A dibenzo-16-crown-5 fluoroionophore for selective emission ratio sensing of Na^+ in basic aqueous dioxane solution †

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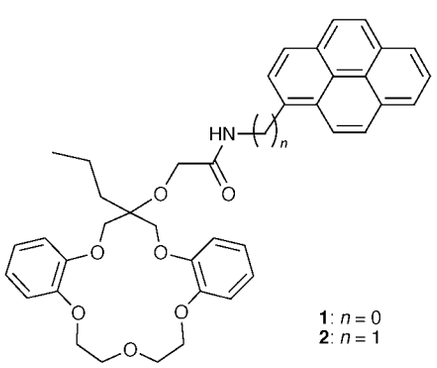
For alkali metal cation sensing in aqueous dioxane solution, a novel dibenzo-16-crown-5‡ (DB16C5) fluoroionophore **1**, *N*-(pyren-1-yl)-*sym*-(propyl)dibenzo-16-crown-5-oxyacetamide, has been synthesized. Examination of fluorescent behavior for **1** in 4:1 1,4-dioxane–water (v/v) containing tetramethylammonium hydroxide (TMAOH) reveals that proton dissociation of the carboxamido moiety is promoted by Na^+ binding, which results in an emission ratio response due to internal charge transfer (ICT) from the donor carboxamido anion to the pyrene acceptor. The emission intensity ratio (I_{459}/I_{387}) increases with enhancement of the Na^+ concentration. No fluorescent response is induced by the presence of Li^+, K^+, or Cs^+. This high Na^+ selectivity is attributed to a preorganized structure of DB16C5 lariat ether binding site in which Na^+ binds tightly to the carbonyl oxygen of the side arm to induce selective proton dissociation. Thus a ratiometric emission response with high Na^+ selectivity has been obtained for **1** in 4:1 1,4-dioxane–water (v/v) containing TMAOH.

Introduction

Sensitive and *in situ* monitoring of alkali metal ion activities in aqueous media is important for the assessment of clinical and biological systems.[1,2] In such analysis, ratiometric fluorometry by measurement of the ratio of signals at two emission or excitation wavelengths is an important method because it allows variations in emission intensities which arise from changes in the analytical environment to be cancelled.[3] For chemosensors in non-aqueous media, we have recently reported ratiometric emission systems for both cation and anion sensing based upon dual monomer/exciplex emissions.[4] In aqueous media, "SBFI" (1,7-diaza-4,10,13-trioxacyclopentadecane, linked *via* its nitrogens to benzofuran isophthalate fluorophores) and related structures developed by Tsien *et al*. are the only reported Na^+-selective fluoroionophores.[5] Although SBFI is well designed and adequate for Na^+ sensing in water,[2] it exhibits only an excitation ratio response to Na^+.[3,5] Previously there has been no rational concept for the design of a Na^+ fluoroionophore which shows efficient emission ratio response in aqueous media.[6,7]



In this study, we report the novel dibenzo-16-crown-5 (DB16C5) fluoroionophore **1** which exhibits an emission ratio response with high Na^+ selectivity in 4:1 1,4-dioxane–water (v/v). Earlier investigations have revealed that attachment of both an oxyacetamide and an alkyl group to the central carbon of the three carbon bridge in DB16C5 compounds orients the functional side arm over the polyether cavity.[8] Such preorganization has been shown to provide high Na^+ binding selectivity; the log $K_{Na,K}^{pot}$ and log $K_{Na,Li}^{pot}$ obtained from the solvent polymeric membrane electrodes of *N*,*N*-(diethyl)-*sym*-(propyl)dibenzo-16-crown-5-oxyacetamide are reported to be −1.98 and −2.84, respectively.[9] Based on this concept, we have introduced a preorganized carboxamide donor side arm into the DB16C5 skeleton and linked it to a pyrene acceptor as an integrated fluorophore-receptor system. Since the *N*-arylcarboxamido proton has a relatively high acidity,[10] Na^+ binding is expected to promote proton dissociation under alkaline conditions by a mechanism similar to that reported for other chromoionophores which function in aqueous media.[11] It has been reported that the oxidation potential of carboxamide is strongly reduced by proton dissociation.[10] Therefore, deprotonation of the carboxamide moiety is expected to affect the fluorescence emission due to internal charge transfer (ICT) from the donor carboxamide anion to the electronically conjugated pyrene acceptor.[12] A new design concept for the construction of DB16C5 fluoroionophore **1** exhibiting a ratiometric emission function for alkali metal ion sensing in basic aqueous dioxane solution is now reported.

