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Metal cation-induced multifluorescence of azacrown-substituted (tetrafluorophenyl)imidazo[1,2-*a*]pyridine

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ortho-Azacrown-substituted (tetrafluorophenyl)imidazo[1,2-*a*]pyridine (**2**) in an acetonitrile solution emits 380 nm light in the presence of Li^+ cation and emits 460 nm light in the presence of Zn^{2+}, Mg^{2+} or H^+ cation. In contrast, *para*-azacrown-substituted analogue (**1**) emits three different fluorescent lights responding to Li^+, Zn^{2+} or H^+ cation, respectively; 388 nm light to Li^+ cation, 433 nm light to Zn^{2+} cation or 469 nm light to H^+ cation.

Keywords: multifluorescence; cation recognition; azacrown; imidazo[1,2-*a*]pyridine

Introduction

Selective recognition of chemical species by a fluorophore modified with a recognition site has been designed for a molecular device such as a logic gate, where a couple of chemical species play a role as input signals and the difference in the fluorescent intensity as an output signal (*1–5*). In most cases, a sole wavelength fluorescence is utilised as an output signal. However, multiple emissions of a single molecule responding to several chemical species have recently been developed as multifluorescent probes (*6–11*). The single-molecular multifluorescence is also of interest from the viewpoint of an optoelectronic device such as a photoconverter.

In a continuing research on the application of fluorinated 2-(2-hydroxyphenyl)benzazoles to fluorescent probes sensing metal cations, we reported that fluorescence of 2-(pentafluorophenyl)imidazo[1,2-*a*]pyridine is strongly enhanced by the protonation with acids (*12*, *13*). In this paper, we wish to describe that azacrown-modified (tetrafluorophenyl)imidazo[1,2-*a*]pyridine (**1**) emits three different fluorescent lights responding to Li^+, Zn^{2+} or H^+ cation, respectively; 388 nm light to Li^+ cation, 433 nm light to Zn^{2+} cation or 469 nm light to H^+ cation.

Results and discussion

Compound **1** was obtained by the substitution of 2-(pentafluorophenyl)imidazo[1,2-*a*]pyridine with 1,4,7-trioxa-10-azacyclododecane in DMSO, together with the *ortho*-substituted isomer **2**. The substituted positions were determined by the ^{19}F NMR analysis. For the comparison of **1**, the piperidine-substituted analogue **3** was prepared in a similar manner. In this case, no formation of *ortho*-substituted products was detected (Scheme 1).

Absorption spectra of **1** in an acetonitrile solution were slightly red-shifted and its absorbance was substantially strong, compared with those of 2-(pentafluorophenyl)imidazo[1,2-*a*]pyridine (*12*). Its fluorescence around 380 nm wavelength was considerably weak and the intensity was affected by the polarity of the solvent; the intensity in nonpolar solvents such as toluene and dioxane was stronger than that in a polar solvent such as acetonitrile (Figure 1). A similar trend was observed with the piperidine analogue **3**. In contrast, fluorescence intensity of **2** was quite small but its wavelength was affected by the polarity of the solvents, around 380 nm in toluene and 460 nm in acetonitrile (Figure 2). The longer wavelength fluorescence in acetonitrile would be ascribed to a charge-transferred species induced by the electron transfer from the azacrown-nitrogen atom into the imidazopyridine ring (*14*).

Cation-induced changes in absorption and fluorescence of the *ortho*-substituted imidazo[1,2-*a*]pyridine **2** were first evaluated in acetonitrile. Although the absorptions of **2** are definitely changed by cations, its fluorescence changes are small, but its trend is clear. Thus, H^+, Zn^{2+} and Mg^{2+} cations induced blueshifts in the absorptions and increased the fluorescence around 460 nm wavelength, whereas Li^+ cation caused blueshifts in both absorption and fluorescence (Figure 3). It should be noted that Na^+ and K^+ cations do not cause any meaningful changes in absorption and fluorescence. Reliable job plots of **2** could not be taken with Li^+ cation but can be obtained with Zn^{2+} or Mg^{2+} cation using the absorbance changes. These results supported the existence of a 1:1 complex

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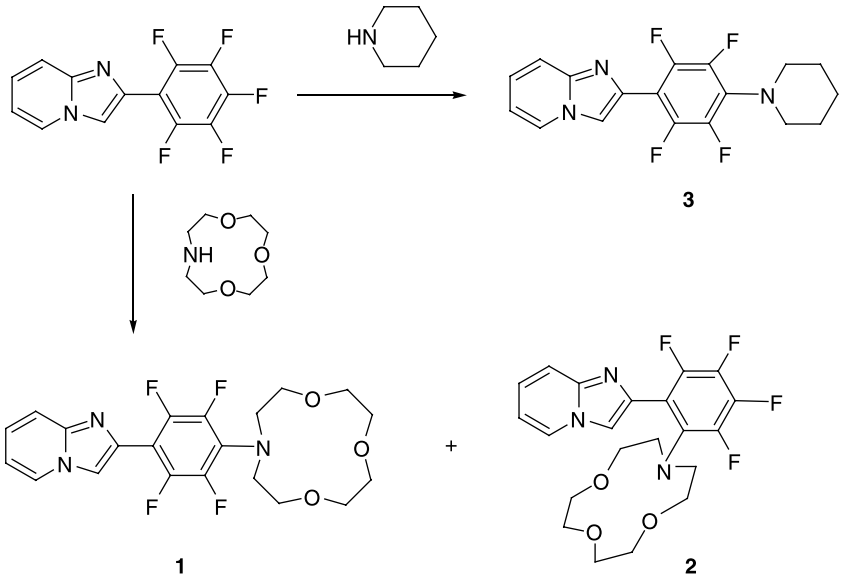

Scheme 1. Synthesis of **1**–**3**.

