recently, several molecules showing selective turn-on response upon Hg^{2+} input have been proposed;[6] however, these molecules form a unique Hg^{2+} complex and, hence, show simple emission enhancement upon Hg^{2+} binding.

Here we report that a bisnaphthyl azadiene ligand, L, 1,6-bis(1-naphthyl)-2,5-diaza-1,5-hexadiene, behaves as a new Hg^{2+}-selective fluorophore, showing an excimer emission depending on the number of coordinated Hg^{2+} atoms. This

---

(1) For books and reviews: (a) Balzani, V. *Molecular Devices and Machines: A Journey into the Nano World*; Wiley-VCH: Weinheim, 2003. (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) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (d) de Silva, A. P.; McClenaghan, N. D.; McCoy, C. P. *Molecular Switches*; Wiley-VCH: New York, 2000. (e) Czarnik, A. W. *Fluorescent Chemosensors for Ion and Molecular Recognition*; American Chemical Society: Washington, DC, 1992.

(2) For example: (a) Uchiyama, S.; Kawai, N.; de Silva, A. P.; Iwai, K. *J. Am. Chem. Soc.* **2004**, *126*, 3032−3033. (b) Gobbi, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 674−678. (c) Fabbrizzi, L.; Licchelli, M.; Mascheroni, S.; Poggi, A.; Sacchi, D.; Zema, M. *Inorg. Chem.* **2002**, *41*, 6129−6136. (d) Callan, J. F.; de Silva, A. P.; McClenaghan, N. D. *Chem. Commun.* **2004**, 2048−2049.

(3) For example: (a) Pina, F.; Passaniti, P.; Maestri, M.; Balzani, V.; Vögtle, F.; Gorka, M.; Lee, S.-K.; van Heyst, J.; Fakhrnabavi, H. *Chem. Phys. Chem.* **2004**, *5*, 473−480. (b) Licchelli, M.; Biroli, A. O.; Poggi, A.; Sacchi, D.; Sangermani, C.; Zema, M. *Dalton Trans.* **2003**, 4537−4545. (c) Amendola, V.; Fernandez, Y. D.; Mangano, C.; Montalti, M.; Pallavicini, P.; Prodi, L.; Zaccheroni, N.; Zema, M. *Dalton. Trans.* **2003**, 4340−4345. (d) Saudan, C.; Balzani, V.; Gorka, M.; Lee, S.-K.; Maestri, M.; Vicinelli, V.; Vögtle, F. *J. Am. Chem. Soc.* **2003**, *125*, 4424−4425. (e) Licchelli, M.; Linati, L.; Biroli, A. O.; Perani, E.; Poggi, A.; Sacchi, D. *Chem.−Eur. J.* **2002**, *8*, 5161−5169. (f) McSkimming, G.; Tucker, J. H. R.; Bouas-Laurent, H.; Desvergne, J.-P.; Coles, S. J.; Hursthouse, M. B.; Light, M. E. *Chem.−Eur. J.* **2002**, *8*, 3331−3342.

(4) McClure, D. S. *J. Chem. Phys.* **1952**, *20*, 682−686.

(5) For example: (a) Chae, M.-Y.; Czarnik, A. W. *J. Am. Chem. Soc.* **1992**, *114*, 9704−9705. (b) Rurack, K.; Kollmannsberger, M.; ReschGenger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968−969. (c) Prodi, L.; Bargossi, C.; Montalti, M.; Zaccheroni, N.; Su, N.; Bradshow, J. S.; Izatt, R. M.; Savage, P. B. *J. Am. Chem. Soc.* **2000**, *122*, 6769−6770. (d) Moon, S.-Y.; Cha, N. R.; Kim, Y. H.; Chang, S.-K. *J. Org. Chem.* **2004**, *69*, 181−183. (e) Moon, S.-Y.; Yoon, N. J.; Park, S. M.; Chang, S.-K. *J. Org. Chem.* **2005**, *70*, 2394−2397.

