

A Color-Switching Molecule: Specific Properties of New Tetraaza Macrocyclic Zinc Complex with a Facile Hydrogen Atom

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Abstract: Unsymmetrical aza-macrocyclic and its zinc complex, which were designed with the aim of exhibiting the hybrid properties of planar and nonplanar macrocycles, were newly synthesized and showed the attractive property of being color-switching molecules. The colors of the solutions, which contain these compounds with a facile hydrogen atom, can be controlled easily by changing the solvent or the acid and base system. The color of the solution containing the free base macrocycle was orange. Importantly, the color of the solution containing the zinc complex of macrocycle depended on the solvent; the solution of zinc complex, which was formed in dichloromethane, showed colorless, and the solutions of acetonitrile and methanol showed yellow and red, respectively. The color of the solution containing the zinc complex was changed by the addition of acids or bases, and the transformation between the colors of the solutions was reversible. This color-switching phenomenon is considered to be related to the change of the conjugation system with the positional change of a facile hydrogen atom on the aza-macrocyclic ring. Furthermore, this new macrocycle exhibited a high selectivity for binding of lithium ion among alkali and alkaline earth metal ions, and the color of its solution changed from orange to colorless with the formation of lithium complex.

Introduction

The macrocyclic compounds including pyridine rings are an interesting and important class of compounds, and numerous studies about this topic have been carried out in a variety of research fields.¹ The discovery by Blau of chelating reagents containing bipyridines has stimulated major efforts to understand the details of the chemical and physical properties of macrocycles containing bipyridine.^{2–4} In particular, studies on the

interaction between aza-macrocyclic and metal ions are of interest for numerous potential applications, such as chemical sensors.⁵

The most successful aza-macrocyclics for practical applications exhibited the possibility of applying the switching system, thereby meeting an important requirement for new systems of displays.⁵ However, this challenging and fascinating problem is interesting primarily from a fundamental rather than a technological point of view because the aza-macrocyclics studied to date do not have enough properties to enable the construction of practical system. This fact has encouraged us to synthesize new aza-macrocyclics having more attractive functionality. Our approach to developing new molecules for the switching system is based on the utilization of unique properties of aza-macrocyclics **1** and **2**, which we synthesized several years ago.^{6,7} The molecular structures of macrocycle **1** having the conjugation system over the whole molecule, macrocycle **2** being the

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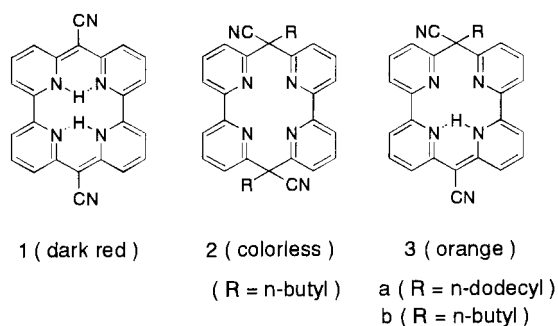
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Chart 1



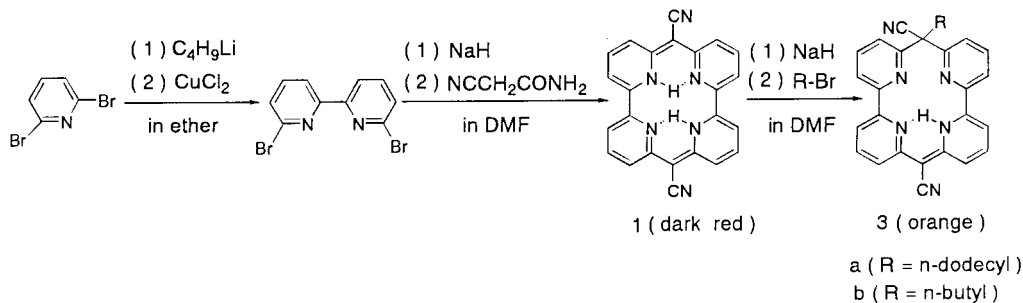
dialkylation substitute of macrocycle **1**, and newly synthesized macrocycle **3** are shown in Chart 1.

A characteristic of macrocycle **1** is the planarity of the macrocyclic ring, which is enhanced by conjugation between the macrocyclic ring and the cyano groups at the bridging positions. In contrast, macrocycle **2** has a distorted nonplanarity, which was clarified by X-ray structure determinations.⁷ The new macrocycle **3** we present has been designed with the aim of exhibiting the hybrid properties of macrocycles **1** and **2**; the 2-pyridyl-2(1*H*)-pyridylideneacetonitrile moiety of macrocycle **1** has been linked to the alkyl di(2-pyridyl)acetonitrile moiety of macrocycle **2**. Therefore, the hydrogen atom in the ring is expected to afford ideal functionality for this purpose because the hydrogen atom of the designed macrocycle **3** is facile due to the unsymmetry and the distorted nonplanarity, which are produced by the combined structures of planar macrocycle **1** and nonplanar macrocycle **2**. Additionally, two types of macrocycles **3a** (with a dodecyl group) and **3b** (with a butyl group) were synthesized in an attempt to probe the effect of the side chains on the conformation of unsymmetrical macrocyclic ring.

An attractive approach to elucidating the chemical nature of new hybrid macrocycle **3** is the clarification of the effect of the solvent on the new compound, because the hydrogen atom in the macrocyclic ring might be affected by the properties of the solvent. Accordingly, the solvent effect has been investigated and the following facts were found: (1) The formation reaction of the zinc complex of macrocycle **3** depended on the solvent, and three types of complexes were formed by the difference in the properties of three solvents (dichloromethane, methanol, acetonitrile).

(2) The color of the solution and the UV–visible spectrum of the zinc complex itself depended on the solvent. Furthermore, we have examined the effect of acid and base on the property of the zinc complex in order to probe the interaction between the zinc complex and the hydrogen atom. It was found that the color of the solution and UV–visible spectrum of the zinc complex were changed by the addition of acids or bases, and this transformation was reversible.

Scheme 1



The key to exhibiting the spectroscopically attractive phenomenon for the macrocycle **3** zinc complex is to control the binding site of the hydrogen atom with the solvent; the conjugation system of the macrocyclic ring of the zinc complex is changed by the binding site of the hydrogen atom on the macrocyclic ring, and as a result, the color of the solution and UV–visible spectrum of the zinc complex were dependent on the solvent.

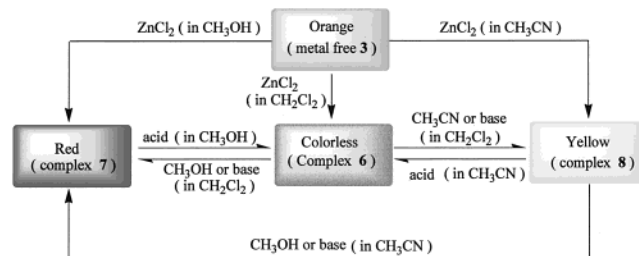
Eventually, the combination of the characteristic structure of macrocycle **1** and that of macrocycle **2** has afforded new color-switching molecules, which exhibit the solvent-responsive property with a positional change of the hydrogen atom as an antenna.

In this paper, we describe the syntheses and properties of new unsymmetrical aza-macrocyclic ring and its zinc complex, of which the color of the solution is capable of being controlled easily by the solvent or the acid and base.

Results

The synthetic route of macrocycle **3** used in this study is shown in Scheme 1.

More detailed synthetic methods and spectroscopic data for macrocycle **3** and its zinc complex are described in the Experimental Section. The complexation reaction of macrocycle **3** with zinc ion depended on the solvent and the resulting solutions showed various colors. The color of the solution containing the zinc complex itself also depended on the solvent and was changed by the addition of acids or bases. The transformation between the colors of the solutions was reversible. The drastic change of the color observed in this experiment was summarized in the following *color cycle*.



The detailed data of UV–visible spectra of macrocycle **3a** and its zinc complex in various solvents were summarized in Table 1.