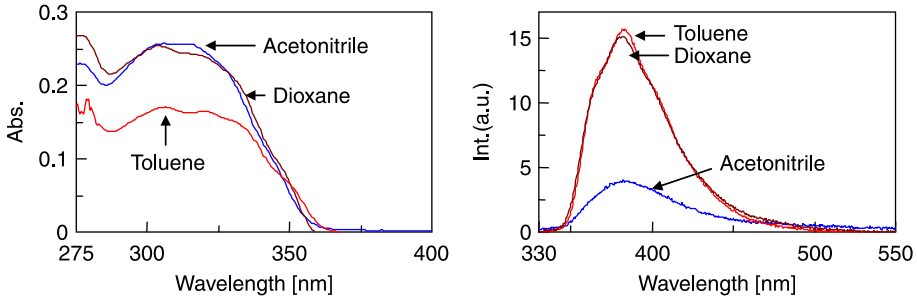

Figure 1. Absorption and fluorescence spectra of **1** in toluene, dioxane and acetonitrile. [**1**] = 1×10^{-5} M, $\lambda_{ex} = 306$ nm.

with Zn^{2+} cation and a 2:1 complex with Mg^{2+} cation (Figure 4). Binding constants were determined by the curve fittings using the absorbance changes and were estimated to be $K = (3.5 \pm 0.7) \times 10^4\,M^{-1}$ for Zn^{2+} cation and $K = (1.9 \pm 0.4) \times 10^9\,M^{-2}$ for Mg^{2+} cation (Figure 5).

Fairly deshielded shift of the 3-proton of the imidazopyridine ring, compared with that of **1**, is characteristic of **2**. In the presence of one equivalent of cation, its proton shifted upfield and the other aromatic protons and the azacrown protons are all shifted downfield. It is noticed that the downfield shift of the aromatic protons

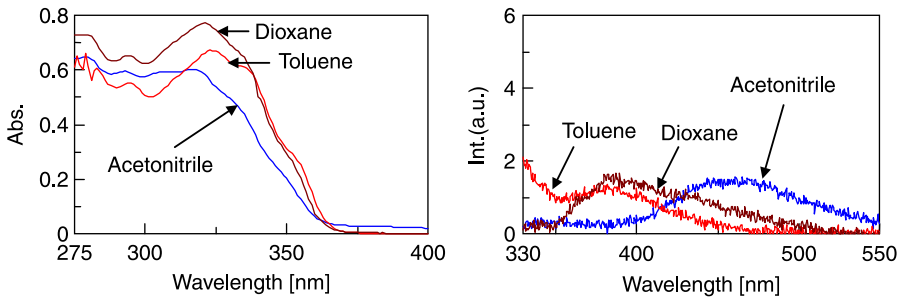

Figure 2. Absorption and fluorescence spectra of **2** in toluene, dioxane and acetonitrile. [**2**] = 1×10^{-4} M for absorption spectra and 1×10^{-5} M for fluorescence spectra, $\lambda_{ex} = 285$ nm.

