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Photoresponsive Tweezers for Alkali Metal Ions. Photochromic Diarylethenes Having Two Crown Ether Moieties

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Alkali metal ion extraction was carried out using photochromic dithienylethene having two benzo-12-crown-4 ethers (**1**), benzo-15-crown-5 ethers (**2**), or benzo-18-crown-6 ethers moieties (**3**) and bis(benzothienyl)ethene having two benzo-18-crown-6 ether moieties (**4**). Two crown ether moieties of the open-ring form captured large metal ions cooperatively like tweezers, while the photogenerated closed-ring form released the ions. The reduced affinities for metal picrates were fully recovered by irradiation with visible light (>480 nm). The ^{1}H NMR spectrum measurement of the solutions ($CDCl_3/CD_3CN$: 5/1) containing both alkali metal picrates and **2** or **3** confirmed that the large alkali metal ions were captured by the two intramolecular crown ethers.

Introduction

Various kinds of photoresponsive host molecules having photochromic bis-anthracene,[1] azobenzene,[2,3] thioindigo,[4] stilbene,[5] or bis-spiropyran[6] as a photoswitch have been synthesized, and switching of host−guest events by use of the host molecules has been investigated. All photochromic compounds used so far for the photoresponsive host molecules are thermally reversible and their durability is limited. The photogenerated isomer of each reported photoresponsive host molecule is thermally unstable and returns to the initial form in the dark. Therefore, it is impossible to maintain the concentration of the extracted guest molecules in the dark. In addition, the photoextraction cycle can be repeated only less than 10 times with keeping the performance.

Recently, new types of photochromic compounds, such as fulgides[7] and diarylethenes,[8,9] have been developed. They undergo thermally irreversible photochromic reactions. Additionally diarylethenes show fatigue resistance; thus, photoresponsive host molecules with a diarylethene photoswitch would show thermally irreversible and fatigue-resistant performance.[10,11]

Figure 1 shows the concept for the photoresponsive tweezers for an alkali metal ion having dithienylethene as a photoswitch and two crown ether moieties as binding sites. The open-ring form of dithienylethene **1** has two conformations, parallel and antiparallel. The antiparallel conformation of the open-ring form undergoes a cyclization reaction when irradiated with UV light. The closed-ring form is thermally stable. Upon irradiation with visible light, the closed-ring form converts to the open-ring form. In the parallel conformation, two intramolecular crown ether moieties can cooperatively bind with a large metal ion like tweezers (photoswitch on), but in the photogenerated closed-ring form the crown ether moieties are separated from each other and cannot capture the metal ion cooperatively (photoswitch off).

Results and Discussions

1. Synthesis and Structure of Diarylethenes Having Two Crown Ethers. Preparation of the photoresponsive tweezers is shown in Schemes 1 and 2. Suzuki coupling reaction[12] of thiophene boronic acid **6** and iodobenzo-crown ethers **7**, **8**, and **9**[13,14] afforded crown ethers **10**-**12**. The dithienylethenes **1**−**3** were obtained by lithiation of **10**−**12** and following treatment with octafluorocyclopentene. Bis(benzothiophene) type **4** was obtained by the coupling reaction of dicarboxylic acid **13** and aminobenzo-18-crown-6 ether **14** in the presence of dicyclohexylcarbodiimide and 1-hydroxybenzotriazole. Compounds **1**−**4** were purified by use of recycle preparative GPC or reversed phase HPLC (eluent: methanol) and were obtained as mixtures of their parallel and antiparallel conformations. The conformations were determined by ^{1}H NMR spectra in $CDCl_3$ at 20 °C.

Dithienylethenes **1**−**3** and bis(benzothienyl)ethene **4** undergo photochromic reactions. As an example, the

