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#### Article

# Argentivorous Molecules with Chromophores in Side Arms: Silver Ion-Induced Turn On and Turn Off of Fluorescence

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**ABSTRACT:** The synthesis of argentivorous molecules ( $L^1$  and  $L^2$ ) having two chromophores (4-(anthracen-9-yl)benzyl or 4-(pyren-1yl)benzyl groups) and two benzyl groups and the fluorescence properties of their silver complexes in a solution and the solid state are reported. A crystallographic approach for the Ag<sup>+</sup> complexes with  $L^1$ and  $L^2$  revealed that the observed fluorescence changes stem from the excimer formation and extinction of fluorescent. Furthermore, binding stabilities of  $L^1$  and  $L^2$  toward Ag<sup>+</sup> ions were estimated by the Ag<sup>+</sup>induced UV-vis and PL spectral changes.



# ■ INTRODUCTION

Excimer is defined as a dimer associated with an excited electronic state and dissociative in its ground electronic state.<sup>1-3</sup> Generally, the excimer band shows a red shift compared with a monomer because of the increasing electron affinity of the acceptor and decreasing the donor's ionization potential.<sup>1-3</sup> Using the fluorescence properties of excimers, the fluorescent sensor molecules for heavy and transition metals have been extensively developed.<sup>4–8</sup> Among well-known fluorophores, anthracene, pyrene, and their derivatives have been investigated into many functions for sensing metal ions, pH, simple inorganic anions, and small organic molecules.<sup>9–19</sup> Pyrene is strong electron donor material, and pyrene excimer from several pyrene derivatives usually exhibits a similar emission color of sky-blue or cyan, resulting from almost the same excited-state geometry.<sup>20-25</sup> Since excellent monomer and excimer emission changes occur at remarkably different wavelengths on the basis of the distance between two anthracene or pyrene moieties, both fluorophores (anthracene and pyrene) acting as a fluorophore have been utilized effectively.<sup>20–29</sup>

On the other hand, our group is interested in tetra-armed cyclens and their silver(I) complexes, incorporating tetraarmed aromatic side chains, giving wide structural diversity in the resulting argentivorous molecules by  $Ag^+-\pi$  and  $CH-\pi$ interactions.<sup>30–39</sup> For example, we demonstrated that doubleand tetra-armed cyclens bearing an anthracene or pyrene unit as side arms behave like an insectivorous plant (Venus flytrap) by  $Ag^+-\pi$  interactions.<sup>30–39</sup> More recently, we reported that an  $Ag^+$  complex with tetra-armed cyclens with styrylmethyl groups incorporates chiral alkyl nitriles to afford a drastic enhancement of the molar ellipticity in CD spectra.<sup>32</sup>



In the case of fluorophore-substituted cyclens, fluorescent complexes where excimers formed were reported.<sup>40–43</sup> We also reported tetra-armed cyclens  $(L^a-L^c)$  with fluorophore as side arms and their silver(I) complexes. However, in the silver(I) complexes of cyclens  $L^a-L^c$ , the excimer formation was not

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observed even if fluorophores have existed in the side arms.<sup>38,39</sup> It is considered that the formation of excimer has been difficult due to the steric hindrance when the complex formed the silver(I) complex. To cover this point, fluorescent cyclens, showing fluorescence changes according to the formation or extinction of the excimer when reacted with the metal ions, are designed. In this work, we proposed tetra-armed cyclens ( $L^1$  and  $L^2$ ) with anthracenyl- or pyrenyl-benzyl groups in the side chains, which exhibits a unique fluorescent response in the presence of  $Ag^+$  (Scheme 1). The fluorescence on—off behaviors via structure—function relationship based on single-crystal X-ray analysis were also determined.

Scheme 1. Ag<sup>+</sup>-Induced Excimer Formation and Extinction Depending on the Fluorogenic Cyclens



## RESULTS AND DISCUSSION

Synthesis of Argentivorous Molecules with Fluorophores ( $L^1$  and  $L^2$ ). New tetra-armed cyclens ( $L^1$  and  $L^2$ ; Supporting Information Figure S1) were prepared by reductive amination of 1,7-dibenzyl-1,4,7,10-tetraazacyclododecane  $(1)^{38}$  with the corresponding aromatic aldehydes (2 and 3) in the presence of NaBH(OAc)<sub>3</sub>. The 4-formyl phenylboronic acid  $(4)^{44}$  and 9-(4-formyl phenyl)anthracene  $(2)^{45}$  were prepared according to the procedure described in the literature. The crystal structure of compound 2 was also determined (Figure S2). The precursor 4-(1-pyrenyl)benzaldehyde (3) was synthesized using the modified condition of the work previously reported.<sup>46</sup> The structures of the new compounds (L<sup>1</sup> and L<sup>2</sup>) were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, FAB-MS, and elemental analysis (Figures S3 and S4).