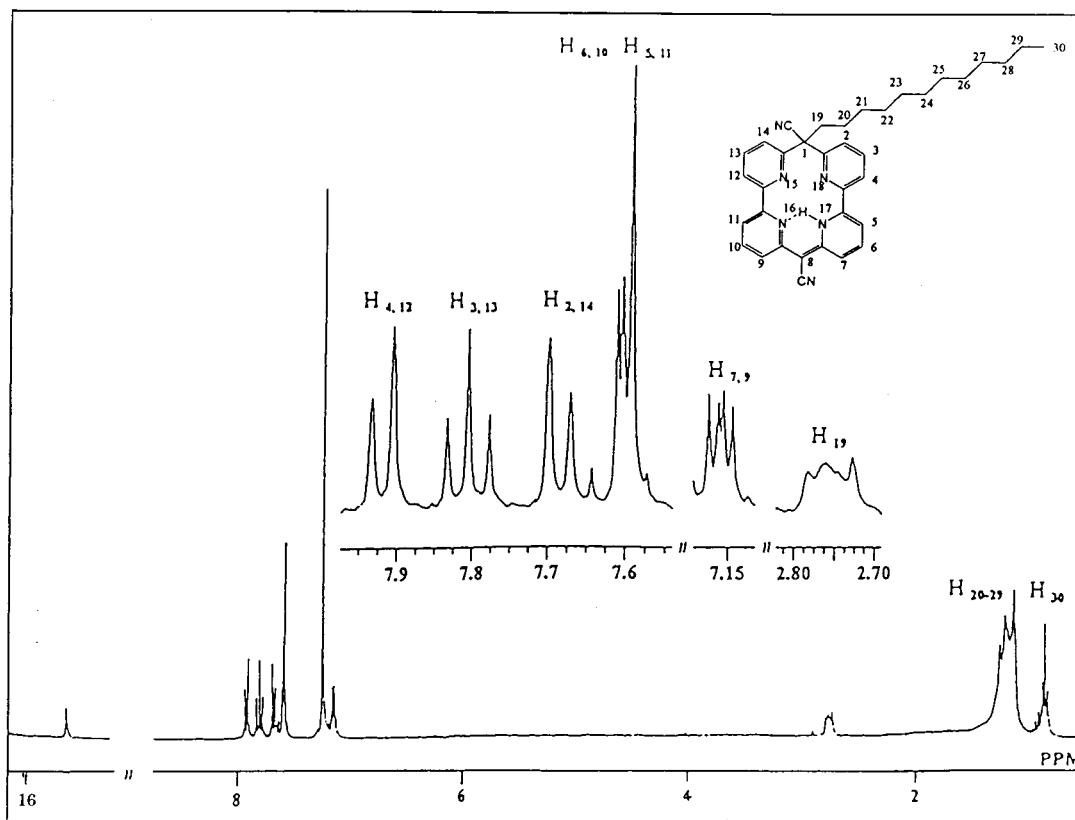
Discussion

Characterization and Properties of Unsymmetrical Macrocycle 3. The molecular structure of macrocycle **3** was assigned by using IR, ¹H NMR, and MS measurements. In IR spectrum, the absorption of nitrile group was observed at 2179 cm⁻¹. The ¹H NMR spectrum of macrocycle **3a** in CDCl₃ was presented

Table 1. UV–Visible Data for the Macrocycle **3a**–Zinc Complexes and Free Base Macrocycle **3a** in Various Solvents^a

compd	solvent	color	λ_{\max} , nm ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)			
3a –Zn	CH ₂ Cl ₂	colorless	303 (2.75)			
	CH ₃ CN	yellow	298 (2.25)	357 (1.81)	440 (1.05)	–
	CH ₃ OH	red	287 (2.50)		381 (2.63)	468 (0.85)
3a	CH ₂ Cl ₂	orange	281 (1.49)	359 (1.42)	378 (1.07)	464 (0.45)
	CH ₃ CN	orange	283 (1.42)	355 (1.39)	378 (1.07)	458 (0.53)
	CH ₃ OH	orange yellow	282 (1.34)	351 (1.41)	378 (0.97)	452 (0.50)

^a The concentrations of the solutions containing compounds measured are as follows: [**3a**–Zn] = $5.45 \times 10^{-5} \text{ M}$; [**3a**] = $5.45 \times 10^{-5} \text{ M}$.

**Figure 1.** ¹H NMR spectrum (270 MHz) of macrocycle **3a** recorded in CDCl₃ at 298 K.**Table 2.** ¹H NMR Data for the Free Base Macrocycle **3a** and its Zinc Complexes (**6** and **7**)^a

compound	δ (ppm)										
	H ₂ , H ₁₄	H ₃ , H ₁₃	H ₄ , H ₁₂	H ₅ , H ₁₁	H ₆ , H ₁₀	H ₇ , H ₉	H ₁₇	H ₈	H ₁₉	H ₂₀ –H ₂₉	H ₃₀
macrocycle 3a	7.69	7.81	7.92	7.59	7.60	7.16	15.65		2.76	1.08–1.31	0.85
complex 6			8.23–8.43					6.71	3.18	1.18–1.28	0.86
complex 7		8.14–8.34			7.55–7.81				3.12	1.13–1.29	0.86

^a Spectra were recorded in CDCl₃ at 298 K with SiMe₄ as internal reference. Chemical shifts downfield from SiMe₄ are defined as positive. Numbering scheme is shown in Figure 1.

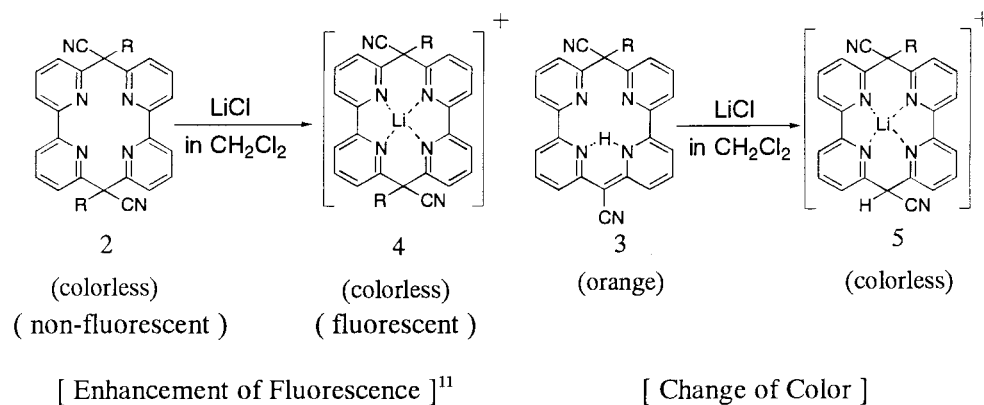
in Figure 1, and its data are summarized in Table 2. A particular noteworthy characteristic of this spectrum is that a single peak is observed at 15.65 ppm and this position is extremely low. This means that this peak corresponds to the proton signal due to the strong intramolecular hydrogen bond. This chemical shift observed for the intramolecular hydrogen bond is very close to that (17.20 ppm) previously described for macrocycle **1** in trifluoroacetic acid.⁸ The proton resonances for the macrocyclic ring give two distinct parts of signals in CDCl₃; the protons of the 2-pyridyl-2(1H)-pyridylideneacetonitrile moiety appear at higher field (7.14–7.64 ppm) and the type of signals shows an ABX pattern. In contrast, the signals at lower field (7.67–7.94 ppm) are assigned to the protons of two pyridine moieties of the alkyldi(2-pyridyl)acetonitrile part and exhibit the pattern of

a first-order AMX system.⁹ Surprisingly, the resonances of 2-pyridyl-2(1H)-pyridylideneacetonitrile protons appear at much higher field than that of pyridine protons. The loss of aromaticity of pyridine itself in the pyridylideneacetonitrile moiety could possibly explain such a result. The resonances of H₄ and H₁₂ appear at much lower field than those of H₂ and H₁₄, respectively, and those of H₅ and H₁₁ appear at much lower field than those of H₇ and H₉, respectively, because of the steric

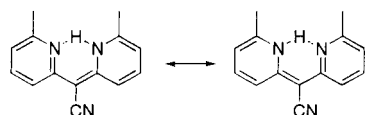
(9) The assignment of these peaks (pyridylideneacetonitrile and pyridine moieties) was confirmed by variable-temperature ¹H NMR measurements. Upon cooling, H₆ and H₇ protons of the 2-pyridyl-2(1H)-pyridylideneacetonitrile moiety moved to lower field. On the other hand, the position of the H₅ proton was nearly independent of the temperature. As a result, the H₅ and H₆ protons appeared at a similar position at room temperature and this spectrum showed an ABX pattern. In contrast, the H₅ and H₆ protons appeared at different positions at low temperature, and this spectrum showed a first-order AMX pattern (Figures 15 and 16).

(8) This macrocycle **1** is insoluble in the usual organic solvents.

Scheme 2



crowdings between H₄ and H₅ and between H₁₁ and H₁₂. One of the most remarkable features of this structure is to include a pyridylideneacetonitrile moiety, which is conjugated with the adjacent pyridine ring. Since this 2-pyridyl-2(1*H*)-pyridylideneacetonitrile moiety consists of long conjugation systems, the orange color for the solution of macrocycle **3** can be explained by this structure.

2-Pyridyl-2(1*H*)-pyridylideneacetonitrile moiety

Macrocycle **3a** exhibited high solubility in most organic solvents. The color of its dilute solution ($\sim 10^{-5}$ M) was orange, and its UV–visible spectrum showed one strong absorption band at 281–283 nm, two absorption bands (a sharp band at 351–359 nm and a weak band at 378 nm), and a broad absorption band at 430–590 nm in CH₂Cl₂, CH₃CN, and CH₃OH. When UV–visible spectra of macrocycle **3a** were measured in these solvents, it was found that there was no difference in the intensity, and shape of absorption bands, except for a hypsochromic shift, with increasing solvent polarity (Table 1).¹⁰

Characteristic Ability of Macrocycle 3 To Form the Lithium Complex. Macrocycle **3** has the hybrid property of planar macrocycle **1** and nonplanar macrocycle **2**. Since the ability to form the complex with metal is expected to be affected by this characteristic property of macrocycle **3**, the complexation reaction of macrocycle **3** with alkali or alkaline earth metal ions was carried out and a pronounced feature in the complexation reaction was found. That is, macrocycle **3** formed the complex only with lithium ion, and the color of the solution changed from orange to colorless, but did not form the complex with alkali or alkaline earth metal ions. The velocity of macrocycle **3** to take up lithium ion in CH₂Cl₂ was much slower than that of macrocycle **2**, which we described previously.⁷ In this case, the UV–visible spectrum of the macrocycle **3** lithium complex resembled much that of the macrocycle **2** lithium complex in CH₂Cl₂. This observation leads us to postulate that the structure of complex **5**, which is formed by the complexation of macrocycle **3** with lithium ion, is similar to that of lithium complex **4** of nonplanar macrocycle **2** as shown in Scheme 2. This fact was confirmed by NMR measurements of complexes **4** and **5**. The aromatic region in the ¹H NMR spectrum of complex **5** (R = butyl) prepared from macrocycle **3b**, as shown

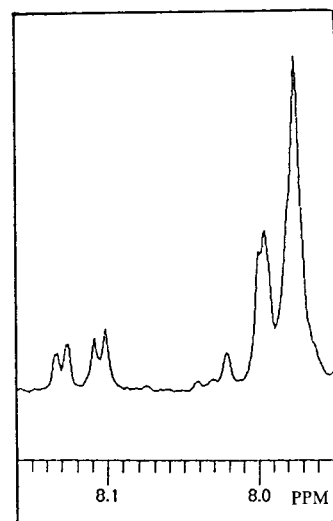


Figure 2. ¹H NMR spectrum (270 MHz) of macrocycle **3a**–lithium (complex **5**) recorded in CDCl₃ at 298 K.

