SYNTHESIS AND EMISSION BEHAVIOR OF DOUBLE-ARMED TETRATHIACROWN CARRYING TWO NAPHTHALENES

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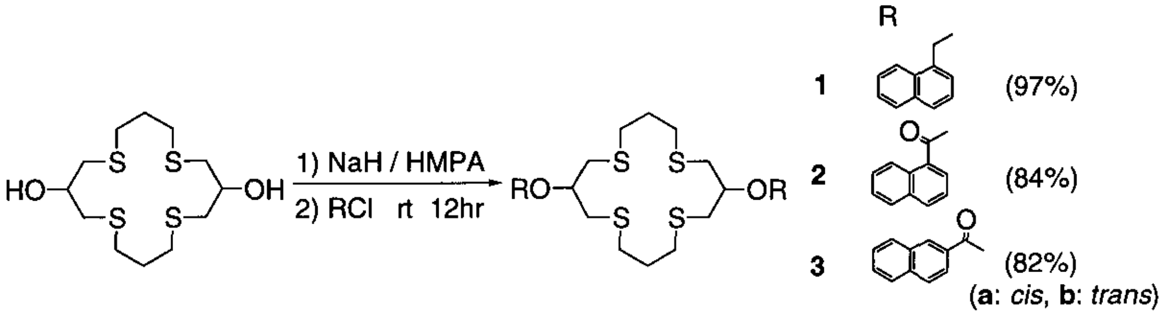
Abstract—Double-armed tetrathiacrown having two naphthalenes shows specific photophysical properties for Pd^{2+} and Au^{3+} ions selectively, based on cooperative actions of parent thiacrown and fluorometric side arms.

Photoresponsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switch.[1] Recently, there are extensive investigations toward the characterization of fluoroionophores including podand, crown ether, calixarene, cyclophane, and cyclodexitrin derivatives with fluorophore.[2] Thus, it is interesting to investigate the complex formation with guest cations using fluorescence spectroscopy. While, armed crown ethers such as lariat ethers and double armed crowns are a class of cation-host molecules, which are characterized by parent macrocyclic ring and ligating arms.[3] Since their cation-binding properties are essentially determined by coordination characters of macrocycle and donor arms, wide variations of basic structures may lead to the design of new and specific host molecules for a given guest cation.[4] By combining armed crown ether and fluorophore,[3,5] a fluoroionophore having a novel property could be produced. Here, we describe the synthesis and fluorescence behavior of the double-armed tetrathiacrown containing two naphthyl pendants.



The naphthalene-functionalized tetrathiacrown derivatives were obtained as a mixture of *cis* and *trans* isomers by reaction of 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (1:1 mixture of *cis* and *trans*), NaH, and the corresponding naphthylmethyl chloride or naphthoyl chloride. The structure and purity of **1**,[6] **2**[7] and **3**[8] were ascertained by NMR spectroscopy and elemental analysis. Fortunately, the *cis* (**3a**) and *trans*

(**3b**) isomers of 2-naphthoyl derivative could be separated by silica gel column chromatography. ^{13}C NMR spectrum of **3a** showed methylene carbons of thiacrown at higher field region (δ=29.51, 31.45, 34.89, 72.93) than that of **3b**, let us to assign it as the "*cis*"-isomer. On the other hand, the higher mp isomer (**3b**) might be the "*trans*"-isomer, showed methylene carbon signals at lower field region (δ=29.89, 31.63, 35.12, 73.36).

Extraction of metal ions into the chloroform solutions containing **1**–**3** was checked by fluorescence spectroscopy; Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pt^{4+}, revealed no change, but Pd^{2+} and Au^{3+} showed a spectral change. In Figure 1 are shown the fluorescence spectra of **1**–**3** obtained with and without Pd^{2+} and Au^{3+}. By addition of metal salts, the fluorescence spectra of **1**–**3** changed dramatically; the spectrum of free **1**–**3** was typical as that of derivatives, showing the emission band at 336 nm for **1**, 374 nm for **2**, and 364 nm for **3**, which were decreased by addition of Pd^{2+} and Au^{3+}.