Structural Description of L<sup>1</sup> and L<sup>2</sup>. The structures of the new ligands,  $L^1$  and  $L^2$ , were also characterized in the solid state by single-crystal X-ray crystallography (Figures S5 and S6, Table S1). Colorless single crystals of  $L^1$  and  $L^2$  were prepared by slow evaporation of their chloroform solutions. Both cyclen  $L^1$  and  $L^2$  are present as the 1,2-alternate conformation (Figures S5 and S6).<sup>31,39</sup> In the packing structure of L<sup>1</sup>, two anthracene molecules from different  $L^1$  were overlapped at a distance of 3.53 Å (Figure 2a). This structure means that the solid state of L<sup>1</sup> forms an anthracene excimer between the nearest neighbor L<sup>1</sup> molecules. Due to intermolecular excimer, the solid-state fluorescence spectrum of L<sup>1</sup> shows strong green emission at 506 nm, as a characteristic emission band for the anthracene excimer<sup>29</sup> (Figure 1a). On the other hand, two pyrene molecules of  $L^2$  were overlapped at a distance of 3.37 Å with about 10% overlap area (Figure 3a). The interplanar distance is almost the same as those reported in the literature.<sup>47–53</sup> Since the pyrene excimer was formed, the solid-state fluorescence spectrum of L<sup>2</sup> shows weak blue emission at 409 nm (Figure 1b). It was reported that the excimer emissions for pyrene dimer could be changed depending on the interplanar distances and overlap degree of pyrene.47



Figure 1. Solid-state fluorescence spectra of (a)  $L^1$  and  $[Ag(BF_4)L^1]$  complex and (b)  $L^2$  and  $[Ag(OTf)L^2]$  complex. The excitation wavelengths ( $\lambda_{ex}$ ) for  $L^1$  and  $L^2$  were 365 and 342.5 nm, respectively.



Figure 2. Crystal structures of (a)  $L^1$  and (b)  $[Ag(BF_4)L^1]$ .

In an attempt to investigate the structure of the Ag<sup>+</sup> complex, <sup>1</sup>H NMR titration was monitored using L<sup>1</sup> and L<sup>2</sup> (Figure S7). The COSY and HOHAHA spectra of a mixture of  $L^2$  with Ag<sup>+</sup> were measured to assign the protons on each aromatic ring (Figures S8 and S9). On the addition of silver(I) to  $L^1$ , the H<sub>a</sub> and H<sub>b</sub> signals of the aromatic ring in the side arms shifted to a higher field by ca. 0.63 and 0.27 ppm, respectively (Figure S7a). The  $H_a$  and  $H_b$  signals in  $L^2$  also shifted to a higher field by ca. 0.70 and 0.98 ppm, respectively (Figure S7b). These chemical shift changes indicate that the H<sub>a</sub> and H<sub>b</sub> protons are located in the shielded area next to the aromatic rings. The NMR data indicate that the Ag<sup>+</sup> ions are covered by the aromatic side arms of  $L^1$  and  $L^2$ . In addition, since there was no change after 1.0 equiv of Ag+, it was confirmed that both cyclen  $(L^1 \text{ and } L^2)$  formed 1:1 Ag<sup>+</sup> complexes.

