JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2007; **20:** 900–907
Published online 9 May 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/poc.1199

Absorption- and fluorescence-spectral sensing of alkali metal ions in anionic micelle solutions containing crowned spirobenzopyrans

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Received 27 December 2006; revised 14 February 2007; accepted 20 March 2007

ABSTRACT: Spirobenzopyran derivatives bearing a monoazacrown ether moiety (monoaza-12-crown-4, -15-crown-5, and -18-crown-6) and an octadecyl group as a lipophilic moiety, called crowned spirobenzopyrans were synthesized, which can be dissolved in anionic micelle solutions. We examined absorption-and fluorescence-spectral changes of micelle solutions containing a crowned spirobenzopyran on addition of alkali metal ions. The crowned spirobenzopyrans are in their merocyanine form in an anionic micelle solution even under dark conditions, showing a significant absorption in the visible region which is attributable to the merocyanine moiety. Crowned spirobenzopyran bearing a monoaza-12-crown-4 moiety exhibited a drastic hypsochromic shift in the absorption and also an enhanced fluorescence on addition of Li^+ to the micelle solutions under alkaline conditions. These spectral changes can be attributed to a strong interaction between Li^+ bound by the crown ether moiety and a phenolate ion of the merocyanine moiety. Similar absorption and fluorescence-spectral changes were induced in the anionic micelle solutions containing the other crowned spirobenzopyrans on addition of alkali metal ions. The intensity of the absorption-spectral changes in the systems of the three crowned spirobenzopyrans, however, differed from each other, depending on the strength of interaction between a metal ion bound to the crown ether moiety and the phenolate ion of the merocyanine moiety. On the other hand, the extent of enhanced relative fluorescence intensity is dependent on the strength of interaction between metal ion and a nitrogen atom of azacrown ether moiety, because the fluorescence spectrum is quenched by photoinduced electron transfer (PET) from the nitrogen atom to the merocyanine moiety.

KEYWORDS: crowned spirobenzopyran; anionic micelle; absorption spectra; fluorescence spectra; lithium ion; metal ion complex; photoinduced electron transfer (PET)

INTRODUCTION

The spirobenzopyran is well-known as a photochromic compound, which isomerizes from its colorless and electrically neutral spiropyran form to the corresponding colored and zwitterionic merocyanine form by UV-light irradiation, and *vice versa* by visible-light irradiation in the non-polar solvent.[1–4] We have studied on the spirobenzopyran derivatives bearing crown ether moiety, called crowned spirobenzopyrans.[5–9] Previously, we reported that the spirobenzopyran moiety of the crowned spirobenzopyran isomerizes to its merocyanine form, even under dark conditions and exhibits a drastic spectral change as mentioned above when its crown ether moiety complexes a metal ion. Thus, crowned spirobenzopyrans are also useful for colorimetric reagents for alkali metal ion.

There is a lot of colorimetric reagents for liquid-liquid extraction of metal ions and/or water miscible organic compounds, and metal-ion concentrations can be measured from the absorption spectra of the reagents in the organic phase for liquid-liquid extraction.[10] Water-immiscible organic solvents such as halogenated hydrocarbons, which are not environment-friendly, have generally been used in liquid-liquid extraction. Thus, for reducing environmental burden, micelle system using lipophilic colorimetric reagents is an alternative to the liquid-liquid extraction for metal-ion determination.[11,12] Surfactants are usually used for forming micelles in aqueous solution, since it is difficult to obtain micelles consisting of only colorimetric reagents because of the structural balance between the lipophilic and hydrophilic

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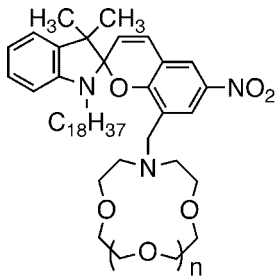
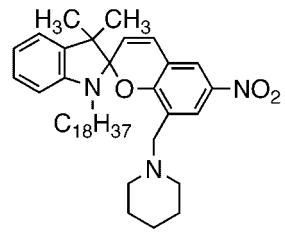
moieties of the reagents. The boundary phase between aqueous media and micelle is hydrophilic and/or has electric charges, while the inner side of the micelle is highly lipophilic. So, lipophilic colorimetric extraction reagents can be applied to micelle systems.[13–16]

In this study, we synthesized crowned spirobenzopyrans **1**–**3**, which have a monoaza-12-crown-4, -15-crown-5, or -18-crown-6 moiety, respectively, as the metal-ion binding moiety as well as an octadecyl group as the lipophilic moiety. Spirobenzopyran derivative **4**, which has a piperidine moiety instead of a crown ether moiety, was also synthesized for comparison. The crowned spirobenzopyrans were dissolved into an anionic micelle solution for colorimetry of alkali metal ions, and our previous study reported remarkable absorption-spectral changes of anionic micelle solutions containing **1**.[17] Here we report that the merocyanine form of the crowned spirobenzopyran exhibits significant changes in fluorescence spectra in the anionic micelle solutions either at neutral pH or in the presence of an appropriate metal ion under alkaline conditions (as shown in the structural formulas). Therefore, their absorption- and fluorescence-spectral changes of micelle solutions containing **1**–**4** were examined in the presence of alkali metal ions.



