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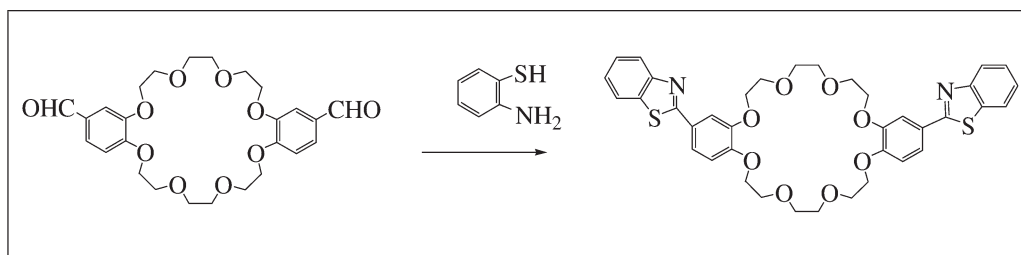
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New crown ether carrying two fluorionophores of *cis*-dibenzothiazolyldibenzo-24-crown-8 was synthesized from *cis*-diformyldibenzo-24-crown-8 and 2-aminobenzethiol. The binding behavior and the optical properties of the crown ether were examined through UV-visible spectroscopy and fluorescence spectroscopy. When complexed with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  ions, it led to intramolecular charge transfer and caused the changes of the fluorescence spectra. The protonation of the crown ether was also studied. With protonation using  $\text{CF}_3\text{COOH}$ , the absorption bands and the fluorescence spectroscopy changed, the maximal fluorescence wavelengths red shifted and the fluorescence intensity with the maximum at 433 nm enhanced strongly.

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## INTRODUCTION

Crown ethers are known to coordinate a variety of metal ions, and the binding behavior of the crown ethers with the cations has been widely investigated [1]. The binding ability of a host is governed by the size, the shape, the rigidity, and the noncovalent interactions of the cavity. When the size of the cation exactly matches the cavity of the crown ether unit, it always forms a 1:1 host/guest complex.

The fluorophores functionalized with crown ethers are of particular importance due to the sensitivity of the resulting fluorophores and the easiness of monitoring the change in the optical signal with respect to metal ion binding. The fluorophore unit with an intramolecular charge-transfer (ICT) excited state is used to produce a strong optical response to the cation-macrocyclic interaction [2–6]. The design and synthesis of crown ether derivatives combining more than one fluorophore with crown ether moiety is one current interest in this area [7–13], they can give rise to a specific fluorescence spectral change upon selective complexation with metal cations. Therefore, it is possible to design fluorescent sensors for metal cation sensing.

In this work, the objective is the preparation and optical properties of *cis*-dibenzothiazolyldibenzo-24-crown-8 (DBTDB24C8), in which benzothiazole is linked to the

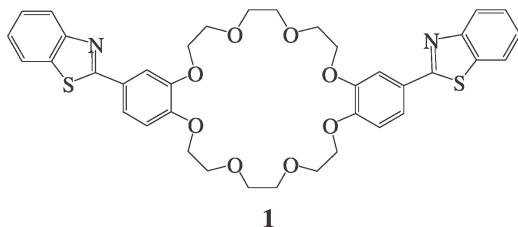
both sides of dibenzo-24-crown-8. The structure of DBTDB24C8 (**1**) is shown in Figure 1.

The comparative study of the complex formation of **1** and its protonation with  $\text{CF}_3\text{COOH}$  was reported. The absorption and fluorescence spectra of **1** were examined in chloroform solution. The effect of complexation on properties was investigated, and comparison was made among  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  cations. Very interesting phenomena was observed when complexing **1** with the cations. The results were also very interesting with the protonation of the new crown ether in different concentrations of  $\text{CF}_3\text{COOH}$  varied from 0.1 to 1%.

