Silver Ion Selective Fluoroionophores Based on Anthracene-Linked Polythiazaalkane or Polythiaalkane Derivatives

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A dozen novel fluoroionophores have been synthesized which are polythiazaalkane and polythia-alkane derivatives coupled with an anthracene moiety by methyl, carbonyl, or methylphenylene bridging groups. The protonation and metal ion complexation behavior of analogues were examined in 1,4-dioxane−water solutions spectrophotometrically and spectrophotofluorometrically. The fluoroionophores, **1**, **2**, **5**, and **6** contain basic nitrogen atoms and quench the fluorescence in the free forms because of photoinduced electron transfer (PET) from a nitrogen atom to a photoexcited anthracene unit. The fluorescence was recovered by the protonation on the nitrogen atom. The fluorescence intensities of the other fluoroionophores used here were not dependent on the pH of the solution. On the complexation of the protonated fluoroionophores **1**, **2**, **5**, and **6** with metal ions under the acidic condition, the fluorescence intensities were decreased by the addition of silver ion selectively. Under the same conditions, the other fluoroionophores exhibited a decrease of the fluorescence intensity with the addition of silver ion selectively. These results imply that the fluoroionophores could form complexes and release a proton from the nitrogen atom of the protonated fluoroionophores. The quenching of the fluorescence of the complexed fluoroionophores **3**, **4**, **7**, and **8**−**12** could be caused by the interaction of a silver ion with a π-electron of the anthracene unit. The degree of spectral change on the complexation with silver ion is primarily dependent on the strength of the interaction of the bound silver ion with nitrogen atom, for **1**, **2**, **5**, and **6**, or with a π-electron of the anthracene unit, for **3**, **4**, **7**, and **8**−**12**.

Introduction

The determination of substrate-specific complexation by spectral changes is one of the most favorable methods from the perspective of the cost of the instruments and the facility of the measurement. In particular, the luminescent probe offers advantages in terms of the sensitivity and the specificity. Thus, fluoroionophores,[1−10] which consist of the fluorescent unit and the complexing part, have been designed for the determination of cations based on the changes of the emission intensity on complexation. Czarnic[11] and de Silva[12] reported that the fluoroionophores, whose cyclic polyamine or monoaza-crown ether moieties were linked with an anthracene unit as a fluorophore by a methylene group, showed chelation-enhanced fluorescence (CHEF) on complexation with a metal ion. On the other hand, Sclafani[13] and Kakizawa[14] reported that the bis-anthracene hosts, which have linear polyamine or polyether moieties linked with anthracene units at both ends, exhibited enhancement of fluorescence due to the formation of an intramolecular photoexcimer by the interaction between both anthracene units upon complexation with a metal ion.[15,16]

We have reported that polythiazaalkane derivatives form stable complexes with silver ion selectively.[17−19] Thus, for the development of fluoroionophores for silver ion, we synthesized the compounds shown in Scheme 1; these compounds contain one or more anthracene units as the fluorophore. We show that spectral changes

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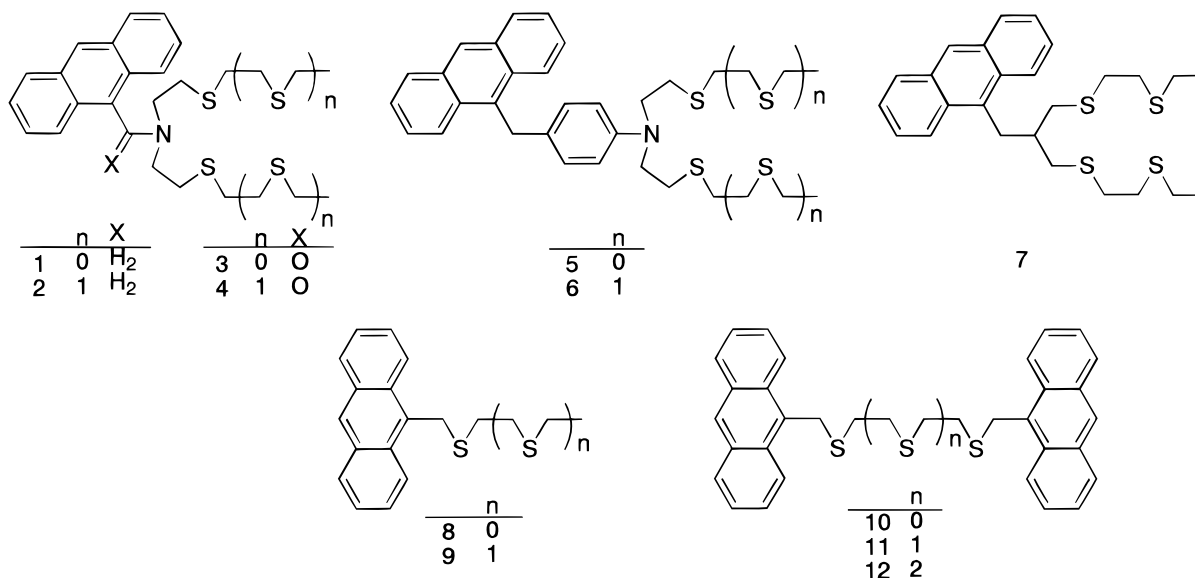(15) Tahara, R.; Hasebe, K.; Nakamura, H. *Chem. Lett.* **1995**, 753.
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Scheme 1. Fluoroionophores

induced by the complexation with silver ion are expected. We also describe the absorbance and the fluorescence spectral properties of the prepared fluoroionophores on the protonation and complexation with some heavy metal ions and their complexation behavior with the silver ion.

Results and Discussion

Design and Synthesis. The ionophores containing some sulfur atoms which act as soft donors in derivatives such as thiacrown ethers have been known to have a specific affinity for silver ion.[20-23] Furthermore, we have found that in solvent−solvent extraction and in aqueous 1,4-dioxane solutions the cyclic and the acyclic polythiazaalkanes[17] and their chromogenic derivatives have selective affinities for silver ion.[18,19] Therefore, a series of anthracene derivatives bearing the multidentate ligands containing sulfur atoms, as shown in Scheme 1, were designed and synthesized to obtain fluoroionophores with the specific recognition properties for silver ion. The fluoroionophores used here, **1−7**, are constructed of three parts as follows: a fluorophore, a bridging unit, and a complexing part. The anthracene unit is selected as a fluorophore. Three different bridging units, carbonyl, methylene, and methylphenylene groups, were used. An acyclic structure composed of polythiazaalkane or polythiaalkane derivatives was selected as the complexing part.

1, **2**, **5**, and **6** contain an anthracene unit and were synthesized in a manner identical to that of *N*-(9-anthrylmethyl)-aza-18-crown-6,[12] which exhibited an emission enhancement following the complexation with alkali metal ion. The fluorescence of the neutral *N*-(9-anthrylmethyl)-aza-18-crown-6 was quenched by an electron transfer from a nitrogen atom to the photoexcited anthracene unit, the so-called photoinduced electron transfer (PET) mechanism.[1,2,24,25] The emission is restored by

the interaction between the nitrogen atom and the bound metal ion on formation of the complex because of the suppression of an electron transfer from the nitrogen atom to the photoexcited anthracene unit. Thus, the anthracene derivatives used here are expected to exhibit the CHEF on complexation with silver ion.

For **3** and **4**, the polythiazaalkane moiety was linked through the nitrogen atom to an anthracene unit by a carbonyl group. Compound **7** consists of a tetrathiaalkane chain bearing the 9-anthrylmethyl group on the central C-pivot of the chain unit. The compounds, **3**, **4**, and **7**, do not have a basic nitrogen atom and are expected to exhibit different spectral changes from those of the polythiazaalkane derivatives, **1**, **2**, **5**, and **6**, by incorporating a basic nitrogen atom when silver ion is complexed.