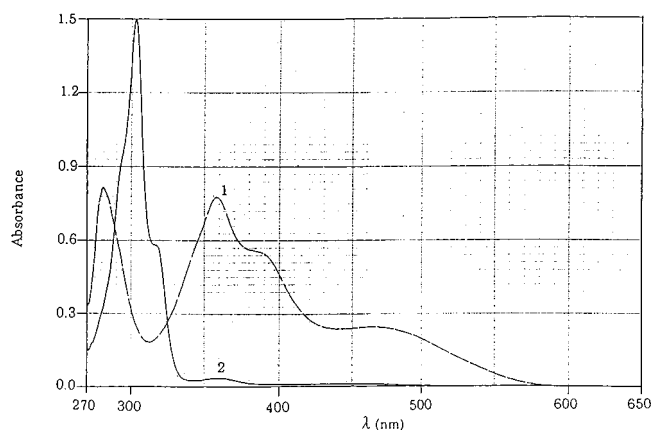


Figure 3. UV–visible spectra of macrocycle **3a** and its zinc complex **6** in CH₂Cl₂: macrocycle **3a** (1); zinc complex **6** (2).

in Figure 2, was similar to that of complex **4** (R = butyl) reported previously by us.⁷ Moreover, the signal (15.65 ppm) of the proton of the inside of the ring of macrocycle **3b** disappeared, and a new singlet peak corresponding to the proton of the outside of the ring of complex **5** (R = butyl) was observed at 7.65 ppm.

Therefore, it is considered that the hydrogen atom in the ring is pushed to the outside of the ring and four pyridine moieties are formed in a macrocyclic ring like nonplanar macrocycle **2**. The experimental fact that the solution changes from orange to

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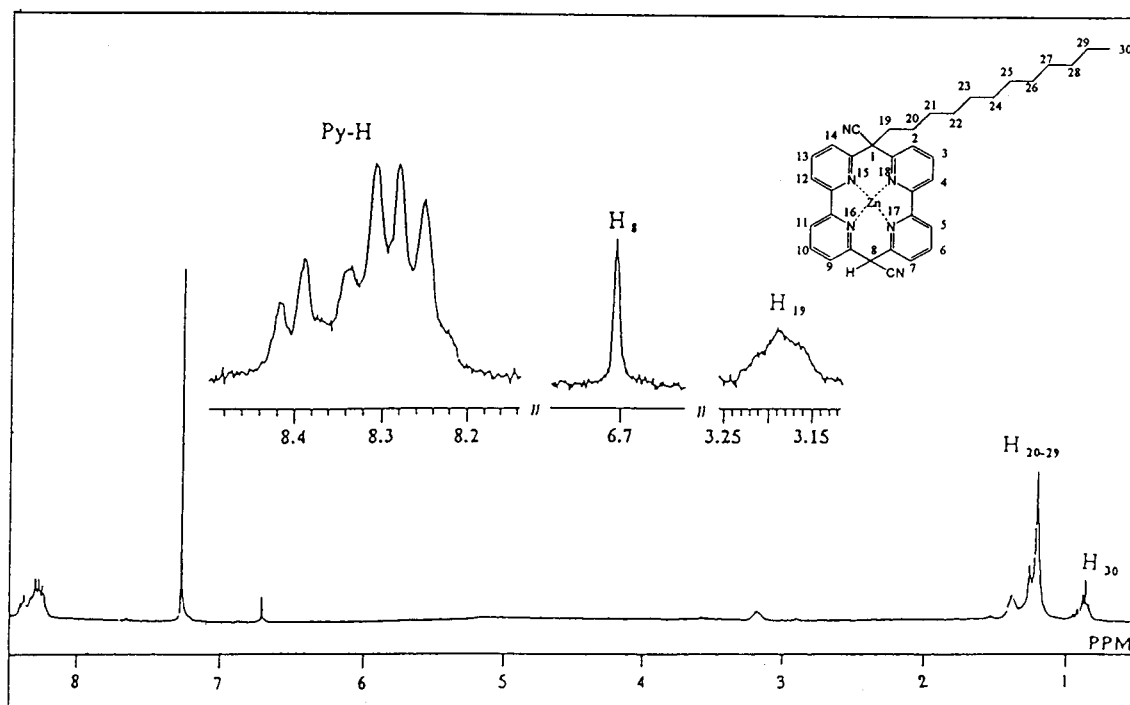


Figure 4. ^1H NMR spectrum (270 MHz) of macrocycle **3a**–zinc (complex **6**) recorded in CDCl_3 at 298 K.

colorless can be explained by the disappearance of the conjugation system of the macrocycle.

As described above, macrocycle **3** did not form any complexes with sodium, potassium, and alkaline earth metal ions. This indicates that macrocycle **3** has a high selectivity for binding of lithium ion, and the color of the solution changes with the formation of the lithium complex. Therefore, there is a possibility that macrocycle **3** is an excellent reagent to detect lithium ion. This is a *new finding in lithium chemistry*.¹²

Structural Changes of the Zinc Complex of Macrocycle 3 in Various Solvents and Its Color-Switching Property. Macrocycle **3** formed the complex with zinc ion and exhibited spectroscopically interesting behavior during the process of complexation in various solvents. While absorption in the visible region (430–590 nm) of macrocycle **3a** in CH_2Cl_2 disappeared, a new absorption of Zn complex appeared at 303 nm (Table 1, Figure 3). Finally, the solution became colorless, and the trend of the change of the spectrum during the reaction of macrocycle **3a** and zinc ion was very similar to that of macrocycle **3a** during uptake of lithium ion in CH_2Cl_2 . In the ^1H NMR spectrum (Figure 4) of this Zn complex in CDCl_3 , the signal (15.65 ppm) of the proton assigned to the intramolecular hydrogen bond of free base macrocycle **3a** disappeared, and a new singlet peak, which is correspondent to the proton of the outside of the ring of complex **6**, was observed at higher field (6.71 ppm).

Additionally, the signals at higher field (7.14–7.64 ppm) that correspond to the protons of the 2-pyridyl-2(1*H*)-pyridylidene-acetonitrile moiety of free base macrocycle **3a** disappeared, and signals that correspond to four pyridine moieties appeared at lower field (8.23–8.43 ppm) (Table 2, Figure 4). This indicates that four pyridine moieties, which are almost equivalent, are formed by coordination of zinc ion. This is evidence for the reason the color of the solution changes from orange to colorless with the formation of the zinc complex. The coordination of zinc to macrocycle **3a** induces significant downfield shifts and

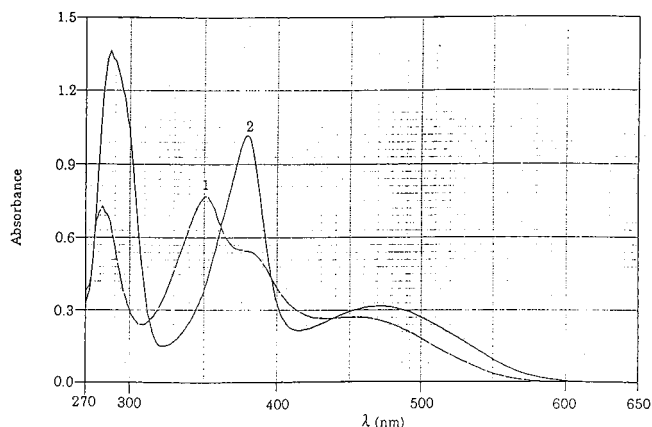


Figure 5. UV–visible spectra of macrocycle **3a** and its zinc complex **7** in CH_3OH : macrocycle **3a** (1); complex **7** (2).

signal broadening for α -methylene protons of the dodecyl group (3.18 ppm). This shift is typical of macrocycle coordinated by metal, owing to the decrease of electron density. The signals of other methylene groups [$(-\text{CH}_2)_{10}-$] were also observed at lower field (1.08–1.31 ppm) compared to those (1.12–1.27 ppm) for the free base macrocycle **3a**.

When the zinc complex was formed in CH_3OH , the absorption intensity of macrocycle **3a** at 378 nm increased with the disappearance of the absorption at 351 nm. The broad band in the visible region was red-shifted from 452 to 468 nm and the orange solution turned to red (Table 1, Figure 5).