Results and discussion

Fluoroionophore **1** was synthesized by conversion of *sym*-(propyl)dibenzo-16-crown-5-oxyacetic acid[13] into the corresponding acid chloride and its condensation with 1-aminopyrene in a conventional manner.[14] For comparison,

† Detailed analysis for determination of binding constant is available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/a9/09638h

‡ The IUPAC name for dibenzo-16-crown-5 is 2,6,8,11,14-pentaoxa-1,7(1,2)-dibenzenacyclotetradecaphane.

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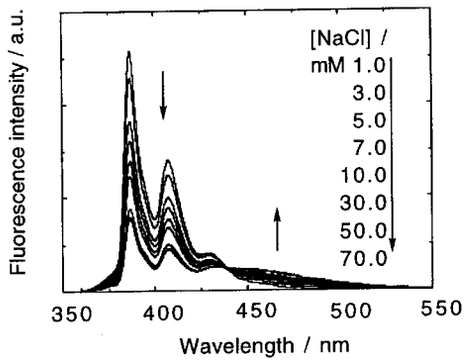

Fig. 1 Fluorescence emission spectra of **1** upon addition of NaCl in 4:1 1,4-dioxane–water (v/v). [**1**] = 8.0×10^{-7} M, [TMAOH] = 33 mM. λ_{ex} = 355 nm.

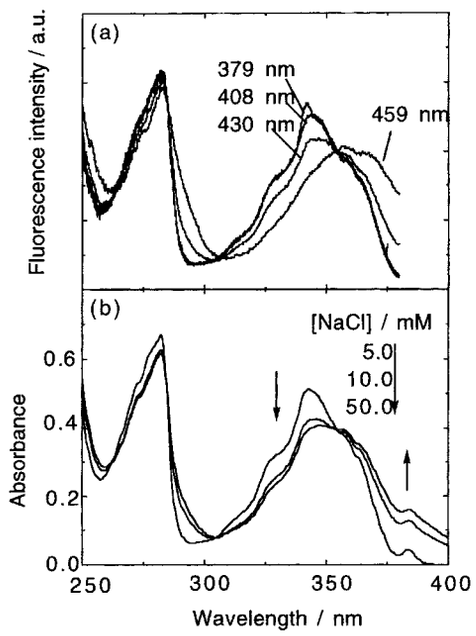

Fig. 2 Excitation and absorption spectra of **1** in 4:1 1,4-dioxane–water (v/v). (a) Excitation spectra of **1** at various emission wavelengths (λ_{em} = 379 nm, 408 nm, 430 nm, and 459 nm). [**1**] = 8.0×10^{-7} M, [TMAOH] = 33 mM, [NaCl] = 10.0 mM. Normalized at 355 nm (isosbestic point in Fig. 2b). (b) Absorption spectra of **1** upon addition of NaCl ([NaCl] = 5.0 mM, 10.0 mM, and 50.0 mM). [**1**] = 2.0×10^{-5} M, [TMAOH] = 33 mM.

fluoroionophore **2**, in which a methylene spacer is introduced between the pyrene and amido moieties to disrupt electronic conjugation, was also prepared. The structures of **1** and **2** were verified by elemental analyses and ^{1}H NMR spectra.

The fluorescent behavior of fluoroionophores **1** and **2** (8.0×10^{-7} M) dissolved in 4:1 1,4-dioxane–water (v/v), was examined in the presence of alkali metal salts. Fig. 1 shows the fluorescent response of **1** in the presence of 33 mM tetramethylammonium hydroxide (TMAOH) upon the addition of NaCl. As can be seen, NaCl addition reduces the fluorescence intensities observed at 387 nm and 408 nm, which are assigned to emission of the pyrene monomer unit, and a new broad fluorescence emission appears in the vicinity of 459 nm with a clear isoemissive point. Thus, an emission ratio response is apparent in the present system.