Linear polythiaalkane derivatives **8−12** with one or two anthryl moieties on the terminal positions were also synthesized. In particular, **10−12**, which have anthracene units on both terminal positions, were modified according to the procedure for N^1,N^4-bis(9-anthrylmethyl)triethylenetetramine, which exhibited enhancement of excimer fluorescence when complexed with zinc(II) ion.[12] The result is likely attributed to a conformational change of the polyamine moiety, resulting in the proximity of the aromatic ends of a ligand. Thus, the bis-anthracene compounds **10−12** were expected to increase the excimer band caused by conformational change when the silver ion complex is complexed.

A series of fluoroionophores were synthesized according to Scheme 2. Anthrylmethyl polythiazaalkane derivatives **1** and **2** were synthesized by the reactions of appropriate polythiazaalkanes with 9-chloromethylanthracene in the presence of potassium carbonate using acetonitrile as a solvent. On the other hand, anthracenecarbonyl analogues **3** and **4** were prepared by the reactions of appropriate polythiazaalkanes with anthracene-9-chlorocarbonyl in the presence of potassium carbonate using benzene as a solvent. In the reactions, little difference in the yields among **1** (41.9%), **2** (32.5%), **3** (33.6%), and **4** (34.8%) was observed.
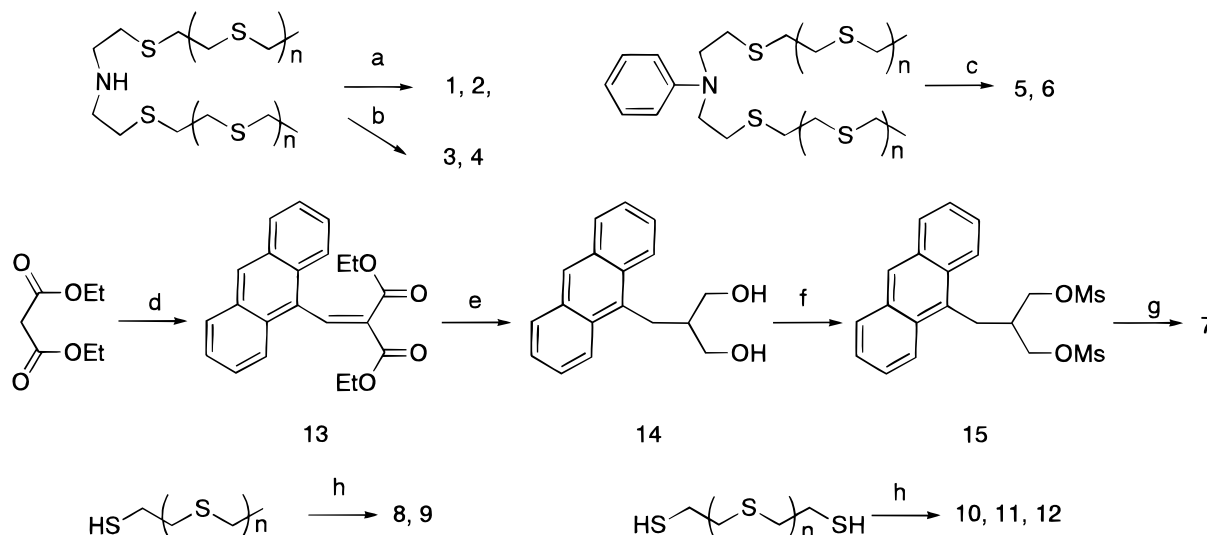
Anthrylmethyl phenylene polythiazaalkane derivatives **5** and **6** were produced by the reactions of appropriate

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Scheme 2[a]

[a] Reagents and conditions: (a) 9-chloromethylanthracene, K$_2$CO$_3$, MeCN; (b) 9-anthracenecarbonyl chloride, K$_2$CO$_3$, benzene; (c) 9-chloromethylanthracene, AlCl$_3$, CHCl$_3$; (d) 9-anthraldehyde, benzene; (e) LiAlH$_4$, THF; (f) methanesulfonyl chloride, Et$_3$N, CH$_2$Cl$_2$; (g) 3-thiapentane-1-thiol, NaOH, EtOH; (h) 9-chloromethylanthracene, NaOH, EtOH.
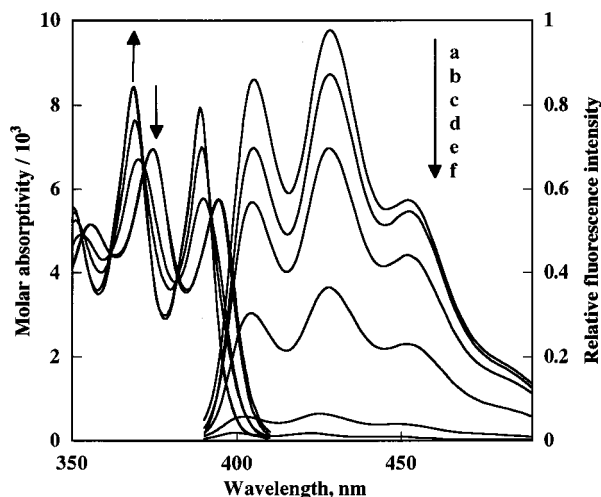

Figure 1. pH-dependent absorbance and fluorescence spectral changes of a 1,4-dioxane−water (52/48 v/v%) solution containing **2**. pH: (a) 1.1; (b) 3.1; (c) 4.3; (d) 4.9; (e) 6.1; (f) 7.1.

Figure 2. Plots of relative fluorescence intensity at 428 nm for **2** (▲) and at 418 nm for **6** (◆) vs pH.

N-phenylpolythiazaalkanes with 9-chloromethylanthracene in the presence of aluminum chloride using chloroform as a solvent. In these reactions, the yields of the compounds **5** and **6** were 60.1 and 56.0%, respectively.

Center C-pivot derivative **7** was synthesized in a four-step procedure as follows: condensation reaction of diethyl malonate with 9-anthraldehyde (84.6%), reduction with LiAlH$_4$ (58.6%), mesylation reaction with methane sulfonyl chloride (95.3%), and then the reaction with 2-thiapentane-1-thiol (75.9%) in the presence of sodium ethoxide as a base. The overall yield was 35.8%.

Terminally modified derivatives **8**−**12** were formed by the reactions of appropriate polythiaalkane (di)thiols with 9-chloromethylanthracene in the presence of sodium ethoxide using ethanol as a solvent; the yields of **8**, **9**, **10**, **11**, and **12** are 55.6, 64.1, 59.1, 54.3, and 60.6%, respectively.

Spectral Properties and Protonation Behavior of Fluoroionophores. The spectral properties of the fluoroionophores were dependent on pH and were measured
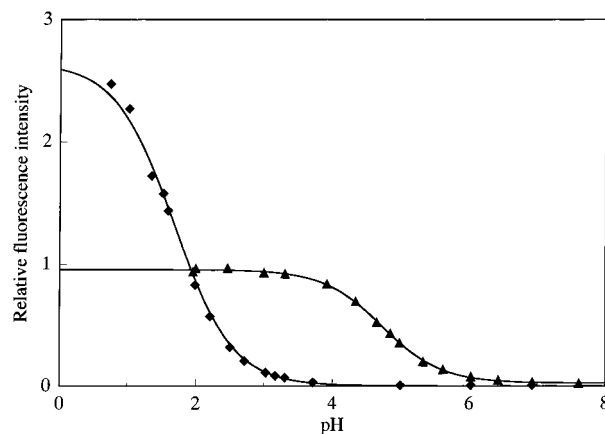
spectrophotometrically and spectrophotofluorometrically in a 1,4-dioxane−water solution. The 1,4-dioxane−water mixture of 52/48 v/v % was used for all molecules except **11** in which a 64/36 v/v % solution was used.

