Preparation of New Red Perylene Fluoroionophores Containing Azacrown and Their Ionophoric Properties

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Introduction

Fluorescent sensors are called 'fluoroionophore' by reason that ionophore is bonded to the fluorescent substance, and the combination of recognition and signal is critical to design sensors. Signal part is to convert recognized information to an optical signal which can be modulated by the optical and physical properties of a fluorescent substance.[1] The changes, which are shown by complex with metal ions, are caused by photo-induced process such as the shift of electrons, electric charges and energy, the generation and degeneration of excimer and exciplex, etc.[2,3] Particularly, the azacrown ethers can effectively influence on the degree of fluorescence in case of bonding with delocalized aromatic compounds.[4-6] Specifically, the degree of fluorescence is increased or decreased in case a positive ionic metal is bonded to the fluorescent substance containing crown ether.[7-18]

Fluorescent photoinduced charge transfer (PCT) has been extensively studied. Although quite a large number of reports exists regarding on the crown ether- and cryptand-based PCT, those based on polymers are limited. Moreover, crown ether-based polymers have just begun to receive attention, and these new polymers were processed into materials suitable for the chemical sensor devices such as ion selective electrodes.[17,19-25] Recently, we prepared polymeric fluoroionophores having azacrown or calix[4]azacrown and investigated their ionophoric properties for various metal cations.[22-24]

N,N'-Dipropyl-3,4,9,10-perylene tetracarboxy diimide has been known to be the red light-emitting fluorescent substance of which fused ring has strong delocalization.[25] In this study, polymeric perylene-based fluoroionophore was synthesized and its ionophoric behaviors were examined.

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Experimental

Materials and Measurements. *N,N'*-Dipropyl-1,7-dibromo-3,4,9,10-perylene tetracarboxy diimide (**1**) were prepared by the method previously reported.[8] 1-Aza-18-crown-6 and 7,16-diaza-18-crown-6 (Aldrich Chem. Co.) were used as received. Tetrahydrofuran and *N,N*-diisoprpopyl ethylamine (Aldrich Chem. Co.) were distilled over sodium and calcium hydride.

FT-IR spectra were obtained with a spectrophotometer (Biorad Excaliber FTS-3000MX) and ^{1}H-NMR spectra were recorded on a spectrometer (Varian Unity Inova, 200 MHz). Elemental analyses were performed using a CHN analyzer (Yanaco MT-3). Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ-Stryragel 10^2, 10^3, and 10^4 Å) in THF and calibrated with polystyrene standards at 20 °C. UV/Vis spectra were obtained on a spectrophotometer (Shimadzu 1601PC). Photoluminescence spectra were obtained on a spectrofluorometer (JASCO FP-6500).

Synthesis of *N,N'*-Dipropyl-1,7-bis(1-aza-18-crown-6-ether)-3,4,9,10-perylene Tetracarboxy Diimide (2). A solution of **1** (0.24 g, 0.38 mmol) and 1-aza-18-crown-6-ether (1 g, 3.79 mmol) dissolved in THF (15 mL) was refluxed with stirring under argon for 96 h. After the solvent was removed by reduced pressure, then distilled water was added and the crude product was extracted with dichloromethane. After the solvent was removed by a rotary evaporator, the product was purified by the column chromatography based on the silica gel and acetonitrile as eluent. The final product was obtained as a red black powder.

Yield 81%. FT-IR (KBr, cm^{-1}) 3120 (aromatic C-H), 2950, 2915, 2865 (aliphatic C-H), 1665 (C=O), 1250 (C-O and C-N). ^{1}H-NMR (CDCl$_3$, ppm) 8.7-9.0 (m, 6 H, ArH-perylene), 1.6-1.7 (m, 4 H, 2 -CH$_2$-), 0.9-1.0 (s, 6 H, 2 -CH$_3$), .4.1-4.3 (m, 4 H, 2 -N-CH$_2$-), 3.5-3.6 (m, 48 H, 20 -O-CH$_2$- and 4 -N-CH$_2$-). Anal. Calcd for C$_{54}$H$_{68}$N$_4$O$_{14}$ (997.14): C, 65.04%; H, 6.87%; N, 5.62%. Found: C, 64.98%; H, 6.69%; N, 5.57%.