1: n = 1
2: n = 2
3: n = 3



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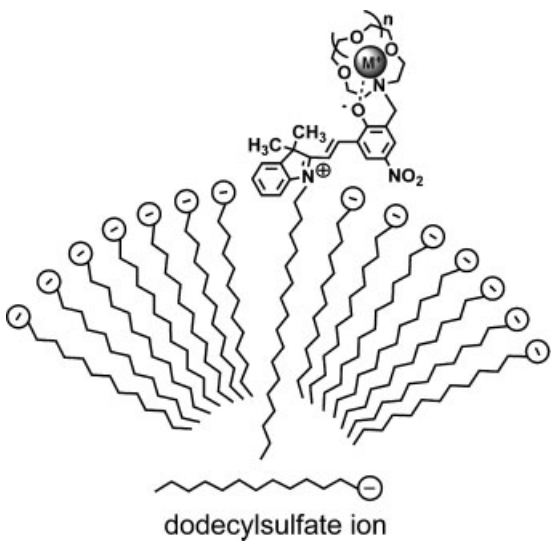

EXPERIMENTAL

Materials and instruments

Crowned spirobenzopyrans **1**–**3** and spirobenzopyran derivative bearing piperidine moiety **4** were synthesized in the same manner as described in a previous paper.[10] Tetramethylammonium dodecylsulfate (TMADS) was prepared by a reported procedure using sodium dodecylsulfate (SDS), which was purchased from Nacalai Tesque, Inc.[18] All metal salts were of analytical grade and were purchased from Kanto Chemical Co. Ltd. Tetramethylammonium hydroxide (TMAOH) from Nacalai Tesque, Inc. was used as received. Neutral Red and quinine sulfate dihydrate were of analytical grade and were purchased from Katayama Chemical Industries Co. Ltd and Wako Pure Chemical Industries Ltd, respectively. Water was deionized. The absorption and fluorescence spectra were measured with HITACHI U-2010 and SHIMAZU Co. RF-5000, respectively.

Measurements of absorption and fluorescence spectra

The measurement solution containing 1.5×10^{-5} mol dm^{-3} crowned spirobenzopyran and 0.01 mol dm^{-3} TMADS was prepared in 50 ml volumetric flask and was allowed to stand for a whole day under dark conditions. The apparent values for pH of the micelle solutions were adjusted by the addition of 1 mol dm^{-3} HCl and 1.1 mol dm^{-3} TMAOH to 10 ml of the above-mentioned solutions. The solutions were prepared just before the measurements. The absorption and fluorescence spectra were measured at ambient temperature. The fluorescence intensity of quinine solution was used as the reference.

RESULTS AND DISCUSSION

Effects of pH on absorption spectra

Spirobenzopyran derivatives **1**–**4** are insoluble in water but they were soluble in anionic micelle solutions which were prepared using TMADS. Typical absorption spectra of the anionic micelle solutions containing **1** under different pH conditions were shown in Fig. 1. The spectrum of the solution showed a maximum absorption wavelength at 521 nm under neutral-pH conditions. This spectrum was attributed to the merocyanine form of the spirobenzopyran moiety of **1**, showing that the spirobenzopyran moiety of **1** isomerizes to its merocyanine form in the anionic micelle solution at neutral pH. This is because of the reason that protonation on the nitrogen atom of monoaza-12-crown-4 moiety occurred in the neutral-pH solution, resulting in the strong interaction between the proton on the nitrogen atom and the

