

Synthesis, Complexation and Fluorescence Properties of *N*-Anthracenylmethyl Dipodal Ligand with Quinoline End-Group

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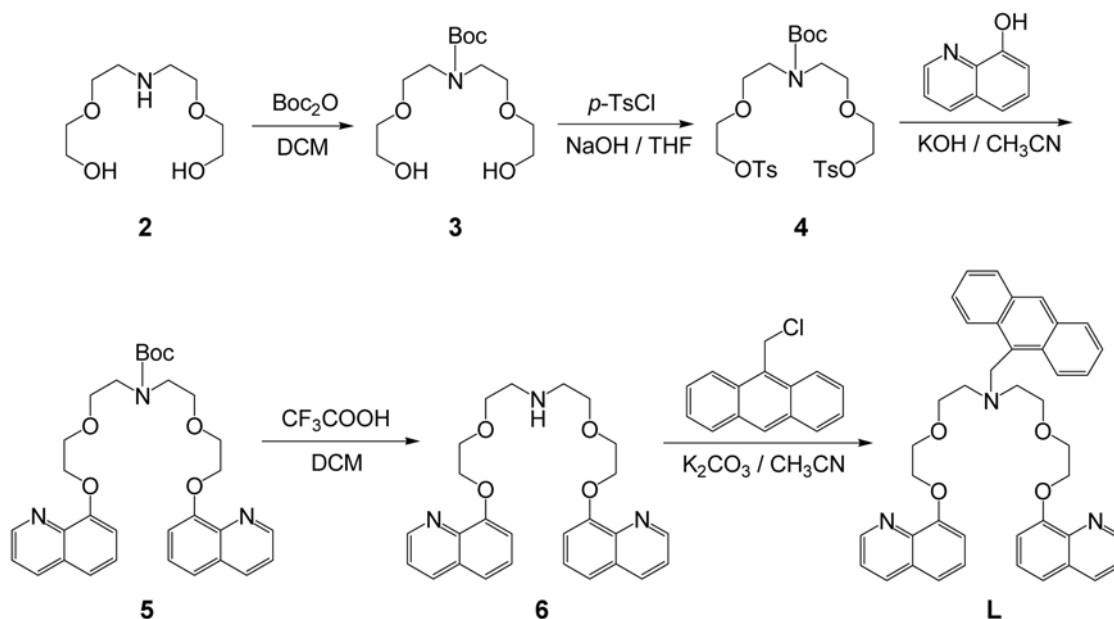
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Recently, many efforts have been devoted to design and construction of fluorescent chemosensors that are capable of detecting metal ions.¹⁻⁵ In many cases, the fluorescent chemosensors have been made through the combination of a receptor molecule and a fluorophore. Owing to their selective complexation with metal species, macrocyclic ligands make them ideal candidates for the receptor molecules. However, the introduction of such cyclic receptors is often limited by high cost and the synthetic complexity. The alternate way to avoid such limitations is to develop the acyclic analogues for the cyclic receptors. Our interest has focused on the dipodal receptors containing quinoline moiety because this receptor has shown not only similar behaviors with cyclic receptors,^{6,7} and the unique coordination ability for some transition metal ions^{8,9} but also been synthesized easily in high yields.¹⁰ Recently, we reported the unique pseudo-cyclic Cd(II) complexes, in which the dipodal receptor with quinoline end-groups wraps around the cadmium atom in a helical manner.⁹ In connection with this reason, we have synthesized *N*-anthracenylmethyl dipodal receptor (**L**) with quinoline end-groups and have further carried out the

exploration of its complexation and metal-induced fluorescence properties.

In the synthesis of **L** (see Scheme 1), the starting material **2** was prepared as previously reported.¹¹ The synthetic procedures for **3-6** are represented in the Supporting Information. **L** was prepared by the reaction of **6** and 9-chloromethylanthracene in CH₃CN in the presence of K₂CO₃ and KI under reflux condition. Purification by column chromatography afforded **L** as a yellow oil in 63% yield. This ligand was fully characterized by conventional methods.

The photophysical properties of **L** were measured in CH₃CN. In fluorescent spectrum of free **L**, upon excitation at 367 nm, typical emission bands from anthracene moiety were observed at 399, 419 and 442 nm. The quantum yield of fluorescence was determined as *ca.* 0.10 using 9-methylanthracene (0.284) as a reference compound. This fact would imply that quenching occurs in **L**, which might suggest that there was an effective quenching of the excited state of fluorophore by the receptor moiety, *via* photo-induced electron transfer (PET) before addition of metal ions (prior to metal ion recognition).



Scheme 1. Synthesis of the dipodal fluorophore **L**.