10.1021/ol0713133 CCC: $37.00

is the first Hg^{2+}-selective turn-on fluorophore containing a naphthalene (NP) fragment and showing a different response to the number of coordinated Hg^{2+} atoms. We report here that the emission is due to the excimer formed via direct excitation of the intermolecular ground-state dimer (GSD) of the NP moieties approaching each other by Hg^{2+} coordination and that the unprecedented emission switching is triggered by the GSD stability controlled by the number of coordinated Hg^{2+} atoms.

The symmetrical L ligand is easily obtained by one-step condensation of nathphthalene-1-carbaldehyde and ethylenediamine in ethanol with 78% yield.[7]

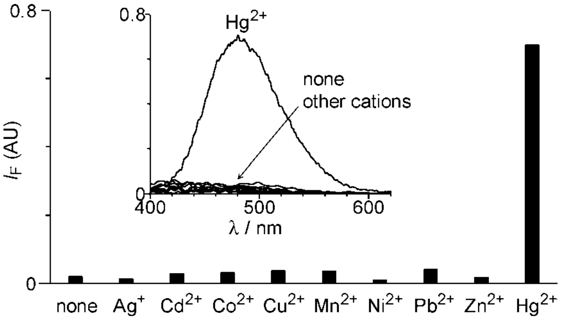


Figure 1. Emission spectra ($\lambda_{exc} = 372$ nm) of L (25 μM) and intensity at 492 nm measured in acetonitrile with and without 1 equiv of respective metal cations as perchlorate salts. The data obtained with 5 equiv of cations are shown in the Supporting Information (Figure S3).

Figure 1 shows emission spectra ($\lambda_{exc} = 372$ nm) of L in acetonitrile measured with 1 equiv of respective metal cations. Without cations, L shows no emission because of an electron transfer from the imine nitrogens to the excited NP fragments.[8] Addition of Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} shows negligible spectrum change. In contrast, Hg^{2+} addition creates strong emission at 400−600 nm, assigned to an excimer formed between the NP fragments.[9] As shown in the graphical abstract picture, a sea-green colored bright emission appears.

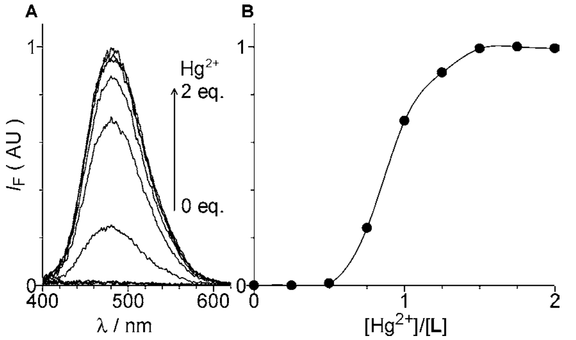


Figure 2. Change in (A) emission spectra and (B) the intensity monitored at 492 nm of L (25 μM) in acetonitrile upon addition of $Hg(ClO_4)_2$ ($\lambda_{exc} = 372$ nm).

Figure 2 shows a change in emission spectrum of L and the intensity monitored at 492 nm with stepwise addition of Hg^{2+}. With <0.5 equiv of Hg^{2+}, no emission appears. In contrast, >0.5 equiv of Hg^{2+} leads to an obvious emission increase. This emission is, however, saturated with >1.5 equiv of Hg^{2+} ($\Phi = 0.246$), implying that, at this condition, an emissive 2:3 L−Hg^{2+} complex exists.

Figure 3A shows a change in the absorption spectra of L with stepwise Hg^{2+} addition. Without Hg^{2+}, L shows a distinctive NP absorption at 260−340 nm ($\lambda_{max} = 305$ nm).[10] This absorption red-shifts ($\lambda_{max} = 311$ nm) with an increase in Hg^{2+} amount. These spectra do not show a clear isosbestic point, indicating that more than two types of L−Hg^{2+} complexes exist. Figure 3B shows excitation spectra collected at 492 nm. A distinctive excitation band is observed at 300−420 nm, which appears at a longer wavelength than the absorption band obtained without Hg^{2+} but is consistent with the red-shifted absorption band obtained with Hg^{2+} (Figure 3A). These indicate that the emission of L is due to the excimer formed via direct photoexcitation of the ground-state dimer (GSD) of the NP fragments associated with each other by Hg^{2+} coordination.