Silver(I)-Induced Excimer Extinction and Formation of L<sup>1</sup> and L<sup>2</sup>. To investigate the luminescence behavior by silver complex formation of L<sup>1</sup> and L<sup>2</sup>, we prepared silver complexes,  $[Ag(BF_4)L^1]$  and  $[Ag(OTf)L^2]$ , and their solidstate fluorescence spectra and quantum yields were measured. As a result, although L<sup>1</sup> showed bright emission ( $\Phi_f = 0.46$ ) at 506 nm (Figure 1a), a silver complex with L<sup>1</sup> exhibited a weak emission ( $\Phi_f = 0.16$ ) at the same wavelength. This quenching effect may reflect an enhancement of photoinduced electron transfer (PET) from the amine to the adjacent anthracene. In contrast, the silver complex with L<sup>2</sup> has a weak blue emission ( $\Phi_f = 0.14$ ) at 409 nm, but the silver complex showed a bright blue luminescence ( $\Phi_f = 0.40$ ) at 462 nm (Figure 1b). In the absence of the silver(I) ion, its fluorescence (pyrenyl excimer emission) is weak due to the PET effect from the nitrogen atom of the cyclen part to the excited state of the Py fluorophore. However, the complexation of the nitrogen atoms by Ag(I) ion inhibits PET, but there is a metal ion-induced chelation-enhanced fluorescence (CHEF) effect that induces fluorescence enhancements.

To obtain further insight for the complexation-based and silver(I)-induced fluorescence enhancement or quenching, we thus decided to reveal the crystal structures of the related complex species. From complexation of  $L^1$  with AgBF<sub>4</sub>, single crystals suitable for X-ray crystallography were obtained. The X-ray analysis revealed that the  $[Ag(BF_4)L^1]$  complex is a crystal in the monoclinic space group  $P2_1/n$  with the formula of  $[Ag(L^1)] \cdot BF_4 \cdot 3CHCl_3$  (Figure 2 and Table S1). The asymmetric unit contains one Ag(I) atom, one  $L^1$  molecule, one  $BF_4$  anion, and three chloroform molecules. The Ag(I)center is four-coordinated to an N4 donor of the cyclen ring. The Ag-N [2.392(2)-2.544(2) Å] bond lengths are within the normal range for these bond types.<sup>54,55</sup> As we expected from <sup>1</sup>H NMR spectral data (Figure S7a), the Ag(I) complex formed argentivorous molecules, in which the four aromatic side arms of the cyclen cover the Ag<sup>+</sup> such as a Venus flytrap. The Ag…C distances were 2.873-3.670 Å (Figure S10a). These distances showed Ag- $\pi$  interactions between the aromatic ring of the cyclen and Ag(I).<sup>56</sup> The CH- $\pi$ interactions between adjacent aromatic side arms were also confirmed (Figure S10b, 2.676-3.156 Å). Comparing the  $[Ag(BF_4)L^1]$  complex with  $L^1$  (Figures 2 and S11), the distance between two anthracene units has become slightly shorter but the overlap degree almost disappeared in the silver complex. Furthermore, the formation of excimer in  $[Ag(BF_4)]$  $L^{1}$  complex was probably disturbed by the existence of anion and solvent molecules between two anthracene units when the silver(I) complex was formed (Figure 2). These crystal structures indicate that the excimer was formed in the solid state of the ligand but excimer is extinct after the complexation with a silver(I).

The slow evaporation of the mixture of  $L^2$  and AgOTf gave colorless crystals suitable for single-crystal X-ray diffraction. The X-ray analysis revealed that the Ag(I) complex [Ag(OTf)  $L^2$ ] is a crystal in the monoclinic space group  $P2_1/c$  with the formula of [Ag( $L^2$ )]·OTf·2CHCl<sub>3</sub> (Figure 3 and Table S1).



Figure 3. Crystal structures of (a)  $L^2$  and (b)  $[Ag(OTf)L^2]$ .

The asymmetric unit contains one formula unit. Similar to complex  $[Ag(BF_4)L^1]$ , complex  $[Ag(OTf)L^2]$  formed argentivorous molecules in which the aromatic side arms of the cyclen and  $Ag-\pi$  and  $CH-\pi$  interactions contributed to the stability of the structure formation (Figure S12). Although the distance between two pyrene units in  $[Ag(OTf)L^2]$  has become slightly longer (0.1 Å) than  $L^2$  (Figures 3 and S13), the overlap degree in the silver complex was drastically increased from 10 (for  $L^2$ ) to 50% (for  $[Ag(OTf)L^2]$ ). This structure means the excimer of  $L^2$  was formed by self-assembling, so the fluorescence intensity increased, and the wavelength changed. The emission for the silver(I) complex of  $L^2$  falls within the typical emission range for pyrene excimer.<sup>47-53</sup>