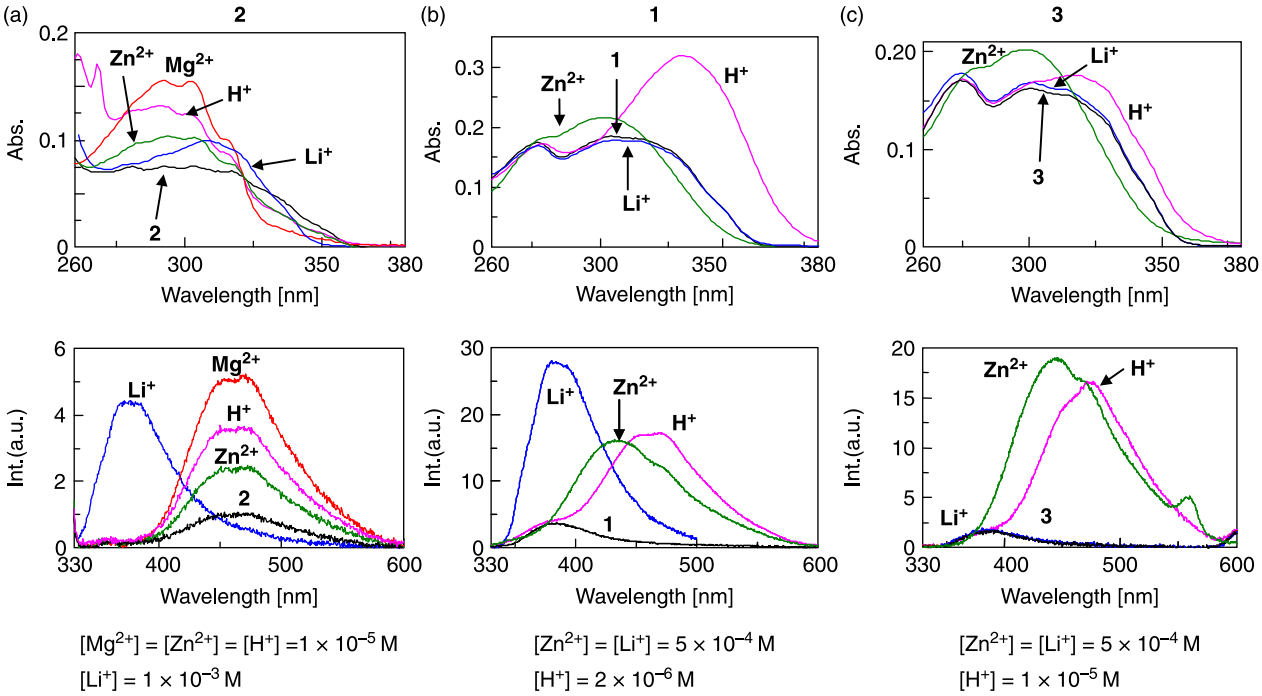

Figure 3. Cation-induced spectral changes of **1**–**3** in acetonitrile**.** [**1**] = [**2**] = [**3**] = 1 × 10^{-5} M, λ_{ex} = 308 nm, metal cation; thiocyanate, H^+; trifluoroacetic acid.

induced by Li^+ cation is relatively small (Figure 6). The deshielded shift of the 3-proton of **2** itself would be ascribed to an effect of the *ortho*-azacrown ring and the upfield shift in the presence of H^+, Zn^{2+} or Mg^{2+} cation would be caused by the ligation of the cation at the 1-nitrogen atom of **2**, which draws the azacrown ring in the direction of the 1-nitrogen atom, in the counter direction of the 3-proton. The azacrown ring associated with Li^+ cation similarly goes in the direction of the 1-nitrogen atom. Assumed structures of the complexes are depicted in Figure 7. It is assumed that, in the excited states, the coordination of H^+, Zn^{2+} or Mg^{2+} cation with the azacrown-nitrogen atom is weakened to result in the formation of a charge-transferred species, which emits the 460 nm light and, reversely, the association of Li^+ cation with the azacrown-nitrogen atom is strong to retard the electron transfer from its nitrogen atom, giving rise to the enhancement of the 380 nm fluorescence (*15*).

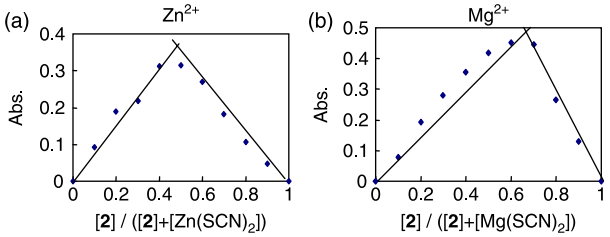

Figure 4. Job plots for the complexations of **2** with (a) $Zn(SCN)_2$ and (b) $Mg(SCN)_2$ in acetonitrile. Total concentration of **2** plus $Zn(SCN)_2$ or $Mg(SCN)_2$ is maintained at 1 × 10^{-4} M.

The effects of cation on absorption and fluorescence of the *para*-substituted imidazo[1,2-*a*]pyridine **1** were next evaluated in an acetonitrile solution. The absorption and the fluorescence were both red-shifted in the presence of trifluoroacetic acid, which is in sharp contrast to the blueshift of the absorption in the case of **2**, and the fluorescence intensity around 469 nm was substantially enhanced with the increase of trifluoroacetic acid (Figures 3 and 8). Addition of excess amount of trifluoroacetic acid caused the slight increase in the fluorescence around the 360 nm wavelength. The ^{1}H NMR spectra of **1** in the presence of an equivalent of trifluoroacetic acid show the deshielded aromatic protons, along with the slightly deshielded protons adjacent to the azacrown-nitrogen atom (Figure 9). These spectral changes support the contribution of the protonation at the 1-nitrogen atom causing the delocalisation of the positive charge to the azacrown-nitrogen atom in the ground state, as depicted in Figure 10. In the case of excess trifluoroacetic acid, the delocalisation would be retarded by the second protonation at the azacrown-nitrogen atom, increasing the fluorescence around the 360 nm wavelength. As anticipated with the piperidine analogue **3**, the similar redshifts of the absorption and the fluorescence were also noticed in the presence of trifluoroacetic acid (Figure 3).