The pH-dependent spectral changes of **2** are shown in Figure 1, which demonstrates a decrease in fluorescence intensity and a minimal change in absorption spectra with increase in pH. Similar spectral changes were observed for *N*-(9-anthrylmethyl)dithiazaundecane **1** and *N*-(9-anthrylmethylphenylene) analogues **5** and **6**. Figure 2 shows the plots of relative fluorescence intensity vs pH for **2** and **6**. Drastic increases in the fluorescence intensity for both compounds were observed under acidic conditions. The results demonstrate that the nitrogen atoms in the polythiazaalkane moieties are protonated under the acidic conditions. That is, the fluorescence is increased by the protonation on the nitrogen atom, which prevents the electron transfer from the nitrogen atom to the photoexcited anthracene unit. The protonation constants were calculated from the fluorescence intensity changes, and the spectral properties and the protonation constants (K_H) are summarized in Table 1. Similar structural analogues (i.e., **1** and **2**, or **5** and **6**) have very

Table 1. Spectral Properties and Protonation Constants for Fluoroionophores

		L			HL		
		absorbance	emission		absorbance	emission	
no.	log $K_H{}^a$	λ_{max}, nm ($\epsilon/10^3$)	λ_{max}, nm	If^d		λ_{max}, nm	If^d
1^b	5.13	350 (5.27), 368 (7.97), 388 (7.57)	399, 422, 446	0.023	354 (4.87), 372 (6.56), 392 (5.43)	404, 426, 450	1.25
2^b	4.69	350 (5.62), 368 (8.61), 388 (8.18)	399, 422, 446	0.025	355 (5.12), 373 (6.94), 393 (5.78)	407, 428, 452	0.98
3^b		349 (5.94), 366 (8.70), 386 (7.97)	396, 416, 442	0.83			
4^b		349 (5.88), 367 (8.52), 387 (7.76)	396, 418, 442	0.89			
5^b	2.08	350 (6.44), 369 (10.00), 390 (9.56)	397, 418, 444	0.024	350 (6.44), 369 (10.00), 390 (9.56)	397, 418, 444	2.74
6^b	1.69	351 (6.29), 369 (9.78), 389 (9.33)	397, 418, 444	0.006	351 (6.29), 369 (9.78), 389 (9.33)	397, 418, 444	2.84
7^b		351 (6.32), 370 (10.12), 390 (9.72)	397, 420, 445	3.40			
8^b		352 (6.11), 371 (9.65), 391 (9.21)	401, 422, 448	0.127			
9^b		353 (6.16), 371 (9.76), 392 (9.28)	400, 422, 447	0.168			
10^b		352 (10.23), 372 (16.07), 392 (15.35)	400, 422, 448	0.208			
11^c		353 (11.91), 372 (18.71), 392 (17.83)	400, 423, 450	0.322			
12^b		353 (11.66), 372 (18.21), 392 (17.25)	401, 423, 450	0.288			

^{a} $K_H = [HL]/[H][L] = 1/K_a$, $\log K_H = pK_a$. ^{b} 1,4-Dioxane–water (52/48 (v/v) %). ^{c} 1,4-Dioxane–water (64/36 (v/v) %). ^{d} A relative fluorescence intensity (If) was calculated on the basis of fluorescence intensity of the anthracene.

close protonation constants and similar spectral properties to each other. The protonation constants of 9-anthrylmethylphenylene derivatives **5** and **6** are about 3 orders of magnitude lower than those of 9-anthrylmethyl derivatives **1** and **2**. These facts demonstrate that the protonation properties are independent of the length of polythiazaalkane chains. For the other analogues **3**, **4**, and **7**–**12**, very small pH-dependent spectral changes were observed under the conditions used here.

The order of the relative fluorescence intensity for the unprotonated fluoroionophores is **7** > **3** ≈ **4** > **10** ≈ **11** ≈ **12** > **8** ≈ **9** ≫ **1** ≈ **2** > **5** ≈ **6**. The anthracene-9-carbonyl polythiazaalkanes **3** and **4** exhibited higher fluorescence intensity than the other polythiazaalkane analogues **1**, **2**, **5**, and **6**. The basicities and oxidation potentials of nitrogen atoms of **3** and **4** which contain the amide bond are extremely low because of the electron-withdrawing effect of the carbonyl group. Thus, the electron transfer from the nitrogen atom to the photoexcited anthracene unit should be suppressed, and the fluorescence is barely quenched.

For the terminally modified derivatives **8** and **9** bearing one anthracene unit and **10**, **11**, and **12** having anthracene units on both sides, the absorbances and fluorescence intensities of the latter are about 2 times those of the former, and the spectral shapes and the maximum absorption and emission wavelengths of the compounds **8**–**10** and **12** are similar to each other. These results indicate that the interaction between both terminal anthracene units to form the intramolecular photoexcimer does not occur in the free form. Only **11** gave a broad peak at higher wavelength (>500 nm) in the emission spectrum, reflecting the partial formation of an intramolecular photoexcimer, comprised of both terminal anthracene units.

Spectral Changes on Complexation with Metal Ions. 1. *N*-(9-Anthrylmethyl)dithiazaundecane 1, *N*-(9-Anthrylmethyl)tetrathiazaheptadecane 2, and *N*-(9-Anthrylmethylphenylene) Analogues 5 and 6. The spectral changes of the solutions containing the fluoroionophores and metal ions were determined using a 1,4-dioxane–water (52/48 v/v%) solution as solvent. The absorption and fluorescence spectral changes of the acidic solution containing **6** with additional silver ion are shown in Figure 3. The fluorescence spectra decrease remarkably with the increase in the silver ion concentration while the absorption spectra was scarcely changed. This means that the complex of **6** with silver ion was formed
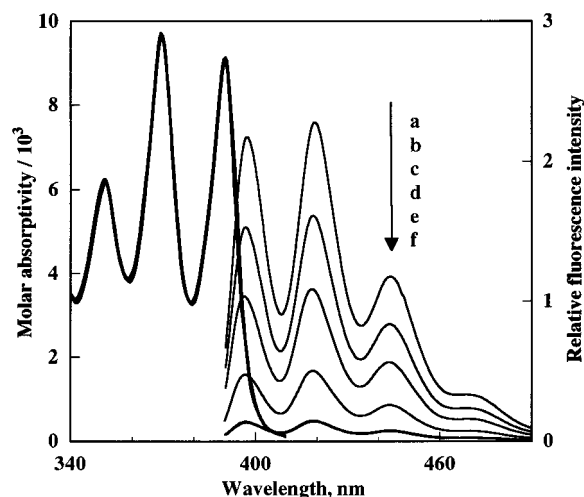

Figure 3. Silver ion concentration dependent absorbance and fluorescence spectral changes of 1,4-dioxane–water (52/48 v/v%) solutions containing **6**. [HNO$_3$] = 0.1 M. [Ag$^+$] = (a) 0; (b) 6.3×10^{-6}; (c) 1.25×10^{-5}; (d) 1.88×10^{-5}; (e) 2.5×10^{-5}; (f) 3.1×10^{-5} M.

and the proton on the nitrogen atom of the polythiazaalkane moiety was replaced by silver ion. Thus, the electron transfer from a nitrogen atom to the photoexcited anthracene unit should be almost restored by the formation of the silver ion complex to quench the fluorescence. Figure 4 depicts the plots of fluorescence intensities at 426 nm of the solutions containing **6** in various concentrations of some metal ions. It is clear from Figure 4 that the fluorescence intensity was decreased markedly by the addition of silver ion, although little change was observed by the addition of the other metal ions. This demonstrates that **6** has high silver ion selectivity, and the 1:1 complex of **6** with silver ion is formed because the fluorescence intensity decreases until the silver ion concentration goes up to being equimolar with **6**. The analogous compounds **1**, **2**, and **5** exhibited similar silver ion selectivity.