Synthesis of Copolymer of 1 and 7,16-Diaza-18-crown-6 (3). A solution of 7,16-diaza-18-crown-6 (0.50 g, 1.9 mmol) and **1** (1.1 g, 1.9 mmol) were dissolved in THF (20 mL), and *N,N*-diisopropyl ethylamine (0.30 g, 2.28 mmol). The solution was refluxed with stirring at 80 °C for 96 h under argon. After the reaction mixture was precipitated in diethyl ether, the powdery product was filtered. The crude product was dissolved in dichloromethane and the solution was washed with distilled water several times. The final product was obtained as a red black powder.

Yield 93%. FT-IR (KBr, cm^{-1}) 3058, 3023 (aromatic C-H), 2950, 2920, 2862 (aliphatic C-H), 1665 (C=O), 1230 (C-O and C-N). ^{1}H-NMR (CDCl$_3$, ppm) 8.7-9.0 (m, 6 H,

ArH-perylene), 1.6-1.7 (m, 4 H, 2 -CH$_2$-), 0.9-1.0 (s, 6 H, 2 -CH$_3$), 4.1-4.3 (m, 4 H, 2 -N-CH$_2$-), 3.5-3.6 (m, 24 H, 8 -O-CH$_2$- and 4 -N-CH$_2$-). Anal. Calcd for C$_{42}$H$_{44}$N$_4$O$_8$ (Mw, 732.83): C, 68.84%; H, 6.05%; N, 7.65%. Found: C, 68.80%; H, 6.09%; N, 7.61%.

General Procedure for Fluorescence Studies. The metal perchlorate or nitrate solution was prepared in EtOH (95%) at a concentration of 1.00 mM. Stock solutions of **2** and **3** (0.06 mM) were prepared in EtOH. For all measurements, excitation was carried out at 522 nm with excitation and emission slit widths at 3 nm. Fluorescence titration experiments were performed using 6 mM solutions of **2** and **3** in EtOH and various concentrations (1-3 eq) of metal ion in EtOH.

Results and Discussion

The synthetic scheme for preparing the azacrown ether-armed perylene model fluoroionophore is shown in Scheme I(a). The reaction of **1** with excess 1-aza-18-crown-6 in THF gave the desired product **2** in 81% yield. Also, the polymeric fluorophore **3** was prepared by the polymerization of **1** with 7,16-diaza-18-crown-6 in the presence of an acid acceptor, as shown in Scheme I(b). The condensation polymerization resulted in 93% yield. To the best of our knowledge, these are the first example of alternating copolymer of perylene fluorophore and azacrown ether, whose structure was confirmed by ^{1}H-NMR, IR spectral assignment and elemental analysis.
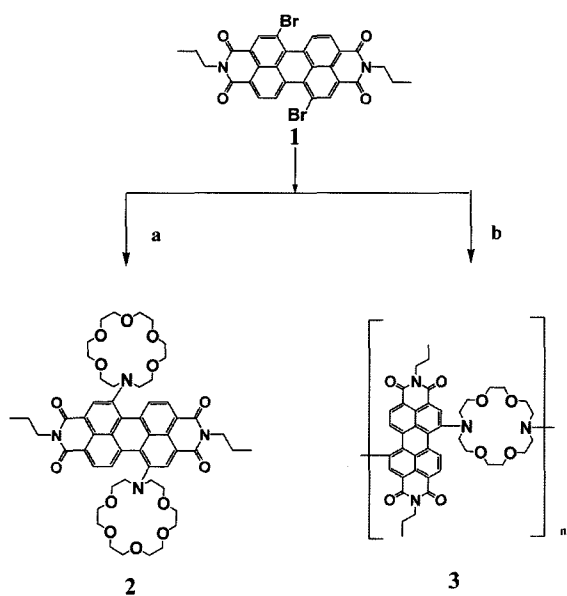
Scheme I. Synthesis of fluoroionophores containing perylene unit; a: 1-aza-18-crown-6-ether, THF, reflux, 96 h, 81%; b: 7,16-diaza-18-crown-6, *N,N*-diisopropyl ethylamine, reflux, 96 h, 93%.