The observation for the experiments in CH_2Cl_2 and CH_3OH leads us to conclude that the complexation reaction of macrocycle **3** with zinc ion is affected by the property of the solvent. When complexation with zinc proceeds in the solvents where the basicity is comparatively small, the hydrogen atom in the ring is extruded on the ring outside, the conjugation system of the macrocycle is lost, and the complex having a structure like complex **6** is formed (Scheme 3). On the other hand, when the more basic solvents are used, complex **7**, which has more an

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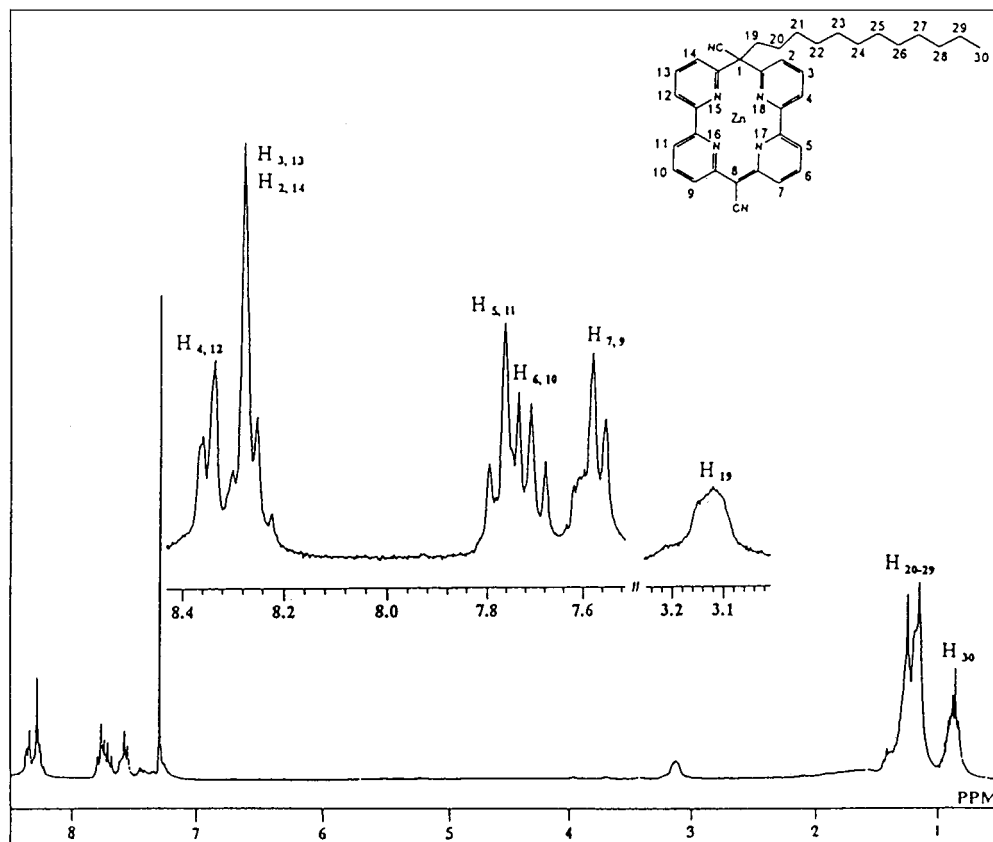
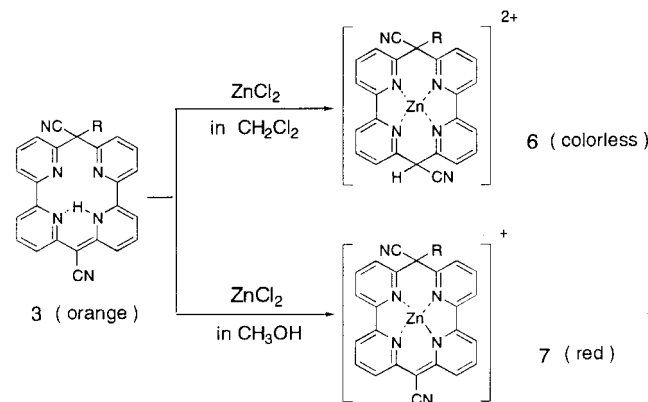


Figure 6. ^1H NMR spectrum (270 MHz) of macrocycle **3a**–zinc (complex **7**) recorded in CDCl_3 at 218 K. This complex **7** was formed in CH_3OH .

Scheme 3¹⁹



enhanced conjugation system compared with macrocycle **3**, is formed (Scheme 3). The reason complex **7** has the structure shown in Scheme 3 is as follows. The free base macrocycle **3** shows the orange color due to the long conjugation system. The coordination by zinc induces the increase of planarity over the macrocyclic ring and the formation of longer conjugation system with pyridine moieties of alkyl di(2-pyridyl)acetonitrile part. As a result, the UV–visible spectrum is red-shifted and the solution shows the red color. The reason complex **7** is formed in the solvent with high basicity is that the hydrogen atom on the ring of complex **6** is removed by the solvent, the longer conjugation system is formed, and the complex is stabilized. This structure of complex **7** is also supported by the ^1H NMR spectrum for complex **7**, which is presented in Figure 6. This indicates the appearance of peaks (7.55–7.81 ppm) assigned to the protons of 2-pyridyl-2(1*H*)-pyridylideneacetonitrile moiety. The ^1H NMR spectrum of complex **6** did not exhibit these peaks (Figure 4).

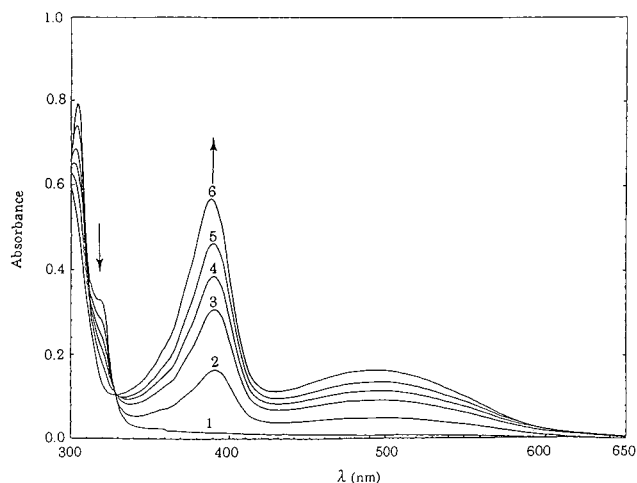


Figure 7. UV–visible spectral changes of macrocycle **3a**–zinc (complex **6**) in CH_2Cl_2 . The amounts of CH_3OH added to the solution were 0 (1), 2.47×10^{-4} (2), 7.41×10^{-4} (3), 9.88×10^{-4} (4), 14.82×10^{-4} (5), and 19.76×10^{-4} mol (6). The concentration of complex **6** in CH_2Cl_2 used in this experiment was 2.50×10^{-5} M.

Of particular interest is the role of the solvent in changing from complex **6** to complex **7**. Attempts were therefore made, using the solvents with various basicities, to explore this effect. The solvents with low basicity were selected in order to probe the sensitive behavior. Dimethyl sulfoxide (DMSO), CH_3OH , and tetrahydrofuran (THF) were used for this experiment. The spectral change of the complex **6** in CH_2Cl_2 by addition of CH_3OH are shown in Figure 7. The relationship between the absorbance ratio at 390 nm and the amount of each solvent added is shown in Figure 8. This figure suggests that there is the correlation between the basicity of the solvent added and

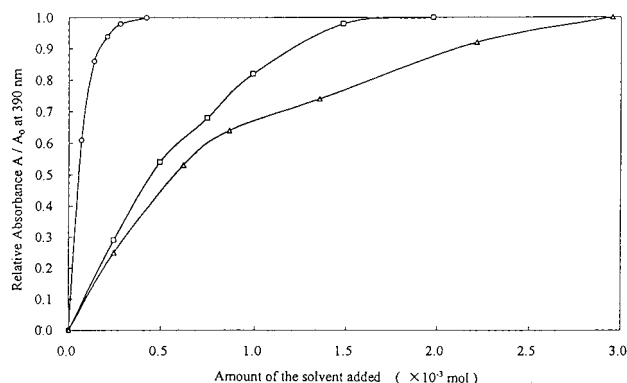
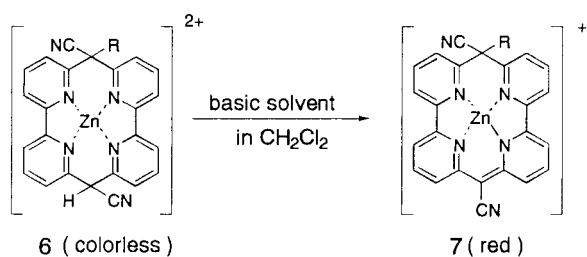


Figure 8. Relationship between the absorbance ratio at 390 nm and the amount of the solvent added. DMSO (O), CH₃OH (□), and THF (Δ). The solvents were added to the solution of macrocycle **3a**–zinc (complex **6**) in CH₂Cl₂, and the concentration of complex **6** was 2.50×10^{-5} M.

Scheme 4¹⁹



the spectral change; the change of the spectrum by DMSO with the higher basicity is more intense than that by THF with lower basicity.¹³ The spectrum obtained by adding this basic medium was in good agreement with that of complex **7** formed in MeOH. These experimental results indicate that complex **6** is transformed to complex **7** by adding the basic solvent. Therefore, the solvent exhibits a large effect in the transformation from complex **6** to complex **7** as shown in Scheme 4.

In addition, we need to explore the interconversion between complex **6** and complex **7** by adding the acid or the base to the solution of the zinc complex of macrocycle **3** in order to confirm the protonation and deprotonation behavior. The experimental procedures and the results are shown in Scheme 5.

Initially, the addition of pyridine to the colorless solution of zinc complex in CH₂Cl₂ was red, and another addition of CF₃COOH to this solution returned it to colorless (Figure 9). In MeOH, zinc complex **7** showing a red color was obtained. The successive addition of the acid and the base to this red solution gave the change of colors to colorless and to red again (Figure 10).