When the neutral solution is used, *N*-(9-anthrylmethyl)polythiazaalkanes **1** and **2** and *N*-(9-anthrylmethylphenylene) analogues **5** and **6** are in their free forms, and the fluorescence of the compounds is quenched due to PET. On addition of silver ion into the solution containing **6**, the fluorescence intensity increased slightly as shown in Figure 5. This observation indicates that the electron transfer from the nitrogen atom to the photoexcited anthracene unit should be weakly depressed by
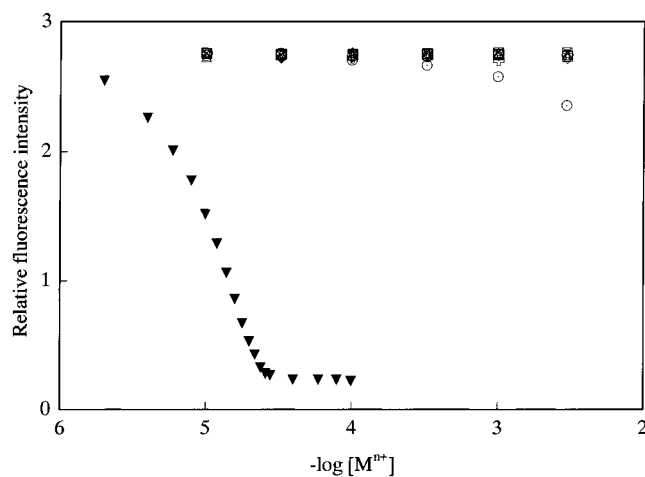
Figure 4. Plots of relative fluorescence intensity at 426 nm for **6** vs $-\log[M^{n+}]$. $[HNO_3] = 0.1$ M. M^{n+}: ⊹, Mn^{2+}; box with ×, Co^{2+}; ▽, Ni^{2+}; ⊙, Cu^{2+}; □, Zn^{2+}; ○, Cd^{2+}; △, Pb^{2+}; ◇, Tl^+; ▼, Ag^+.

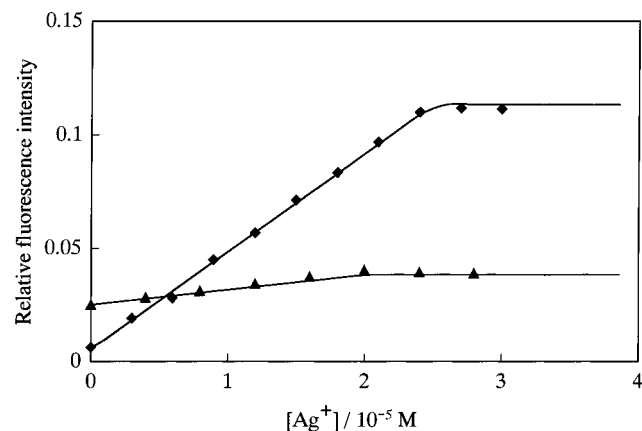**Figure 5.** Plots of relative fluorescence intensity at 422 nm for **2** (▲) and at 418 nm for **6** (◆) vs silver ion concentration. pH 8 for **2**, and pH 5 for **6**.

the complexation of **6** with silver ion. In other words, the weak interaction between the nitrogen atom of the polythiazaalkane moiety and silver ion is induced by the formation of the complex. On the other hand, the extent of the increase in the fluorescence intensity of the solution containing 9-anthrylmethyl derivative **2**, which has the same tetrathiazapentadecane moiety as **6**, was much smaller than that of **6** (see Figure 5). This effect is probably due to the bound silver ion that is brought close to the anthracene unit and can interact with the π-electrons of the anthracene unit of **2** to quench the fluorescence. Such quenching phenomena were observed in the case of anthraceno-cryptands.[26−29] The anthracene unit

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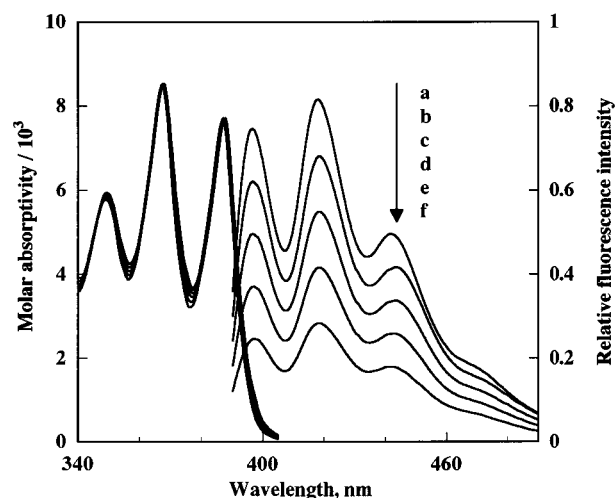

Figure 6. Silver ion concentration dependent absorbance and fluorescence spectral changes of a 1,4-dioxane−water (52/48 v/v%) solution containing **4**. $[HNO_3] = 0.1$ M. $[Ag^+] =$ (a) 0; (b) 6.3×10^{-6}; (c) 1.25×10^{-5}; (d) 1.88×10^{-5}; (e) 2.5×10^{-5}; (f) 3.1×10^{-5} M.
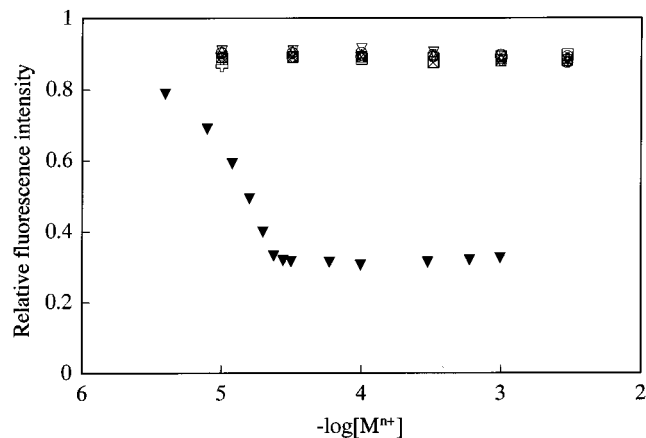

Figure 7. Plots of relative fluorescence intensity at 418 nm for **4** vs $-\log[M^{n+}]$. $[HNO_3] = 0.1$ M. M^{n+}: ⊹, Mn^{2+}; box with ×, Co^{2+}; ▽, Ni^{2+}; ⊙, Cu^{2+}; □, Zn^{2+}; ○, Cd^{2+}; △, Pb^{2+}; ◇, Tl^+; ▼, Ag^+.

of the 9-anthrylmethylphenylene derivative **6** is far from the bound silver ion when it forms the complex with silver ion. This is obvious by examining the appropriate conformers in space-filling models.