## RESULTS AND DISCUSSION

**Absorption spectra after complexation.** The absorption spectra of dibenzo-24-crown-8 (DB24C8), *cis*-diformyldibenzo-24-crown-8 (DFDB24C8) and **1** were examined in chloroform solution. Figure 2 displayed that the absorption maximum of the DB24C8 was at 278 nm. Two absorption peaks at 277 nm and 309 nm were observed for DFDB24C8. **1** had the absorption maximum at 324 nm.

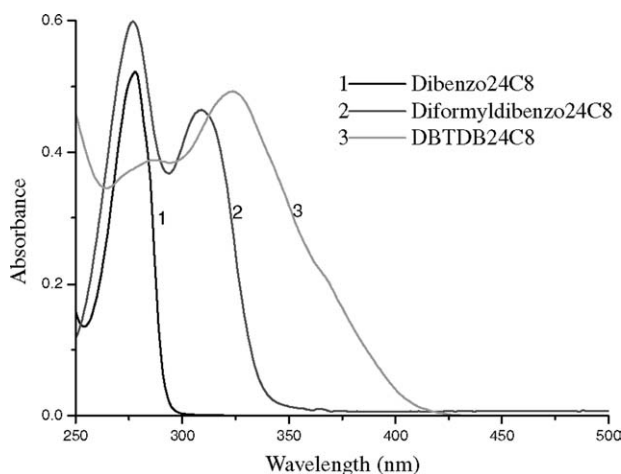
The absorption spectra reflect the complexation behavior. It was suggested that the crown ether could show not only improved cation-binding selectivity, but



**Figure 1.** The structure of *cis*-DBTDB24C8.

also specific optical response due to cation-induced intramolecular stacking of the units and “rigidification.” With the addition of the guest cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  to the solution of **1** in chloroform, the absorption spectra were changed, respectively. It was found that the absorption maximum indicating the complexation ability of **1** with guest cations of different sizes were varied. For example, with increasing the amount of  $\text{CsSCN}$  in the solution of **1** in chloroform, the absorption maximum was blue shifted from 324 to 316 nm. The blue-shifted  $\Delta\lambda$  values of **1** along with various sizes of cations are summarized in Table 1.

**Absorption spectra after protonation.** The addition of  $\text{CF}_3\text{COOH}$  into the solution of **1** with the concentration varied from 0.1 to 1% caused the absorption maximum to blue shifted from 324 to 307 nm,  $\Delta\lambda = -17$  nm. The absorption investigation was also used to compare the different addition order of the alkali metal ions and  $\text{CF}_3\text{COOH}$  into the solution. Figure 3 shows the absorption spectral changes of **1** with the addition of  $\text{CsSCN}$  and  $\text{CF}_3\text{COOH}$  in different orders. When  $\text{CsSCN}$  was first added, the absorption maximum shifted from 324 nm to 316 nm (1 $\rightarrow$ 2), and the absorbance increased. Then  $\text{CF}_3\text{COOH}$  was added to reach the concentration of 1%, the absorption maximum shifted from 316 to 309 nm (2 $\rightarrow$ 3), and the absorbance decreased. In contrast, when  $\text{CF}_3\text{COOH}$  was first added to



**Figure 2.** Absorption spectra of DB24C8 and its derivatives in chloroform.

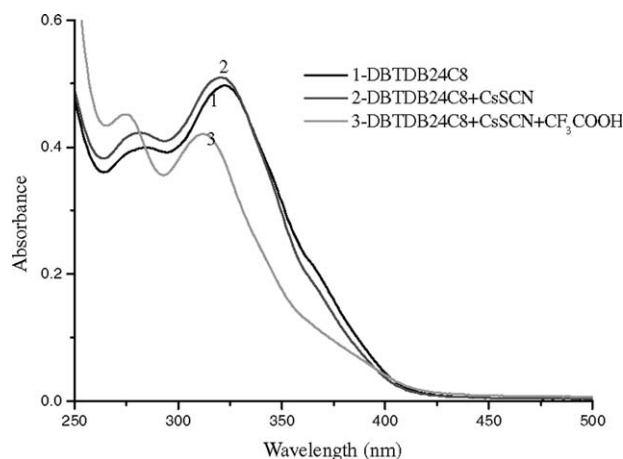
**Table 1**  
Absorption spectra of **1** in chloroform in the presence of cations.