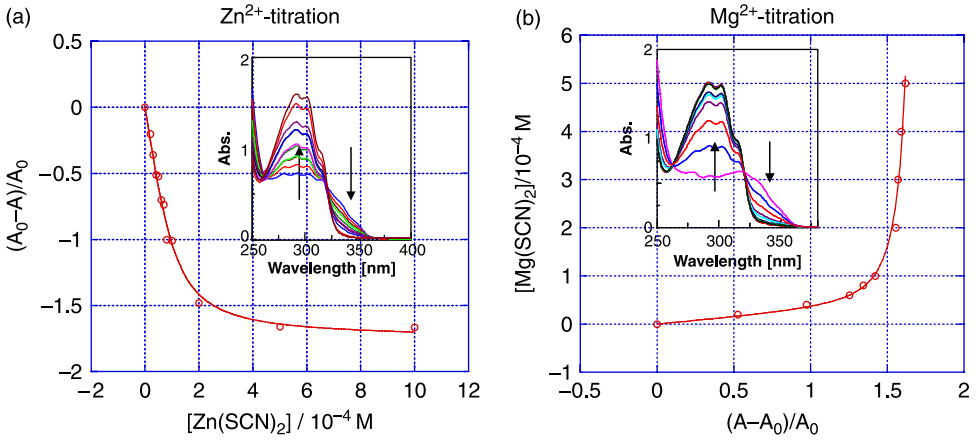

Figure 5. Titration of **2** with (a) $Zn(SCN)_2$ and (b) $Mg(SCN)_2$ in acetonitrile. [**2**] = 1 × 10^{-4} M, $[Zn(SCN)_2] = 0–10 \times 10^{-4}$ M, $[Mg(SCN)_2] = 0–5 \times 10^{-4}$ M.

Addition of Li^+ cation to an acetonitrile solution of **1** did not cause the appreciable change in the absorption but enhanced the fluorescence around the 388 nm wavelength (Figure 3). Although Li^+ cation did not affect the ^{1}H NMR spectra of **1** distinctly, this fluorescence enhancement would be ascribed to the association of Li^+ cation with the azacrown site from the fact that a similar fluorescence enhancement was not observed in the case of **3** and from the consideration of the size-matching of Li^+ cation with the 12-azacrown ring (*16*). The curve fitting of the fluorescence intensity of **1** supported the formation of a 1:1 complex of **1** and Li^+ cation, its binding constant being estimated to be $K = (4.7 \pm 0.7) \times 10^2\ M^{-1}$ (Figure 11).

The effects of Zn^{2+} cation on the spectral properties of **1** are very complicated. Thus, the absorption was slightly blue-shifted in the presence of Zn^{2+} cation but its fluorescence was reversely red-shifted and the emission around the 433 nm wavelength was enhanced with the increase of Zn^{2+} cation. The ^{1}H NMR spectra of **1** in the presence of an equivalent of Zn^{2+} cation show a similar tendency to those with trifluoroacetic acid, and also show the deshielded aromatic protons, along with the slightly deshielded protons adjacent to the azacrown-nitrogen atom (Figure 9). In this case, it is not so likely that the ligation of Zn^{2+} cation at the 1-nitrogen atom causes the delocalisation of the positive charge to the

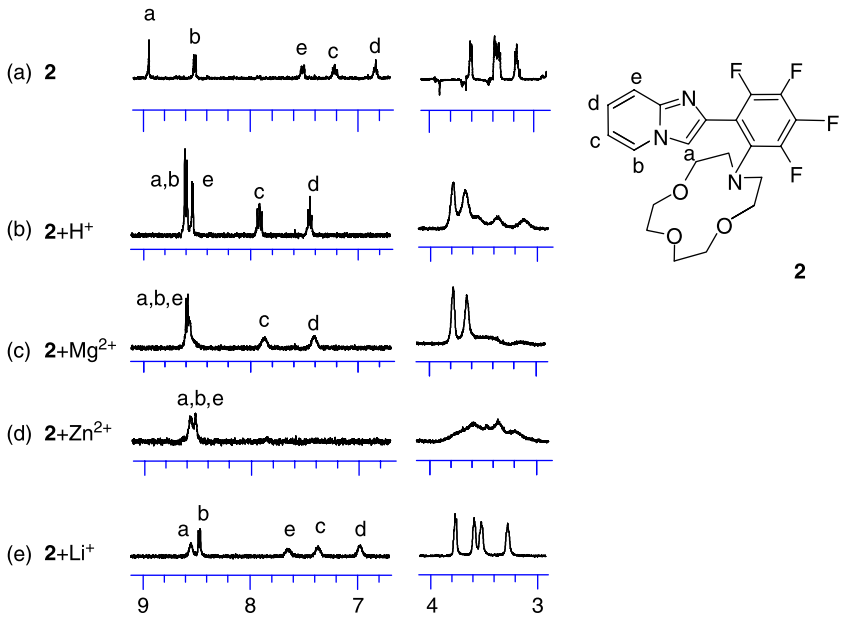

Figure 6. ^{1}H NMR spectra of **2** (a) itself, (b) with trifluoroacetic acid, (c) with $Mg(SCN)_2$, (d) with $Zn(SCN)_2$ and (e) with LiSCN. Solvent; CD_3CN, [**2**] = $[CF_3COOH] = [Mg(SCN)_2] = [Zn(SCN)_2] = [LiSCN] = 1 \times 10^{-3}$ M.