2. 9-Anthracenecarbonyl Polythiazaalkane 3 and 4 and Center C-Pivot Tetrathiapentadecane Derivative 7. 9-Anthracenecarbonyl polythiazaalkane **3** and **4** have an amido nitrogen atom in the polythiazaalkane moiety, and the center C-pivot tetrathiapentadecane derivative **7** has no nitrogen atom in the molecule. The spectral changes of the solutions containing **3**, **4**, and **7** were, therefore, barely observed under the pH conditions used in this study. The typical spectra of the acidic solutions containing **4** and silver ion are shown in Figure 6, in which the fluorescence spectra are remarkably changed with the concentration of silver ion while the absorption spectra are barely effected. Figure 7 depicts the plots of fluorescence intensity at 418 nm of the solution of **4** vs the concentration of some metal ions. The remarkable decrease in the fluorescence intensity was observed only during the addition of silver ion. The spectral changes were caused by the complexation of **4**
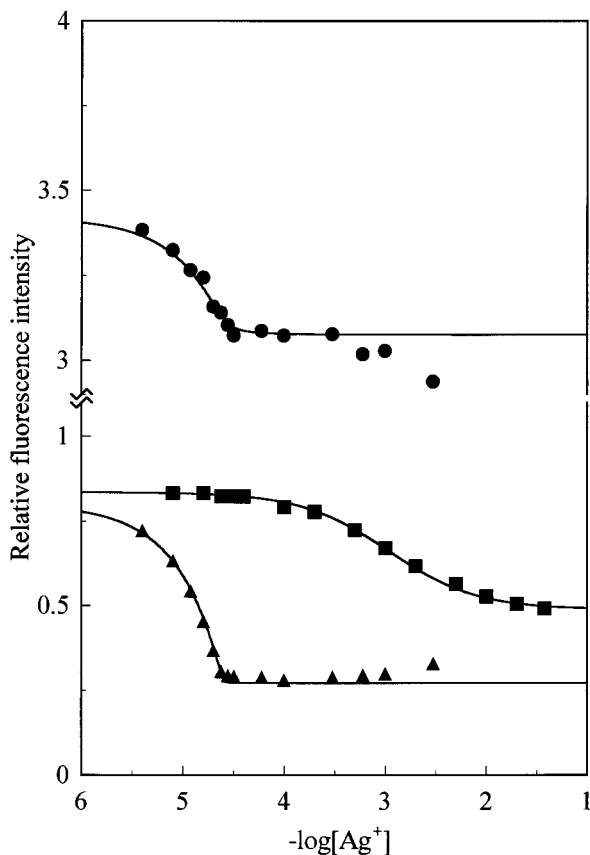
Figure 8. Plots of relative fluorescence intensity at 416 nm for **3** (■), at 418 nm for **4** (▲) and at 420 nm for **7** (●) vs −log-[Ag⁺]. [HNO₃] = 0.1 M.

with silver ion and demonstrated that **4** has excellent silver ion selectivity. Such spectral changes seem to be similar to those of the acidic solutions containing **6** as mentioned above. The quenching mechanisms of **4** and **6**, however, are different from one another. The decrease in the fluorescence intensity of the acidic solution of **6** is primarily caused by the recovery of PET due to conversion from protonation of the nitrogen atom of **6** to the formation of the silver ion complex. The spectral changes

of the solutions of **4** are attributable to the interaction between the π-electrons of the anthracene unit and the silver ion bound to the polythiazaalkane moiety. As described above, in this case silver ion is an effective quencher for the fluorescence.[26−29] Similar phenomena were seen for the solutions of **3** and **7**, although the degrees of the decrease in the fluorescence were much smaller than that of **4** (Figure 8). The stability constant of **3** is much smaller than that of **4** and the intensity of the spectral change should be affected according to the stability of the complex. On the other hand, the structure of **7** differs from those of polythiazaalkane derivatives. Compound **7** does not take a favorable conformation for quenching where the anthracene unit can approach the bound silver ion well.

3. Terminally Modified Polythiaalkane Monoanthryl Derivatives 8 and 9 and Dianthryl Analogues 10, 11, and 12. The absorption and the fluorescence spectral changes of the acidic solutions containing **8**−**12** were examined on addition of silver ion. Figures 9a and 9b show the changes in the molar absorptivity at 371 nm and the fluorescence intensity at 423 nm on addition of silver ion, respectively. All compounds exhibited a remarkable decrease in the fluorescence spectra upon increasing concentration of silver ion while the absorption spectra were not changed as much. The patterns of the decreases in the fluorescence intensity of **9**, **11**, and **12** were similar to each other. It is obvious from Figure 9b that these compounds form the stable complexes with silver ion and the bound silver ion quenches the fluorescence effectively. In particular, **12** interacts most strongly with silver ion. The fluorescence intensities of **8** and **10** were more loosely decreased upon the increase in the concentration of silver ion than those of **9**, **11**, and **12**. This means that the complexes of **8** and **10** are not so stable as those of **9**, **11**, and **12**. Formation of the intramolecular photoexcimer between two anthracene rings was not observed for dianthryl derivatives **10**, **11**, and **12** on complexation with silver ion.

Silver Ion Complexation Behavior. The stability constants of the silver ion complexes of the fluoroionophores were calculated from the changes of the fluorescence intensity at their maximum emission wavelengths
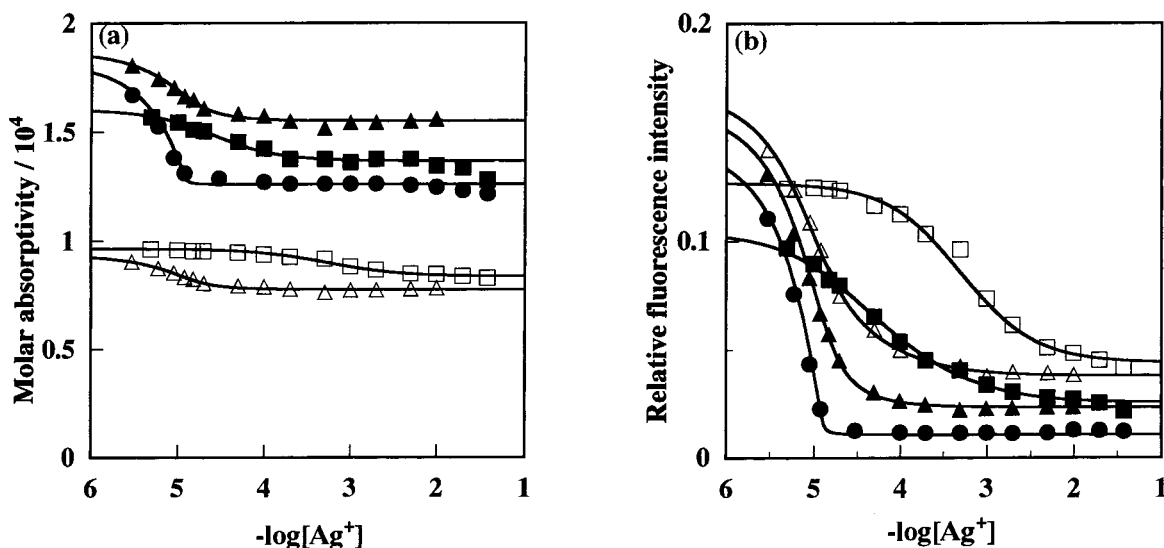

Figure 9. Plots of molar absorptivity at 423 nm (a) and relative fluorescence intensity at 321 nm (b) vs −log[Ag⁺]. [HNO₃] = 0.1 M. Fluoroionophore: □, **8**; △, **9**; ■, **10**; ▲, **11**; ●, **12**.