DOI: 10.1002/poc

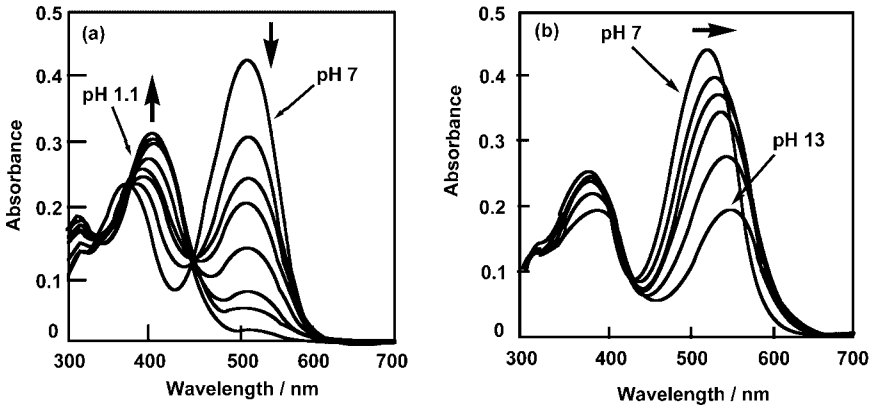

Figure 1. Absorption-spectral changes of micelle solution containing **1** under (a) acidic, and (b) basic conditions. (**1**) = 1.5×10^{-5} mol dm^{-3}, (TMADS) = 0.01 mol dm^{-3}; apparent pH: (a) 7.0, 3.5, 3.2, 3.1, 2.7, 2.3, 2.1, 2.0, 1.7, 1.4, 1.1, (b) 7.0, 10.5, 10.8, 11.0, 11.3, 11.7, 11.9, 12.1, 12.3, 12.7, 13.0

phenolate anion induced by the ring opening. Under acidic conditions (Fig. 1(a)), the absorbances at 521 nm and at 404 nm were decreased and increased, respectively, with the decreasing pH. The increase in the absorbance at 404 nm is caused by protonation on the phenolate ion of the merocyanine moiety. On the other hand, under alkaline conditions, the maximum absorption wavelength exhibited a bathchromic shift from 521 nm at pH 7 to 549 nm at pH 13 with the increase in pH, as shown in Fig. 1(b). This result shows that the proton on the nitrogen atom of monoaza-12-crown-4 moiety strongly interacts with the phenolate ion of the merocyanine moiety at neutral pH to withdraw electrons from the merocyanine moiety. With increasing pH, the protonation on the nitrogen atom is suppressed and the electron density of the merocyanine moiety is increased to cause a bathochromic shift in the absorption spectra.[11,19] Similar spectral shifts with a pH change were also observed for the anionic micelle solution containing crowned spirobenzopyrans **2**, **3**, and **4**.

Absorption-spectral change on addition of alkali metal ion

The effects of the addition of an alkali metal ion on the absorption spectra for crowned spirobenzopyrans were examined for anionic micelle solutions containing spirobenzopyran derivatives **1**–**4** under dark conditions. Since the nitrogen atom on the crown ether moiety of crowned spirobenzopyran is protonated under neutral-pH conditions as mentioned above, the crown ether moiety hardly forms complexes with a metal ion. Thus, the micelle solutions were adjusted to pH 13 using TMAOH for deprotonation on the nitrogen atom of monoazacrown ether moiety. Tetramethylammonium ion forms no complex with 12-crown-4, 15-crown-5, and 18-crown-6 moieties, and rarely interacts with the phenolate ion of the merocyanine moiety.

For the micelle solution containing **1**, the absorption-spectral change and the shift of maximum absorption wavelength on addition of Li^+ were as shown in Fig. 2 and Fig. 3, respectively. The maximum absorption wavelength was 549 nm at pH 13 in the absence of metal ion, and was then shifted to 523 nm. The spectral change was accompanied by the largest hypsochromic shift in the presence of 8.0×10^{-2} mol dm^{-3} Li^+.[17] Monoaza-12-crown-4 of **1** forms stable complexes with Li^+ due to the size-fit of Li^+ with monoaza-12-crown-4. Lithium ion bound by the crown ether moiety strongly interacts with the phenolate ion of the merocyanine moiety because of the high charge density of Li^+. The interaction brings about the electron withdrawal from the merocyanine moiety, causing the hypsochromic shift of the absorption spectra. Some shift of the maximum absorption wavelength was observed on the addition of Na^+, the maximum absorption wavelength being 545 nm at the metal ion concentration of 8.0×10^{-2} mol dm^{-3}. The interaction between Na^+ and the phenolate ion of the merocyanine moiety is

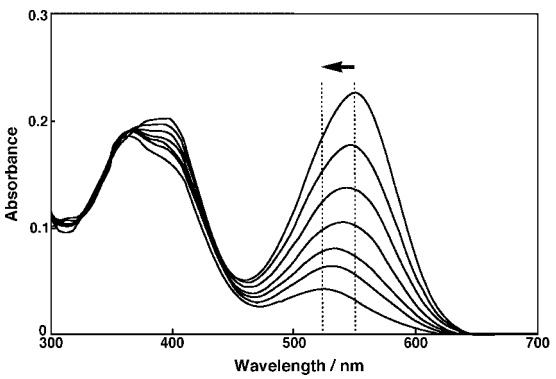

Figure 2. Absorption-spectral changes of micelle solution containing **1** and Li^+ at different concentrations. (**1**) = 1.5×10^{-5} mol dm^{-3}, (TMADS) = 0.01 mol dm^{-3}; pH = 13. (Li^+) = 0, 2.8×10^{-3}, 5.5×10^{-3}, 8.1×10^{-3}, 1.6×10^{-2}, 2.4×10^{-2}, 3.9×10^{-2}, 7.6×10^{-2} mol dm^{-3}