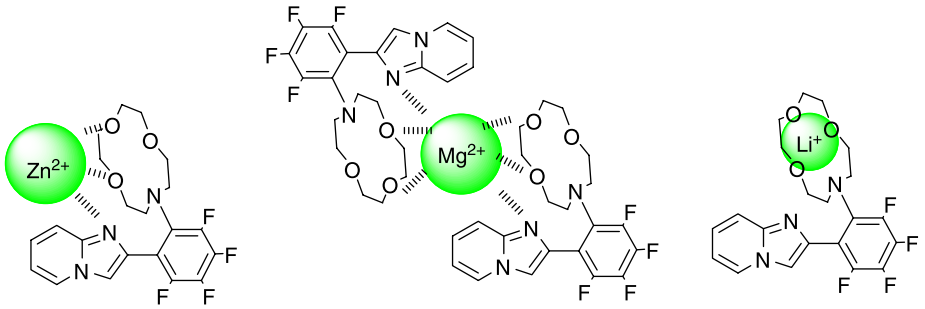

Figure 7. Assumed structures of the complexes of **2** with Zn^{2+}, Mg^{2+} or Li^{+}.

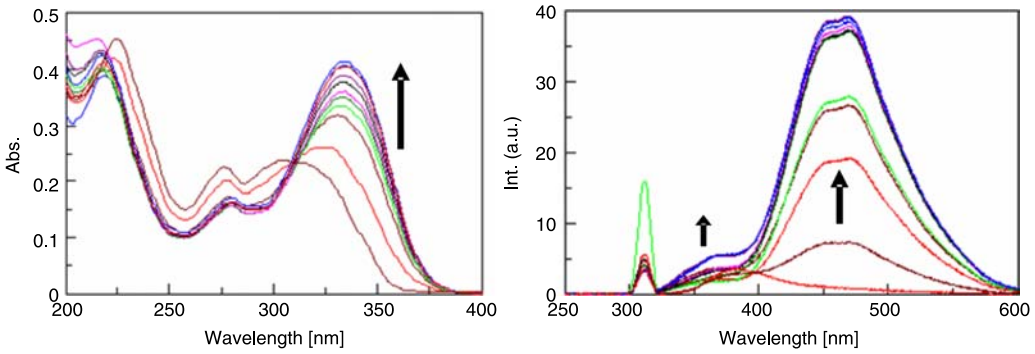

Figure 8. Spectral changes of **1** with the increase of trifluoroacetic acid in acetonitrile. [**1**] = 1×10^{-5} M, λ_{ex} = 308 nm, [trifluoroacetic acid] = 0–1 equiv. of **1**.

azacrown-nitrogen atom in the ground state, because the absorption of **1** is not red-shifted but slightly blue-shifted. Although the Job plot using ^{1}H NMR analysis supports the existence of a 1:1 complex of **1** with Zn^{2+} cation (Figure 12), titration was found to be difficult because of the non-existence of reliable isosbestic points in the absorption spectra. A similar trend in absorption and fluorescence was observed with **3** (Figure 3), suggesting

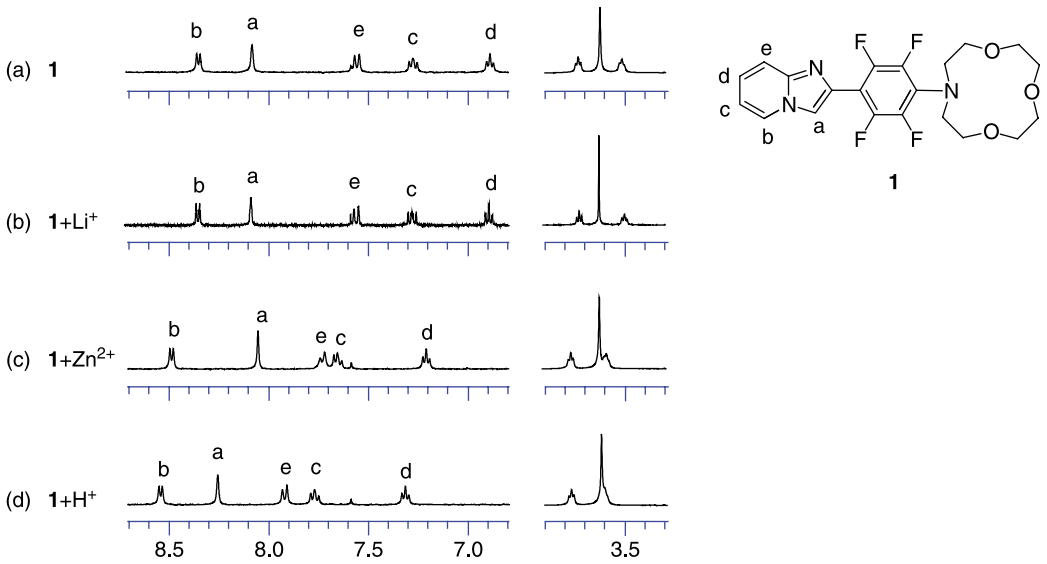

Figure 9. ^{1}H NMR spectra of **1** (a) itself, (b) with LiSCN, (c) with $Zn(SCN)_2$ and (d) with trifluoroacetic acid. Solvent; CD_3CN, [**1**] = [CF_3COOH] = [$Mg(SCN)_2$] = [$Zn(SCN)_2$] = [LiSCN] = 1×10^{-3} M.

