Synthesis and Properties of *N,N'*-Bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane. Metal Ion-Induced Monomer and Excimer Emission Enhancement

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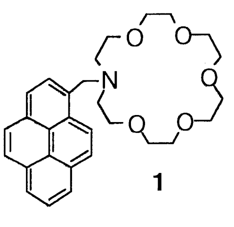
N,N'-Bis(1-pyrenylmethyl)-4,13-diaza-18-crown-6 ether was found to display unique photophysical properties in the presence of the guest metal salts. The binding of metal ions to the azacrown ether cavity inhibited the exciplex formation and changed the distance between two pyrenyl groups. This caused not only the emission-intensity enhancement but also a large change in the monomer/excimer fluorescence-intensity ratio.

Photoresponsive supramolecular systems are of great interest particularity for their potential application to nanoscale devices that can be used for cation sensors and switches, etc. Several fluoroionophores including fluorescence sensor (or fluorophore) such as naphtalene, umbelliferone, anthracene, or pyrene have been synthesized.[1] Fluorescence spectroscopy has detected the complex formed between these compounds and various metal salts in high sensitivities. Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor.[2] The addition of metal salts enhanced the fluorescence emission intensity of *N*-(1-pyrenylmethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**1**),[3] while the presence of metal ions exerted a strong effect on the ratio of the monomer vs. excimer emission intensity of fluorophores that containing two pyrenyl groups.[4] We are reporting the synthesis and fluorescence properties of the azacrown ether **2** containing two chromophoric pyrenyl pendants, as a new approach that takes advantage of the formation of both exciplex and excimer.[5]



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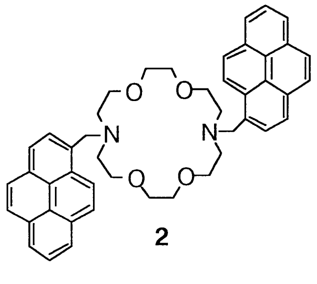

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Pyrene-functionalized diazacrown ether **2** was prepared by the *N*-alkylation of 4,13-diaza-18-crown-6 with 1-pyrenylmethyl bromide in tetrahydrofuran-triethylamine (95% yield). The structure and purity of **2** were ascertained by NMR spectroscopy and elemental analysis.[6]

The fluorescence spectral behavior of **2** (1.0×10^{-6} M, 1.0 M=1.0 moldm^{-3}) in methanol-chloroform (9:1 v/v)[7] at room temperature is illustrated in Figure 1. Fluoroionophore **2**, (when excited at 342 nm), gave a broad emission band with a maximum of 464 nm in addition to the monomer emission (378, 398 nm). The formation of intramolecular exciplex should be responsible for the appearance of the former emission band. The latter emission-band intensity that has an azacrown ether unit was reduced to approximately one-200th that of the pyrene (2×10^{-6} M) that accompanied by the occurrence of the exciplex fluorescence, indicating that the quenching of the excited pyrene chromophore by the azacrown unit proceeds in a mechanism similar to that for the classical pyrene-dimethylaniline system[8] or a pyrene-azacrown system.[2]

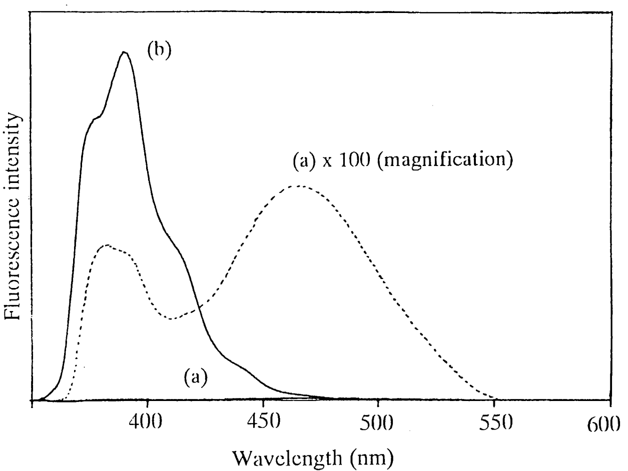

Figure 1. Fluorescence spectra of (a) **2** (1.0×10^{-6} M) and (b) pyrene (2.0×10^{-6} M) in methanol-chloroform (9:1 v/v).