Table 2. Spectral Properties and Stability Constants for Silver Ion Complexes of Fluoroionophores

no.	log K_{ML}[a]	log K_{ML2}[a]	AgL		
			absorbance	emission	
			λ_{max}, nm ($\epsilon/10^3$)	λ_{max}, nm	If[d]
1[b]	>7	e	354 (4.47), 372 (6.16), 392 (5.31)	399, 422, 446	0.028
2[b]	>7	e	353 (5.23), 370 (7.40), 390 (6.63)	399, 422, 446	0.040
3[b]	2.97	e	349 (6.06), 367 (8.49), 387 (7.66)	396, 416, 442	0.486
4[b]	>7	e	349 (6.00), 367 (8.68), 387 (7.88)	396, 418, 442	0.310
5[b]	5.65	5.56	350 (6.52), 369 (10.12), 389 (9.68)	397, 418, 444	0.168
6[b]	>7	e	351 (6.29), 369 (9.78), 389 (9.33)	397, 418, 444	0.129
7[b]	6.27	e	351 (6.72), 369 (10.76), 389 (10.36)	397, 420, 445	3.08
8[b]	3.31	e	354 (5.99), 373 (9.05), 394 (8.32)	402, 425, 450	0.044
9[b]	4.93	5.28	355 (5.80), 373 (8.68), 394 (7.96)	403, 425, 450	0.038
10[b]	3.87	5.15	355 (9.91), 374 (14.79), 395 (13.75)	402, 424, 450	0.052
11[c]	5.76	e	353 (11.91), 372 (18.71), 392 (17.83)	403, 425, 451	0.046
12[b]	>7	e	356 (9.98), 375 (14.70), 396 (12.53)	403, 425, 450	0.020

[a] K_{ML} = [AgL$^+$]/([Ag$^+$][L]), K_{ML2} = [AgL$_2^+$]/([AgL$^+$][L]). [b] 1,4-Dioxane−water (52/48 (v/v) %). [c] 1,4-Dioxane−water (64/36 (v/v) %). [d] A relative fluorescence intensity (If) was calculated on the basis of the fluorescence intensity of anthracene. [e] A value was not calculated because the maximum ratio of the species was under 10%.

and are summarized in Table 2. It can be concluded from Table 2 that the stabilities of the silver ion complexes increase with the number of the sulfur atoms in the complexing parts of the fluoroionophores. The derivatives containing four sulfur atoms, **2**, **4**, **6**, **7**, and **12**, form very stable complexes almost quantitatively with silver ion.

On comparison among the derivatives containing two sulfur atoms, **5**, **9**, and **10** form a small amount of 1:2 complex (silver ion:fluoroionophore), and the order of the stability of 1:1 complexes is **3** < **10** < **9** < **5** < **1**. Amide derivative **3** exhibits the lowest silver ion complexation ability among the analogues. Because the two sulfur atoms of **3** are far apart from each other and the amide nitrogen atom plays a minor role as a donor atom upon complexation with silver ion, the chelate ring could not be formed effectively. Among the terminally modified dithiaalkane derivatives, monoanthryl derivative **9** and dianthryl one **10** have lower complexation ability than the other fluoroionophores containing two sulfur atoms such as **1** and **5**. This should be true because of the steric hindrance of anthracene moiety(s) on complexation with silver ion. Dithiazaalkane derivatives, **1** and **5**, exhibited relatively high complexation ability with silver ion compared with the other dithiazaalkane **3** and the dithiaalkane analogues **9** and **10**, because the nitrogen atom on the polythiazaalkane moieties of **1** and **5** should be involved during the complexation with silver ion.

The stability constants of the complexes with the other metal ions (i.e., Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Tl$^+$) were difficult to calculate because the spectral changes were rarely observed by addition of metal ions.

Experimental Section

Preparation of 6-(9′-Anthrylmethyl)-3,9-dithia-6-aza-undecane (1). 9-Chloromethylanthracene (0.75 g, 3.3 mmol), 3,9-dithia-6-azaundecane (0.58 g, 3 mmol), and potassium carbonate (0.45 g, 3.3 mmol) were dissolved in acetonitrile (50 mL) and refluxed with stirring for 3 h. After the reaction was completed, the solvent was evaporated in vacuo and then 100 mL of water was added to the residue. The aqueous solution was extracted with three 100 mL portions of CHCl$_3$. The extract was dried over MgSO$_4$. After removal of the solvent, the crude product was subjected to column chromatography and yielded **1** as a yellow oil: yield 0.53 g(41.9%); ^{1}H NMR (CDCl$_3$) δ 1.20 (t, 6H), 2.32−2.94 (m, 12H), 4.63 (s, 2H), 7.25−7.54 (m, 4H), 7.93−8.04 (m, 2H), 8.40−8.57 (m, 3H); MS (EI) m/z 383 (M$^+$). Anal. Calcd for C$_{23}$H$_{29}$NS$_2$: C, 72.01; H,7.62; N, 3.65. Found: C, 71.80; H,7.61; N, 3.60.

Preparation of 9-(9′-Anthrylmethyl)-3,6,12,15-tetrathia-9-azaheptadecane (2). In a manner similar to that for **1**, the reaction of 9-chloromethylanthracene (0.50 g, 2.2 mmol) with 3,6,12,15-tetrathia-9-azaheptadecane (0.63 g, 2 mmol) afforded **2** as a yellow oil: yield 0.33 g (32.5%); ^{1}H NMR (CDCl$_3$) δ 1.20 (t, 6H), 2.40−2.89 (m, 20H), 4.62 (s, 2H), 7.26−7.58 (m, 4H), 7.94−8.05 (m, 2H), 8.42−8.56 (m, 3H); MS (EI) m/z 503 (M$^+$). Anal. Calcd for C$_{27}$H$_{37}$NS$_4$: C, 64.37; H,7.40; N, 2.78.Found: C, 64.78; H,7.38; N, 2.75.

Preparation of 6-(9′-Anthracenecarbonyl)-3,9-dithia-6-azaundecane (3). Crude 9-anthracenecarbonyl chloride, 3,9-dithia-6-azaundecane (0.58 g, 3.0 mmol), and potassium carbonate (0.45 g, 3.3 mmol) were dissolved in dry benzene (50 mL) at 0 °C. The solution was then stirred for 3 h at room temperature. After the reaction was complete, the solvent was evaporated in vacuo and then 100 mL of water was added to the residue. The aqueous solution was extracted with three 100 mL portions of CHCl$_3$. The extract was dried over MgSO$_4$. After the removal of the solvent, the crude product was subjected to the column chromatography and yielded **3** as a pale yellow solid: yield 0.40 g (33.6%); mp 64−65 °C; ^{1}H NMR (CDCl$_3$) δ 0.57 (t, 3H), 1.31−1.66 (m, 5H), 2.23−3.24 (m, 8H), 4.01 (t, 2H), 7.43−7.60 (m, 4H), 7.92−8.06 (m, 4H), 8.46 (s, 1H); MS (EI) m/z 397 (M$^+$). Anal. Calcd for C$_{23}$H$_{27}$NOS$_2$: C, 69.48; H,6.84; N, 3.52. Found: C, 69.72; H, 6.72; N, 3.63.

Preparation of 9-(9′-Anthracenecarbonyl)-3,6,12,15-tetrathia-9-azaheptadecane (4). In a manner similar to that for **3**, the reaction of crude anthracenecarbonyl chloride (0.48 g, 2.0 mmol) with 3,6,12,15-tetrathia-9-azaheptadecane (0.63 g, 2 mmol) afforded **4** as a pale yellow solid: yield 0.36 g (34.8%); mp 31−32 °C; ^{1}H NMR (CDCl$_3$) δ 1.02−3.21 (m, 24H), 4.08 (t, 2H), 7.44−7.56 (m, 4H), 7.90−8.08 (m, 4H), 8.48 (s, 1H); MS (EI) m/z 517 (M$^+$). Anal. Calcd for C$_{27}$H$_{35}$NOS$_4$: C, 62.63; H,6.81; N, 2.70. Found: C, 62.43; H,6.63; N, 2.72.