Examination of the excitation spectra for each of the emission bands reveals that the structureless emission at 459 nm arises from a change in electronic structure at the ground state (Fig. 2a). The absorption spectra recorded for **1** at 25-fold higher concentration (2.0×10^{-5} M) exhibit a bathochromic shift with an isosbestic point at 355 nm upon the addition of NaCl under the same alkaline conditions (Fig. 2b), revealing

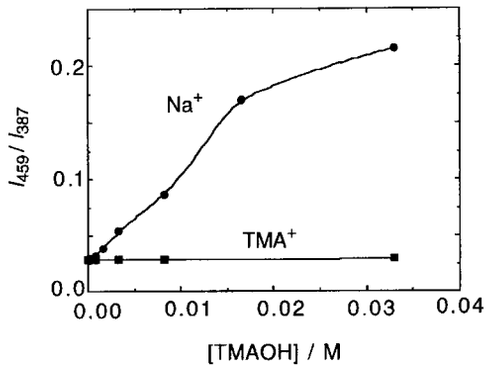

Fig. 3 Effect of TMAOH concentration upon the fluorescent behavior of **1** in 4:1 1,4-dioxane–water (v/v). [**1**] = 5.0×10^{-7} M in the presence of (■) 0.050 M TMACl and (●) 0.050 M NaCl. λ_{ex} = 355 nm.

that proton dissociation of the carboxamide moiety takes place in the ground state. It should be noted that this bathochromic shift of the absorption spectra is only observed when Na^+ is present in the system.

The effect of TMAOH concentration upon the ratio of fluorescence intensities at 459 nm and 387 nm (I_{459}/I_{387}) in the presence of (a) 0.050 M TMACl and of (b) 0.050 M NaCl is shown in Fig. 3. The upper limit for the TMAOH concentration was 33 mM due to the solubility of TMAOH in 4:1 1,4-dioxane–water (v/v). No significant response is apparent in the absence of TMAOH or when TMAOH is added in the presence of 0.050 M TMACl. In contrast, the addition of TMAOH dramatically enhances the I_{459}/I_{387} ratio when 0.050 M NaCl is present. Under the present experimental conditions, excimer formation is improbable because the concentration of **1** (5.0×10^{-7} M) is sufficiently low. The pK_a of the acetanilide proton ($CH_3CONHC_6H_5$) is reported to be 13.8 in water,[10] and this value will increase when the solvent polarity is decreased. Thus it is difficult to measure the intrinsic pK_a value for **1** in aqueous dioxane solution.

Under the assumption that the carboxamide and pyrene moieties have independent redox potentials, the free energy changes of photoinduced electron transfer (ΔG_{PET}/kcal mol^{-1}) is roughly assessed from the Rohm–Weller equation (1),[15] where

$$\Delta G_{PET} = 23.06[E_{ox}(D) - E_{red}(A)] - \omega_p - \Delta G_{00}(A) \quad (1)$$

E_{ox}(D), E_{red}(A), ω_p, and ΔG_{00}(A) are the oxidation potential of donor (D), the reduction potential of acceptor (A), the ion-pairing energy, and the excitation energy of acceptor (A). The reduction potential of pyrene, E_{red}(Py), is 2.09 V in DMF (*vs.* SCE),[16] which should be similar in CH_3CN, and ΔG_{00}(Py) is 77 kcal mol^{-1}.[15] The ω_p is estimated to be −1.3 kcal mol^{-1} in CH_3CN.[15] The oxidation potential of acetamide and the acetamide anion are 3.29 V in CH_3CN (*vs.* NHE) and 0.73 V in DMSO (*vs.* NHE), respectively.[10] Thus the calculation gives a change in ΔG_{PET} from *ca.* 40 kcal mol^{-1} for an acetamide–pyrene model to *ca.* −18 kcal mol^{-1} for an acetamide anion–pyrene model in CH_3CN. The oxidation potential of the acetamide anion is inferred from the data in DMSO and we anticipate that the oxidation potential will be lower in CH_3CN than in DMSO. These results support the theory that proton dissociation of the carboxamido moiety in **1** is promoted by Na^+ binding, which results in a fluorescence emission due to ICT from the donor carboxamido anion to the pyrene acceptor. This is in agreement with fluoroionophore **2** in which the acidity of the carboxamido proton is reduced by introducing a methylene spacer between the carboxamido and pyrene moieties, for which no fluorescent response was obtained.