Three types of L−Hg^{2+} complexes with 2:1, 2:2, and 2:3 stoichiometry exist. As shown in Figure 2B, no emission appears with <0.5 equiv of Hg^{2+}, implying that a nonemis-

---

(6) (a) Nolan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 14270−14271. (b) Descalzo, A.; Martinez-Mañez, R.; Radeglia, R.; Rurack, K.; Soto, J. *J. Am. Chem. Soc.* **2003**, *125*, 3418−3419. (c) Guo, X.; Qian, X.; Jia, L. *J. Am. Chem. Soc.* **2004**, *126*, 2272−2273. (d) Ono, A.; Togashi, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 4300−4302. (e) Hennrich, G.; Sonnenschein, H.; Resch-Genger, U. *J. Am. Chem. Soc.* **1999**, *121*, 5073−5074. (f) Hennrich, G.; Walther, W.; Resch-Genger, U.; Sonnenschein, H. *Inorg. Chem.* **2001**, *40*, 641−644. (g) Zhang, G.; Zhang, D.; Yin, S.; Yang, X.; Shuai, Z.; Zhu, D. *Chem. Commun.* **2005**, 2161−2163. (h) Yoon, S.; Albers, A. E.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 16030−16031. (i) Caballero, A.; Martínez, R.; Lloveras V.; Ratera, I.; Vidal-Gancedo, J.; Wurst, K.; Tárraga, A.; Molina, P.; Veciana, J. *J. Am. Chem. Soc.* **2005**, *127*, 15666−15667. (j) Sasaki, D. Y.; Padilla, B. E. *Chem. Commun.* **2005**, 1581−1582. (k) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2006**, *128*, 14474−14475. (l) Avirah, R. R.; Jyothish, K.; Ramaiah, D. *Org. Lett.* **2007**, *9*, 121−124.

(7) **L.** Naphthalene-1-carbaldehyde (1.0 g, 6.4 mmol) and ethylenediamine (0.19 g, 3.2 mmol) were refluxed in ethanol (50 mL) for 36 h under dry N_2. The white precipitate formed was recovered by filtration, washed thoroughly with ethanol, and dried in vacuo. The white solid obtained was recrystallized from $CHCl_3$/ethanol, affording a white powder of L (0.85 g, 2.5 mmol, yield 78 %). ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 4.19$ (s, 4H, CH_2 of ethylenediamine), 7.34−7.49 (m, 6H, Ar*H*), 7.82−7.88 (m, 6H, Ar*H*), 8.78 (d, 2H, Ar*H*), 8.96 (s, 2H, C*H*=N). ^{13}C NMR (68MHz, $CDCl_3$, TMS): δ 62.6, 124.5, 125.1, 125.9, 126.9, 128.4, 128.6, 130.7, 131.3, 133.8, 162.3. FAB-MS: Calcd for $C_{24}H_{20}N_2$ 336.2, found *m/z* 337.2 ($M + H^+$, 79%). Elemental Anal. Calcd: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.56; H, 5.89; N, 8.55. ^1H and ^{13}C NMR spectra of L are shown in Supporting Information (Figures S1 and S2).

(8) (a) Shiraishi, Y.; Tokitoh, Y.; Nishimura, G.; Hirai, T. *Org. Lett.* **2005**, *7*, 2611−2614. (b) Shiraishi, Y.; Tokitoh, Y.; Hirai, T. *Chem. Commun.* **2005**, 5316−5318. (c) Shiraishi, Y.; Tokitoh, Y.; Hirai, T. *Org. Lett.* **2006**, *8*, 3841−3844. (d) Shiraishi, Y.; Tokitoh, Y.; Nishimura, G.; Hirai, T. *J. Phys. Chem. B* **2007**, *111*, 5090−5100.

(9) (a) Albelda, M. T.; García-España, E.; Gil, L.; Lima, J. C.; Lodeiro, C.; Seixas de Melo, J.; Melo, M. J.; Parola, A. J.; Pina, F.; Soriano, C. *J. Phys. Chem.* **2003**, *107*, 6573−6578. (b) Métivier, R.; Leray, I.; Valeur, B. *Chem. Commun.* **2004**, *10*, 4480−4490.