Preparation of 6-(9′-Anthrylmethylphenylene)-3,9-dithia-6-azaundecane (5). 9-Chloromethylanthracene (1.34 g, 5 mmol), 6-phenyl-3,9-dithia-6-azaundecane (1.94 g, 5 mmol), and AlCl$_3$(0.73 g, 5 mmol) were dissolved in dry CHCl$_3$ (50 mL) at 0 °C. The solution was refluxed with stirring for 6 h. After the reaction was complete, the solution was cooled and washed with three 100 mL portions of water. The organic solution was dried over MgSO$_4$. After evaporation of the solvent, the crude product was subjected to column chromatography and yielded **5** as a pale yellow solid: yield 1.38 g (60.1%); mp 103−104 °C; ^{1}H NMR (CDCl$_3$) δ 1.23 (t, 6H), 2.42−2.72 (m, 8H), 3.44 (t, 4H), 4.90 (s, 2H), 6.50 (d, 2H), 6.98 (d, 2H), 7.35−7.55 (m, 4H), 7.93−8.09 (m, 2H), 8.15−8.36 (m, 2H), 8.41 (s, 1H); MS (EI) m/z 459 (M$^+$). Anal. Calcd for C$_{29}$H$_{33}$NS$_2$: C, 75.77; H,7.24; N, 3.05. Found: C, 75.63; H,7.32; N, 2.99.

Preparation of 9-(9′-Anthrylmethylphenylene)-3,6,12,15-tetrathia-9-azaheptadecane (6). In a manner similar to that for **5**, the reaction of 9-chloromethylanthracene (1.13 g, 5

mmol) with 9-phenyl-3,6,12,15-tetrathia-9-azaheptadecane (1.94 g, 5 mmol) afforded **6** as a pale yellow solid: yield 1.62 g (56.0%); mp 47−48 °C; ^{1}H NMR (CDCl$_3$) δ 1.19 (t, 6H), 2.38−2.83 (m, 16H), 3.46 (t, 4H), 4.90 (s, 2H), 6.49 (d, 2H), 6.99 (d, 2H), 7.35−7.53 (m, 4H), 7.96−8.07 (m, 2H), 8.18−8.29 (m, 2H), 8.40 (s, 1H); MS (EI) *m/z* 579 (M$^+$). Anal. Calcd for C$_{33}$H$_{41}$-NS$_4$: C, 68.36; H,7.13; N, 2.42. Found: C, 68.24; H,7.10; N, 2.40.

Preparation of 8-(9′-Anthrylmethyl)-3,6,10,13-tetra-thiapentadecane (7). 9-Anthraldehyde (10.3 g, 0.05 mol) and diethyl malonate (8.80 g, 0.055 mol) were dissolved in benzene (200 mL) and refluxed with stirring and with the use of a Dean−Stark water trap. After the reaction was complete, the solution was cooled and washed with three 100 mL portions of water. The organic solution was dried over MgSO$_4$. After the solvent was evaporated in vacuo, the crude product was subjected to column chromatography and yielded **13** as a pale yellow solid: yield 14.72 g (84.6%); mp 76−77 °C; ^{1}H NMR (CDCl$_3$) δ 0.34 (t, 3H), 1.40 (t, 3H), 3.62 (q, 2H), 4.43 (q, 2H), 7.38−8.62 (m, 10H). Compound **13** (13.92 g of 0.04 mol) was then reduced by LiAlH$_4$ (3.12 g, 0.08 mol) in THF to yield **14** as a white solid: yield 6.23 g (58.6%); mp 130−131 °C; ^{1}H NMR (CDCl$_3$) δ 1.95−2.31 (br, 3H), 3.62−3.81 (m, 6H), 7.34−7.56 (m, 4H), 7.92−8.03 (m, 2H), 8.23−8.34 (m, 3H). The resulting **14** (3.46 g, 0.013 mol) was converted to the corresponding dimethylsulfonate **15** by using methanesulfonyl chloride (3.12 g, 0.08 mol) and triethylamine (3.03 g, 0.03 mol) as a base in dry CH$_2$Cl$_2$ (100 mL). Compound **15** was isolated as a pale yellow solid: yield 5.23 g (95.3%); mp 157−158 °C; ^{1}H NMR (CDCl$_3$) δ 2.80−2.95 (m, 7H), 3.78 (d, 2H), 4.22−4.31 (m, 4H), 7.43−7.59 (m, 4H), 7.97−8.25 (m, 4H), 8.40 (s, 1H). NaOH (0.40 g, 10 mmol) was dissolved in EtOH (100 mL) under a nitrogen atmosphere. After the addition of 3-thiapentane-1-thiol (1.22 g, 10 mmol) to the solution, the mixture was stirred at room temperature for 1 h. Compound **15** (2.11 g, 5 mmol) was added to the solution, and the mixture was stirred overnight at ambient temperature. After the reaction was complete, the solvent was evaporated in vacuo and 100 mL of water was added to the residue. The aqueous solution was extracted with three 100 mL portions of CHCl$_3$, and the extract was dried over MgSO$_4$. After evaporation of the solvent in vacuo, the crude product was subjected to the column chromatography and yielded **7** as a white solid: yield 0.90 g (75.9%); mp 40−41 °C; ^{1}H NMR (CDCl$_3$) δ 0.91 (t, 6H), 1.99−2.86 (m, 17H), 3.82 (d, 2H), 7.42−7.53 (m, 4H), 7.94−8.04 (m, 2H), 8.34−8.45 (s, 3H); MS (EI) *m/z* 474 (M$^+$). Anal. Calcd for C$_{26}$H$_{34}$S$_4$: C, 65.77; H,7.22. Found: C, 65.64; H, 7.15.

Preparation of 1-(9′-Anthryl)-2-thiabutane (8). NaOH (0.16 g, 4 mmol) was dissolved in EtOH (50 mL) under a nitrogen atmosphere. After the addition of ethanethiol (0.19 g, 3 mmol) to the solution, the mixture was stirred at room temperature for 1 h. To the solution was added 9-chloro-methylanthracene (0.75 g, 3.3 mmol), and the mixture was stirred overnight. After the reaction was complete, the solvent was evaporated in vacuo and 100 mL of water was added to the residue. The aqueous solution was extracted with three 100 mL portions of CHCl$_3$, and the extract was dried over MgSO$_4$. After concentrating the solution in vacuo, the crude product was subjected to column chromatography and yielded **8** as a pale yellow solid: yield 0.42 g (55.6%); mp 78−79 °C; ^{1}H NMR (CDCl$_3$) δ 1.30 (t, 3H), 2.49−2.79 (m, 2H), 4.68 (s, 2H), 7.27−7.57 (m, 4H), 7.88−7.99 (m, 2H), 8.23−8.32 (m, 3H); MS (EI) *m/z* 252 (M$^+$). Anal. Calcd for C$_{17}$H$_{16}$S: C, 80.91; H, 6.39. Found: C, 80.72; H, 6.46.

Preparation of 1-(9′-Anthryl)-2,5-dithiaheptane (9). In a manner similar to that for **8**, the reaction of 9-chlorometh-ylanthracene (0.75 g, 3.3 mmol) with 3-thiapentane-1-thiol (0.37 g, 3 mmol) afforded **9** as a pale yellow solid: yield 0.60 g (64.1%); mp 52−53 °C; ^{1}H NMR (CDCl$_3$) δ 1.16 (t, 3H), 2.48−2.89 (m, 6H), 4.77 (s, 2H), 7.37−7.61 (m, 4H), 7.92−8.09 (m, 2H), 8.26−8.36 (m, 3H); MS (EI) *m/z* 312 (M$^+$). Anal. Calcd for C$_{19}$H$_{20}$S$_2$: C, 73.03; H, 6.45. Found: C, 73.12; H, 6.45.

