Highly Selective Fluorescent Signaling for Al^{3+} in Bispyrenyl Polyether

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A series of bispyrenyl-polyether have been synthesized and investigated as a fluorescent chemosensor for metal ions. The results showed that bispyrenyl-polyether system is selective towards Al^{3+} ion over other ions tested. In free ligand, excited at 343 nm, it displays a strong excimer emission at around 475 nm with a weak monomer emission at 375 nm. A ratiometry of monomer (375 nm) increase and excimer (475 nm) quenching was shown only when Al^{3+} ion is bound to ligand, because two facing pyrene groups form a less efficient overlap of π–π stacking compared with that of free ligand.

Key Words : Pyrene, Excimer, Fluorescence, Aluminium ion

Introduction

The design of fluorescent chemosensors able to selectively recognize and sense specific cations has attracted considerable interests due to their importance in biological and environmental settings.[1,2] The main issue in design of effective fluorescent chemosensor is to easily convert molecular recognition into photochemical changes with a high selectivity and sensitivity. On account of their high sensitivity and selectivity,[3-5] fluorescent chemosensors can be effectively used as a tool to analyze and clarify such roles of charged chemical species in living system as well as to measure the amount of metal ions from the sources contaminated with them.

In the biochemistry centered on the toxicity of the metal ions,[6] Al^{3+} ion has gained prominence through a possible link to Alzheimer's disease.[7] For detection of Al^{3+} ion, we reported a 1,3-alternate calix[4]arene with fluorescent dipyreneyl polyether groups showing a complex with Al^{3+} ion. The compounds showed fluorescence change of both the pyrene excimer and its monomer by a conformational change of the ligand to suppress an efficient HOMO-LUMO interaction between two pyrenes (Py-Py*).[8]

The Pb^{2+} ion has been also considered as one of the important target ions to be selectively removed because of its adverse effects to people, particularly to children.[9] A wide variety of symptoms which include memory loss, irritability, anemia, muscle paralysis, and mental retardation have been ascribed to lead exposure, suggesting that Pb^{2+} ion affects multiple targets *in vivo*.[10]

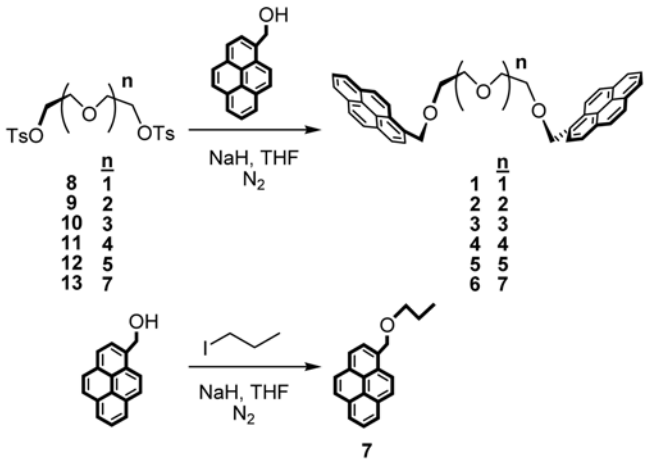
Most of the fluorescent chemosensors for cations are composed of a cation recognition unit (ionophore) together with a fluorogenic unit (fluorophore) and are called fluoroionophores.[11] An effective fluorescence chemosensor must convert the event of cation recognition by the ionophore into an easily monitored and highly sensitive light signal from the fluorophore.

Among fluorophores, pyrenes are known as one of the most useful fluorogenic units because they display not only a well-defined monomer emission at 375 nm but also an efficient excimer emission at around 475 nm.[12] With an intensity ratio of excimer to monomer emission (I_E/I_M) being sensitive to the conformational changes of the pyrene-appended receptor, the I_E/I_M changes upon the metal ion complexation can be an informative parameter in various sensing systems.[13,14] In addition, polyethers in which the proper-sized polyether oxygen rings are incorporated into the pyrene have attracted intense interest as a selective extractant for specific metal ions.[15]

From this standpoint, we herein report the synthesis of new series of bispyrene polyether compounds **1-6**, which exhibit a unique fluorescent response with Al^{3+} ion. **7** was also synthesized as a reference material to elucidate the binding mechanism of **1-6** to metal cations.

Results and Discussion

The general synthetic procedures for **1-7** are summarized in Scheme 1. Starting materials **8-13** were prepared accord-



Scheme 1. Synthetic routes to fluorescent chemosensors **1-7**.