(10) Albelda, M. T.; Bernard, M. A.; Díaz, P.; García-España, E.; Seixas de Melo, J.; Pina, F.; Soriano, C.; Luis, S. V. *Chem. Commun.* **2001**, 1520−1521.

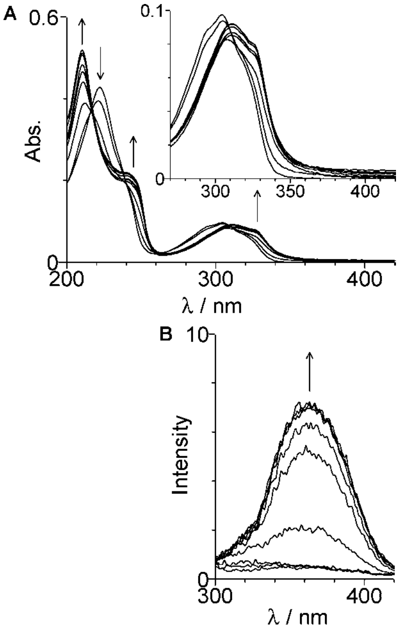


Figure 3. Change in (A) absorption and (B) excitation ($\lambda_{em} = 492$ nm) spectra of L (25 μM) in acetonitrile upon addition of 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, and 2 equiv of $Hg(ClO_4)_2$.

sive 2:1 complex exists. With >0.5 equiv of Hg^{2+}, emissive 2:2 and 2:3 complexes form in response to the increas in Hg^{2+} amount. An absorption-based Job's plot (A_{350}) shows a maximum absorption at X ($= [Hg^{2+}]/([Hg^{2+}] + [L]) =$ 0.33 and an inflection point at $X = 0.5$ (Supporting Information, Figure S4), indicative of the 2:1 and 2:2 complex formation. An emission-based Job's plot shows a maximum emission at $X = 0.6$ (Supporting Information, Figure S5). These clearly suggest that three types of L−Hg^{2+} complexes with 2:1, 2:2, and 2:3 stoichiometry exist. The existence of the emissive 2:2 and 2:3 complexes is further confirmed by time-resolved emission decay measurements (Supporting Information, Figure S6). With 1 equiv of Hg^{2+}, the decay is fitted by single exponential (decay time: 7.9 ns). With 1.25 equiv of Hg^{2+}, the profile is fitted with the sum of two exponentials with decay times of 7.9 ns (58%) and 11.4 ns (42%). In contrast, with 1.5 equiv of Hg^{2+}, the decay is fitted only with the long lifetime component (11.4 ns). These suggest that both 2:2 and 2:3 complexes are the emissive species. No negative preexponential, i.e., a rise time, is detected in all decay profiles; this supports the direct GSD photoexcitation mechanism for excimer formation.

The different emission properties of 2:1, 2:2, and 2:3 L−Hg^{2+} complexes are due to the alignment of the NP fragments depending on the number of coordinated Hg^{2+} atoms. Figure 4 shows a change in the ^{1}H NMR spectra of L (CD_3CN at 233 K). With 0.5 equiv of Hg^{2+} (Figure 4b), where a 2:1 complex forms, iminic H_a protons (−CH=N; 8.94 ppm) disappear and move downfield (9.60 ppm; $\Delta\delta = +0.66$ ppm), meaning that one Hg^{2+} atom coordinates with four imine nitrogens of the two L molecules. At this condition, some of the NP protons shift upfield, while the others shift downfield. The downfield shift of the NP protons is due to the decrease in electron density of the NP moieties by the adjacent electron-withdrawing Hg^{2+} atom.[11] The upfield shift is due to the anisotropic effect by the decrease in the ring current of the imine moieties with the Hg^{2+} binding.[12] The coordination behavior of the 2:1 complex is supported by the calculated geometry of the complex. Figure 5a shows the structure of the 2:1 complex optimized at the DFT level (Supporting Information, Computational Details). Hg^{2+} is coordinated with four nitrogen atoms of two L molecules, where the Hg−N bond distances are 2.30, 2.33, 2.34, and 2.34 Å, which are below the upper limit of a covalent bond (2.75 Å).[13] Notably, NP fragments of the complex are separated from each other and are nonparallel (distances of C1 positions of the NP fragments are >4.82 Å). This is due to the electrostatic repulsion of the NP fragments. It is well-known that excimer formation requires a parallel configuration of the NP fragments.[14] This means that the separation of the NP fragments within the 2:1 complex suppresses the GSD formation, resulting in no excimer emission.