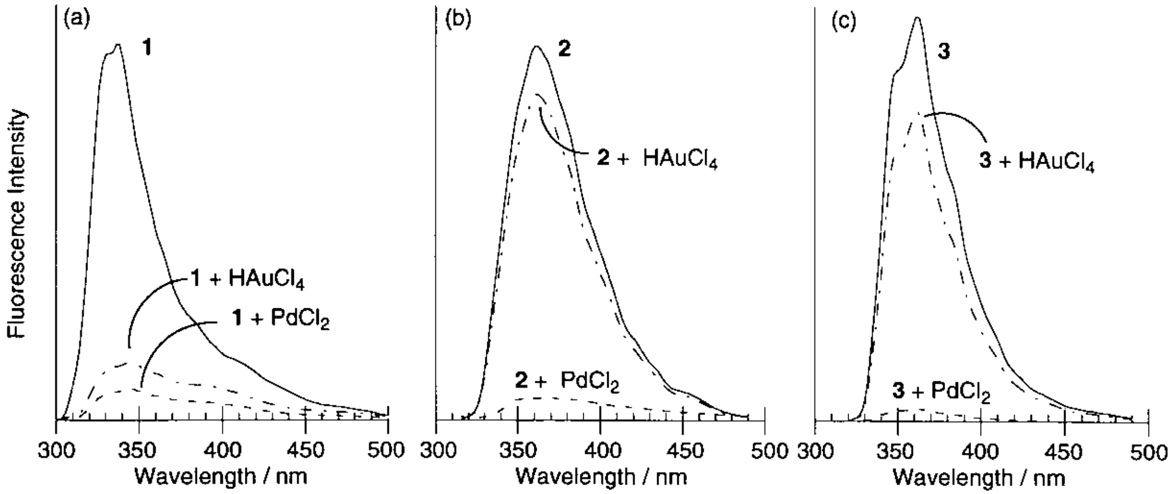


Figure 1. Fluorescence spectral changes of (a) **1**, (b) **2**, and (c) **3** (2.00 x 10^{-5} M) in chloroform that was equilibrated with aqueous $PdCl_2$ and $HAuCl_4$ (2.00 x 10^{-4} M); as excited at 282 nm for **1**, 299 nm for **2**, and 284 nm for **3**.

Figure 2 illustrated the relative emission intensity of **1**–**3** against the guest salt concentration. The composition of the complexes was determined as 2 (metal):1 (ligand) for the Pd^{2+}-thiacrown (**1**–**3**) system

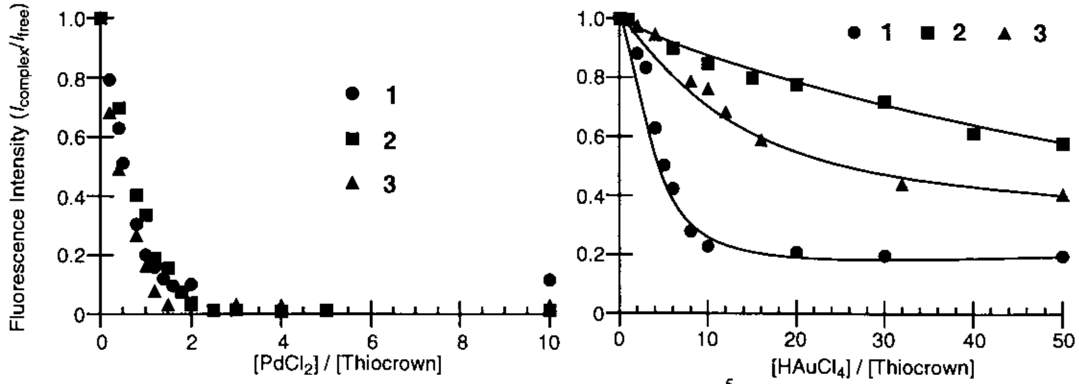


Figure 2. Dependence of fluorescence intensities of **1**–**3** (2.00 x 10^{-5} M) at 336 nm for **1**, 374 nm for **2**, and 364 nm for **3** on concentration of $PdCl_2$ and $HAuCl_4$ in chloroform.

by the molar ratio method. The extraction equilibrium constants were determined by the non-liner curve-fitting method.[9] The equilibrium constants of Pd^{2+} complex were larger than those of Au^{3+} complex and the increasing order of equilibrium constants for Au^{3+} was **2** (2500 ± 750 M^{-1}) < **3** (3280 ± 980 M^{-1}) < **1** (25000 ± 5000 M^{-1}). This result means that the ester sidearm does not participate in the coordination with Au^{3+}. The relative emission intensities of **3a**, **3b**, and **3** against the guest salt concentration are shown in Figure 3. The equilibrium constant of **3a** (2600 ± 390 M^{-1}) for Au^{3+} complex was similar to that of **3b** (2730 ± 120 M^{-1}). Comparison of the selectivity order for **1**–**3**, **3a**, and **3b** confirms that the thiacrown and fluorometric side arm property may control the selectivity of the host toward guest cations in a delicate manner.

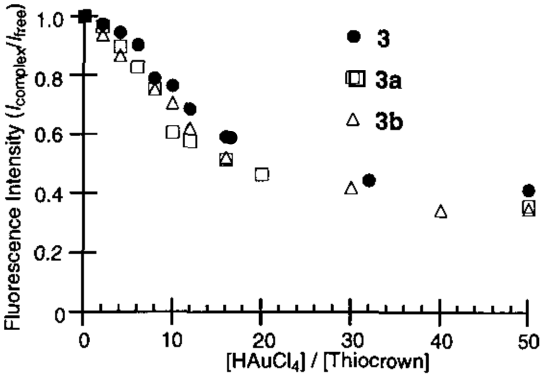


Figure 3. Dependence of fluorescence intensities of **3**, **3a**, and **3b** (2.00 x 10^{-5} M) at 364 nm on concentration of $HAuCl_4$.

In conclusion, the double armed tetrathiacrown (**1**–**3**) recognized Pd^{2+} and Au^{3+}, based on cooperative actions of parent thiacrown and fluorometric side arms. These double-armed tetrathiacrown having naphthyl pendants may be utilized as a new fluorescent sensor for guest salts. Further investigations are now in progress and will be reported elsewhere.