Cations	In the absence of cations $\lambda_{\text{max}}$ (nm)	In the presence of cations $\lambda_{\text{max}}$ (nm)	$\Delta\lambda$ (nm)
$\text{Na}^+$	324	319	-5
$\text{K}^+$	324	319	-5
$\text{Rb}^+$	324	318	-6
$\text{Cs}^+$	324	316	-8

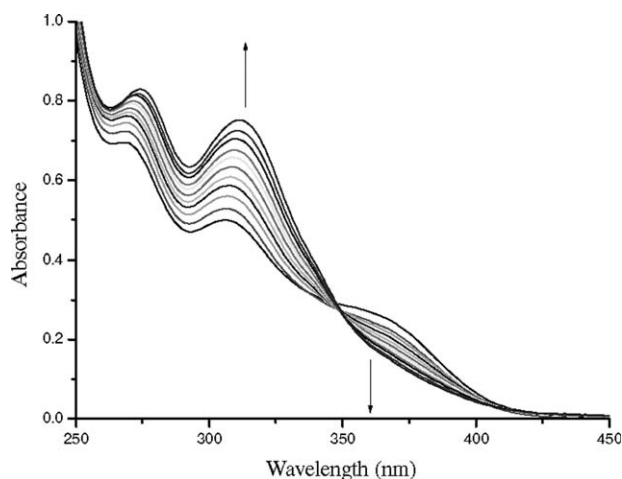
reach the concentration of 1%, the absorption maximum shifted from 324 to 307 nm, the absorbance increased slightly, while that the absorbance at 380 nm increased evidently. Then  $\text{CsSCN}$  was added, as was shown in Figure 4, the absorption maximum red shifted from 307 to 312 nm, and the absorbance increased significantly. Meanwhile, the absorption at 380 nm decreased greatly. It indicated that the intramolecular charge transfer took place between the metal ions in dibenzo-crown ether center moiety with the two benzothiazole groups.

**Fluorescence spectra after complexation.** Fluorescence study is useful in examining the interaction between the metal ions and benzo-crown ether moiety. Figure 5 gives fluorescence spectra of **1** with the addition of  $\text{CsSCN}$  in chloroform solution. The fluorescence intensity of free **1** reached its maximum at 383 nm with the excitation at 324 nm. The maximum increased with the addition of  $\text{Cs}^+$  and its maximal intensity wavelength slightly shifted from 383 to 385 nm.

The fluorescence properties of **1** with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  ions were all examined in chloroform solution with the excitation at 324 nm. The fluorescence data were summarized in Table 2. The effect of the cations studied depends on the size of the cations as well as the macrocycle moiety cavity size. The order of the fluorescence intensity increased ratio  $I/I_0$  of the cations was  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$ .



**Figure 3.** Absorption spectra of **1** after added  $\text{CsSCN}$  and then  $\text{CF}_3\text{COOH}$ .

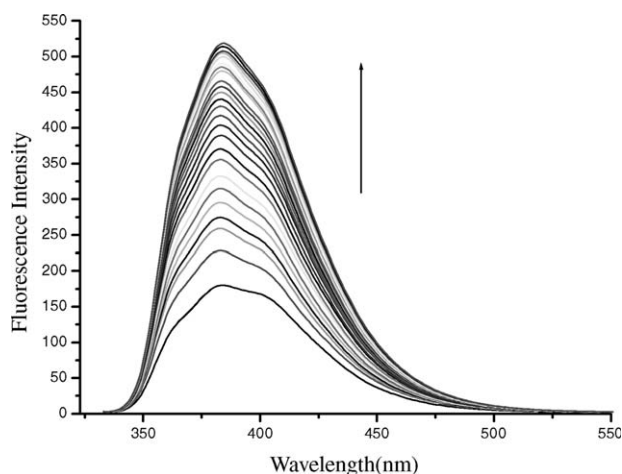


**Figure 4.** The absorption spectra of **1** gradually changed with the addition of CsSCN after its protonation with CF<sub>3</sub>COOH.