Preparation of 1,6-Bis(9′-anthryl)-2,5-dithiahexane (10), 1,9-Bis(9′-anthryl)-2,5,8-trithianonane (11), and 1,12-Bis- (9′-anthryl)-2,5,8,11-tetrathiadodecane (12). In a manner similar to that for **8**, the reaction of 9-chloromethylanthracene (0.50 g, 2.2 mmol) with the corresponding dithiols (1 mmol) in EtOH (50 mL) in the presence of NaOH (0.1 g, 2.5 mmol) gave **10**, **11**, and **12** as the yellow solids. **10**: yield 0.28 g (59.1%); mp 213-214 °C; ^{1}H NMR (DMSO-d_6 + CDCl$_3$) δ 2.89 (s, 4H), 4.67 (s, 4H), 7.42−7.64 (m, 8H), 7.95−8.05 (m, 4H), 8.22−8.40 (m, 6H); MS (EI) *m/z* 474 (M$^+$). Anal. Calcd for C$_{32}$H$_{26}$S$_2$: C, 80.97; H, 5.52. Found: C, 80.90; H, 5.54. **11**: yield 0.29 g (54.3%); mp 182−183 °C; ^{1}H NMR (CDCl$_3$) δ 2.53−2.75 (m, 8H), 4.75 (s, 4H), 7.42−7.59 (m, 8H), 7.97−8.12 (m, 4H), 8.27−8.39 (m, 6H); MS (EI) *m/z* 534 (M$^+$). Anal. Calcd for C$_{36}$H$_{34}$S$_3$: C, 76.36; H, 5.65. Found: C, 76.34; H, 5.63. **12**: yield 0.36 g (60.6%); mp 141−142 °C; ^{1}H NMR (CDCl$_3$) δ 2.47−2.80 (m, 12H), 4.76 (s, 4H), 7.35−7.61 (m, 8H), 7.92−8.02 (m, 4H), 8.24−8.35 (m, 6H); MS (EI) *m/z* 594 (M$^+$). Anal. Calcd for C$_{36}$H$_{34}$S$_4$: C, 72.68; H, 5.76. Found: C, 72.71; H, 5.74.

Protonation Behavior for Fluoroionophores. The protonation behavior of fluoroionophores was measured spectrophotometrically at 25.0 ± 0.2 °C in a 1,4-dioxane−water solution because the fluoroionophores used here are insoluble in pure water. The solution (25 mL) contained 2.5×10^{-5} M anthracene unit of fluoroionophore and 0.1 M potassium nitrate for adjusting the ionic strength. The pH of the solution was controlled by Good's buffers, HNO$_3$, and KOH. UV−vis absorption spectra and emission spectra were obtained on a Hitachi 150-20 spectrophotometer and Shimadzu RF-5000 spectrofluorometer with 1-cm quartz cells, respectively. Absorption and emission spectra were measured at each pH. On the determination of the relative fluorescence intensity, the fluorescence intensity of the solution containing anthracene under the same conditions is defined that the relative fluorescence intensity is 1.0.

The protonation constants (K_H) were determined from the pH-dependent fluorescence intensity changes at the maximum emission wavelengths of the fluoroionophores as follows: the protonation constants, K_H, are defined in eq 1,

$$K_H = [HL^+]/[H^+][L] \tag{1}$$

where L and HL$^+$ are the fluoroionophore and the protonation form of fluoroionophore, respectively. The total concentration of the ligand (C_L) is represented as eq 2, where x_L and x_{HL} are molar fractions of L and HL$^+$, respectively.

$$C_L = [L] + [HL^+] = C_L(x_L + x_{HL}) \tag{2}$$

The relative fluorescence intensity (If) of the solution at an appropriate wavelength is given by eq 3, where If$_L$ and If$_{HL}$ are the relative fluorescence intensity of L and HL$^+$, respectively.

$$\text{If} = \text{If}_L x_L + \text{If}_{HL} x_{HL} \tag{3}$$

$$= \text{If}_{HL} + (\text{If}_L - \text{If}_{HL})/(1 + [H^+]K_H) \tag{4}$$

The value (If$_L$) of relative fluorescence intensity for L was determined by previous work. For determination of the constants If$_{HL}$ and K_H, we made an original calculation program as follows: the appropriate values for If$_{HL}$ and K_H are used as initially substituted values in eq 4 for calculation and the first value for a calculated fluorescence intensity If$_{cal}$ is obtained. The value If$_{cal}$ is compared with the experimentally obtained fluorescence intensity If$_{obs}$. Then the substituted values of K_H and If$_{HL}$ in eq 4 were changed 0.01 or 0.00001 each stepwise, and the calculated value (If$_{cal}$) is compared with the value of If$_{obs}$ again. The optimum values of K_H and If$_{HL}$ can be finally obtained simultaneously by minimizing the error square sum (U) defined by $U = \sum(\text{If}_{obs,i} - \text{If}_{cal,i})^2$, where If$_{obs,i}$ and If$_{cal,i}$ are the experimentally observed fluorescence intensity and the calculated one, respectively.

Spectral Properties and Complexation Behavior of Fluoroionophores with Metal Ions. The spectral properties and the complexation behavior of fluoroionophores were measured spectrophotofluorometrically in a similar manner as described in the measurement of the protonation constants. 1,4-Dioxane−water (52/48 v/v %) solutions were used for the measurements except for the case of **11**, where 1,4-dioxane−water (64/36 v/v %) was used. The stability constants were determined by keeping the pH value constant and changing the metal ion concentration. The pH in the solution was adjusted to pH 8.0 by *N*-cyclohexyl-3-aminopropanesulfonic acid (CAPS)−KOH buffer for **1** and **2**, pH 5.0 by 2-morpholinoethanesulfonic acid (MES)−KOH buffer for **5** and **6**, and pH 1 by 0.1 M HNO_3 for the other fluoroionophores used here.

The complexation equilibria of the fluoroionophore with silver ion and the stability constants, K_{ML} and K_{ML2}, are defined as follows:

$$Ag^+ + L \rightleftharpoons AgL^+ \qquad K_{ML} = \frac{[AgL^+]}{[Ag^+][L]} \qquad (5)$$

$$AgL^+ + L \rightleftharpoons AgL_2^+ \qquad K_{ML2} = \frac{[AgL_2^+]}{[AgL^+][L]} \qquad (6)$$

The stability constants for the silver ion complexes were determined in a manner similar to the spectrophotometric method described elsewhere.[17,19] The total concentrations of silver ion (C_{Ag}) and ligand (C_L) are represented in eqs 7 and 8.

$$C_{Ag} = [Ag^+] + [AgL^+] + [AgL_2^+] \qquad (7)$$

$$C_L = [L] + [AgL^+] + 2[AgL_2^+] \qquad (8)$$

The concentration of silver ion is given by combining eqs 5−7

$$[Ag^+] = C_M/(1 + K_{ML}[L] + K_{ML}K_{ML2}[L]^2) \qquad (9)$$

Equation 10 is likewise obtained from eqs 5, 6, and 8:

$$[L] + K_{ML}[Ag^+][L] + 2\,K_{ML}K_{ML2}[Ag^+][L]^2 - C_L = 0 \qquad (10)$$

Substituting $[Ag^+]$ of eq 9 into eq 10 yields the polynomial of $[L]$, $f([L]) = 0$. The concentration of ligand in the system can be obtained by solving the above equation, $f([L]) = 0$, with the bisection method.

The fluorescence intensity (I_f) of the solution at an appropriate wavelength is given by eq 11, where I_{f_L}, $I_{f_{ML}}$, and $I_{f_{ML2}}$ are the fluorescent intensities of L, AgL^+, and AgL_2^+, respectively.

$$I_f = I_{f_L}[L] + I_{f_{ML}}[AgL^+] + I_{f_{ML2}}[AgL_2^+] \qquad (11)$$

Because the values of I_{f_L} and $I_{f_{ML2}}$ are known, the values of $I_{f_{ML}}$, $K_{ML,}$ and K_{ML2} can be obtained by minimizing the error square sum (U), defined by $U = \sum (I_{f_{obs,i}} - I_{f_{cal,i}})^2$, where $I_{f_{obs,i}}$ and $I_{f_{cal,i}}$ are the experimentally observed fluorescent intensity and the calculated one, respectively.