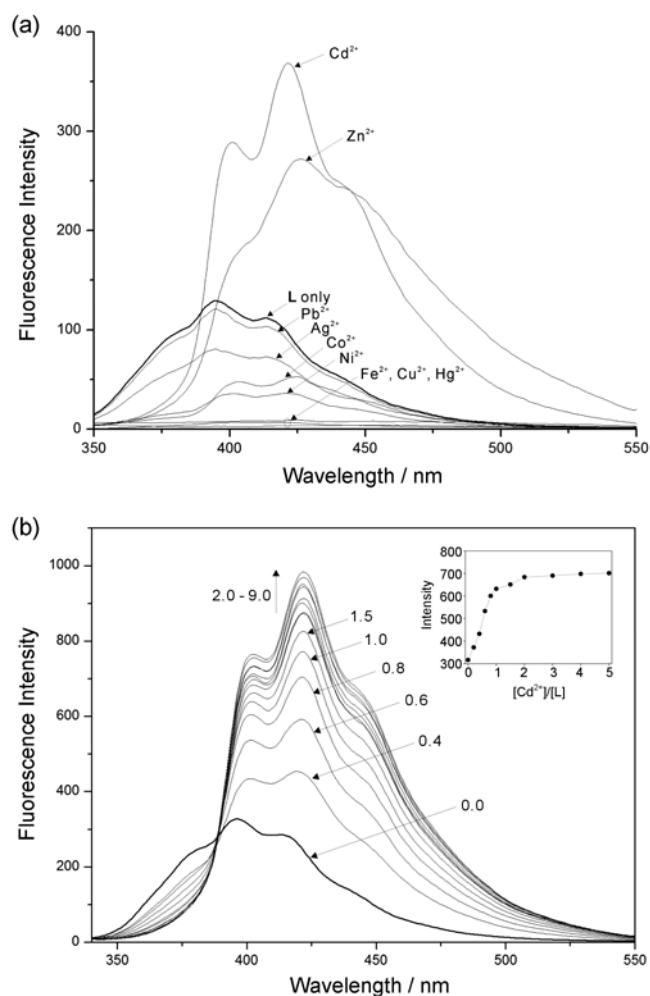


Figure 1. (a) Fluorescence spectra of **L** ($1.0 \mu\text{M}$) in the presence of the metal ions in CH_3CN , and (b) fluorescence changes of **L** ($1.0 \mu\text{M}$) upon titration with $\text{Cd}(\text{NO}_3)_2$ (0-9 equiv., CH_3CN). The excitation wavelength was 302 nm.

We next investigated the metal-induced fluorescent changes of the ligand in acetonitrile by adding the transition and heavy metal ions such as $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Ag}(\text{I})$, $\text{Pb}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Hg}(\text{II})$. Figure 1 shows the spectral changes of **L** after adding 50 equiv of metal nitrates. It is noteworthy that the large metal-induced increases of fluorescent intensity for $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$ were observed. In particular, the largest intensity enhancement induced by $\text{Cd}(\text{II})$ is clearly visible to the naked eye (see photo in Figure S2 of Supporting Information). Whereas, no significant changes or decreases of fluorescent intensity (*quenching*)¹² was observed upon addition of other metal ions except $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$. On the other hand, no significant changes were observed upon addition of same metal species to the solution of 9-methylanthracene as a reference compound, suggesting the above metal-induced changes for **L** are due to the complexation. In addition, the observed longer-wave shift by addition of $\text{Cd}(\text{II})$ also suggests that an intramolecular charge-transfer complex (intramolecular exciplex) is formed between $\text{Cd}(\text{II})$ and **L**.¹³