The results showed that the binding ability of Cs<sup>+</sup> was higher than other alkali metal ions since the size of 24-crown-8 cavity matches the radius of Cs<sup>+</sup>.

**Fluorescence spectra after protonation.** Figures 6 and 7 showed the fluorescence spectra changes due to the different addition order of CsSCN and CF<sub>3</sub>COOH into **1**. When CF<sub>3</sub>COOH was added to reach the concentration of 1% at first, the fluorescence intensity with the maximum at 433 nm suddenly increased strongly. Then CsSCN was titrated into the solution. With increasing the amount of CsSCN, the fluorescence intensity at 433 nm decreased, meanwhile the fluorescence intensity at 385 nm increased (Figure 6).

In contrast, when CsSCN was added at first, the fluorescence intensity with the maximum at 385 nm increased, but the increased value was not so high than that of the CF<sub>3</sub>COOH. The shape of fluorescence spectra



**Figure 5.** Fluorescence spectra of **1** with the addition of CsSCN in chloroform.

**Table 2**

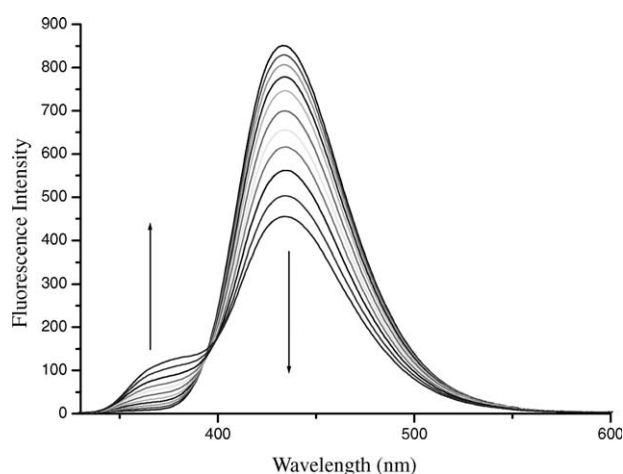
Fluorescence spectra of **1** in CHCl<sub>3</sub> after addition of cations.

Cations	In the absence of cations		In the presence of cations	
	$\lambda_f$ (nm)	Stokes shift (nm)	$\lambda_{fmax}$ (nm)	Stokes shift (nm)
Na <sup>+</sup>	383	59	384	65
K <sup>+</sup>	383	59	384	65
Rb <sup>+</sup>	383	59	384	66
Cs <sup>+</sup>	383	59	385	69

changed, the fluorescence intensity maximum red shifted from 385 to 433 nm and subsequently increased distinctly with the titration of CF<sub>3</sub>COOH from the concentration of 0.1 to 1%, meanwhile the fluorescence intensity at 385 nm decreased.

From the results of comparison, it was supposed that it led to a change in the equilibrium position of the metal cation, which was predominantly bound to six of the eight oxygen atoms of the DB24C8 moiety in the macroheterocycle. When a metal ion was added, the interaction between crown ether cavity and the cation took place, the cation in close interaction with the donor or the acceptor moiety would change the photophysical properties of the fluorophore because the complexed cation affected the efficiency of intramolecular charge transfer [14].