Perylene dyes are known to have low solubility in common organic solvents. However, the incorporation of the azacrown ether into the polymer backbone greatly enhanced the solubility of the perylene dye in common organic solvents. The polymer was soluble in DMF, ethyl acetate, chloroform and ethanol, while displaying virtually no solubility in *n*-hexane and ethyl ether.

Polymer **3** has an inherent viscosity of 0.39 dL/g along with a weight average molecular weight (Mw) of 12,000 g/mole and a polydispersity of 1.65. The polymer synthesized by the condensation polymerization reaction had a somewhat moderate molecular weight, judging from the viscosity and GPC data. When films were cast by allowing the solvent of polymer **3** to evaporate on a glass, hard and brittle films were obtained. The model compound **2** and polymeric fluoroionophore **3** showed a UV-vis absorption at λ_{max}=522 in ethanol as shown in Figure 1. The dibromoperylene precursor **1** was compared with **2** and **3**.

When an amino group playing the role of an electron donor within the fluorophore interacts with a cation, a blue shift of the absorption spectrum is observed. The absorption bands of compound **2** in the visible region are blue shifted (1-4 nm) by metal ion binding, as shown in Figure 2. Also, the fluorescence spectra are in principle shifted in the same direction as those of the absorption spectra. However, the fluorescence spectrum exhibits only a slight blue shift in most cases.[26]

The blue shift of **2** upon K$^+$ binding can be explained by the photo-induced charge transfer (PCT).[3] The PCT might have its origin in the interaction between the azacrown ether and K$^+$.

The emission intensities of model and polymeric fluoroionophores for various cations are summarized in Table I. The metal ion binding properties of **2** and **3** were investigated by monitoring the fluorescence induced upon the addition of Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+},
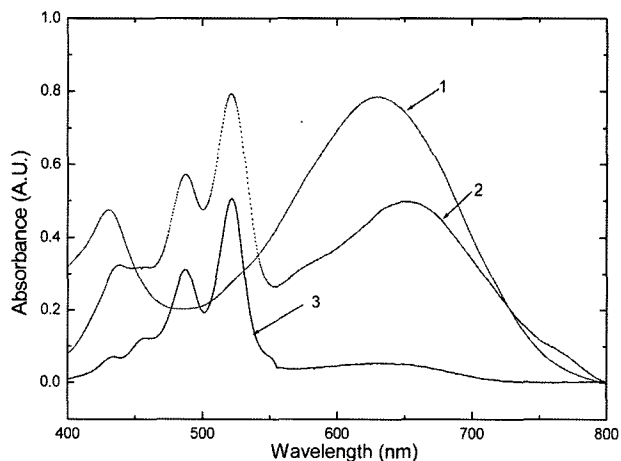

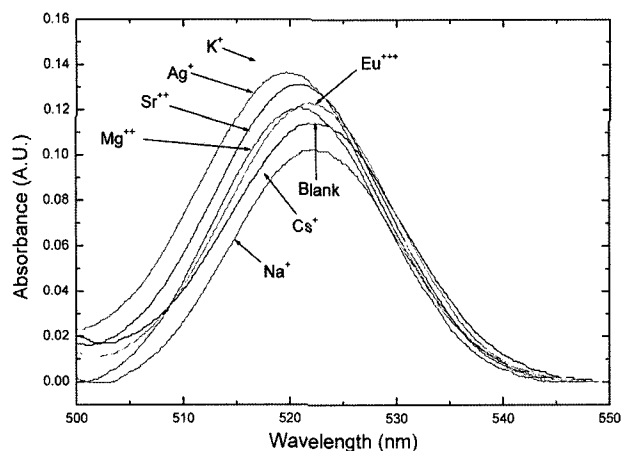**Figure 1.** UV-visible absorption spectra of **1** (6 μM), **2** (9 μM), and **3** (3 μM) in ethanol.