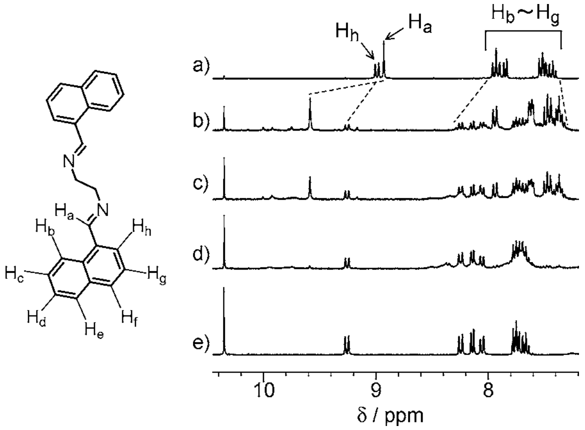


Figure 4. Change in ^{1}H NMR spectra of L in CD_3CN upon addition of (a) 0, (b) 0.5, (c) 1, (d) 1.5, and (e) 2.0 equiv of $Hg(ClO_4)_2$.

As shown in Figure 5b, within an emissive 2:2 complex, one Hg^{2+} atom is also coordinated with four nitrogens. Another Hg^{2+} atom is sandwiched in between the two NP fragments. These NP moieties are forced to stay close and coplaner (the C1−C1 distance of the NP fragments is 4.52 Å). This is probably due to the cation−π interaction between the π-electron of the NP moieties and electron-withdrawing

---

(11) Wang, J.; Qian, X. *Chem. Commun.* **2006**, 109−111.

(12) (a) Jaźwiński, J.; Duddeck, H. *Magn. Reson. Chem.* **2003**, *41*, 921−926. (b) Pazderski, L.; Szłyk, E.; Sitkowski, J.; Kamieñski, B.; Kozerski, L.; Toušek, J.; Marek, R. *Magn. Reson. Chem.* **2006**, *44*, 163−170. (c) Pazderski, L.; Toušek, J.; Sitkowski, J.; Kozerski, L.; Marek, R.; Szłyk, E. *Magn. Reson. Chem.* **2007**, *45*, 24−36.

(13) (a) Wang, M.-C.; Sue, L.-S.; Liau, B.-C.; Ko, B.-T.; Elango, S.; Chen, J.-H. *Inorg. Chem.* **2001**, *40*, 6064−6068. (b) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George, E. E.; Hayhurst, G. *Inorg. Chem.* **1981**, *20*, 2414−2422. (c) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George, E. E.; Hayhurst, G. *Inorg. Chem.* **1981**, *20*, 4293−4300.

(14) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586−3593.

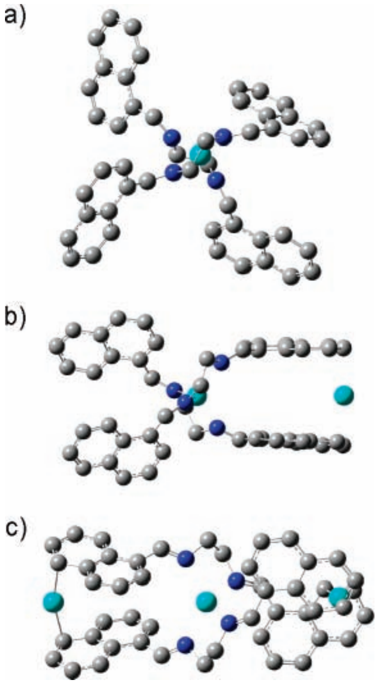


Figure 5. Calculated structures of (a) 2:1, (b) 2:2, and (c) 2:3 L−Hg^{2+} complexes (B3LYP/6-31G* for (a) or B3LYP/3-21G for (b) and (c), with the Stuttgart Relativistic Small-Core basis set for the Hg atom with effective core potential).