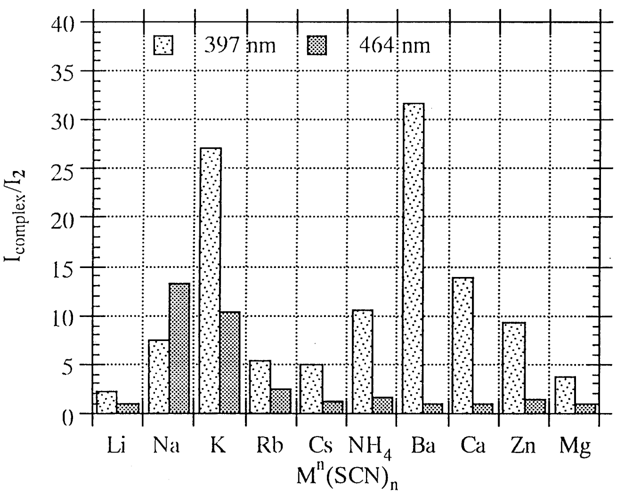

Figure 2. The influence of various metal cations (added as thiocyanate salts) on the emission-intensity ratio ($I_{complex}/I_2$); [**2**]=1.0×10^{-6} M, [Metal salts] =2.0×10^{-2} M, excitation at 342 nm.

A dramatic change in the monomer-emission intensity of **2** (I_2) was observed upon the addition of various metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ca^{2+}, Ba^{2+}, Zn^{2+}, and Mg^{2+}). When the metal salts were added (2 x 10^4 molar equivalent), the emission-intensitiy ratio ($I_{complex}/I_2$), (which was being used as a measure of the molecular recognition sensing), changed from 2 to 32 at 397 nm (monomer emission) and from 1 to 13 at 464 nm (excimer emission) depending on the nature of the added metal cations as demonstrated in Figure 2.

It is interesting that the ratio order of excimer (I_{ex}) and monomer (I_m) emission intensities (I_{ex}/I_m) are different among bound metal ions. The order of this ratio was Na^+ (1.89) > K^+(0.66) > Li^+ (0.65) > Rb^+ (0.49) > Cs^+ (0.34). This result indicate that the binding of bigger alkali metal ions to the azacrown ether hinders the excimer formation to a greater extent. The smaller I_{ex}/I_m values for Li^+ and bivalent metal ions imply that the coordinated structure differs from that of the other alkali metal ions.

From the intensity ratio of the monomer and excimer fluorescences of the pyrene pendant, one can estimate the size and the valence of metal ions that were incorporated into host **2**.

Table 1. Association constants (K, mol dm^{-3}) of **1** and **2** for metal salts in methanol-chloroform (9:1)

Metal cation source	**1**	**2**
LiSCN	48	3
NaSCN	1010	389
KSCN	56200	2400
RbSCN	15100	345
CsSCN	4630	117
NH_4SCN	2530	50
$Ca(SCN)_2$	847	145
$Ba(SCN)_2$	22300	142
$Zn(SCN)_2$	158	7
$Mg(SCN)_2$	513	1420

Using changes in the emission intensity as well as in the metal ion concentration, the association constants (K) were determined by the curve-fitting method[9] (Table 1). The K values of **2** are smaller than those of **1**, suggesting that the two large pyrene rings of **2** inhibit the complexation with metal ions. In spite of the low association constant of **2** in methanol-chloroform, the enhancement of the monomer and/or excimer emission intensity of **2** by bound metal salts establishes that **2** has a high fluorescence switch-on ability for complexation with various metal ions.

In conclusion, aza crown ether **2** has the following properties. 1) Fluorescence quenching via intramoleculer electron transfer between the pyrenyl group and the nitrogen atom in the crown ring and cation recognition by emision-intensity enhancement. 2) Fluorescence sensing of the alkali metal(I) ions using the monomer/excimer emission intensity ratio. The introduction of two pyrenyl pendants into the azacrown ether, therefore, makes it possible to develop a new fluorescence sensor.

References and Notes

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6 **2**: yellow prism, Mp 149.0−150.0 °C, ^{1}H NMR ($CDCl_3$, 500MHz) δ= 3.60 (8H, t, J=5.8 Hz), 3.67 (8H, s), 3.95 (8H, t, J=5.8 Hz), 4.37 (4H, s), 7.96 (2H, t, J=7.6 Hz), 8.01 (4H, s),8.04 (2H, d, J=7.9 Hz), 8.08 (2H, d, J=9.2 Hz), 8.09 (2H, d, J=7.9 Hz), 8.14 (2H, d, J=7.6 Hz), 8.15 (2H, d, J=7.6 Hz), and 8.58 (2H, d, J=9.2 Hz); ^{13}C NMR ($CDCl_3$) δ=54.32 (4C), 58.60 (2C), 70.21 (4C), 70.80 (4C), 129.83 (2C), 130.66 (2C), 130.94 (2C), 131.33 (2C), 133.36 (2C), 124.44 (2C), 124.82 (2C), 124.87 (2C), 124.92 (2C), 125.01 (2C), 125.78 (2C), 126.96 (2C), 127.03 (2C), 127.46 (2C), and 128.08 (2C). Found: C, 79.89; H, 6.67; N, 3.95%. Calcd for $C_{46}H_{46}N_2O_4$: C, 79.97; H, 6.71; N, 4.05%.

7 The solubility of **2** for methanol is poor.

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