Figure 2. *UV-vis absoption spectral changes of fluoroionophore* **2** (1 μM) upon binding various metal ions (3 μM) in ethanol.
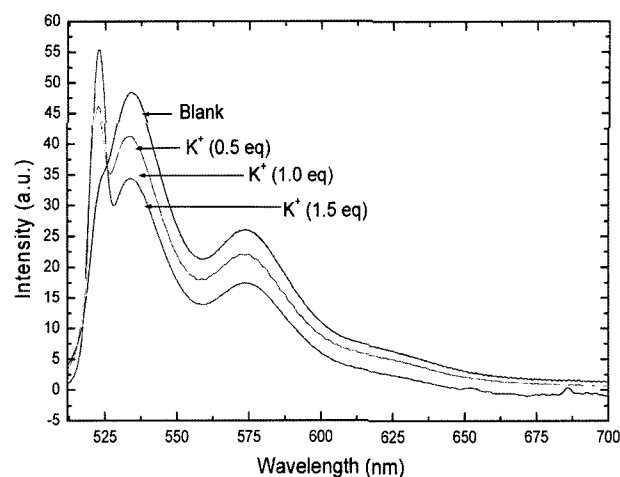

Figure 3. Fluorescence emission spectral changes of model fluoroionophore **2** (6 μM) upon addition of potassium ion in ethanol.

Ag^+, Cu^+, Al^{3+}, and Eu^{3+} ions.

When alkali metal ions were added to model fluoroionophore **2**, all of the emission intensities decreased. Especially, the fluorescence of **2** decreased substantially upon the addition of K^+ and Rb^+, whereas only a relatively small decrease was observed upon the addition of Na^+ and Cs^+ ions. The chelation-enhanced quenching effect of the Cs^+ ion was negligible compared with that of the K^+ ion. K^+ and Rb^+ ions are known to have effective sizes for azacrown-6.[27] The variation in the emission intensity of **2** with increasing concentration of K^+ ions is shown in Figure 3. When 3 equivalents of K^+ were added, the emission intensity decreased by 24%.

Divalent positive ions induced less emission changes (<20%). The sequence of interaction of the azacrown ether with alkali earth metal ions is $Ca^{2+}<Mg^{2+}<Sr^{2+}<Ba^{2+}$, as shown in Figure 4 and Table I, and thus the emission intensity is slightly decreased. It was observed that **2** displayed a moderate ion-dipole interaction between divalent ion and azacrown cavity. Very similar results were observed for the polymeric fluoroionophore **3** upon the addition of the alkali metal ions, Na^+, K^+, Rb^+, and Cs^+, in ethanol. The sequence of emission intensity changes for the addition of alkali metal cations to polymeric fluoroionophore **3** is $Na^+<Cs^+<Rb^+<K^+$, as shown in Figure 5. Although the azacrown cavity (ca. 2.7-3.2 Å) of **3** is relatively larger than the K^+ ion (2.66 Å), it strongly recognizes the K^+ ion because of the ion-dipole
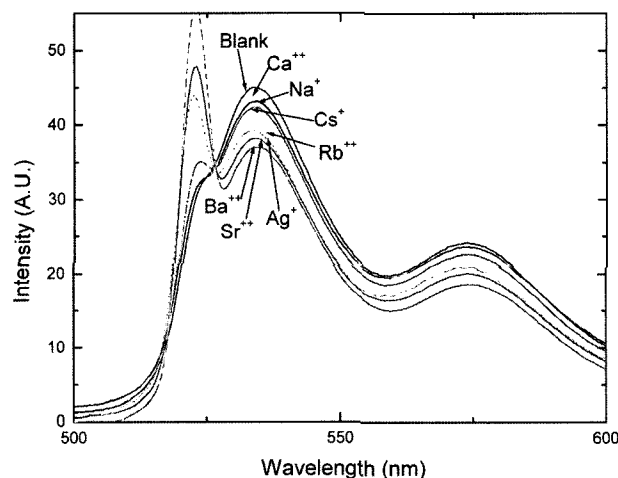

Figure 4. Fluorescence emission spectral changes of model fluoroionophore **2** (6 μM) upon addition of various alkali and alkali earth metal ions (3.0 eq) in ethanol.

interaction between the azacrown cavity and ion.[18,28]

The fluorescence of polymer **3** decreased slightly upon the addition of Mg^{2+} and Ca^{2+} in ethanol. On the other hand, the addition of Sr^{2+} and Ba^{2+} led to a substantial decrease in the fluorescence of **3**. We also attempted to observe the changes in the fluorescence intensity of **3** upon the addition of Ag^+ ions in ethanol.