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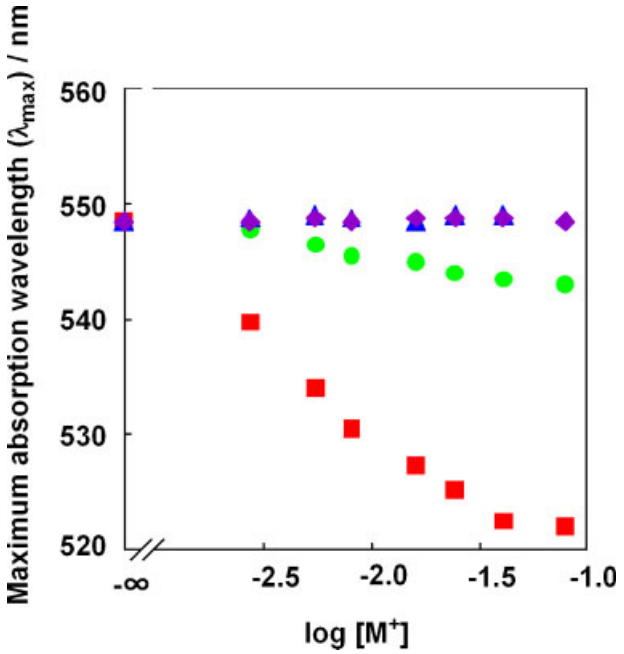

Figure 3. Changes in maximum absorption wavelength of micelle solution containing **1** in the presence of alkali metal ion (from Ref. 17). (**1**) = 1.5×10^{-5} mol dm^{-3}, (TMADS) = 0.01 mol dm^{-3}, (TMAOH) = 0.1 mol dm^{-3}; ■: Li^+, ●: Na^+, ▲: K^+, ◆: Cs^+ (This figure is available online at www.interscience.wiley.com/journal/poc)

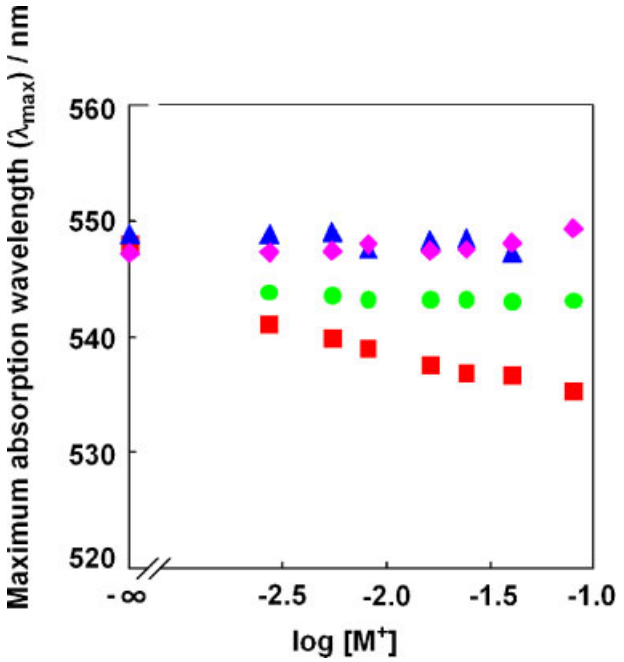

Figure 4. Changes in maximum absorption wavelength of micelle solution containing **2** in the presence of alkali metal ion. (**2**) = 1.5×10^{-5} mol dm^{-3}, (TMADS) = 0.01 mol dm^{-3}, (TMAOH) = 0.1 mol dm^{-3}; ■: Li^+, ●: Na^+, ▲: K^+, ◆: Cs^+ (This figure is available online at www.interscience.wiley.com/journal/poc)

weak due to the lower charge density than that of Li^+, although the Na^+ complex with monoaza-12-crown-4 is as stable as Li^+ complex. No shift in the maximum absorption wavelength was observed on the additions of K^+ and Cs^+, which hardly form any complex with monoaza-12-crown-4.