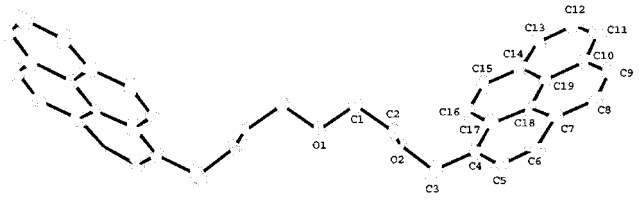


Figure 1. X-ray crystal structure of **1**.

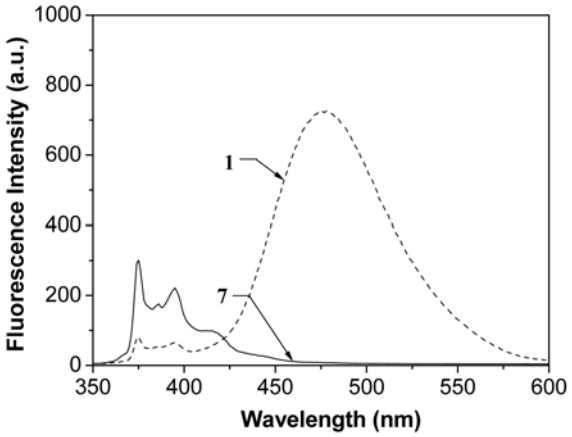


Figure 2. Fluorescence spectra of free **1** and **7** (6.0 μM) in CH_3CN. The excitation wavelength is 343 nm.

ing to the literature.[16,17] Reaction of **8** with 2.1 equiv of 1-pyrenemethol and NaH as a base in dry THF afforded **1** in quantitative yield. Alkylation of 1-pyrenemethanol with 1-iodopropane and NaH in THF provided **7** in 74% yield. Compounds **2-6** were prepared by the same method used in **1**. All structures were ascertained by ^{1}H NMR and ^{13}C NMR, and Mass spectrometry. Also, the solid-state structure of **1** (Figure 1, Table 1) provided convincing evidence for its conformation.

Excited at 343 nm, **1** displays both monomer and excimer emission at 375 and 475 nm, respectively, whereas **7** emits its only monomer at 375 nm (Figure 2). This means that the excimer emission is formed by the intramolecular not by the intermolecular pattern. Host molecules with more than one pyrenyl group exhibit an intramolecular excimer emission by two different mechanisms.[18] One arises from π-π stacking of the pyrene rings in the ground-state, which results in a characteristic decrease of the excimer emission intensity and a concomitant increase of monomer emission intensity. The other mechanism is due to interaction of the excited pyrene (Py*) with the ground-state pyrene (Py). As a result, it is apparent that the excited state of one pyrene unit shows a strong interaction with the ground state of the other pyrene unit through the π-π stacking in **1**.

To obtain insight into the metal ion binding properties of **1-7**, we investigated fluorescence changes upon addition of the perchlorate salt of Ag^+, Cs^+, K^+, Li^+, Na^+, Mg^{2+}, Co^{2+}, Ca^{2+}, Zn^{2+}, Pb^{2+}, and Al^{3+} to the CH_3CN solutions of **1-7**. The results are presented in Table 2 and show that they have similar binding properties for the metal ions. On the other hand, **7** hardly responds to the most metal ions tested,

Table 1. Crystal data and structure refinement for **1**

Identification code	Reflections collected / unique
Empirical formula	Completeness to theta = 28.35°
Formula weight	Absorption correction
Temperature	Max. and min. transmission
Wavelength	Refinement method
Crystal system, space group	Data / restraints / parameters
Unit cell dimensions	Goodness-of-fit on F^2
	Final R indices [I>2sigma(I)]
	R indices (all data)
Volume	Absolute structure parameter
Z, Calculated density	Extinction coefficient
Absorption coefficient	Largest diff. peak and hole
F(000)	**1**
Crystal size	$C_{38}H_{30}O_3$
Theta range for data collection	534.62
Limiting indices	233(2) K
0.71073 Å	6083 / 3275 [*R*(int) = 0.1281]
Monoclinic, C2	99.7%
a = 34.72(2) Å α = 90°.	Semi-empirical from equivalents
b = 4.562(3) Å β = 96.840(13)°.	0.9983 and 0.1421
c = 8.472(6) Å γ = 90°.	Full-matrix least-squares on F^2
1332.6(16) Å^3	3275 / 1 / 187
2, 1.332 Mg/m^3	1.364
0.083 mm^{-1}	R_1 = 0.2332, wR_2 = 0.5090
564	R_1 = 0.3870, wR_2 = 0.5756
0.10 × 0.05 × 0.02 mm	−10(10)
1.18 to 28.35°.	0.13(3)
$-45 \le h \le 46$, $-6 \le k \le 6$, $-10 \le l \le 11$	0.967 and −0.683 e.Å^{-3}