For the investigation on complexation of the $\text{Cd}(\text{II})$ ion

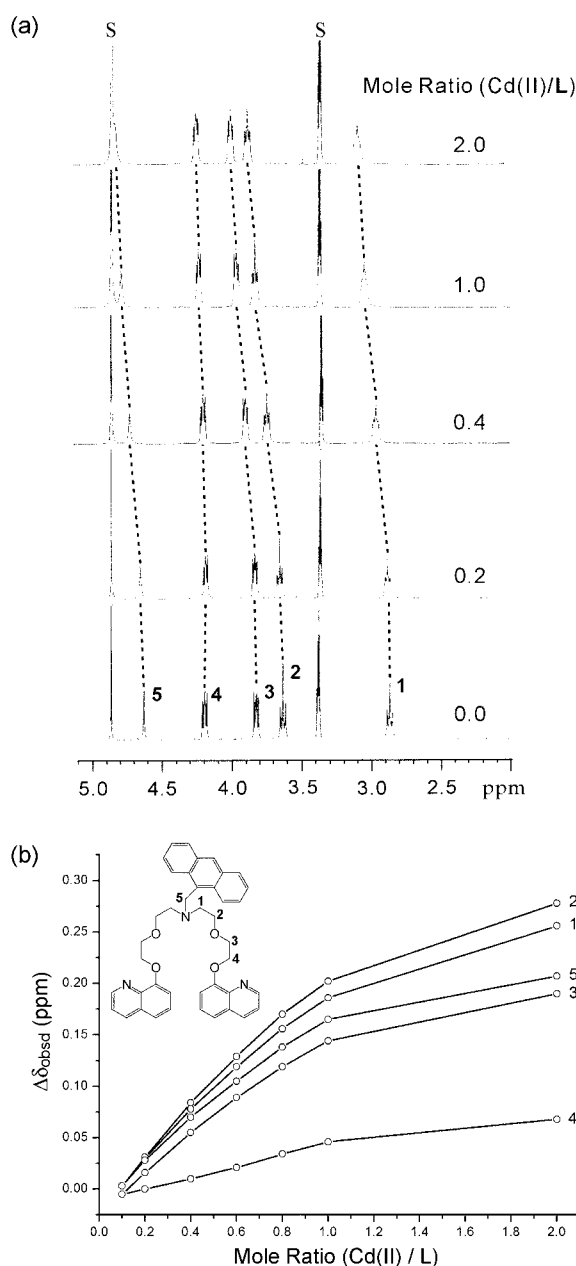


Figure 2. (a) Aliphatic region of ^1H NMR (300 MHz, CD_3OD) of **L** by stepwise addition of $\text{Cd}(\text{NO}_3)_2$ in CD_3OD and (b) the ^1H NMR titration curves for **L** with $\text{Cd}(\text{NO}_3)_2$. For labeling of protons, see a formula in this figure.

with **L**, ^1H -NMR titration experiments were performed. As shown in Figure 2, well resolved peaks for free **L** were observed in alkyl region. The $\text{Cd}(\text{II})$ guest, $\text{Cd}(\text{NO}_3)_2$, was added to **L** (0.01 mol dm^{-3}) in CD_3OD and shifts of the H_1 , H_2 , H_3 , H_4 and H_5 noted after each addition. Upon increasing molar ratio of the $\text{Cd}(\text{II})$ ions, remarkable down field shifts of each protons were observed. These observations strongly suggest the possibility of coordination between the donor set ($-\text{O}-\text{N}-\text{O}-$) for **L** and the $\text{Cd}(\text{II})$ ion. The magnitude of variation in chemical shift is following order; $\text{H}_2 \approx \text{H}_1 > \text{H}_5 \approx \text{H}_3 \gg \text{H}_4$, indicating that the $\text{Cd}(\text{II})$ ion binds more strongly to the bridgehead nitrogen atoms than to oxygen atoms

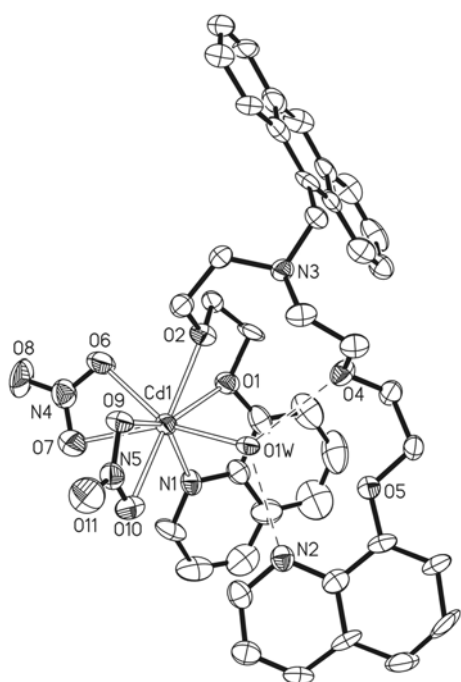


Figure 3. Crystal structure of **1**, $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})]\text{CH}_3\text{CN}$, with 50% thermal ellipsoids. Uncoordinated solvent molecule and H atoms are omitted for clarity.

attached quinoline moieties.

To gain deeper insight of coordination pattern between receptor **L** and the Cd(II) ions, X-ray single crystal analysis was conducted. Contrary to our expectations, however, X-ray structure analysis reveals that the structural feature of the solid-state does not coincide with the results from the solution state. Thus, in the solid state, the Cd atom is not coordinated by the nitrogen atom (N3) with methylanthracene moiety (Figure 3), although the cadmium ion affects to the N3 atom in the solution state as described above. This structural difference in both solid and solution states may be arise from the steric hindrance of two bulky and bidentate nitrate anions coordinated to the Cd atom in the course of the formation of crystalline **1** from the solution.