Silver-Induced UV–Vis and Fluorescence Spectral Changes of L<sup>1</sup> and L<sup>2</sup>. To estimate the stability constants for silver complexes of L<sup>1</sup> and L<sup>2</sup>, UV–vis and fluorescence titration were carried out in chloroform:methanol (=1:9) and THF at 298 K, respectively (Figures S14 and S15). From UV–vis titration data, the stability constants (log  $\beta$ ) between silver(I) and L<sup>1</sup> and L<sup>2</sup> are 7.3(1) and 7.2(1), respectively (Figures S14c and S15c).<sup>57</sup> On the other hand, in the titration experiments using fluorescence spectroscopy, the log  $\beta$  values of L<sup>1</sup> and L<sup>2</sup> were 7.3(1) and 6.9 (1), respectively, roughly similar to the values of log  $\beta$  from UV–vis titration. These results strongly support that the 1:1 silver(I) complexes of L<sup>1</sup>

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and  $\boldsymbol{L}^2$  were thermodynamically stable species in the solution state.

The <sup>13</sup>C NMR and CSI-MS titration experiments were also performed to suggest further information for the complexation of  $L^1$  and  $L^2$  with Ag(I) (Figures S16–S18). These results supported that  $L^1$  and  $L^2$  formed 1:1 complex.

# CONCLUSION

We have designed and prepared two fluorogenic argentivorous molecules  $(L^1 \text{ and } L^2)$  with anthracenyl- or pyrenyl-benzyl units as side arms. X-ray structures of the ligands and the silver complexes were investigated to confirm their fluorescent responses by silver(I) ion in the solid state. These results revealed that the observed fluorescence changes stem from the excimer formation and extinction of fluorescent. That is, when  $L^1$  forms a silver(I) complex, the fluorescence emission strongly quenched because the formation of excimer is disturbed by the position of anion between anthracene units, while in the silver(I) complex with  $L^2$ , the silver(I) ioninduced significant red shift with the increase of fluorescence intensity because of formation of excimer. These results would be contributing not only to the design of new fluorogenic cyclen for heavy metal ions but also to the development of the relationship between the structure and the fluorescence change for the cyclen-based receptor.

# EXPERIMENTAL SECTION

**General Method.** All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL ECP400 spectrometer (400 MHz). The <sup>1</sup>H–<sup>1</sup>H COSY and HOHAHA NMR spectra were recorded on a Bruker Avance II 400. The FAB mass spectrum was obtained on a JEOL 600H mass spectrometer. The absorption spectra were recorded on a JASCO V-650 UV–visible spectrophotometer. Stability constants were calculated using Hyper-Spec ver. 1.1.33.<sup>57</sup> The fluorescence spectra were recorded in a HORIBA SPEX Fluorolog-3 spectrophotometer. The absolute quantum yields were measured with a Hamamatsu Quantaurus-QY C11347-11 absolute PL quantum yield measurement system. Cold ESI mass spectra were recorded on a JEOL JMST100CS mass spectrometer. The elemental analysis was carried out on a Yanako MT-6 CHN Micro Corder.

Synthesis of 4-(1-Pyrenyl)benzaldehyde (3). We prepared compound 3 using the modified condition of the work previously reported.<sup>46</sup> A mixture of 1-bromopyrene (1.41 g, 5.0 mmol), 4-formylphenylboronic acid (0.595 g, 3.97 mmol), benzene (20.0 mL), and ethanol (6.0 mL) was added to a 100 mL two-necked round-bottom flask under a nitrogen atmosphere. The mixture was stirred at 80 °C. After the compounds dissolved, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.0614 g, 0.0531 mmol), K<sub>2</sub>CO<sub>3</sub> (1.73 g, 12.5 mmol) and water (6.5 mL) were added. And then, the mixture was stirred for 1 day at 80 °C under nitrogen. After benzene was added, the organic layer was extracted, washed with brine, and dried with NaSO<sub>4</sub>. The residue was separated by silica gel column chromatography (benzene) and recrystallized from chloroform/hexane to obtain 3 as a yellow solid. Mp: 147.0–148.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.16 (s, 1H), 8.26–7.82 (m, 13H). FAB-MS (m/z) (DTT:TG = 1:1): 283 ([M + 1]<sup>+</sup>, 100%).