The ^{1}H NMR spectra of **1** and **2** in 4:1 d_4-1,4-dioxane–D_2O (v/v) containing 0.10 M Na^+ were measured in the absence and presence of 30 mM OD^- and adjusted with NaSCN and NaOD (Fig. 4). For **1**, the chemical shift of the α-methylene proton in

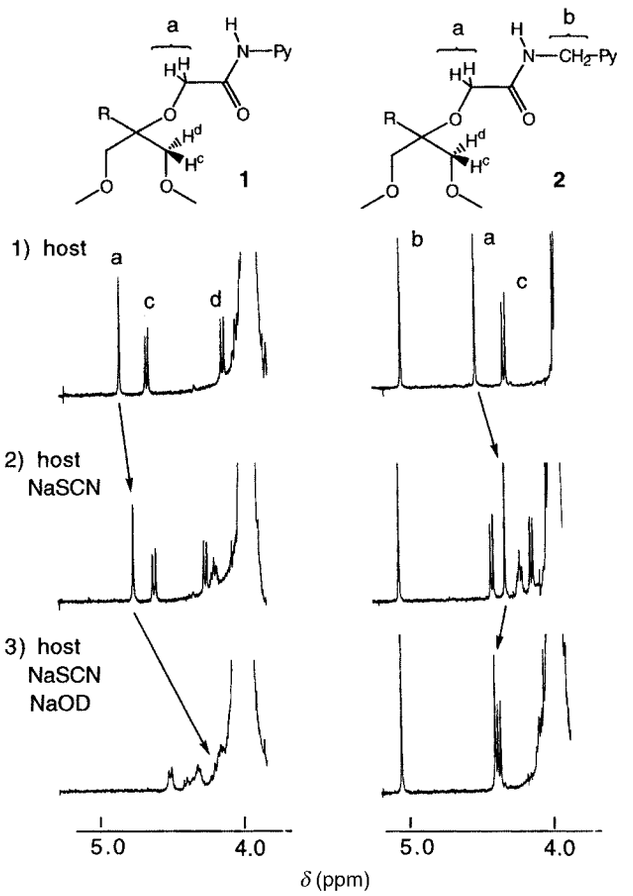

Fig. 4 ^{1}H NMR spectra of **1** and **2** in 4:1 d_4-dioxane–D_2O (v/v) containing 0.10 M Na^+ and 30 mM OD^- adjusted with NaSCN and NaOD.

the carboxamide side arm observed at 4.82 ppm shifted to 4.70 ppm in the presence of 0.10 M NaSCN. This peak was found to disappear upon the addition of 30 mM OD^-, being shifted to a higher magnetic field inside the large solvent peaks at 3.4–4.1 ppm. In contrast, the signal for the α-methylene protons in **2** merely shifted from 4.51 ppm (host only) to 4.26 ppm (host with 0.10 M NaSCN) to 4.36 ppm (host with 0.10 M NaSCN containing 30 mM OD^-). These results provide additional support for the metal-induced proton dissociation for **1**.