Hg^{2+}.[15] This indicates that the second Hg^{2+} coordination brings the two NP fragments closer and, hence, leads to GSD formation, thus allowing the excimer emission. As shown in Figure 4c, with 1 equiv of Hg^{2+} where the 2:2 complex exists, the upfield NP protons (7.3−7.5 ppm) decrease and move downfield, suggesting that the electron density of the NP moieties actually decreases by the Hg^{2+}−NP cation−π interaction.[15] At this condition, the iminic H$_a$ protons (9.60 ppm) also decrease and shift downfield (10.35 ppm; $\Delta\delta = +0.75$ ppm). This is because the decrease in electron density of the NP moieties by the Hg^{2+}−NP interaction leads to a decrease in the ring-current effect on the iminic protons, resulting in a downfield shift of the iminic protons. These NMR behaviors support the 2:2 complex structure optimized by calculation.

As shown in Figure 5c, for an emissive 2:3 complex, one Hg^{2+} atom is also coordinated by four imine nitrogens, and the other two Hg^{2+} atoms are sandwiched in between the two sets of two NP fragments via Hg^{2+}−NP cation−π interaction. As shown in Figure 4d and e, with >1.5 equiv of Hg^{2+}, upfield NP protons disappear and move downfield completely. This suggests that all NP moieties undergo Hg^{2+}−NP cation−π interaction. In this condition, the iminic H$_a$ protons (9.60 ppm) disappear completely and shift downfield (10.35 ppm). This also supports the Hg^{2+}−NP cation−π interaction. These findings strongly support the calculated 2:3 complex structure (Figure 5c). As shown in Figure 5c, both sets of NP fragments are forced to stay close and to be parallel, where the average distance of the C1−C1 positions of NP fragments is determined to be 4.32 Å, which is shorter than that of the 2:2 complex (4.52 Å). As a result of this, the 2:3 complex forms a more stable GSD of the NP fragments, thus demonstrating strong and long-lived excimer emission.

Another notable feature of L is the high emission reversibility (Supporting Information, Figure S7). When L is added to the solution containing the 2:3 complex (mole ratio L:Hg^{2+} = 1:1.5), the emission intensity decreases with the L amount and becomes zero accurately at the mole ratio of L:Hg^{2+} = 3:1.5. This suggests that the 2:2 and 2:3 complexes are easily transformed to a 2:1 complex. This is because the Hg^{2+}−NP cation−π interaction is much weaker than that of the N−Hg^{2+} coordination.[16]

In conclusion, we have synthesized a new ligand capable of showing Hg^{2+}-selective excimer emission, which is due to the excimer formed by direct excitation of the intermolecular GSD of the NP fragments approaching each other by Hg^{2+} coordination. The on/off switching of the excimer emission is precisely controlled by the number of coordinated Hg^{2+} atoms. The simple molecular design presented here may contribute to the development of more useful fluorescent signaling materials using Hg^{2+} input and more sophisticated molecular level devices with multiple functions.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research (No. 19760536) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

Supporting Information Available: Experimental procedure, calculation detailes, spectral data (Figures S1−S7), and Cartesian coodinates for L−Hg^{2+} complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0713133

---

(15) (a) Kang, J.; Choi, M.; Kwon, J. Y.; Lee, E. Y.; Yoon, J. *J. Org. Chem.* **2002**, *67*, 4384. (b) Iyoda, M.; Kuwatani, Y.; Yamauchi, T.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1988**, 65. (c) Pierre, J.-L.; Baret, P.; Chautemps, P.; Armand, M. *J. Am. Chem. Soc.* **1981**, *103*, 2986. (d) Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P.; Lehne, V. *J. Org. Chem.* **1993**, *58*, 2781.

(16) Bashall, A.; McPartlin, M.; Murphy, B. P.; Powell, H. R.; Waiker, S. *J. Chem. Soc., Dalton Trans.* **1994**, 1383−1390.