The formation reaction of zinc complex in acetonitrile provides another series of color changes. The intensity of the shorter wavelength band (355 nm) for two absorption bands of macrocycle **3a** itself increased and that of the longer wavelength band (378 nm) diminished. Moreover, the broad band in the visible region is blue-shifted from 458 to 440 nm and the color of the solution became yellow (Table 1, Figure 11). Experiments using the acid–base system were also made as well as the cases of CH₂Cl₂ and CH₃OH in order to characterize the complex, which was formed in CH₃CN. Initially, when HCOOH was added to the yellow solution, it changed to colorless. Additionally, it became red when the base was added to this solution. In the reverse order, it became red when pyridine was added to

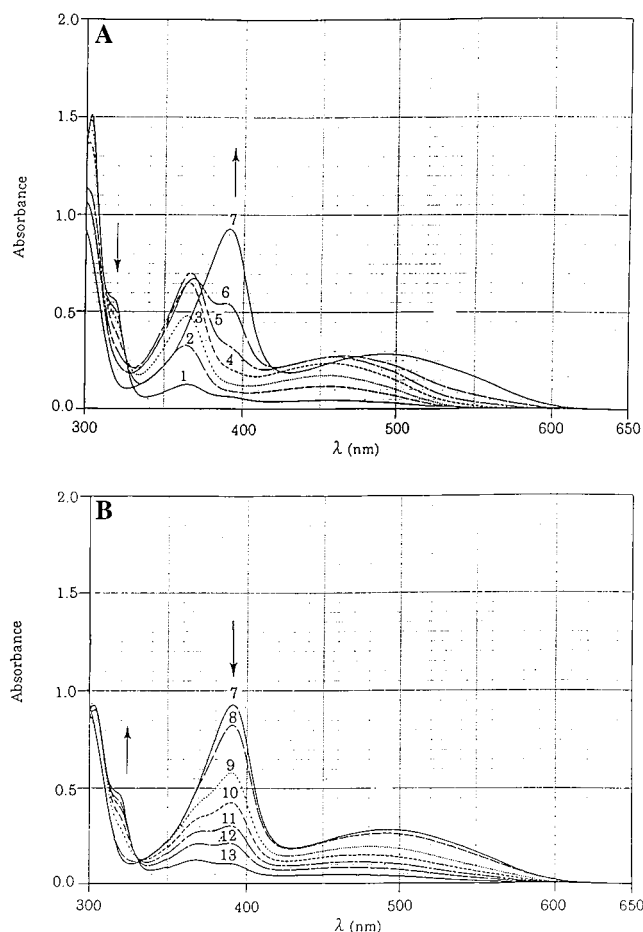


Figure 9. (A) UV–visible spectral changes of macrocycle **3a**–zinc (complex **6**) in CH₂Cl₂. The amounts of pyridine added to the solution were 0 (1), 0.34×10^{-4} (2), 1.02×10^{-4} (3), 1.36×10^{-4} (4), 1.71×10^{-4} (5), 2.05×10^{-4} (6), and 2.73×10^{-4} mol (7). The concentration of complex **6** in CH₂Cl₂ used in this experiment was 4.93×10^{-5} M. (B) UV–visible spectral changes of macrocycle **3a**–zinc (complex **6**) in CH₂Cl₂. The amounts of CF₃COOH added to the solution after addition of 2.73×10^{-4} mol of pyridine were 0 (7), 0.32×10^{-4} (8), 0.75×10^{-4} (9), 0.96×10^{-4} (10), 1.17×10^{-4} (11), 1.39×10^{-4} (12), 1.81×10^{-4} (13), and 2.24×10^{-4} mol (14).

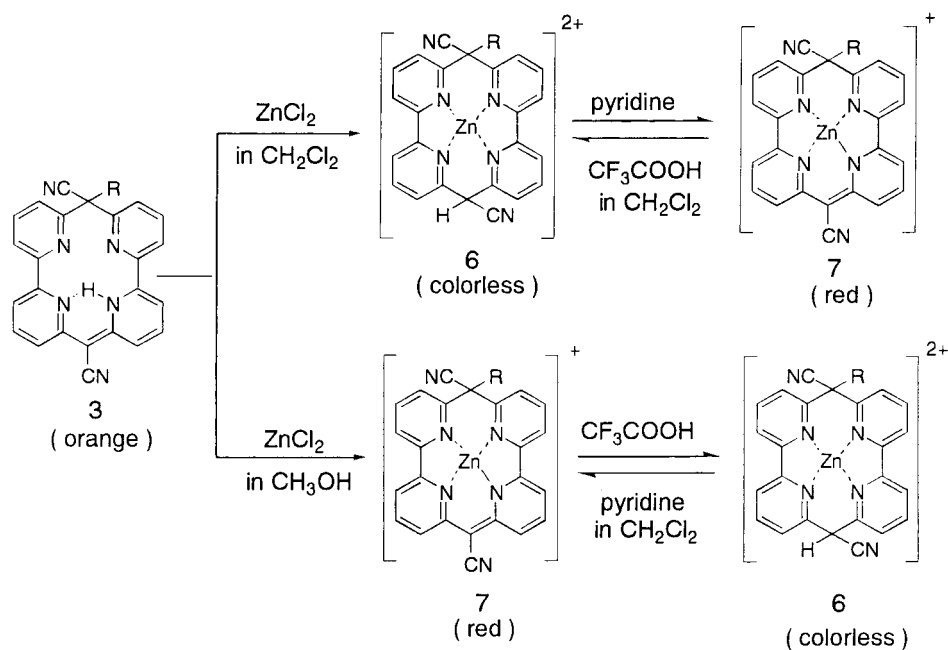
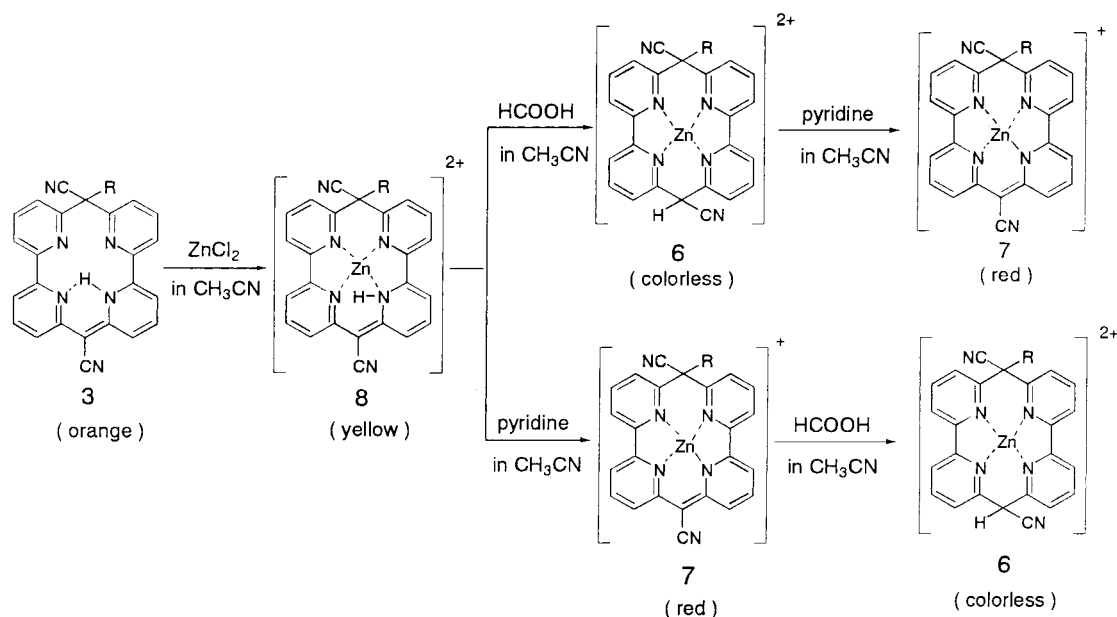
this yellow solution, and when HCOOH was added to this red solution, it became colorless. The changes of UV–visible spectra accompanied by these operations are shown in Figures 12 and 13, respectively, and the structural changes that correspond to the change of spectra are presented in Scheme 6. In this case, the spectra of the colorless and red solutions are very similar to the spectra of zinc complex obtained in CH₂Cl₂ and CH₃OH, respectively. These spectroscopic findings have led the consideration about the structure of the complex in the yellow solution; this complex has a conjugation system spreading over the macrocycle and a hydrogen atom in the ring. Therefore, macrocycle **8** shown in Scheme 6 is considered to be the structure of this complex.

Fluorescence measurements of free base macrocycle **3a** (orange), complex **6** (colorless), complex **7** (red), and complex **8** (yellow) were carried out in an attempt to obtain supporting information about each structures. The fluorescence spectra of these complexes are presented in Figure 14.¹⁵ The pronounced

(14) Takano, K.; Furuhashi, A.; Ogawa, S.; Tsuchiya, S. *J. Chem. Soc., Perkin Trans 2*, **1999**, 1063.

(15) This fluorescence spectrum of macrocycle **3a** was almost the same as that of complex **8**, and the two spectra appeared to be superimposable.

(13) Riddick, J. A.; Bunger, W. A.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of chemistry 2; John Wiley & Sons: New York, 1986.