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6. **1** (mixture of *cis* and *trans*): yellow oil, ^{1}H NMR ($CDCl_3$) δ = 1.79–1.89 (8H, m), 2.45–2.86 (32H, m), 3.75 (4H, qui, J =6.1 Hz), 5.07 (4H, s), 5.08 (4H, s), 7.41 (4H, dd, J =8.2, 7.0 Hz), 7.44–7.55 (12H, m), 7.79 (4H, d, J =8.2 Hz), 7.83 (4H, d, J =8.9 Hz), 8.18 (2H, d, J =8.2 Hz), and 8.19 (2H, d, J =8.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 29.50, 29.72, 31.66, 31.72, 35.59, 35.71, 70.67, 78.14, 78.23, 124.39, 124.44, 125.19, 125.87, 126.12, 126.81, 126.90, 127.71, 127.92, 128.23, 128.50, 128.84, 131.79, 133.56, and 133.80. Anal. Calcd for $C_{34}H_{40}O_2S_4$: C, 67.06; H, 6.62. Found: C, 66.86; H, 6.41.
7. **2** (mixture of *cis* and *trans*): yellow oil, ^{1}H NMR ($CDCl_3$) δ = 2.01–2.09 (8H, m), 2.67–2.87 (16H, m), 2.96–3.00 (8H, m), 3.07-3.11 (8H, m), 5.45 (4H, qui, J =6.1 Hz), 7.44-7.53 (8H, m), 7.58–7.02 (4H, m), 7.84 (4H, d, J =7.9 Hz), 7.97 (4H, d, J =8.6 Hz), 8.21-8.25 (4H, m), and 8.94 (4H, d, J =8.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 29.54, 29.97, 31.36, 31.55, 34.86, 35.11, 72.52, 72.91, 124.49, 124.54, 125.77, 125.80, 126.22, 126.99, 127.78, 128.80, 128.53, 130.34, 131.35, 133.46, 133.48, 133.80, 166.85 and 166.17. Anal. Calcd for $C_{34}H_{36}O_4S_4$: C, 64.12; H, 5.70. Found: C, 64.42; H, 6.12.
8. **3a**: yellow powder, mp 144–145°C (Recrystallization from ethyl acetate:hexane (1:1 *v/v*)), ^{1}H NMR ($CDCl_3$) δ = 2.06 (4H, qui, J =7.0 Hz), 2.78–2.88 (8H, m), 3.02 (4H, dd, J =14.2, 6.1 Hz), 3.13 (4H, dd, J =13.7, 6.1 Hz), 5.42 (2H, qui, J =6.1 Hz), 7.54 (2H, ddd, J =8.2, 7.9, 1.1 Hz), 7.59 (2H, ddd, J =8.2, 7.9, 1.1 Hz), 7.87 (2H, d, J =7.9 Hz), 7.88 (2H, d, J =8.5 Hz), 7.96 (2H, d, J =8.2 Hz), 8.07 (2H, dd, J =8.5, 1.1), and 8.63 (2H, s); ^{13}C NMR ($CDCl_3$) δ = 29.51 (2C), 31.45 (4C), 34.89 (4C), 72.93 (2C), 125.30 (2C), 126.68 (2C), 127.19 (2C), 127.78 (2C), 128.24 (2C), 128.36 (2C), 129.43 (2C), 131.35 (2C), 132.51 (2C), 135.67 (2C), and 166.17 (2C). Anal. Calcd for $C_{34}H_{36}O_4S_4$: C, 64.12; H, 5.70. Found: C, 64.18; H, 5.91. **3b**: colorless powder, mp 148–149°C (Recrystallization from ethyl acetate:hexane (1:1 *v/v*)), ^{1}H NMR ($CDCl_3$) δ = 2.05 (4H, qui, J =7.0 Hz), 2.17-2.88 (8H, m), 3.02 (4H, dd, J =14.0, 6.1 Hz), 3.12 (4H, dd, J =14.0, 6.1 Hz), 5.42 (2H, qui, J =6.1 Hz), 7.53 (2H, ddd, J =7.9, 6.7, 1.2 Hz), 7.59 (2H, ddd, J =7.9, 6.7, 1.2 Hz), 7.86 (2H, d, J =6.4 Hz), 7.88 (2H, d, J =6.7 Hz), 7.96 (2H, d, J =7.9 Hz), 8.07 (2H, dd, J =8.9, 1.8), and 8.63 (2H, s); ^{13}C NMR ($CDCl_3$) δ = 29.89 (2C), 31.63 (4C), 35.12 (4C), 73.36 (2C), 125.30 (2C), 126.68 (2C), 127.20 (2C), 127.77 (2C), 128.25 (2C), 128.36 (2C), 129.45 (2C), 131.35 (2C), 132.51 (2C), 135.67 (2C), and 166.28 (2C). Anal. Calcd for $C_{34}H_{36}O_4S_4$: C, 64.12; H, 5.70. Found: C, 64.15; H, 5.97.
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