The largest shift in the maximum absorption spectra of the micelle solution containing **2**, which has a monoaza-15-crown-5 moiety, was also observed on the addition of Li^+, as shown in Fig. 4. Contrary to the general understanding that monoaza-15-crown-5 forms the most stable complex with Na^+ of all alkali metal ions, the present spectral changes might conflict with the size-fit coccept.[20] It is worth to note (Fig. 4) that the hypsochromic shift of maximum absorption wavelength was already leveled off on the addition of 2.7×10^{-3} mol dm^{-3} Na^+, because monoaza-15-crown-5 of **2** forms stable complexes with Na^+ quantitatively at this concentration. On the other hand, the hypsochromic shift in the maximum absorption wavelength lasted with the increase in the Li^+ concentration up to 8.0×10^{-2} mol dm^{-3}. These results show that the interaction of the phenolate ion of the merocyanine moiety with Li^+ is much stronger than that with Na^+, although monoaza-15-crown-5 forms more stable complexes with Na^+ than Li^+. That is to say, the extent of the shifts in the maximum absorption wavelength reflect the strength of the interaction with the phenolate ion of the merocyanine moiety, but do not necessarily do the stabilities of the crown ether complexes with the metal ions.

In the absorption-spectral changes of micelle solutions containing **3**, which has a monoaza-18-crown-6 moiety, similar phenomena described above were typically observed, as shown in Fig. 5. The largest hypochromic shift was also attained in the presence of Li^+, which is not easy to form complexes with monoaza-18-crown-6. On the other hand, an anomalous bathochromic shift in the maximum absorption wavelength was observed on the addition of K^+, which is well known to form most stable complexes with monoaza-18-crown-6 of all the alkali metal ions. The shift is leveled off at 2.7×10^{-3} mol dm^{-3} in K^+. It is anticipated that some protons, which interacts with the phenolate ion of the merocyanine moiety most powerfully, remained on the nitrogen atom of monoaza-18-crown-6 at pH 13, and that the ion exchange between the proton and K^+ formed stable monoaza-18-crown-6 – K^+ complexes. Monoaza-18-crown-6 – K^+ complex should rarely affect the charge density of the merocyanine moiety and therefore its absorption spectrum, since K^+ hardly interacts with the phenolate ion of the merocyanine moiety. In order to investigate the change in the acidity constant in the anionic micelle, we titrated Neutral Red as a pH indicator by using TMAOH (Fig. 6). The titration curve was shifted to the alkaline side by about pH 2.5 in the anionic micelle solution, probably because sulfonate anions covering the surface of the

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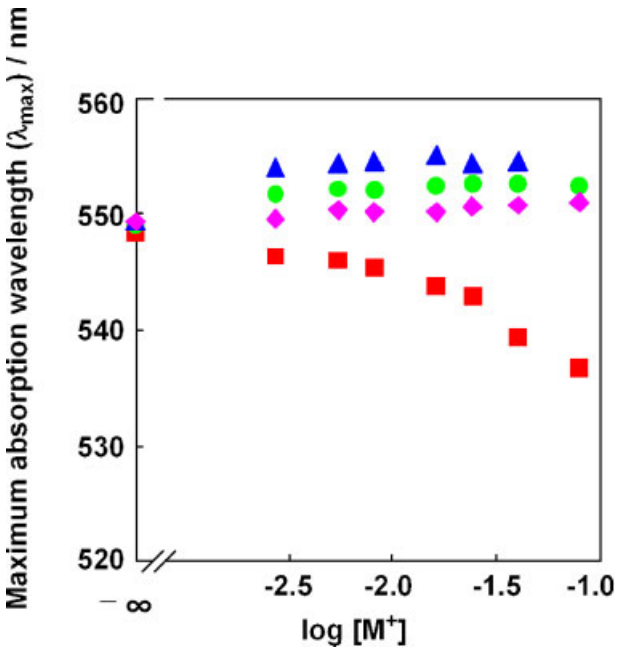

Figure 5. Changes in maximum absorption wavelength of micelle solution containing **3** in the presence of alkali metal ion. (**3**) = 1.5×10^{-5} mol dm^{-3}, (TMADS) = 0.01 mol dm^{-3}, (TMAOH) = 0.1 mol dm^{-3}; ■: Li^+, ●: Na^+, ▲: K^+, ◆: Cs^+ (This figure is available online at www.interscience.wiley.com/journal/poc)

anionic micelle prevent approaching of hydroxide ions to the lipophilic compound in the micelle core. The minus logarithmic value of acid dissociation constant for monoaza-18-crown-6 was shifted to *ca.* 11.5, which shows that 3–6% of the nitrogen atom in the monoaza-18-crown-6 moiety of **1** is protonated even at pH 13. For the micelle solution of compound **4**, no absorption-spectral change was observed in the presence of any alkali metal ion at apparent pH 13. These results demonstrate that the absorption-spectral changes of the micelle solution containing spirobenzopyran derivatives at pH 13 are caused by the interaction between a metal ion bound by crown ether and the phenolate ion of the merocyanine moiety. That is to say, the crown ether moiety is absolutely essential for inducing the absorption-spectral change of spirobenzopyran derivatives in the anionic micelle solution.