Table I. Emission Intensity of Red Fluoroionophore Containing Azacrown with Various Cations

Product	Intensity	Alkali Metal						Alkali Earth Metal				etc.			
	Blank	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ag^+	Cu^+	Zn^{2+}	Al^{3+}	Eu^{3+}	Cr^{3+}
2	45	43.1	34.4	39.6	43.9	39.0	43.9	38.1	36.0	39.2	39.8	40.2	38.4	38.2	37.5
3	106	104	84.5	89.6	102	104	97	94.4	84.8	89.7	96.9	101	96.2	95.4	96.5

Excitation at λ_{max}= 522±1 nm and emission at λ_{max}= 534±1 nm for **2**. Excitation at λ_{max}= 522±1 nm and emission at λ_{max}= 549±1 nm for **3**.
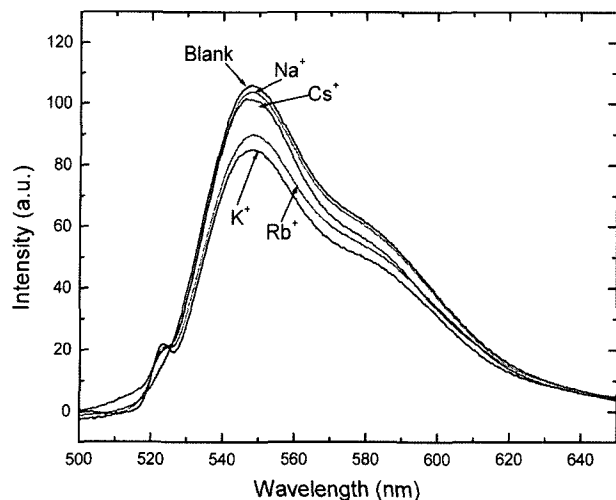
Figure 5. Fluorescence emission spectra of **3** (6 μM) upon addition of alkali metal cations (3 eq).

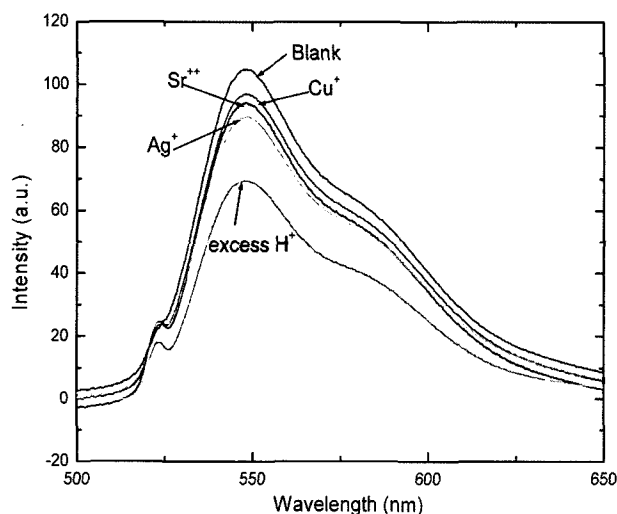**Figure 6.** Fluorescence emission spectra of **3** (6 μM) upon addition of various metal cations (3eq) and proton.

As shown in Figure 6, the addition of Ag^+ ion ions led to a 17% variation in the fluorescence intensity of **3**. A gradual decrease in the fluorescent emission was observed when the concentration of Ag^+ ions was increased. In the case of trivalent ions, the fluorescent intensity was slightly decreased, even at a low-concentration, due to the interaction between the crown ether and trivalent ions. This pronounced fluorescence decrease can be rationalized in terms of PCT.[1-5]

Upon the addition of trifluoroacetic acid to a solution of **2** and **3** in ethanol, the emission was decreased by 35%, as shown in Figure 6. As the pH of the solution decreased, the fluorescence intensities of **2** and **3** decreased, due to the protonation of the tertiary amine group.

In conclusion, we reported the synthesis and of a new aza-crown-based perylene fluoroionophore and polymeric fluor-

oionophore with alternating azacrown and perylene blocks and studied their binding properties. By the PCT mechanism, we observed a decrease in the fluorescence emission of up to 25% in ethanol. When metal ions were added, the polymer displayed large PCT effects, especially with K^+, Ba^{2+} and Ag^+.

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