indicating that the polyether spacer between two pyrenes plays an important role in the fluorescence ratiometrical changes in both monomer and excimer emissions toward metal ions.

To obtain quantitative insight into the ionic affinity of **1-6**, we determined the intensity changes upon complexation of Al^{3+} and Pb^{2+}. The fluorescence changes of receptors are found to be highly dependent on the polyether spacer length. As shown in Table 3, association constants[19] of Al^{3+} decrease from **1** to **5** in order of increasing polyether length. In contrast, addition of Pb^{2+} gives an enhanced association constant with increasing polyether length. Compound **6** responds to metal ion, exhibiting a fluorescence behavior unlikely to that of **1-5**. This is presumably because the podand length of **6** is too large to entrap the cations.

On the basis of fluorescence changes upon metal cation complexation, we found that **1-6** exhibit Pb^{2+} and Al^{3+} selectivity over other metal cations tested. Compound **1** with a short spacer is observed to be selective for Pb^{2+} ion in terms of decreasing fluorescence, which is due to the PET effect and the heavy metal ion effect.[20] The fluorescence intensity was gradually decreased by the addition of the Pb^{2+} ion until 1,000 equiv. of ion was added. However, decreasing extent of the excimer emission in **2-6** by Pb^{2+} is much greater than that in **1**.

Table 2. Fluorescence changes ($I-I_0$) of **1-7** upon the addition of various metal cations[a]

Ligand	λ_{em} (nm)	Ag^+	Cs^+	K^+	Li^+	Na^+	Mg^{2+}	Co^{2+}	Ca^{2+}	Zn^{2+}	**Pb^{2+}**	**Al^{3+}**
1	375	8	3	5	5	6	4	2	40	5	**−4**	**865**
	475	−13	44	62	23	45	47	−176	5	8	**−248**	**−622**
2	375	6	12	0	7	0	−2	−1	306	16	**−10**	**745**
	475	−19	181	−32	93	−38	−69	−159	−213	203	**−383**	**−342**
3	375	0	2	2	0	−2	20	−11	93	10	**−83**	**713**
	475	−52	28	24	−2	−9	70	−168	−75	16	**−595**	**−437**
4	375	8	0	0	0	5	8	0	3	8	**−42**	**304**
	475	−24	22	23	19	−2	29	−206	−16	21	**−609**	**−332**
5	375	29	20	31	3	19	25	28	58	18	**−34**	**316**
	475	163	22	30	41	46	49	−54	29	25	**−696**	**−275**
6	375	−1	34	37	4	31	198	36	184	55	**0**	**262**
	475	−69	−60	−138	−20	34	−131	−259	−143	−27	**−596**	**−151**
7	375	30	29	26	22	28	34	−69	35	36	**25**	**37**

[a]Conditions: **1-7**: 6.0 μM in CH_3CN; excitation at 343 nm; metal ions, 500 equiv. in CH_3CN. I_0: fluorescence emission intensity of free **1-7**; I: fluorescence emission intensity of metal ion-complexed **1-7**. (+) and (−) denote fluorescence intensity increase and decrease, respectively.

Table 3. The association constants (K_a) of receptors **1-6** with cations in CH_3CN[a]

Ligand	Al^{3+}(K_a)	Pb^{2+}(K_a)
1	4.94×10^3 M^{-1}	2.56×10^2 M^{-1}
2	3.21×10^3 M^{-1}	4.22×10^3 M^{-1}
3	1.01×10^3 M^{-1}	5.12×10^4 M^{-1}
4	3.52×10^2 M^{-1}	5.54×10^7 M^{-1}
5	1.23×10^4 M^{-1}	4.52×10^5 M^{-1}
6	9.29×10^3 M^{-1}	3.17×10^7 M^{-1}

[a]Conditions: **1-6** (6.0 μM): Determined by fluorescence spectroscopy in CH_3CN; excitation at 343 nm; metal ions, 500 equiv. in CH_3CN. The errors in the association constants were less than 10%.