Effects of pH on fluorescence spectra

The anionic micelle solutions containing spirobenzopyran derivatives **1**–**4** exhibited strong fluorescence under neutral-pH conditions. The fluorescence spectra for the micelle solutions containing crowned spirobenzopyran **1** under different pH conditions were examined at an excitation wavelength of 535 nm (Fig. 7). The fluorescence intensity at the maximum fluorescence wavelength was decreased with an increase of pH and was almost quenched at pH 13. It is probably because the photoinduced electron transfer (PET) from the nitrogen atom of the crown ether moiety to the fluorescence-emitting merocyanine moiety reduced the fluorescence intensity due to the deprotonation of the nitrogen atom at pH 13. Such a phenomenon was also observed for the other crowned spirobenzopyrans **2** and **3**. Several reviews covering PET and photoinduced charge transfer (PCT) have been reported for the interaction between an electron donor site on substrate recognition moiety

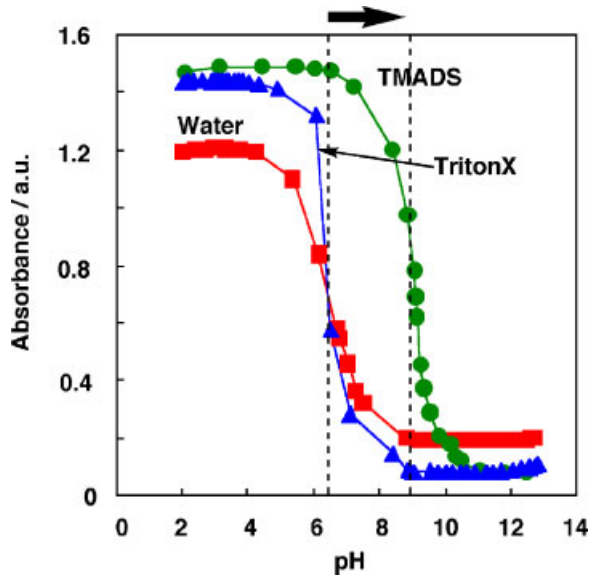

Figure 6. Plots of absorbance at different pH in aqueous solutions and micelle solutions containing Neutral Red (This figure is available online at www.interscience.wiley.com/journal/poc)

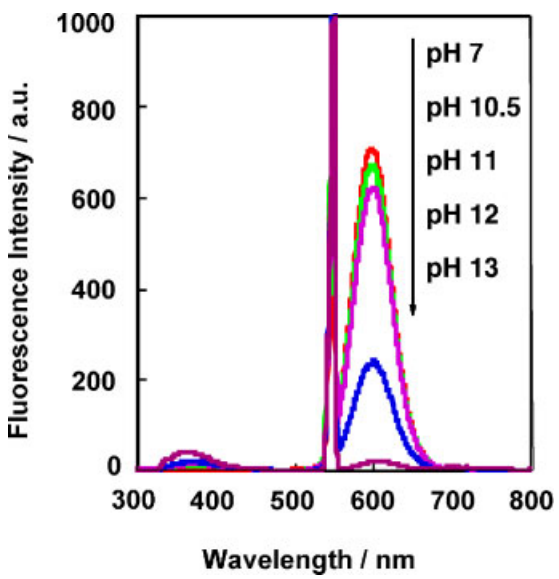

Figure 7. Fluorescence-spectral change with increasing pH of micelle solutions containing **1**. Excitation wavelength is 540 nm (This figure is available online at www.interscience.wiley.com/journal/poc)

