Fluorescence Enhancement Observed in Tetra-aza Macrocycles by Lithium Complexation

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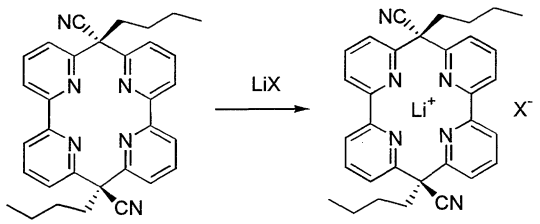
The fluorescence spectra of tetra-aza macrocycles containing pyridine rings and their lithium complexes were measured and specific fluorescence behaviors were found. That is, the complexation of tetra-aza macrocycle with lithium ion dramatically enhances the fluorescence intensity (over 1100 fold).

A variety of compounds whose fluorescence emission spectra are markedly affected by the complexation have been synthesized,[1-8] because these studies are expected to provide more useful informations about biological system.

We found that tetra-aza macrocycle **1** containing two 2,2'-bipyridine moieties shows specific fluorescent behaviors; that is, although the fluorescence of tetra-aza macrocycle **1** is extremely weak, the strong fluorescence intensity was observed in the spectrum of its lithium complex **2**. This behavior of fluorescence emission with lithium complex **2** is markedly noticed.

This lithium complex **2** was synthesized by the reaction of macrocycle **1** with lithium halide or lithium perchlorate in acetonitrile as shown in below.[9-10] In order to clarify the exact composition of lithium complex **2** in solid, the elemental analysis of this complex was performed and the ratio of macrocycle **1** to lithium ion was determined as 1:1. In addition, a plot of UV-Visible absorbance versus proportion of molar concentration of macrocycle **1** to lithium halide indicated the formation of the 1:1 complex in solution.



1 **2**

The fluorescence emission spectra of macrocycle **1** and its lithium complex **2** were measured and the results were summarized in Table. The relative quantum yield of macrocycle **1**, which was measured by using quinine sulfate solution, was extremely low (< 10^{-3}). However, the complexation of the macrocycle with lithium ion dramatically enhances the fluorescence intensity (over 1120 fold) as seen in Table 1 (relative quantum yield of complex **2** : 0.978). Similar enhancement of fluorescence was not observed in other alkali metal complexes, because their equilibrium constants were very small due to the small cavity of macrocycle **1**. Thus, this phenomenon is very specific.

This great enhancement of fluorescence would probably come from the specific structure and property of macrocycle **1**, because macrocycle **1** has small cavity and its macrocyclic inversion occurs easily.[9]

Table 1. Data of fluorescence spectra of tetra-aza macrocycles(**1** and **3**) and their lithium complexes(**2** and **4**), and relative fluorescence emission intensity of lithium complexes to macrocycles[a]

Compound	Solvent	λ_{max}(nm)[b]	Relative intensity[c]
Macrocycle **1**	CH_3CN	390	1
	CH_2Cl_2	393	1
Lithium Complex **2**	CH_3CN	345	1050
	CH_2Cl_2	347	1120
Macrocycle **3**	CH_3CN	423	1
	CH_2Cl_2	425	1
Lithium Complex **4**	CH_3CN	330	3.0
	CH_2Cl_2	335	3.5

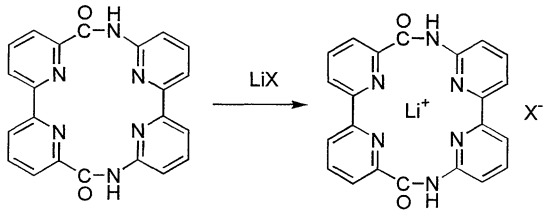
[a]The concentration of macrocycles and lithium complexes used for measurements were 1 x 10^{-4} M and their fluorescence measurements were conducted at 20℃

The excitation wavelengths were 260 nm for **1** and **2**, and 285 nm for **3** and **4**, which were the wavelengths of the maximum peaks in UV-Visible spectra of **1** and **3**, respectively.

[b]The maximum peak of fluorescence spectrum.

[c]The relative fluorescence quantum yields of lithium complexes **2** and **4** were also measured by using quinine sulfate solution and the calculations using these values also gave similar values.

In order to confirm this, new macrocycle **3** relative to macrocycle **1** was synthesized and fluorescent properties of new macrocycle **3** and its lithium complex **4** were compared with those of macrocycle **1** and lithium complex **2**. The structures of new macrocycle **3** and its lithium complex **4** are shown below.



3 **4**

This macrocycle **3** was synthesized by the coupling reaction of 2,2'-bipyridine-6,6'-diacid chloride and 6,6'-diamino-2,2'-bipyridine under high dilution.[11] The reaction of macrocycle **3** with lithium halide proceeded easily and the complex of 1:1 was obtained as well as the case of macrocycle **1**. The table contains the fluorescence data of new compounds (**3** and **4**). The relative quantum yield of macrocycle **3** was 0.273 and the ratio of increase of fluorescence intensity for lithium complex **4** was 3.5 fold, which is much smaller than that (1120 fold) for lithium complex **2**. Thus, the great fluorescence enhancement observed for lithium complex **2** seems to be the specific phenomenon. Though several factors explained for this fluorescence enhancement are considered such as (1) the increased energy of the n- π * singlet state relative to the fluorescent π - π * singlet excited state[12] or (2) the flexibility of molecule[8], the detailed discussion about this will appear in our future paper.

The studies on practical applications using these results are in progress.

References and Notes

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11 Details will be reported elsewhere. There is a possibility that the rigidity of the molecule affects the fluorescence intensity.

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