To assess the selectivity for alkali-metal cations, the fluorescent response of **1** upon the addition of alkali-metal chlorides in 4:1 1,4-dioxane–water (v/v) containing 33 mM TMAOH is examined. The resultant dependences of the intensity ratio at 459 nm to that at 387 nm (I_{459}/I_{387}) on the concentrations of various alkali metal cations are shown in Fig. 5. It is evident that no fluorescent response is induced by the presence of Li^+, K^+, or Cs^+ in the concentration range 0 to 50 mM. The I_{459}/I_{387} value only rises with an increase in Na^+ concentration above 1.0 mM. The 1:1 binding constant of **1** for Na^+ as calculated from a Benesi–Hildebrand plot[17] is 219 ± 17 M^{-1}.† This high Na^+ selectivity is attributed to the preorganized structure of the DB16C5 lariat ether binding site in which Na^+ binds tightly to the carbonyl oxygen of the side arm to induce selective proton dissociation.[11] Thus high Na^+ selectivity has been obtained for **1** in 4:1 1,4-dioxane–water (v/v) containing TMAOH.

In conclusion, we have designed the novel dibenzo-16-crown-5 (DB16C5) fluoroionophore **1** which exhibits an emission ratio response with high Na^+ selectivity in 4:1 1,4-dioxane–water (v/v). It is found that proton dissociation of the carboxamido moiety in **1** is promoted by Na^+ binding, which results in a ratiometric emission due to internal charge transfer (ICT) from the donor carboxamido anion to the pyrene acceptor. Although

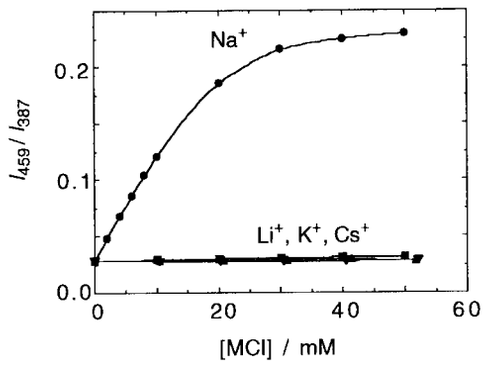

Fig. 5 Dependence of I_{459}/I_{387} on the concentrations of alkali metal cations in 4:1 1,4-dioxane–water (v/v). [**1**] = 5.0×10^{-7} M, [TMAOH] = 33 mM, (▲) LiCl. (●) NaCl, (■) KCl, and (▼) CsCl. λ_{ex} = 355 nm.

the fluoroionophore **1** requires basic conditions, the acidity of the carboxamide proton is tunable by introducing sulfonylcarbamoyl linkages such as the (dimethylamino)naphthalene-1-sulfonamide (dansyl) moiety.[18] Thus the present results establish a new system for the construction of ratiometric chemosensors for alkali metal ion sensing in aqueous dioxane media.

Experimental

Fluorescence spectra were measured by a JASCO FP-770 spectrophotometer (Japan Spectroscopic Co. Ltd.) at 25 °C; the slits for the excitation and emission monochrometers were 3.0 nm and 1.5 nm, respectively; and the spectral scan rate was 50.0 nm min^{-1}. All emission spectra were uncorrected. Absorption spectra were recorded with a Hitachi U-3000 UV-Vis spectrophotometer (Hitachi, Ltd.) by using a quartz cell of 1 cm path length at 25 °C. ^{1}H NMR spectra were obtained with a JEOL α-500 (500 MHz; JEOL DATUM), with chemical shifts (ppm) reported downfield from tetramethylsilane.

Reagents

All solvents and reagents were obtained as the highest commercial quality and used without further purification, unless otherwise noted. 1,4-Dioxane (specially prepared reagent for HPLC) was purchased from Nacalai Tesque, Inc. Tetrahydrofuran (THF) was distilled from Na–benzophenone. *sym*-(Propyl)dibenzo-16-crown-5-oxyacetic acid was prepared according to the literature procedure.[13] Free pyren-1-ylmethylamine solution was prepared as follows: pyren-1-ylmethylamine hydrochloride (105 mg, 0.39 mmol) was dissolved in CH_2Cl_2 (30 mL) and the solution was washed with aqueous 0.1 M NaOH (30 mL). The organic layer was dried over $MgSO_4$, concentrated, and diluted with THF (10 mL). All aqueous solutions were prepared with distilled water that was subsequently deionized using a Millipore Milli-Q water system.