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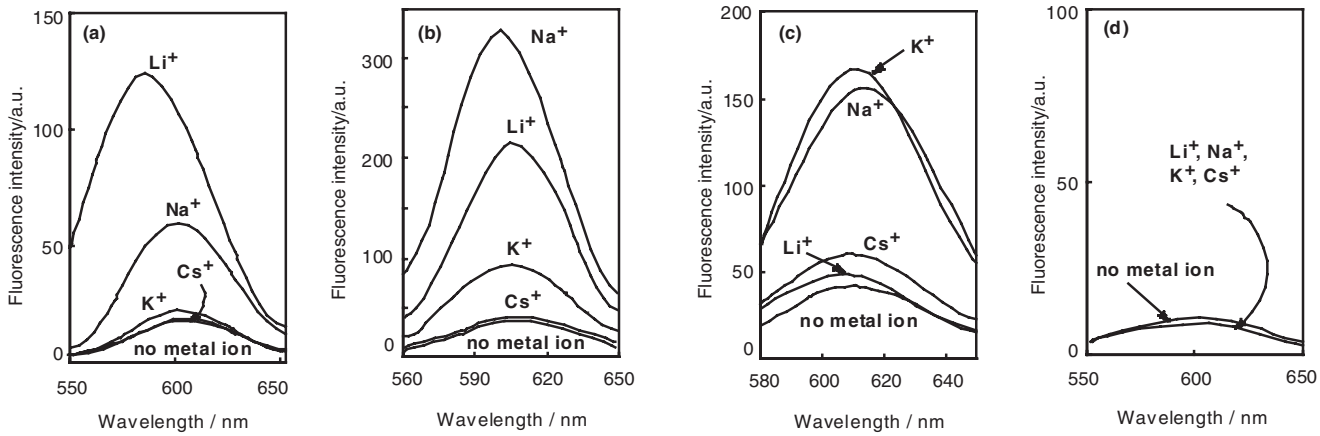

Figure 8. Fluorescence spectra in micelle solutions containing alkali metal ions and (a) **1**, (b) **2**, (c) **3**, and (d) **4** at pH 13

bearing a fluorophore and a complexed substrate, such as metal ions and organic compounds.[21–23]

Fluorescence-spectral change on addition of alkali metal ion

The changes in the relative fluorescence intensities of crowned spirobenzopyrans **1–3** on addition of a metal ion were examined in the anionic micelle solution at pH 13. The fluorescence spectra of the micelle solutions containing spirobenzopyran derivatives **1–4** in the presence of alkali metal ions were shown in Fig. 8. The largest increase in the fluorescence spectrum was observed on the addition of Li^+ for micelle solution containing **1** (Fig. 8(a)). This result is in accord with the change in the maximum absorption wavelength for the micelle solution of **1** in the presence of Li^+ (Fig. 3). Monoaza-12-crown-4 moiety forms stable complexes with Li^+, the nitrogen atom of monoazacrown ether moiety tightly interacting with Li^+. Therefore, the PET from the crown-ether nitrogen atom to the merocyanine moiety is strongly depressed to increase the relative fluorescence intensity. An enhancement in the fluorescence was also observed on the addition of Na^+ which forms the complexes with monoaza-12-crown-4, although it was not so remarkable as the corresponding Li^+ addition system due to the lower charge density as well as the larger ion size.

For the micelle solution containing **2**, the largest fluorescence-spectral change was observed on the addition of Na^+ [Fig. 8(b)]. Sodium ion forms the most stable complex with monoaza-15-crown-5 moiety of **2** of all alkali metal ions. This result, however, does not agree with the change in the maximum absorption spectra of the micelle solution containing **2**, which exhibited the largest change on the addition of Li^+. It is because that the change in the maximum absorption wavelength of the merocyanine moiety depends upon the strength of interaction between a metal ion and the phenolate ion of the merocyanine moiety, thus Li^+ interacting with the phenolate ion stronger than Na^+ to cause the largest change in the maximum absorption wavelength. On the other hand, Na^+, which forms the most stable complex with monoaza-15-crown-5 moiety of **2**, interacts most powerfully with the nitrogen atom to suppress the PET, should increase the fluorescence intensity, as the fluorescence spectrum changed depending on the extent of PET from the nitrogen atom of the crown ether moiety to the merocyanine moiety. Such a phenomenon was also observed for the micelle solution containing **3** (Fig. 8(c)). The fluorescence spectra of the micelle solution containing **3** showed the largest change on the addition of K^+, since monoaza-18-crown-6 generally forms stable complexes with K^+ selectively. In this case, Li^+ hardly affects the fluorescence spectrum for the micelle solution of **3**. This result shows that the fluorescence-spectral change is governed by the strength of the interaction between the metal ion and nitrogen atom of the crown ether moiety of the crowned spirobenzopyran derivative. That is to say, the more stable complex a metal ion forms with the monoazacrown ether moiety, the larger the fluorescence-spectral change is. For comparison, no fluorescence spectral change of the micelle solution containing **4** was observed in the presence of any alkali metal ion (Fig. 8(d)).