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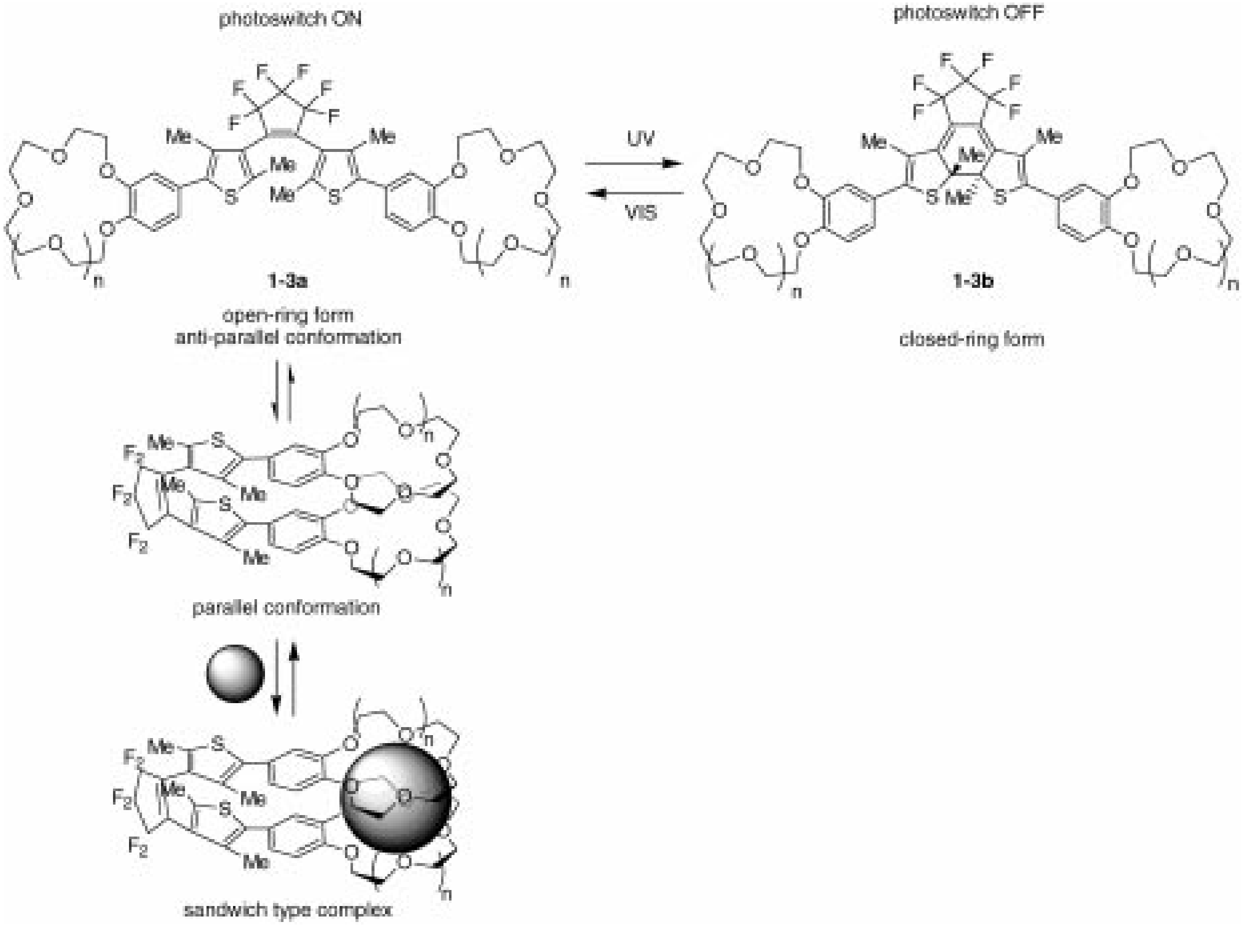
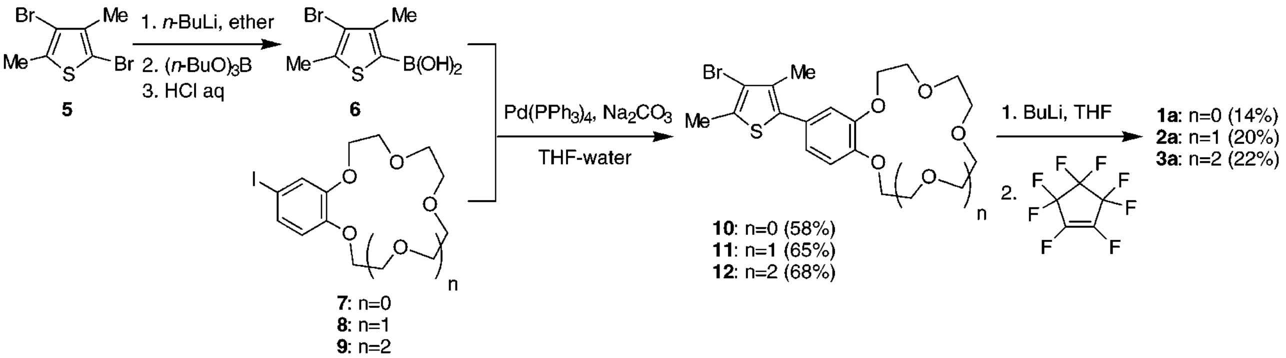


Figure 1. Concept for photoresponsive tweezers having dithienylethene and two crown ether moieties

Scheme 1



photochromic reaction of **1** is shown in Figure 2. Upon irradiation with 313 nm light, the absorption maxima appeared at 583 and 375 nm which are attributed to the closed-ring form **1b**.[8] The spectrum returned to the initial one by irradiation with >480 nm light. The ratio of **1a** and **1b** in photostationary state at 313 nm (PSS_{313}) in CH_2Cl_2 was 9:91 which was determined by the ^1H NMR and absorption spectra.[15] On the other hand, the ratio of **4a** and **4b** at the photostationary state (313 nm) was 45:55. The small conversion of **4** upon irradiation with 313 nm light is due to high ring-opening quantum yield of the bis(benzothienyl)ethene.[16] The extinction coefficient of the both isomers were the same at 313 nm; therefore, the ratio of quantum yields of the ring-closing reaction and that of the ring-opening reaction is 91:9.