Scheme 5¹⁹Scheme 6¹⁹

feature of these spectra is that the fluorescence intensity of complex **6** is very large and, in contrast, that of complex **8** is almost the same as that of free base macrocycle **3a**. It seems rather difficult to explain this result by a simple mechanism. However, some explanation might be found by using results previously reported. By using lithium complex **4**, we were able to observe the great enhancement of fluorescence.^{11,14} The structure of complex **6** is very similar to that of lithium complex **4**, exhibiting large intensity of fluorescence. Thus, the large fluorescence intensity observed for complex **6** might be explained in terms of the similarity of the system of macrocyclic rings. Additionally, this explanation was confirmed by the experimental result about lithium complex **5**; lithium complex **5** exhibited the enhanced fluorescence intensity. A similar explanation would be applied for complex **8**; the structure of complex **8** is almost the same as that of free base macrocycle **3a** as shown in the above schemes, and complex **8** shows a fluorescence intensity similar to that of free base macrocycle **3a**.

As stated above, the position of the hydrogen atom in the zinc complex of macrocycle **3** depends on the property of the solvent, and its conjugation system changes largely with this binding site. As a result, the color of the solution containing this zinc complex dramatically changes to colorless, yellow, and red.¹⁶ This phenomenon is exhibited distinctly by Table 3, which contains the shifts of hydrogen atoms of some compounds as a function of conditions.¹⁷

Both structures of macrocycles **1** and **2** are fully symmetrical, but macrocycle **3** takes an unsymmetrical structure, possibly taking a highly distorted structure, which produces various conformations. There is a possibility that this fact is confirmed by the variable-temperature ^1H NMR spectroscopy. Therefore,

(16) The complexation reaction was attempted by using other solvents. As a result, the following colors were observed: (i) colorless in benzene, toluene and CHCl_3 , (ii) yellow in acetone, and (iii) red in DMSO and THF.

(17) The clear ^1H NMR spectrum of complex **8** was not obtained by our NMR system.

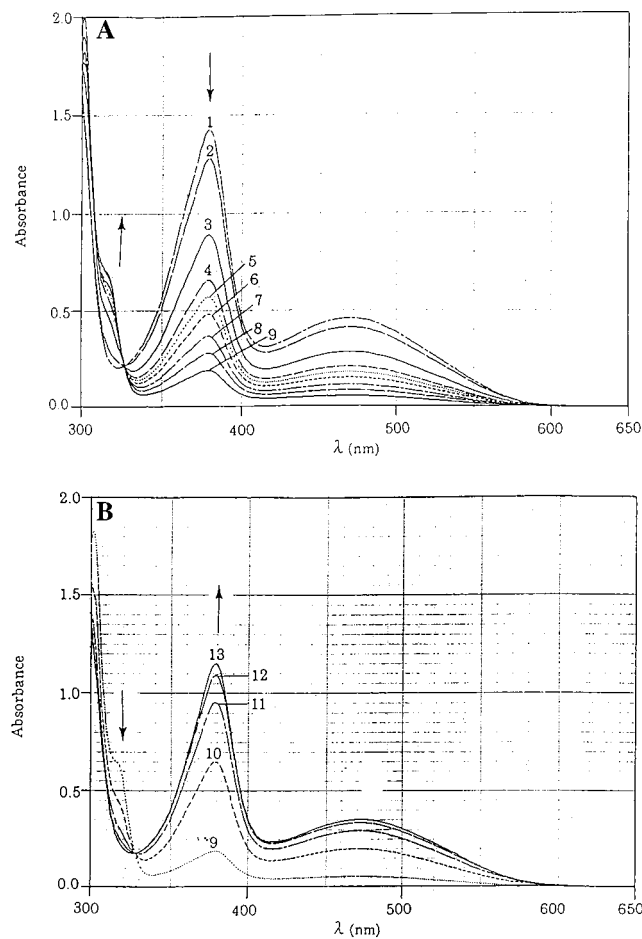


Figure 10. (A) UV-visible spectral changes of macrocycle **3a**–zinc (complex **7**) in CH_3OH . The amounts of CF_3COOH added to the solution were 0 (1), 0.32×10^{-4} (2), 0.53×10^{-4} (3), 0.75×10^{-4} (4), 0.96×10^{-4} (5), 1.28×10^{-4} (6), 2.13×10^{-4} (7), 4.26×10^{-4} (8), and 10.6×10^{-4} mol (9). The concentration of complex **7** in CH_3OH used in this experiment was 8.06×10^{-5} M. (B) UV-visible spectral changes of macrocycle **3a**–zinc (complex **7**) in CH_3OH . The amounts of pyridine added to the solution after addition of 10.6×10^{-4} mol of CF_3COOH were 0 (9), 0.85×10^{-4} (10), 1.71×10^{-4} (11), 2.56×10^{-4} (12), and 3.41×10^{-4} mol (13).

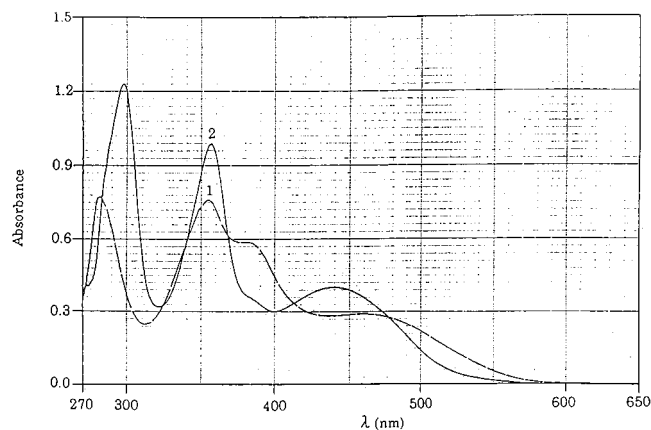


Figure 11. UV-visible spectra of macrocycle **3a** and its zinc complex **8** in CH_3CN : macrocycle **3a** (1), complex **8** (2).

this measurement was carried out and the temperature dependence of the ^1H NMR spectra was found. The ^1H NMR spectrum of macrocycle **3a** as a function of temperature is shown in Figure 15. This result indicates some variations of conformation with

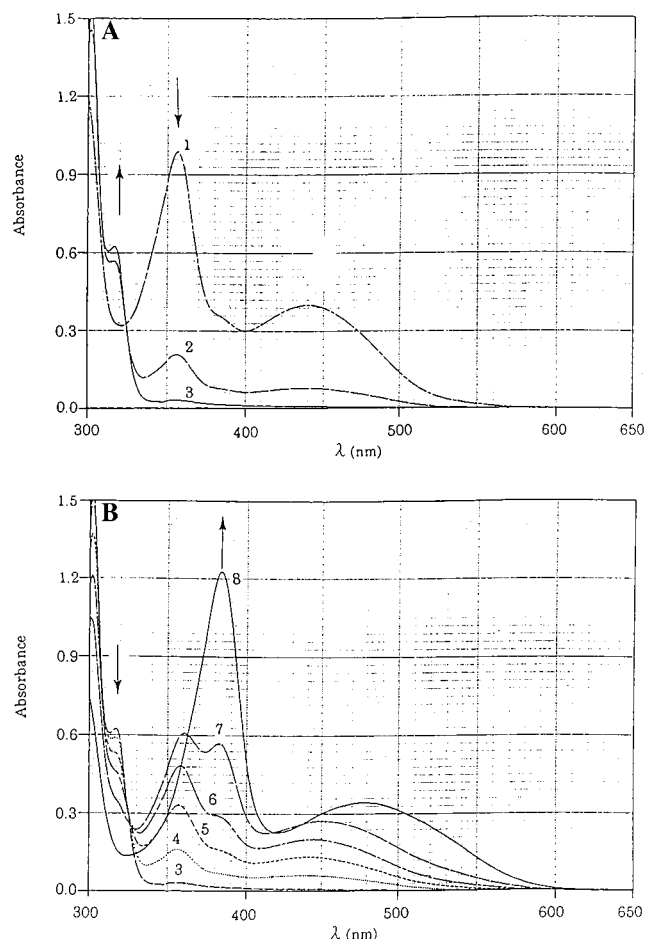


Figure 12. (A) UV-visible spectral changes of macrocycle **3a**–zinc (complex **8**) in CH_3CN . The amounts of HCOOH added to the solution were 0 (1), 0.20×10^{-5} (2) and 1.57×10^{-5} mol (3). The concentration of complex **8** in CH_3CN used in this experiment was 5.45×10^{-5} M. (B) UV-visible spectral changes of macrocycle **3a**–zinc (complex **8**) in CH_3CN . The amounts of pyridine added to the solution after addition of 1.57×10^{-5} mol of HCOOH were 0 (3), 0.34×10^{-4} (4), 1.02×10^{-4} (5), 1.71×10^{-4} (6), 2.39×10^{-4} (7), and 4.09×10^{-4} mol (8).

change of temperature; upon cooling, the signals seen for the H_6 (H_{10}) and H_7 (H_9) protons of the pyridylideneacetonitrile moiety moved to lower field, while that of the H_5 (H_{11}) proton was virtually invariant as shown in Figure 16. This unusual shifts of protons H_6 (H_{10}) and H_7 (H_9) must be due to the increases of planarity of the 2-pyridyl-2(1H)-pyridylideneacetonitrile and the effect of the ring current of the cyano group; at low temperature, the degree of planarity of the 2-pyridyl-2(1H)-pyridylideneacetonitrile moiety increases, this leads to an increasing degree of conjugation with the cyano group and increasing effect of the ring current, and this affords the appearance of these signals at lower field.