Synthesis of 1,7-Bis(4-(9-anthracenyl)benzyl)-4,10-dibenzyl-1,4,7,10-tetraazacyclododecane (L<sup>1</sup>). 1,7-Dibenzylcyclen<sup>38</sup> (1, 0.177 g, 0.5 mmol), 4-(9-anthracenyl)benzaldehyde<sup>45</sup> (2, 0.750 g, 2.7 mmol), and NaBH(OAc)<sub>3</sub> (0.63 g, 2.7 mmol) were added to 1,2-dichloroethane (12 mL) under a nitrogen atmosphere. The mixture was stirred for 7 days at room temperature. Saturated aqueous Na<sub>2</sub>CO<sub>3</sub> was then added before the mixture was extracted with chloroform. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. The residue was separated by silica gel column chromatography (chloroform:methanol = 2:1) and recrystallized from chloroform/ethanol to obtain L<sup>1</sup> as yellow solid. Yield: 68% (0.29 g). Mp: 120.0–130.0 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.48 (s, 2H), 8.02 (d, *J* = 8.3 Hz, 4H), 7.58–7.62 (m, 8H), 7.48 (d, 4H, *J* = 7.1), 7.40 (t, 4H, *J* = 7.4), 7.22–7.32 (m, 12H), 7.14 (m, 2H), 3.61 (s, 4H), 3.57 (s, 4H), 2.84 (s, 16H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 140.60, 140.01, 137.58, 137.15, 131.77, 131.24, 130.59, 129.49, 129.40, 128.58, 128.44, 127.18, 126.92, 126.64, 125.61, 125.44, 60.53. 60.40. Anal. Calcd for [C<sub>64</sub>H<sub>60</sub>N<sub>4</sub> + 1.5H<sub>2</sub>O]: C, 84.27; H, 6.96; N, 6.14. Found: C, 83.99; H, 6.67; N, 6.23%. FAB-MS (*m*/*z*) (DTT:TG = 1:1): 886 ([M + 1]<sup>+</sup>, 40%).

Synthesis of 1,7-Bis(4-(1-pyrenyl)benzyl)-4,10-dibenzyl-1,4,7,10-tetraazacyclododecane (L<sup>2</sup>). 1,7-Dibenzylcyclen<sup>38</sup> (1. 0.178 g, 0.5 mmol), 4-(1-pyrenyl)benzaldehyde (3, 0.616 g, 2.0 mmol), and NaBH(OAc)<sub>3</sub> (0.44 g, 2.1 mmol) were added to 1,2dichloroethane (10 mL) under a nitrogen atmosphere. The mixture was stirred for 7 days at room temperature. Saturated aqueous Na<sub>2</sub>CO<sub>3</sub> was then added before the mixture was extracted with chloroform. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. The residue was separated by silica gel column chromatography (chloroform:methanol:ammonia = 5:1:0.2) and recrystallized from chloroform/ acetonitrile to obtain  $L^2$  as yellow solid. Yield: 78% (0.37 g). Mp: 182.0–184.0 °C (dec.). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.20–7.18 (*m*, 36H), 3.60 (*s*, 4H), 3.56 (*s*, 4H), 2.84 (*s*, 16H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 139.65, 138.25, 131.88, 131.35, 130.79, 130.64, 129.43, 129.37, 128.78, 128.45, 128.09, 127.78, 127.67, 127.62, 126.93, 126.37, 125.68, 125.38, 125.26, 125.19, 125.10, 125.01, 60.57, 60.30. Anal. Calcd for  $[C_{68}H_{60}N_4 + 1.5H_2O]$ : C, 85.05; H, 6.61; N, 5.83. Found: C, 85.25; H, 6.40; N, 5.88%. FAB-MS (m/z) (DTT:TG  $= 1:1): 933 ([M + 1]^+, 10\%)$ 