Synthesis of *N*-(pyren-1-yl)(4-propyl-2,6,8,11,14-pentaoxa-1,7(1,2)-dibenzenacyclotetradecaphan-4-yl)oxyacetamide (1)

To a solution of *sym*-(propyl)dibenzo-16-crown-5-oxyacetic acid (143 mg, 0.32 mmol) in dry benzene (20 mL) was added oxalyl chloride (81 mg, 0.64 mmol). The mixture was stirred at room temperature for 15 h. The solvent and excess oxalyl chloride were evaporated *in vacuo* and the residue was diluted with THF (20 mL). To the solution was added 1-aminopyrene (90 mg, 0.42 mmol) and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated *in vacuo* and the residue was diluted with dichloromethane (25 mL). The solution was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica

gel with ethyl acetate–hexane (1 : 1) as eluent to afford **1** (138 mg, 67%). Calcd for $C_{40}H_{39}NO_7$: C, 74.40; H, 6.09; N, 2.17. Found: C, 74.25; H, 6.35; N, 1.97%. ^{1}H NMR ($CDCl_3$, 500 Mz) 1.13 (3H, t, J = 7.3 Hz), 1.63–1.72 (2H, m), 2.09–2.15 (2H, m), 3.73–3.79 (2H, m), 3.89–4.02 (4H, m), 4.09–4.18 (4H, m), 4.76 (2H, d, J = 10.0 Hz), 5.00 (2H, s), 6.78–7.02 (8H, m), 7.71 (1H, d, J = 9.0 Hz), 7.96 (1H, t, J = 7.6 Hz), 7.98 (1H, d, J = 9.0 Hz), 8.02 (1H, d, J = 9.0 Hz), 8.06 (1H, d, J = 7.6 Hz), 8.12 (1H, d, J = 9.0 Hz), 8.14 (1H, d, J = 7.6 Hz), 8.15 (1H, d, J = 8.4 Hz), 8.59 (1H, d, J = 8.4 Hz), 10.03 (1H, s).

Synthesis of *N*-(pyren-1-ylmethyl)(4-propyl-2,6,8,11,14-pentaoxa-1,7(1,2)-dibenzenacyclotetradecaphan-4-yl)oxyacetamide (2)

To a solution of *sym*-(propyl)dibenzo-16-crown-5-oxyacetic acid (134 mg, 0.30 mmol) in dry benzene (20 mL) was added oxalyl chloride (76 mg, 0.60 mmol). The mixture was stirred at room temperature for 15 h. The solvent and excess oxalyl chloride were evaporated *in vacuo* and the residue was diluted with THF (20 mL). To the solution was added freshly prepared pyren-1-ylmethylamine (90.2 mg, 0.39 mmol) in THF (10 mL) and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated *in vacuo* and the residue was diluted with CH_2Cl_2 (25 mL). The solution was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel with ethyl acetate–hexane (1 : 1) as eluent to afford **2** (120 mg, 61%). Calcd for $C_{41}H_{41}NO_7 \cdot 2H_2O$: C, 70.78; H, 6.52; N, 2.01. Found: C, 70.56; H, 6.54; N, 2.23%. ^{1}H NMR ($CDCl_3$, 500 Mz) 0.93 (3H, t, J = 7.6 Hz), 1.34–1.44 (2H, m), 1.79–1.85 (2H, m), 3.59–3.66 (2H, m), 3.69–3.76 (4H, m), 3.88 (2H, d, J = 10.8 Hz), 3.91–3.98 (2H, m), 4.40 (2H, d, J = 10.4 Hz), 4.67 (2H, s), 5.17 (2H, d, J = 6.0 Hz), 6.57–6.85 (8H, m), 7.58 (1H, t, J = 6.0 Hz), 7.86 (1H, d, J = 9.0 Hz), 7.89 (1H, d, J = 9.0 Hz), 7.93 (1H, d, J = 9.2 Hz), 7.95 (1H, d, J = 8.8 Hz), 7.99 (1H, t, J = 7.6 Hz), 8.02 (1H, d, J = 8.8 Hz), 8.13 (1H, d, J = 7.6 Hz), 8.16 (1H, d, J = 7.6 Hz), 8.24 (1H, d, J = 9.2 Hz).

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