On the other hand, fluorescence changes of **1-6** for Al^{3+} ion complexation are found to be different from those for heavy metal ions and divalent ions. Figure 3(a) shows the fluorescence spectrum of **1** with increasing amount of Al^{3+}. Despite a different length of the spacer between two pyrenes, they show same tendency of the fluorescence ratiometry towards Al^{3+} ion. However, in **3-6**, the fluorescence changes are saturated with more than 1,000 equiv of Al^{3+}, whereas in the case of **1** and **2** they are with only 200 equiv of Al^{3+}, reflecting that **1** and **2** seem to coordinate with Al^{3+} more readily than **3-6** do. When the Al^{3+} ion is entrapped by a pair of polyether units, the two pyrenes seem to cross each other. As a result, the excimer emission of the pyrene is decreased along with the monomer emission increased, causing a suppression of the efficient intramolecular HOMO(π)-LUMO(π^*) interaction of two pyrene units.

Job plot experiments indicate a 1:1 complex formation of **1** or **5** with Al^{3+}. Receptors-Al^{3+} complex concentration approached the maximum when the molar fraction of [L]/([L] + [Al^{3+}]) was about 0.5, meaning that it formed a 1:1 complex (Figure 4). In addition, one isoemissive point at 428 nm in the fluorescence titration spectra supports that the complex stoichiometry for ligand with Al^{3+} ion is 1:1. A 1:1 complex of **1** or **5** with Pb^{2+} is also evidenced by Job plot experiments.

In conclusion, a series of dipyrene spacing with polyethylene glycol units were synthesized and studied for a ratiometric fluorescence changes for metal cations. **1-6** display a high selectivity towards Al^{3+} ion over other metal

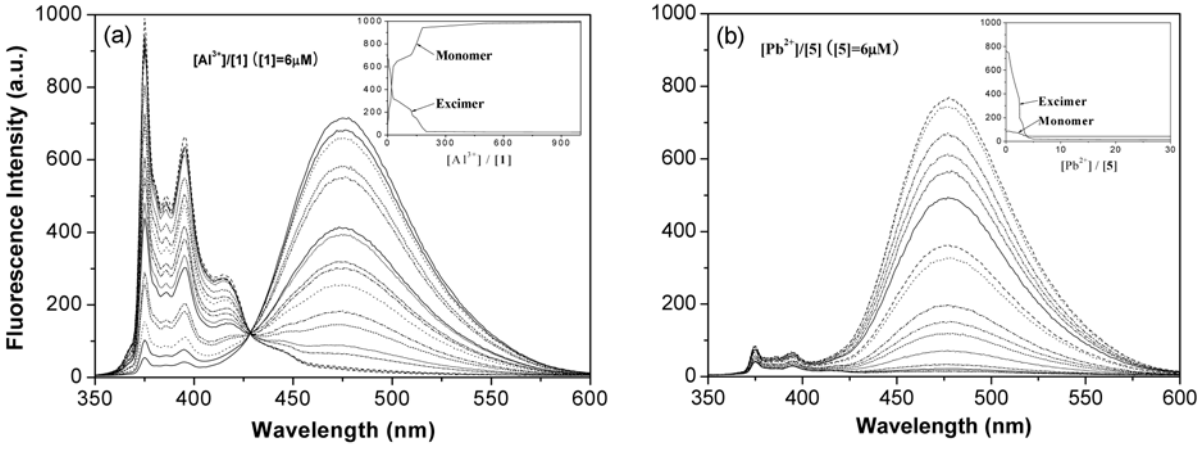


Figure 3. Fluorescence spectra of (a) **1** (6.0 μM) upon the addition of Al^{3+} and (b) **5** (6.0 μM) upon the addition of Pb^{2+} in acetonitrile. (The excitation wavelength is 343 nm).