**Preparation of [Ag(BF<sub>4</sub>)L<sup>1</sup>], [Ag(L<sup>1</sup>)]·BF<sub>4</sub>·3CHCl<sub>3</sub>.** AgBF<sub>4</sub> (3.9 mg, 0.020 mmol) in methanol (1 mL) was added to a solution of L<sup>1</sup> (17.7 mg, 0.020 mmol) in chloroform (1 mL). Acetonitrile and 1,2-dichloroethane were added to the mixture to dissolve a fine powder that precipitated the solution. The slow evaporation of the solution afforded a colorless crystalline product ([Ag(BF<sub>4</sub>)L<sup>1</sup>]) suitable for X-ray analysis. Because the sample was dried under vacuum for the elemental analysis sample, some lattice solvent (CHCl<sub>3</sub>) was reduced. Mp: 125.0–130.0 °C (dec.). Anal. Calcd for [C<sub>64</sub>H<sub>60</sub>N<sub>4</sub>B<sub>1</sub>F<sub>4</sub>Ag<sub>1</sub> + 1.5CHCl<sub>3</sub> + 0.5H<sub>2</sub>O]: C, 62.05; H, 4.97; N, 4.42. Found: C, 61.91; H, 4.93; N, 4.24%.

**Preparation of [Ag(OTf)L<sup>2</sup>], [Ag(L<sup>2</sup>)]·OTf·2CHCl<sub>3</sub>.** AgOTf (5.1 mg, 0.020 mmol) in methanol (1 mL) was added to a solution of L<sup>2</sup> (18.6 mg, 0.020 mmol) in chloroform (1 mL). The acetonitrile was added to the mixture for dissolving a fine powder that precipitated from the solution. The slow evaporation of the solution afforded a colorless crystalline product ([Ag(OTf)L<sup>2</sup>]) suitable for X-ray analysis. Because the sample was dried under vacuum for the elemental analysis sample, lattice solvent (CHCl<sub>3</sub>) was removed. Anal. Calcd for [C<sub>69</sub>H<sub>60</sub>N<sub>4</sub>O<sub>3</sub>F<sub>3</sub>S<sub>1</sub>Ag + H<sub>2</sub>O]: C, 68.59; H, 5.17; N, 4.64. Found: C, 68.79; H, 5.08; N, 4.52%.

UV–Vis Titration with AgOTf for L<sup>1</sup> and L<sup>2</sup>. All titrations were performed in a mixed solvent of chloroform and methanol (1:9). For titration,  $1.25 \times 10^{-5}$  and  $1.25 \times 10^{-5}$  M solutions of L<sup>1</sup> and L<sup>2</sup> were prepared, respectively. Both titrations were performed with the 0.0– 6.0 equiv of silver(I) triflate. Titration data were fitted into a desired binding model with HyperSpec.<sup>57</sup>

Fluorescence Titration with AgOTf for L<sup>1</sup> and L<sup>2</sup>. All titrations were performed in a THF solvent. The  $2.0 \times 10^{-7}$  and  $2.0 \times 10^{-5}$  M solutions of L<sup>1</sup> and L<sup>2</sup> were prepared, respectively. The titration of L<sup>1</sup> was performed with 0.0–3.0 equiv of silver(I) triflate. In the case of L<sup>2</sup>, titration was performed with the 0.0–10.0 equiv of silver(I) triflate. Also, titration data were fitted into a desired binding model with HyperSpec.<sup>57</sup> The excitation wavelengths ( $\lambda_{ex}$ ) for L<sup>1</sup> and L<sup>2</sup> were 365 and 342.5 nm, respectively.

**Metal-Induced Fluorescence Change in a Solution.** Metal ion-induced fluorescence spectral changes were carried out. THF solutions of metal salts  $(AgNO_3, Ni(NO_3)_2, Cu(NO_3)_2, Zn(NO_3)_2, Cd(NO_3)_2)$  and  $Hg(NO_3)_2$  were prepared. After the addition of 1.0

equiv of metal salts to the L<sup>1</sup> and L<sup>2</sup> THF solutions, the fluorescence spectroscopies were measured. The excitation wavelengths ( $\lambda_{ex}$ ) for L<sup>1</sup> and L<sup>2</sup> were 365 and 342.5 nm, respectively.

Metal-Induced Fluorescence Change in the Solid State. To preparation for solid-state metal complexes of  $L^1$ , metal nitrate salts (0.020 mmol) in methanol (1 mL) were added to a solution of  $L^1$  (17.7 mg, 0.020 mmol) in chloroform. Acetonitrile and 1,2-dichloroethane were added to the mixture to dissolve a fine powder that precipitated the solution. The mixture was slowly evaporated until a solid product was afforded. Obtained solid products were confirmed by elemental analysis.