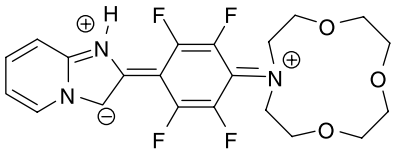

Figure 10. Assumed structure of the protonated **1**.

the formation of a similar species to that with **1**. From these observations, we assume that the **1**–Zn^{2+} complex ligated at the 1-nitrogen atom by Zn^{2+} cation forms a dimer or an oligomer where the Zn^{2+} cation is weakly bridged with the azacrown-nitrogen atom of the other **1**–Zn^{2+} complex in the ground state, this weak bridging is released in the excited state (*15*), followed by the electron transfer from the azacrown-nitrogen atom into the imidazopyridine ring, and then the formed charge-transferred species emits the 433 nm light (*14*). This consideration would be supported by the difference between the absorption spectra and the excitation spectra of **1** in the presence of 10 equiv. of Zn^{2+} cation as shown in Figure 13, where the similar spectra of **3** with Zn^{2+} cation is depicted.

It was confirmed that fluorescence and absorption of **1** were not affected by Mg^{2+} cation, which is in contrast to those of **2**. It is assumed that ligation of Mg^{2+} cation at the 1-nitrogen atom of the imidazopyridine ring is weaker than that of Zn^{2+} cation, from the considerations of the rule of hard and soft acids and bases. Therefore, ligation at the 1-nitrogen atom of the imidazopyridine ring and cooperative association with the *ortho*-substituted azacrown ring in **2** would be necessary for the complexation of Mg^{2+} cation. It is also noted that other metal cations such as Na^+, K^+ and Ca^{2+} do not cause any meaningful changes in the absorption and fluorescence.

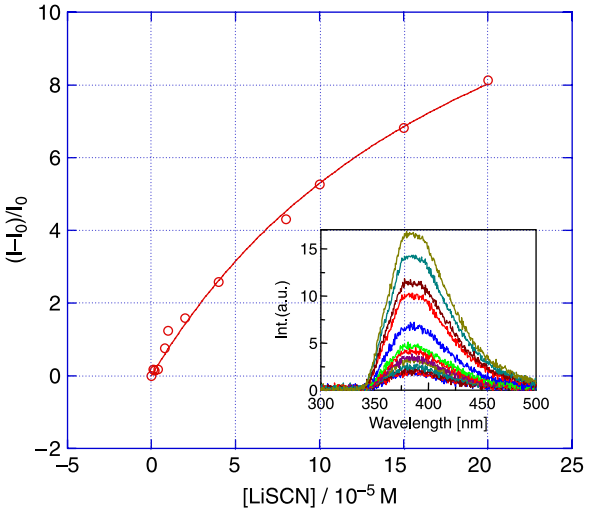

Figure 11. Titration of **1** with LiSCN in acetonitrile. [**1**] = 1 × 10^{-5} M, [LiSCN] = 0–20 × 10^{-5} M.

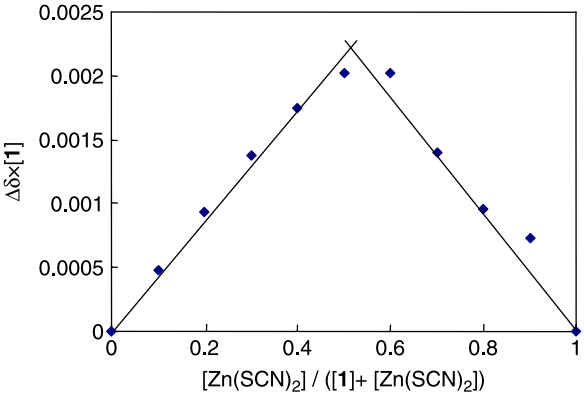

Figure 12. Job plot for the complexation of **1** with Zn^{2+} in acetonitrile. Total concentration of **1** plus $Zn(SCN)_2$ is maintained at 1 × 10^{-2} M.

Conclusions

para-Azacrown-substituted (tetrafluorophenyl)imidazo-[1,2-*a*]pyridine (**1**) and its *ortho*-analogue (**2**) were simply prepared by the substitution of 2-(pentafluorophenyl)imidazo[1,2-*a*]pyridine with 1,4,7-trioxa-10-azacyclododecane. Multiple fluorescence was found to be enhanced by several kinds of cations in an acetonitrile solution. Thus, **2** emits the 380 nm light in the presence of Li^+ cation and emits the 460 nm light in the presence of Zn^{2+}, Mg^{2+} or H^+ cation. In contrast, **1** emits three different fluorescent lights responding to Li^+, Zn^{2+} or H^+ cation, respectively; 388 nm light to Li^+ cation, 433 nm light to Zn^{2+} cation or 469 nm light to H^+ cation.

Experimental

The FT/IR spectra were recorded on a JASCO FTIR-460 plus spectrophotometer and samples were run as potassium bromide pellets. The UV–vis and fluorescence spectra were recorded with JASCO V-530 and JASCO FP-6500 spectrometers, respectively, and measured in solvents of the highest quality for spectroscopy (KOKUSAN Chemical Co., Tokyo, Japan) without further purification. The ^1H and ^{19}F NMR spectra were recorded with a JEOL JNM-LA400 spectrometer and the chemical shifts are given in δ (ppm) downfield using tetramethylsilane as an internal standard for ^1H NMR spectra and trifluoroacetic acid as an external standard for ^{19}F NMR spectra; J values are given in Hz. The MALDI-TOF MS spectra were taken with a SHIMAZU AXIMA-CFR Plus mass spectrometer. The elemental analyses were measured with a Perkin-Elmer 2400 II CHN analyser.