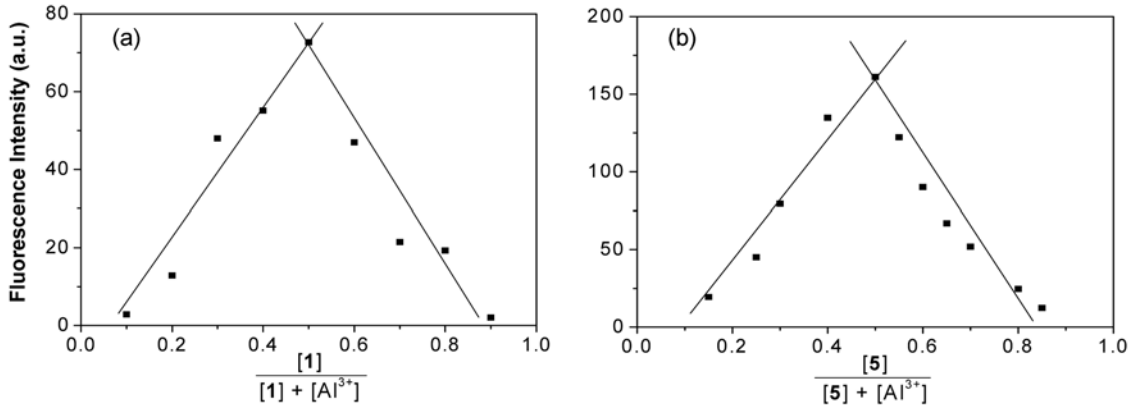


Figure 4. Job plot of (a) **1** and (b) **5** with Al^{3+} in CH_3CN. The excitation wavelength is 343 nm (Ligand:Al^{3+}=1:1).

ions. In free ligand, they show strong excimer emission at 475 nm with weak monomer emission at 375 nm. The monomer emission increases, concomitantly with an excimer emission decreased when Al^{3+} was bound to dipyrene polyether system. Upon addition of Pb^{2+} ion, both monomer and excimer emissions were decreased, due to a heavy-metal ion effect.

Experimental Section

Diethylene glycol bis(1-pyrenylmethyl) ether (1). To a mixture of 1.0 g (2.41 mmol) of **8** and 1.17 g (4.82 mmol) of 1-pyrenmethanol in 100 mL of dry THF, anhydrous NaH 24 mg (24.1 mmol) were added under nitrogen atmosphere. The reaction mixture was refluxed for 24 hours. After removal of the solvent *in vacuo*, HCl solution (100 mL) and CH_2Cl_2 (100 mL) were added and organic layer was separated and then washed two times with 50 mL of water. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated *in vacuo* to give a yellowish oil which was purified by column chromatography on silica gel with ethyl acetate:hexane (1:2) to provide 0.8 g (62.5%) of **1** as a yellow oil. Compound **1** was prepared by almost the same method used for **7**. 56% yield. Mp: 83-92 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.35-7.93 (m, 18H, Ar-*H*), 5.23 (s, 4H, Ar-*CH*$_2$-O), 3.73-3.71 (m, 8 H, O*CH*$_2$CH$_2$). ^{13}C NMR ($CDCl_3$): 131.3, 131.1, 130.7, 127.5, 127.3, 127.2, 126.9, 125.9, 125.7, 125.2, 125.0, 125.0, 124.8, 124.6, 124.3, 123.4, 71.8, 77.0, 76.3, 71.8, 70.8, 69.5 ppm. FAB MS *m/z* (m^+): Calcd, 534.64. Found, 534.63.

Triethylene glycol bis(1-pyrenylmethyl) ether (2). Compound **2** was prepared by the same method used for **1**. Mp: 94-99 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.35-7.94 (m, 18 H, Ar-*H*), 5.20 (s, 4H, Ar-*CH*$_2$-O), 3.68-3.65 (m, 12H, O*CH*$_2$CH$_2$). ^{13}C NMR ($CDCl_3$): 131.3, 131.1, 130.7, 129.3, 127.5, 127.3, 127.2, 126.9, 125.8, 125.1, 124.3, 123.4, 71.7, 70.7, 70.6, 69.5 ppm. FAB MS *m/z* (m^+): Calcd, 578.7. Found, 578.7.

Tetraethylene glycol bis(1-pyrenylmethyl) ether (3). Compound **3** was prepared by the same method that used for **1**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.12-7.98 (m, 18H, Ar-*H*), 4.07 (S, 4H, Ar-*CH*$_2$-O), 3.68-3.61 (m, 16H, O*CH*$_2$CH$_2$). ^{13}C NMR ($CDCl_3$): 131.2, 129.7, 127.9, 127.5, 127.3, 127.3, 126.9, 125.8, 125.1, 124.4, 123.4, 71.7, 70.6, 70.5, 69.4 ppm. FAB MS *m/z* (m^+): Calcd, 622.7. Found, 622.