 $[{\rm Ag}({\rm NO}_3){\rm L}^1]$ : Anal. Calcd for  $[{\rm C}_{64}{\rm H}_{60}{\rm N}_5{\rm O}_3{\rm Ag}$  + 2CHCl\_3]: C, 61.27; H, 4.83; N, 5.41. Found: C, 61.28; H, 4.99; N, 5.59%.

 $[Cu(NO_3)_2L^1]$ : Anal. Calcd for  $[C_{64}H_{60}N_6O_6Cu + 0.5CHCl_3]$ : C, 68.41; H, 5.38; N, 7.42. Found: C, 68.47; H, 5.62; N, 7.61%.

 $[Zn(NO_3)_2L^1]$ : Anal. Calcd for  $[C_{64}H_{60}N_6O_6Zn + 0.25CHCl_3]$ : C, 69.87; H, 5.50; N, 7.61. Found: C, 69.90; H, 5.63; N, 7.54%.

 $[Cd(NO_3)_2L^1]$ : Anal. Calcd for  $[C_{64}H_{60}N_6O_6Cd + 2.4CHCl_3 + 6CH_3CN]$ : C, 56.92; H, 4.90; N, 10.16. Found: C, 57.10; H, 5.11; N, 10.34%.

 $[Hg(NO_3)_2L^1]$ : Anal. Calcd for  $[C_{64}H_{60}N_6O_6Hg + 0.5CHCl_3]$ : C, 61.02; H, 4.80; N, 6.62. Found: C, 61.15; H, 4.82; N, 6.80%.

The metal nitrate salts (0.020 mmol) in methanol (1 mL) were added to a solution of  $L^2$  (18.6 mg, 0.020 mmol) in chloroform. Acetonitrile was added to the mixture for dissolving a fine powder that precipitated from the solution. The mixture was slowly evaporated until a solid product was afforded. Obtained solid products were confirmed by elemental analysis.

 $[Ag(NO_3)L^2]$ : Anal. Calcd for  $[C_{68}H_{60}N_5O_3Ag + H_2O]$ : C, 72.85; H, 5.57; N, 6.25. Found: C, 72.76; H, 5.46; N, 6.06%.

 $[\rm Ni(\rm NO_3)_2 L^2]$ : Anal. Calcd for  $[\rm C_{68} H_{60} N_6 O_6 Ni$  + 0.5CHCl\_3 + 0.5H\_2O]: C, 69.45; H, 5.23; N, 7.09. Found: C, 69.25; H, 5.52; N, 7.29%.

 $[Cu(NO_3)_2L^2]$ : Anal. Calcd for  $[C_{68}H_{60}N_6O_6Cu$  + 0.5CHCl<sub>3</sub> + H<sub>2</sub>O]: C, 68.65; H, 5.35; N, 7.01. Found: C, 68.72; H, 5.35; N, 7.28%.

 $[Zn(NO_3)_2L^2]$ : Anal. Calcd for  $[C_{68}H_{60}N_6O_6Zn + 1.5H_2O]$ : C, 71.04; H, 5.52; N, 7.31. Found: C, 70.99; H, 5.34; N, 7.28%.

 $[Hg(NO_3)_2L^2]$ : Anal. Calcd for  $[C_{68}H_{60}N_6O_6Hg + 0.5CHCl_3]$ : C, 62.45; H, 4.63; N, 6.38. Found: C, 62.66; H, 4.74; N, 6.58%.

X-ray Crystallographic Analysis. X-ray data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package of APEX2.  $^{58}$  All of the calculations for the structure determination were carried out using the SHELXTL package.<sup>59</sup> In all cases, non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures are summarized in Table S1. Crystallographic data for 2075285 (L<sup>1</sup>), 2075286 (L<sup>2</sup>), 2075287 ([Ag(BF<sub>4</sub>)L<sup>1</sup>]), 2075288 ([Ag(OTf)L<sup>2</sup>]), and 2075289 (2) have been deposited with CCDC.

### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01161.

NMR spectra, UV-vis spectra PL spectra, crystal structures, and CSI-MS spectra (PDF)

#### Accession Codes

CCDC 2075285–2075289 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The pubs.acs.org/IC

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#### Notes

The authors declare no competing financial interest.

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