This macrocycle **3** formed complexes with some other metal ions (Cu^{2+} , Co^{2+} , Fe^{2+} , Eu^{3+} , Sn^{2+}) in CH_2Cl_2 or CHCl_3 . The shapes of the UV-visible spectra of these complexes resembled that of the zinc complex **7** obtained in CH_3OH , and their solutions showed a red-shift compared with that of complex **7**. The solutions of these complexes were very sensitive to the addition of acid or base; when acid was added to the deeply colored solutions, they became colorless. Additionally, when the base was added to this, the solution returned to its original color. These processes were found to be reversible and occur repeatedly with good reproducibility.

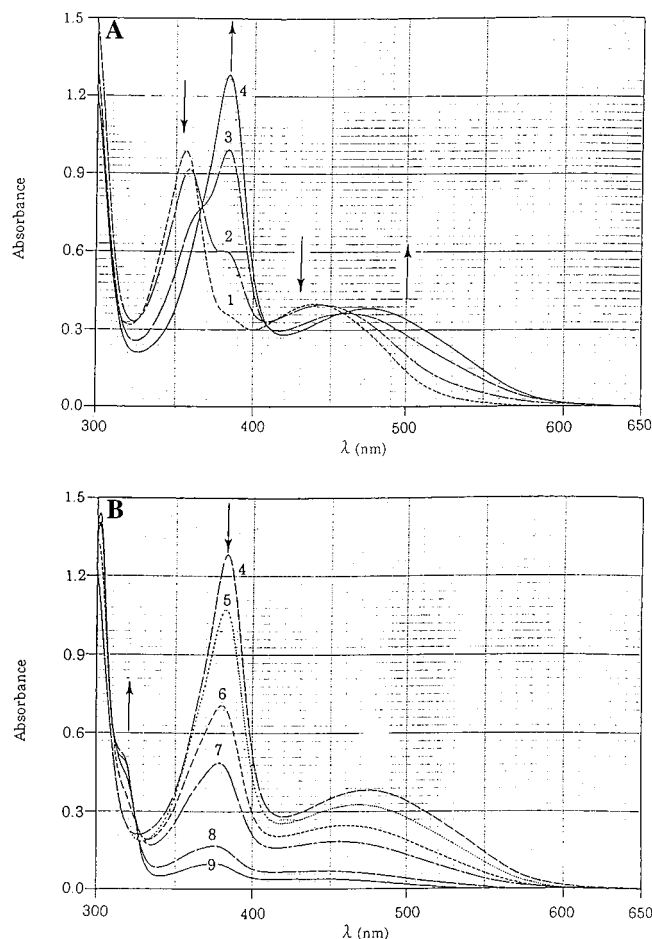


Figure 13. (A) UV-visible spectral changes of macrocycle **3a**–zinc (complex **8**) in CH_3CN . The amounts of pyridine added to the solution were 0 (1), 2.21×10^{-4} (2), 3.06×10^{-4} (3), and 3.40×10^{-4} mol (4). The concentration of complex **8** in CH_3CN used in this experiment was 5.45×10^{-5} M. (B) UV-visible spectral changes of macrocycle **3a**–zinc (complex **8**) in CH_3CN . The amounts of HCOOH added to the solution after addition of 3.40×10^{-4} mol of pyridine were 0 (4), 0.98×10^{-4} (5), 3.32×10^{-4} (6), 5.09×10^{-4} (7), 9.80×10^{-4} (8), and 11.76×10^{-4} mol (9).

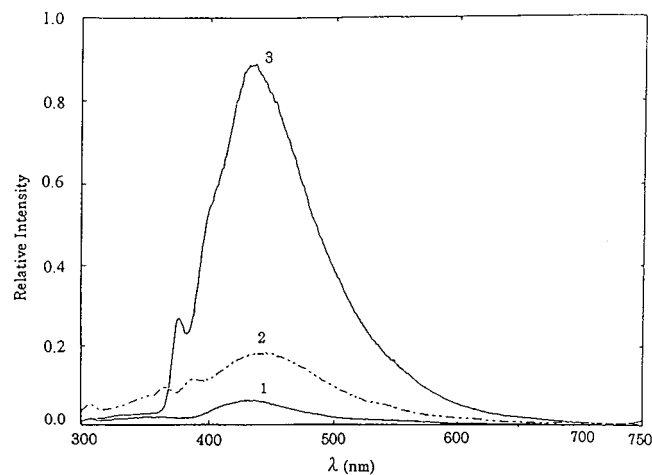


Figure 14. Fluorescence spectra of macrocycle **3a** and its zinc complexes **6**, **7**, and **8** in CH_2Cl_2 : macrocycle **3a** and complex **8** (1), complex **7** (2), and complex **6** (3). The excitation wavelength was 285 nm.

Conclusion

Unsymmetrical aza-macrocycle **3**, which has the combined structures of planar macrocycle **1** and nonplanar macrocycle **2**,

Table 3. Chemical Shifts of the Facile Hydrogen Atoms

compound	solvent	chemical shift
1	trifluoroacetic acid	17.20
3a	CDCl_3	15.65
5 (R = butyl)	CDCl_3	7.65
6 (R = dodecyl)	CDCl_3	6.71

was newly synthesized and found to exhibit a new functionality; a zinc complex of this macrocycle **3** has various conformations due to its unsymmetrical and distorted structure, giving a facile hydrogen atom. As a result, this hydrogen atom on the macrocyclic ligand moves easily by complexation with Zn ion. The binding site of this facile hydrogen atom is also changed by the property of the solvent. In other words, the binding site of the hydrogen atom on the macrocyclic ring is capable of being controlled by the solvent. The conjugation system of the macrocycle changes with the binding site of the hydrogen atom, and as a consequence, the colors of the solutions containing these compounds are capable of being controlled by solvent. It was also found that the conjugation system of the macrocyclic ring is changed reversibly by using the acid–base system.

The characteristic color change by this color-switching molecule was summarized in the color cycle given above.

In summary, a new aza-macrocycle and its zinc complexes, of which the colors of the solutions are controlled easily by the solvent or the acid–base system, were synthesized. This color-switching molecule has some advantages over the previously known compounds,⁵ because the facile hydrogen atom as an antenna is very sensitive to the chemical environment, such as solvent and pH. The results observed in this experiment provide an important strategy for syntheses of new color-switching molecules. In addition to providing the color-switching molecule, this method to design the unsymmetrical and distorted system generates considerable activation of the development of a molecule to catch the lithium ion easily.

Experimental Section

Chemicals. All reagents and solvents were purchased from Wako Chemical Co. and used as received. Dimethylformamide (DMF) used in the synthesis was dried over 3-Å molecular sieves and distilled under vacuum. For column chromatography, Wakogel (silica gel) C-300 (particle size 45–75 μm) was used. Macrocycle **1** was prepared by a literature procedure.⁷

Instrumentation. UV-visible spectra were obtained on a Shimadzu UV-2200 spectrophotometer at room temperature in 1-cm quartz cell. IR spectra were measured on a Perkin-Elmer FT-IR 1720 X spectrometer with a KBr method. The fluorescence spectra were collected by using a Shimadzu RF-5300PC spectrometer under an argon atmosphere at room temperature. Mass spectra were taken in a JEOL JMS-700 spectrometer. ^1H NMR spectra were measured on a JEOL JNM GX-270 spectrometer (270 MHz). When variable-temperature ^1H NMR measurements were carried out, a liquid nitrogen-cooled variable-temperature controller was used. Chemical shifts are reported with ppm units with SiMe_4 as an internal standard. Since the solutions of free base macrocycle **3**, its Zn complexes **7** and **8**, and its other metal complexes described above were photosensitive, these solutions were kept in the dark.

Syntheses. Macrocycle 3a. A dispersion of 60% sodium hydride in mineral oil (0.6 g, 1.50×10^{-2} mol) was placed in a 100-mL four-necked flask under an argon atmosphere. After the mineral oil had been removed by washing with ethyl ether, anhydrous DMF (50 mL) was charged at room temperature, and then, macrocycle **1** (0.3 g, 7.77×10^{-4} mol) was added. The reaction mixture was stirred for 2 h at 50 $^\circ\text{C}$. While hydrogen gas was evolved, the color of the reaction mixture turned to deep red. After cooling to 30 $^\circ\text{C}$, 1-bromododecane (3 mL, 1.30×10^{-1} mol) in 25 mL of DMF was added to its reaction mixture, and the reaction temperature was raised to 135 $^\circ\text{C}$. At this temperature,