Addition of CF<sub>3</sub>COOH to the chloroform solution caused red shifts of the long wavelength absorption band. It is understandable that the protonation of the basic benzothiazole nitrogen with CF<sub>3</sub>COOH would cause enhancement of the  $\pi$ -acceptor properties of this heteroring. The consequent increased ICT transition from the HOMO of the  $\pi$ -rich benzo-crown ring to the LUMO of the benzothiazolium ring is responsible for the observed red shifts upon protonation [14–18].



**Figure 6.** Fluorescence spectra of **1** first added CF<sub>3</sub>COOH and then CsSCN.

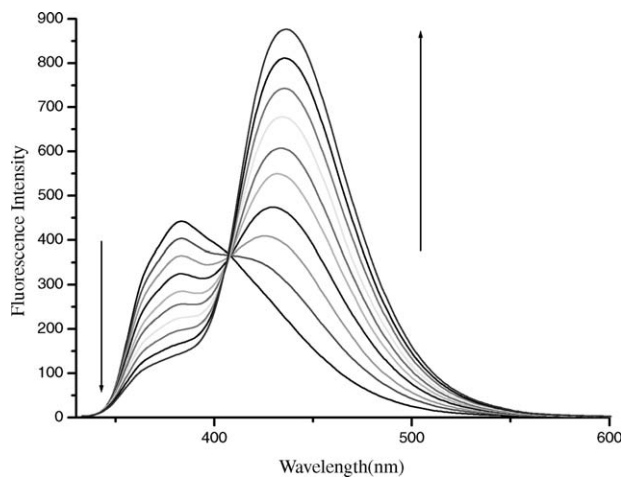


Figure 7. Fluorescence spectra of **1** first added CsSCN and then CF<sub>3</sub>COOH.

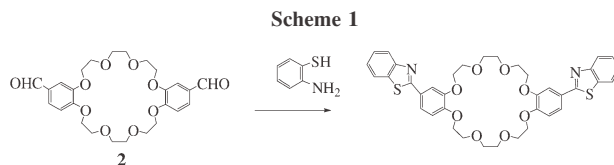
After CF<sub>3</sub>COOH was added, the protonation of the two benzothiazole nitrogen atoms with CF<sub>3</sub>COOH caused the enhancement of the  $\pi$ -acceptor properties of the heterorings [15]. As the alkali metal ions were added into the DBTDB solution, the intramolecular charge transfer between the crown moiety center and the benzothiazole group led to the change of the fluorescence intensity.

## CONCLUSION

The new crown ether carrying two fluoroionophores of **1** was synthesized and characterized. The binding behavior of **1** with alkali metal ions and the optical properties were investigated through UV-visible spectra and fluorescence spectra. The results showed that the intramolecular charge transfer took place between the metal ions in dibenzo-crown ether center moiety with the two benzothiazole groups when alkali metal ions were added. The Cs<sup>+</sup> ions was very effective for **1** due to the fact that it can form stable complexes than other alkali ions. CF<sub>3</sub>COOH can cause great enhancement of the fluorescent properties owing to the effect of protonation.

## EXPERIMENTAL

**Equipment and reagents.** Elemental analyses were performed using a Vario EL Elementar analyser. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained on a Varian Mercury 300 MHz NMR spectrometer in CDCl<sub>3</sub> solution. The chemical shifts were expressed in ppm ( $\delta$  scale) using tetramethylsilane as an internal standard. GC-MS data were obtained from a Shimadzu GC-mass spectrometer of GCMSD-QP5050. FAB MS data were obtained from a Jeol JMS 700 mass spectrometer. FTIR spectra were recorded on a Mattson Instrument Genesis II spectrometer. The melting points were recorded on a MEL melting point apparatus and were uncorrected. The absorption spectra were taken on a Hewlett Packard UV-visible spectro-



photometer of type UV-8453. Fluorescence spectra were recorded on a JASCO FP-6300 spectrofluorometer.

All the reagents were purchased from Aldrich Company and used as received. Spectral grade solvents were obtained from Junsei Chemical Co. Ltd. of Japan.