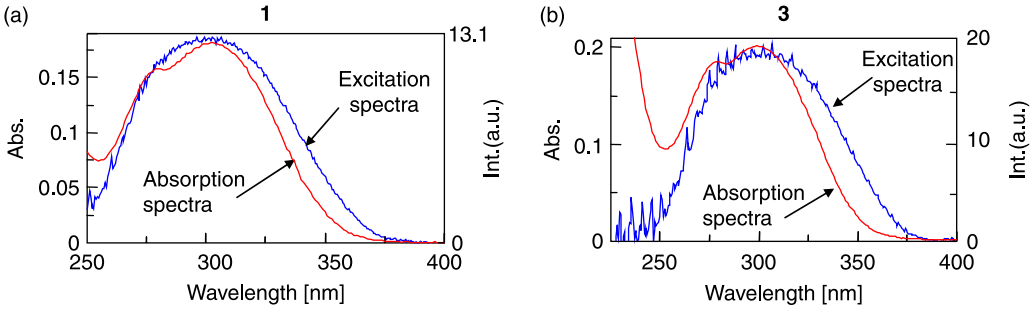

Figure 13. Absorption and excitation spectra of (a) **1** and (b) **3** with $Zn(SCN)_2$ in acetonitrile. [**1**] = [**3**] = 1×10^{-5} M, $[Zn(SCN)_2] = 1 \times 10^{-4}$ M, $\lambda_{em} = 434$ nm.

2-(Pentafluorophenyl)imidazo[1,2-*a*]pyridine was prepared by the reaction of bromomethyl pentafluorophenyl ketone, according to the previously reported paper (*12*).

2-(2,3,5,6-Tetrafluorophenyl-4-piperidino)imidazo[1,2-a]pyridine (3)

A mixture of 2-(pentafluorophenyl)imidazo[1,2-*a*]pyridine (220 mg, 0.77 mmol), piperidine (2 ml) and triethylamine (3 ml) in 10 ml of dried DMSO was stirred at 65°C for 2 h. Ethyl acetate was added to the reaction mixture and the mixture was washed with water and brine, dried over magnesium sulphate and evaporated. The resulting solid was chromatographed on silica gel (hexane–ethyl acetate, 1:1) to give 170 mg (63% yield) of **3**, which was recrystallised from hexane–ethyl acetate. Yellow crystals; mp 153–154°C; FT/IR (KBr): ν 3179 (C—H), 3045 (C—H), 2930 (C—H), 2845 (C—H), 1648 (C—F) cm^{-1}; UV–vis (acetonitrile): λ_{max} [log ε (litres mol^{-1} cm^{-1})] 275 (4.31), 301 (4.29), 312 (4.27) nm; ^{1}H NMR ($CDCl_3$): δ 1.66 (m, 6H), 3.26 (t, $J = 4.3$ Hz, 4H), 6.83 (dd, $J = 6.8$, 6.5 Hz, 1H), 7.21 (ddd, $J = 9.2$, 6.5, 0.97 Hz, 1H), 7.70 (d, $J = 9.2$ Hz, 1H), 7.91 (s, 1H), 8.15 (dd, $J = 6.8$, 0.97 Hz, 1H); ^{19}F NMR ($CDCl_3$): δ −76.2 (AA′BB″, 2F), −68.0 (AA′BB″, 2F); MS (MALDI-TOF) *m/z*: calcd for $C_{18}H_{15}F_4N_3$ $[M+H]^+$ 350.12; found $[M+H]^+$ 350.10. Anal. Calcd for $C_{18}H_{15}F_4N_3$: C, 61.89; H, 4.33; N, 12.03. Found: C, 61.95; H, 4.31; N, 11.97.

10-(2,3,5,6-Tetrafluoro-4-(imidazo[1,2-a]pyridin-2-yl)phenyl)-1,4,7-trioxa-10-azacyclododecane (1) and 10-(3,4,5,6-tetrafluoro-2-(imidazo[1,2-a]pyridin-2-yl) phenyl)-1,4,7-trioxa-10-azacyclododecane (2)

A mixture of 2-(pentafluorophenyl)imidazo[1,2-*a*]pyridine (420 mg, 1.48 mmol), 1,4,7-trioxa-10-azacyclododecane (250 mg, 1.43 mmol) and triethylamine (3 ml) in 25 ml of dried DMSO was stirred at 100°C for 3 days. Ethyl acetate was added to the reaction mixture and the mixture was washed with water and brine, dried over magnesium sulphate and evaporated. The resulting solid was chromatographed on silica gel (hexane–ethyl acetate, 1:1 and then 1:2) to give 110 mg (18% yield) of **1** and 90 mg (14% yield) of **2**, which were recrystallised from hexane–ethyl acetate.