Reaction of **L** and $\text{Cd}(\text{NO}_3)_2$ in acetonitrile afforded a colorless crystalline product **1** suitable for X-ray structure analysis. The crystallographic analysis reveals that **1** is an 1:1 (metal to ligand) complex of formula $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})]\text{CH}_3\text{CN}$. As depicted in Figure 3, the Cd atom in **1** is eight-coordinated by one N and two O atoms from **L**, four O atoms from two bidentate nitrate ions, and one O atom from a water molecule. Considering the narrow bite angle [O6-Cd1-O7: $51.3(2)^\circ$, O9-Cd1-O10: $52.6(2)^\circ$] of the bidentate nitrate ions, the geometry of the Cd atom may be described a highly distorted pseudo-octahedral arrangement. The Cd atom deviates by 0.26 \AA from the equatorial plane defined by one N and two O atoms from **L**, and two O atoms (O9 and O10) from one bidentate nitrate ion. In crystal structure, a coordinated water molecule forms to the intramolecular H-bonds with two un-coordinated heteroatoms of **L**; O1W \cdots N2: $2.816(9) \text{ \AA}$ and O1W \cdots O4: $2.838(8) \text{ \AA}$. In the packing

structure, two parallel anthracene planes of the adjacent molecules related to the inversion center interact through the intermolecular π - π stacking with a distance of $3.46(2) \text{ \AA}$ between the their planes (Figure S3 of Supporting Information).

In summary, the fluoroionophore **L** functionalized with anthracene was synthesized and its selective Cd(II) detection by fluorescence intensity increase was confirmed. In particular, the propose probe allows discrimination of Cd(II) over other heavy metals except Zn(II). The selective recognition is attributed to the stable 1:1 complexation between the ligand and Cd(II) in solution (inset of Figure 1(b)).

Experimental Section

General methods. All solvents were freshly distilled over appropriate drying reagents prior to use. All starting materials were purchased from either Aldrich or Strem and used without further purification. NMR spectra were recorded on a Bruker Avance-300 spectrometer (300 MHz). Microanalyses of C, H, and N were carried out using LECO CHN-932 analyzer.

Synthesis of $[\text{Cd}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})]\text{CH}_3\text{CN}$ (1**).** Reaction of $\text{Cd}(\text{NO}_3)_2$ with **L** in acetonitrile afforded colorless X-ray quality crystalline product **1**: Mp $281\text{--}283^\circ$ decomp.) Anal. Calcd (Found) % for $\text{C}_{43}\text{H}_{44}\text{CdN}_6\text{O}_{11}$: C, 55.34 (55.48); H, 4.75 (4.96); N, 9.01 (8.92). IR (KBr, cm^{-1}) 3403, 2935, 2803, 2708, 1598, 1460, 1382, 1349, 1295, 1105, 1026, 825, 760.

Fluorescence measurement. UV/Vis and photoluminescent spectra were obtained with UV/Vis spectrometer Lambda 900 and a Perkin Elmer Luminescence spectrometer LS 50B, respectively. The stock solution of $\text{Cd}(\text{NO}_3)_2$ was prepared in CH_3CN . All solutions for photophysical experiments were degassed with more than three repeated freeze-

Table 1. Crystallographic data and structure refinement for complex **1**

Chemical formula	$\text{C}_{43}\text{H}_{44}\text{CdN}_6\text{O}_{11}$
T (K)	173(2)
Crystal system, Space group	Triclinic, $P\bar{1}$
a (\AA)	13.195(2)
b (\AA)	13.923(3)
c (\AA)	14.664(3)
α ($^\circ$)	115.276(4)
β ($^\circ$)	94.183(4)
γ ($^\circ$)	116.561(4)
V (\AA^3)	2059.7(6)
Z	2
Absorption coefficient (mm^{-1})	0.600
$F(000)$	960
Crystal size (mm^3)	$0.20 \times 0.15 \times 0.10$
θ range ($^\circ$)	1.62 to 26.37
Reflections collected / Unique	12197 / 8258
Goodness-of-fit on F^2	0.930
Final R indices	$R_1 = 0.0705$, $wR_2 = 0.1258$

pump-thaw cycles in a vacuum line. The emission slit width was at 3-5 nm. The relative quantum yields of PL (Φ_{PL}) for all compounds were determined relative to 9-methylantracene ($\Phi_{\text{PL}} = 0.284$) as the standard. The quantum yield was then measured by the previously known process.¹⁴

X-ray crystallography. All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation, and a CCD detector. The program SAINTPLUS¹⁵ was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS program of the SHELXTL package¹⁶ and refined by full matrix least squares against F^2 for all data using SHELXL. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions [$U_{\text{iso}} = 1.2U_{\text{eq}}$ (parent atom)] and refined using a riding model with the exception of the hydrogen atoms of the coordinated water molecule. The initial positions of the hydrogen atoms of water molecule were obtained from difference electron density maps and then refined using a riding model. The summary of the crystal data, experimental details and refinement results for **1** is listed in Table 1.

Supplementary data. Crystallographic data for the structure reported here have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 639441. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk, or electronically via www.ccdc.cam.ac.uk/data_request/cif.

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