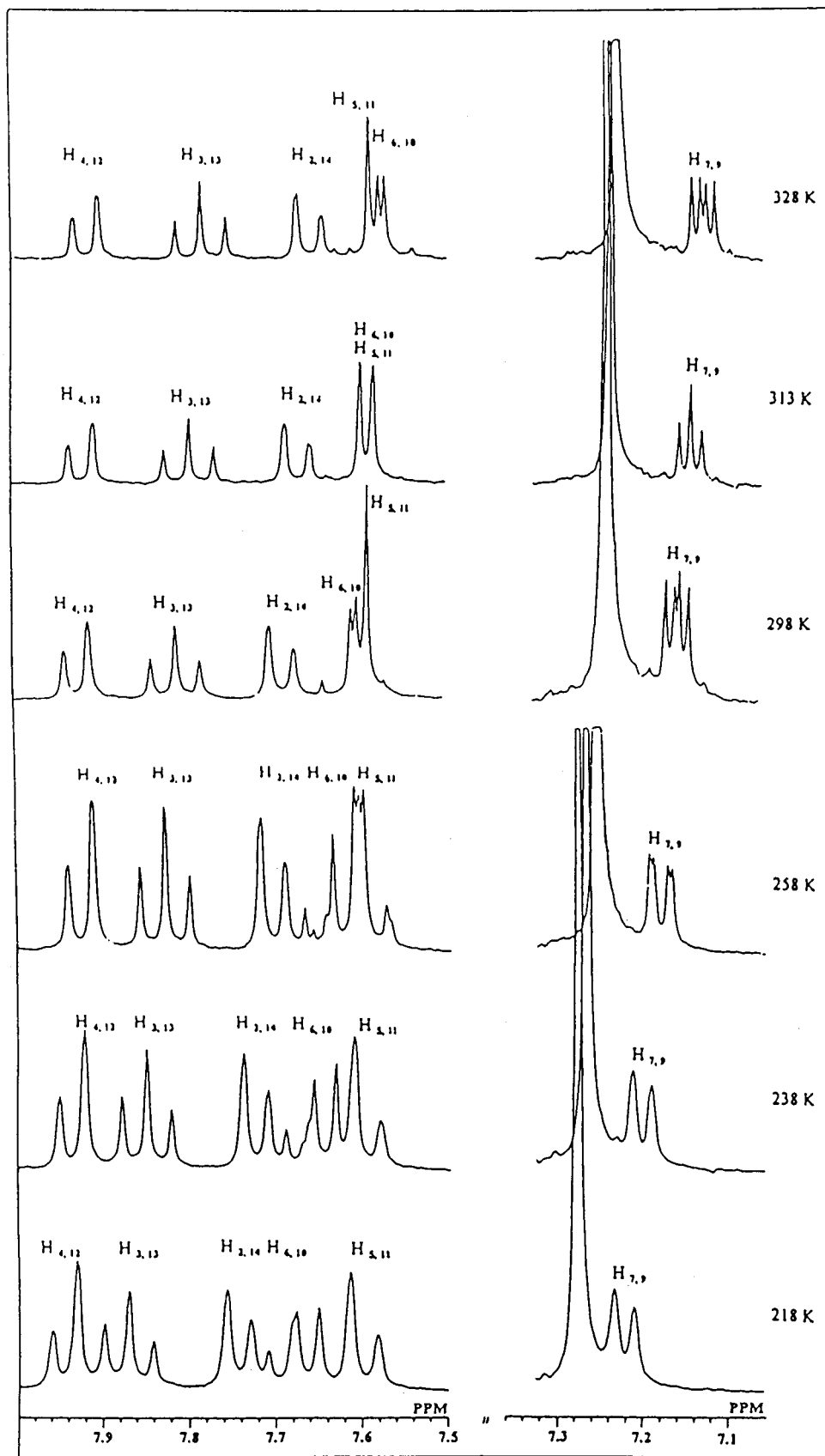


Figure 15. ^1H NMR (270 MHz) spectra of the macrocycle **3a** in CDCl_3 at various temperatures.

the reaction mixture was stirred for 16 h. The reaction was stopped by adding of water, and DMF was removed under vacuum to give a crude product as a red oil. This product was extracted by chloroform and purified by silica gel (particle size 45–75 μm) column chromatography by using chloroform as elute. Macrocycle **3a** was isolated from the

third fraction as bright-red needles in 55% yield: ^1H NMR (CDCl_3 , 298 K) δ 15.65 (s, H_{17}), 7.92 (d, $\text{H}_{4,12}$), 7.81 (t, $\text{H}_{3,13}$), 7.69 (d, $\text{H}_{2,14}$), 7.60 ($\text{H}_{6,10}$), 7.59 ($\text{H}_{5,11}$), 7.16 ($\text{H}_{7,9}$), 2.76 (H_{19}), 1.08–1.31 (m, H_{20-29}), 0.85 (t, H_{30}), $J_{23} = J_{1314} = 7.56$ Hz, $J_{34} = J_{1213} = 7.29$ Hz, $J_{56} = J_{1011} = 7.31$ Hz, $J_{67} = J_{910} = 8.91$ Hz, $J_{57} = J_{911} = 0.79$ Hz; m/z 554 (M^+),

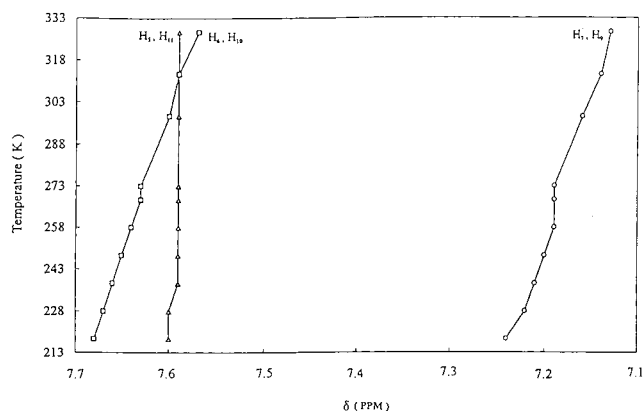


Figure 16. Variable-temperature ^1H NMR (270 MHz) data for the 2-pyridyl-2(1H)-pyridylideneacetonitrile group of free base macrocycle **3a** in CDCl_3 .

$385 (\text{M}^+ - (-\text{CH}_2)_{11}-\text{CH}_3)$. Anal. Calcd (%) for $\text{C}_{36}\text{H}_{38}\text{N}_6$: C, 77.98; H, 6.86; N, 15.16. Found (%): C, 77.19; H, 7.34; N, 14.49. UV-vis (CH_2Cl_2) λ_{max} (ϵ) 281 nm (14 900), 359 (14 200), 378 (10 700), 464 (4500); IR (KBr) (cm^{-1}) 2925, 2186, 1625, 1572, 1501, 1458, 1423, 1171, 784.

Macrocycle 3b.¹⁸ The synthesis and the procedure of purification were similar to the preparation of macrocycle **3a**, though 1-bromobutane was substituted for 1-bromododecane. The reaction mixture was heated at 100 °C for 8 h with stirring. Tetraazadicyanomobutyl macrocycle

(18) The properties of macrocycle **3b** were very similar to those of macrocycle **3a**.

(19) R = dodecyl.

3b was isolated from the third fraction by column chromatography and obtained as pale red powder in 65% yield: ^1H NMR (CDCl_3 , 298 K) δ 15.65 (s, H_{17}), 7.94 (d, $\text{H}_{4,12}$), 7.83 (t, $\text{H}_{3,13}$), 7.72 (d, $\text{H}_{2,14}$), 7.61 ($\text{H}_{6,10}$), 7.60 ($\text{H}_{5,11}$), 7.18 ($\text{H}_{7,9}$), 2.77 (H_{19}), 1.23–1.33 (m, H_{20-21}), 0.78 (t, H_{22}), $J_{23} = J_{1314} = 7.56$ Hz, $J_{34} = J_{1213} = 7.29$ Hz, $J_{56} = J_{1011} = 7.31$ Hz, $J_{67} = J_{910} = 8.91$ Hz, $J_{57} = J_{911} = 0.79$ Hz; m/z 442 (M^+), 385 ($\text{M}^+ - (-\text{CH}_2)_3-\text{CH}_3$); UV-vis (CH_2Cl_2) λ_{max} (ϵ) 281 nm (14 500), 359 (14 000), 378 (10 700), 464 (4100); IR (KBr) (cm^{-1}) 2935, 2183, 1628, 1582, 1518, 1465, 1434, 1180, 795.

Zn Complex 6 of Macrocycle 3a. A mixture of macrocycle **3a** (0.05 g, 9.02×10^{-7} mol) and ZnCl_2 (0.25 g, 1.83×10^{-4} mol) in 15 mL of CH_2Cl_2 were stirred for 10 min at room temperature. By complexation with ZnCl_2 , the orange solution changed to colorless solution. The resulting solution was used for UV-visible and ^1H NMR investigation: ^1H NMR (CDCl_3 , 298 K) δ 8.23–8.43 (m, 12 H, Py-H), 6.71 (s, 1 H, H_8), 3.18 (br. 2 H, H_{19}), 1.18–1.28 (m, 20 H, H_{20-29}), 0.86 (t, 3 H, H_{30}); UV-vis (CH_2Cl_2) λ_{max} (ϵ) 303 nm (27 500).

Zn Complex 7 of Macrocycle 3a. A mixture of macrocycle **3a** (0.05 g, 9.02×10^{-5} mol) and ZnCl_2 (0.25 g, 1.83×10^{-3} mol) in 15 mL of CH_3OH was stirred for 10 min at room temperature. The complexation of macrocycle **3a** gave a red solution, the reaction mixture was stood for 30 min at room temperature, and a red solid was precipitated. The red solid was collected by filtration and washed with water. After drying under vacuum, the red solid was obtained as a zinc complex **7**: ^1H NMR (CDCl_3 , 218 K) δ 8.35 (d, 2 H, $\text{H}_{4,12}$), 8.22–8.31 (m, 4 H, $\text{H}_{4,12}$, $\text{H}_{3,13}$), 7.78 (d, 2 H, $\text{H}_{5,11}$), 7.71 (t, 2 H, $\text{H}_{6,10}$), 7.57 (d, 2 H, $\text{H}_{7,9}$), 3.12 (t, 2 H, H_{19}), 1.16–1.38 (m, 20 H, H_{20-29}), 0.85 (t, 3 H, H_{30}); UV-vis (CH_3OH) λ_{max} (ϵ) 287 (25 000), 381 (26 300), 468 (8500). IR (KBr) (cm^{-1}) 2924, 2168, 1595, 1553, 1467, 1421, 1387, 1013, 795.

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