*Compound **1***

Yellow crystals; mp 110–111°C; FT/IR (KBr): ν 3157 (C—H), 3042 (C—H), 2942 (C—H), 2858 (C—H), 1650 (C—F), 1130 (C—O—C) cm^{-1}; UV–vis (acetonitrile): λ_{max} [log ε (litres mol^{-1} cm^{-1})] 276.5 (4.36), 306.5 (4.41), 313 (4.41) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.55 (t, $J = 4.9$ Hz, 4H), 3.71 (m, 8H), 3.81 (t, $J = 4.9$ Hz, 4H), 6.83 (ddd, $J = 6.8$, 6.8, 0.98 Hz, 1H), 7.21 (ddd, $J = 9.2$, 6.8, 0.98 Hz, 1H), 7.69 (d, $J = 9.2$ Hz, 1H), 7.91 (s, 1H), 8.16 (d, $J = 6.6$ Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ −74.2 (AA′BB″, 2F), −67.5 (AA′BB″, 2F); MS (MALDI-TOF) *m/z*: calcd for $C_{21}H_{21}F_4N_3O_3$ $[M+H]^+$ 440.15; found $[M+H]^+$ 440.09. Anal. Calcd for $C_{21}H_{21}F_4N_3O_3$: C, 57.40; H, 4.82; N, 9.56. Found: C, 57.26; H, 4.73; N, 9.29.

*Compound **2***

Yellow crystals; mp 180–182°C; FT/IR (KBr): ν 3165 (C—H), 2906 (C—H), 2858 (C—H), 1631 (C—F), 1132 (C—O—C) cm^{-1}; UV–vis (acetonitrile): λ_{max} [log ε (litres mol^{-1} cm^{-1})] 279 (3.83), 293 (3.81), 317 (3.82) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (t, $J = 4.2$ Hz, 4H), 3.38 (m, 8H), 3.71 (t, $J = 4.1$ Hz, 4H), 6.76 (dd, $J = 6.8$, 6.6 Hz, 1H), 7.14 (dd, $J = 9.0$, 6.6 Hz, 1H), 7.61 (d, $J = 9.0$ Hz, 1H), 8.48 (d, $J = 6.8$ Hz, 1H), 9.12 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ −83.6 (dd, $J = 21.0$, 21.0 Hz, 1F), −81.7 (dd, $J = 21.0$, 20.0 Hz, 1F), −69.6 (dd, $J = 20.0$, 9.0 Hz, 1F), −63.8 (m, 1F); MS (MALDI-TOF) *m/z*: calcd for $C_{21}H_{21}F_4N_3O_3$ $[M+H]^+$ 440.15; found $[M+H]^+$ 440.13. Anal. Calcd for $C_{21}H_{21}F_4N_3O_3$: C, 57.40; H, 4.82; N, 9.56. Found: C, 57.47; H, 4.94; N, 9.51.

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References

(1) Guo, Z.; Zhu, W.; Shen, L.; Tian, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5549–5553.
(2) Magri, D.C.; Brown, G.J.; McClean, G.D.; de Silva, A.P. *J. Am. Chem. Soc.* **2006**, *128*, 4950–4951.
(3) Lankshear, M.D.; Cowley, A.R.; Beer, P.D. *Chem. Commun.* **2006**, 612–614.
(4) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley: Weinheim, Germany, 2003; Chapter 9.
(5) de Silva, A.P.; McClenaghan, N.D.; McCoy, C.P. In *Molecular Switches*; Feringa, B.L., Ed.; Wiley: Weinheim, Germany, 2001; Chapter 11.
(6) Tolosa, J.; Zucchero, A.J.; Bunz, U.H. *J. Am. Chem. Soc.* **2008**, *130*, 6498–6506.
(7) Choi, J.K.; Kim, S.H.; Yoon, J.; Lee, K.-H.; Bartsch, R.A.; Kim, J.S. *J. Org. Chem.* **2006**, *71*, 8011–8015.
(8) Tanaka, K.; Sano, K.; Katoh, T.; Iwata, S.; Nemoto, K.; Kurushima, T. *J. Fluorine Chem.* **2006**, *127*, 1073–1078.
(9) Komatsu, H.; Miki, T.; Citterio, D.; Kubota, T.; Shindo, Y.; Kitamura, Y.; Oka, K.; Suzuki, K. *J. Am. Chem. Soc.* **2005**, *127*, 10798–10799.
(10) Komatsu, H.; Citterio, D.; Fujiwara, Y.; Oka, K.; Suzuki, K. *Org. Lett.* **2005**, *7*, 2857–2859.
(11) Martinez, R.; Espinosa, A.; Tárraga, A.; Molina, P. *Org. Lett.* **2005**, *7*, 5869–5872.
(12) Tanaka, K.; Kurushima, T.; Iwata, S.; Shimada, S. *J. Heterocycl. Chem.* **2007**, *44*, 303–307.
(13) Tanaka, K.; Kumagai, T.; Aoki, H.; Deguchi, M.; Iwata, S. *J. Org. Chem.* **2001**, *66*, 7328–7333.
(14) Rettig, W. *Angew. Chem., Int. Ed.* **1986**, *25*, 971–988.
(15) Martin, M.M.; Plaza, P.; Hung, N.D.; Meyer, Y.H.; Bourson, J.; Valeur, B. *Chem. Phys. Lett.* **1993**, *202*, 425–430.
(16) Katayama, Y.; Nita, K.; Ueda, M.; Nakamura, H.; Takagi, M.; Ueno, K. *Anal. Chim. Acta* **1985**, *173*, 193–209.