Pentaethylene glycol bis(1-pyrenylmethyl) ether (4). Compound **4** was prepared by the same method used for **1**. ^{1}H NMR (200 MHz: $CDCl_3$): δ 8.31-7.95 (m, 18H, Ar-*H*), 5.20 (s, 4H, Ar-*CH*$_2$-O), 3.67-3.56 (m, 20H, O*CH*$_2$CH$_2$). ^{13}C NMR ($CDCl_3$): 131.3, 127.5, 127.3, 127.2, 126.9, 125.8, 125.0, 124.3, 123.4, 71.7, 70.6, 70.5, 70.4, 69.4 ppm. FAB MS *m/z* (m^+): Calcd, 666.8. Found, 666.5.

Hexaethylene glycol bis(1-pyrenylmethyl) ether (5). Compound **5** was prepared by the same method used for **1**. 84% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.39-7.95 (m, 18 H, Ar-*H*), 5.24 (s, 4H, Ar-*CH*$_2$-O), 3.72-3.56 (m, 24H, O*CH*$_2$CH$_2$). ^{13}C NMR ($CDCl_3$): 131.3, 131.2, 130.7, 129.3, 127.5, 127.3, 127.3, 126.9, 125.8, 125.1, 124.8, 124.6, 124.3, 123.4, 71.7, 70.6, 70.5, 70.4, 69.4 ppm. FAB MS *m/z* (m^+): Calcd, 710.8. Found, 710.5.

Octaethylene glycol bis(1-pyrenylmethyl) ether (6). Compound **6** was prepared by the same method used for **1**. 74% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.45-7.98 (m, 18 H, Ar-*H*), 5.25 (s, 4H, Ar-*CH*$_2$-O), 3.73-3.55 (m, 32 H, O*CH*$_2$CH$_2$). ^{13}C NMR ($CDCl_3$): 131.3, 131.2, 130.7, 129.3, 128.1, 127.6, 127.3, 125.8, 125.1, 124.8, 124.6, 124.4, 123.5, 97.7, 74.3, 71.7, 70.6, 70.5, 69.4 ppm. FAB MS *m/z* (m^+): Calcd, 798.96. Found, 798.95.

Propyl 1-pyrenemethyl ether (7). A mixture of 1-pyrenemethanol (1.00 g, 4.30 mmol), NaH (1.03 g, 42.9 mmol), and THF (60 mL) was stirred magnetically for 20 min, and then 1-iodopropane (2.19 g, 12.8 mmol) was added. The reaction miture was refluxed for 2 days and evaporated *in vacuo*. The residue was extracted with CH_2Cl_2, and the organic solution was washed with water, dried over $MgSO_4$, and evaporated *in vacuo* to yield 0.87 g (74%) of **7** as a yellowish oil. ^{1}H NMR (200 MHz: $CDCl_3$): δ 8.30-7.95 (m, 9H, Ar-*H*), 5.15 (s, 2H, Ar-*CH*$_2$-O), 3.53-3.50 (m, 2H, O*CH*$_2$CH$_2$CH$_3$), 1.68-1.65 (m, 2H, OCH$_2$*CH*$_2$CH$_3$), 0.88-0.84 (m, 3H, OCH$_2$CH$_2$*CH*$_3$) ^{13}C NMR ($CDCl_3$): 131.8, 131.2, 131.1, 130.8, 129.2, 127.5, 127.3, 127.2, 126.8, 125.8, 125.1, 124.4, 123.4, 72.2, 71.4, 31.9, 29.6, 29.3, 23.0,

22.6, 14.1, 10.7 ppm. FAB MS *m/z* (m^+): Calcd, 274.36. Found, 274.35.

General Procedure for Fluorescence Studies. Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. Stock solutions (1.00 mM) of the metal perchlorate salts were prepared in MeCN. Stock solutions of **1-6** (0.06 mM) were prepared in MeCN. For all measurements, excitation was at 343 nm with excitation slit widths at 1.5 nm and emission slit widths at 3 nm. Fluorescence titration experiments were performed using 6 μM solutions of **1-6** in MeCN and various concentrations of metal perchlorate in MeCN. After calculating the concentrations of the free ligands and complexed forms of **1-6** from the fluorescence titration experiments, the association constants were obtained using the computer program ENZFITTER.[19]

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