**Synthesis and characterization.** The synthetic route of DBTDB24C8 is outlined in Scheme 1. The synthesis of *cis*-diformyldibenzo-24-crown-8 was described elsewhere [19].

**Synthesis of diformyldibenzo-24-crown-8 (2).** **2** was synthesized according to the method described [19]. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 3.83–3.87 (m, 8H), 3.90–3.98 (m, 8H), 4.19–4.25 (m, 8H), 6.92–6.95 (d, 2H), 7.40(d, 2H), 7.44 (dd, 2H), 9.82 (s, 2H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 190.87, 154.21, 149.12, 130.19, 126.95, 111.74, 110.84, 71.63, 71.50, 69.60, 69.50, 69.42, 69.39; IR (KBr, cm<sup>-1</sup>): 3067.3, 2954.4, 2888.7, 2849.1, 2735.9, 1697.6, 1578.0, 1517.3, 1437.7, 1272.5, 1126.0, 1058.3, 953.5, 792.3, 821.4, 753.1; MS(GC): *m/z* 504.1 [M]<sup>+</sup>, calc. for C<sub>26</sub>H<sub>32</sub>O<sub>10</sub>, M, 504.2; Anal. calc. for C<sub>26</sub>H<sub>32</sub>O<sub>10</sub>: C, 61.90; H, 6.39; Found: C, 62.17; H, 6.14.

**Synthesis of 1.** Diformyldibenzo-24-crown-8 **2** (108 mg, 0.2 mmol) and 2-aminobenzothiazole (76 mg, 0.6 mmol) were dissolved in absolute ethanol (8 mL). The mixture was stirred and refluxed for 24 h. After cooled to r.t. and filtered, the crude product was purified by recrystallization from ethanol, to give 67 mg deep yellow solid. Yield 47%. mp: 74–77°C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 3.71–3.78 (m, 8H), 3.87–3.93 (m, 8H), 4.12–4.25 (m, 8H), 6.80 (d, 2H), 7.05–7.07 (m, 2H), 7.24–7.28 (m, 2H), 7.47–7.56 (dd, 2H), 7.73–7.76 (d, 2H), 7.85–7.92 (d, 2H), 8.21–8.26 (dd, 2H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 167.82, 154.09, 152.13, 149.08, 148.99, 148.89, 136.78, 134.87, 134.36, 131.91, 131.91, 126.82, 126.56, 126.19, 124.84, 122.79, 121.50, 112.34, 111.50, 71.50, 71.41, 69.77, 69.33; IR(KBr, cm<sup>-1</sup>): 3031.3, 2917.3, 2859.7, 1617.5, 1598.1, 1564.4, 1507.6, 1466.9, 1432.2, 1356.7, 1321.1, 1267.3, 1166.9, 1128.3, 1102.4, 1061.0, 1004.7, 852.5, 839.4, 737.5; MS(FAB): *m/z* 715.5[M+H]<sup>+</sup>, calc. for C<sub>38</sub>H<sub>38</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>, M, 714.2; Anal. calc. for C<sub>38</sub>H<sub>38</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: C, 63.79; H, 5.36; N, 3.92; S, 8.97. Found: C, 63.51; H, 5.47; N, 4.13, S, 9.21.

**Absorption and fluorescence measurements.** **1** was dissolved in chloroform to make a  $2 \times 10^{-6}$  M solution. The alkali metal salts of NaSCN, KSCN, RbSCN, and CsSCN were made into  $1 \times 10^{-4}$  M solutions in methanol, respectively. Complexation was studied by the titration of the metal salt solution into the chloroform solution of **1**. CF<sub>3</sub>COOH was used as the protonation reagent to check the absorption and fluorescence spectra with the different concentrations from 0.1 to 1% in chloroform solution. The absorption and fluorescence spectra were examined at 25°C.

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