Fluorescence-spectral change with metal ion concentration

Changes in the relative fluorescence intensity at the maximum fluorescence wavelength of the micelle solutions containing crowned spirobenzopyrans **1–3** were examined at different metal ion concentrations, which were varied in the concentration range between 5.0×10^{-4} and 8.0×10^{-2} mol dm^{-3} (Fig. 9). The relative fluorescence intensities increased with increasing

DOI: 10.1002/poc

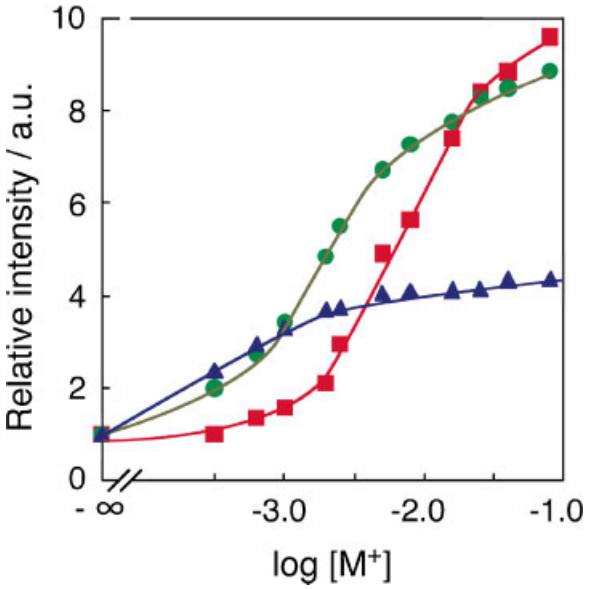

Figure 9. Changes in relative fluorescence spectra in micelle solutions containing (■) **1** and Li^+, (●) **2** and Na^+, (▲) **3**, and, K^+ at pH 13 (This figure is available online at www.interscience.wiley.com/journal/poc)

metal ion concentrations in all of the cases. However, the linearly increasing concentration ranges of the relative fluorescence intensities of the micelle solutions containing **1**, **2**, and **3** were 2.5×10^{-3}–5.0×10^{-2} mol dm^{-3} for Li^+, 5.0×10^{-4}–1.0×10^{-2} mol dm^{-3} for Na^+, and up to 5.0×10^{-3} mol dm^{-3} for K^+, respectively. Such a difference in the linear range is dependent on the different stabilities of the metal ion complexes of crowned spirobenzopyrans. We tried to calculate approximate values of complex stability constants (K) from the plots in Fig. 9 to obtain the values as follows: $\log K = 2.2$, 2.6 and 3.3 for Li^+-**1**, Na^+-**2**, and K^+-**3** complexes, respectively. Furthermore, the plots of the relative fluorescence intensities for Li^+-**1** and Na^+-**2** can be used as the calibration curves for fluorescence analyses of these metal ions.[24]

The fluorescence intensities of these micelle solutions containing 8.0×10^{-2} mol dm^{-3} metal ion were different from each other. It is because the extent of PET from the electron on the crown-ether nitrogen atom governs its fluorescence intensity. Thus, Li^+, which has the highest charge density among the alkali metal ions, strongly withdraws electrons on the nitrogen atom by complexing with the monoazacrown ether moiety to suppress the PET drastically and then to increase the fluorescence intensity most significantly. It is supported by the result that the fluorescence intensity of the micelle solution of K^+-**3** complex was much smaller than that of Li^+-**1** complex, although a combination of K^+ and monoaza-18-crown-6 forms much more stable complexes than that of Li^+ and monoaza-12-crown-4.

CONCLUSIONS

Crowned spirobenzopyrans dissolved in anionic micelle solutions, whose spirobenzopyran moieties turned out to be their corresponding merocyanine form considerably. This induced the significant changes in fluorescence spectra as well as the absorption spectra in the visible region. Their absorption- and fluorescence-spectral behavior were strongly dependent on pH conditions of the micelle solutions. The maximum absorption wavelength of the micelle solutions containing crowned spirobenzopyrans **1** showed hypsochromic shifts drastically on the addition of Li^+ at pH 13 under dark conditions. The relative fluorescence intensities of the micelle solution containing a crowned spirobenzopyran decreased with increasing the pH from 7 to 13. Such fluorescence changes are caused by the photoinduced electron transfer (PET) from the nitrogen atom of the azacrown ether moiety to the fluorescence-emitting merocyanine moiety. The fluorescence for the micelle solutions containing a crowned spirobenzopyran at pH 13 was increased by the addition of an alkali metal ion, which forms the most stable complexes with the azacrown ether moiety of crowned spirobenzopyrans to reduce the PET from the nitrogen atom to the merocyanine moiety. The relative fluorescence intensities were also increased with the concentration of the added metal ion. Thus, the micelle solutions containing a crowned spirobenzopyran are promising candidates as the colorimetric and fluorimetric sensing systems for alkali metal ions.

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