The energy barriers between parallel and antiparallel conformations were estimated by dynamic ^1H NMR in $CDCl_3$ or $CDCl_2CDCl_2$. The methyl protons of **1a** appeared as four singlets with same intensity at 290 K. Therefore, there is no exchange between the parallel and the antiparallel conformations in the NMR time scale in this condition, and the ratio of conformations is 1:1. Upon raising the temperature, the methyl signals were broadened, and two sets of methyl protons were coalesced at 303 K. Figure 3 shows the dynamic ^1H NMR spectrum of methyl protons in part. The lifetime of the each

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[15] The conversion of diarylethenes by irradiation was determined from the extinction coefficients of their closed-ring forms which were calculated from the ratio in ^1H NMR spectra and absorption spectra of the solutions with same conversion.

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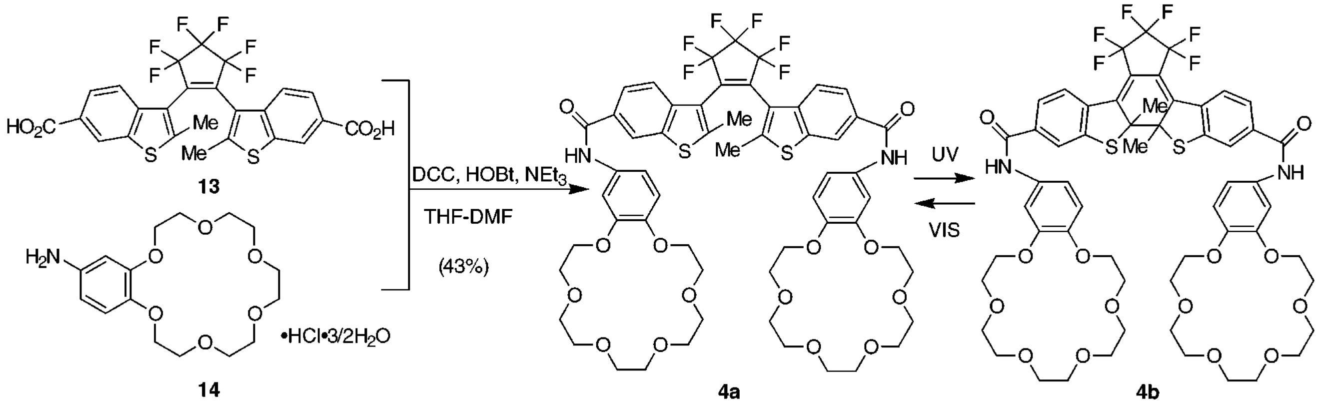
Scheme 2



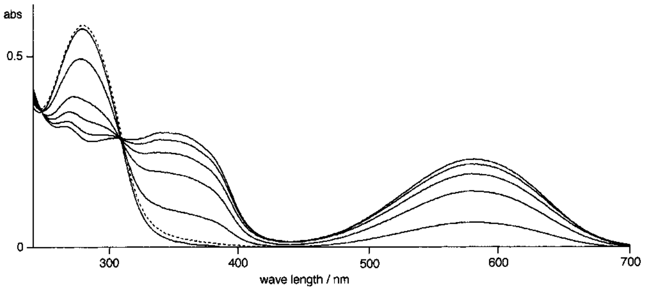


Figure 2. Photochromic reaction of **1** ([**1**] = 1.0 × 10^{-5} mol dm^{-3}, in CH_2Cl_2, solid line: irradiation with 313 nm light for 0, 2, 4, 6, 8, 10 min, dotted line: irradiation of PSS_{313} with >480 nm light for 5 min).

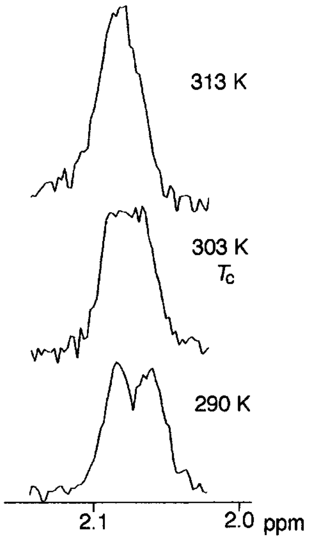


Figure 3. Dynamic ^1H NMR spectra of **1a** (in part) in $CDCl_3$ (200 MHz).

conformation was determined as 0.25 s at 303 K in $CDCl_3$. The energy barrier ($\Delta G_{303}^{\ddagger}$) between two conformations was estimated[17] to be 67 kJ mol^{-1}. The coalescence temperature and the energy barriers of **2a** and **3a** are 303 K and 67 kJ mol^{-1} in $CDCl_3$, respectively. These values are independent of the ring size of crown ethers. The coalescence temperature and $\Delta G_{353}^{\ddagger}$ between two conformations of **4a** were also determined to be 353 K and 71 kJ mol^{-1} in $CDCl_2CDCl_2$, respectively. The lifetime of each conformation is about 0.019 s at 353 K. These values are similar to those reported for 2,3-bis(2-methylbenzo[*b*]thiophen-3-yl)maleic anhydride ($\Delta G_{318}^{\ddagger}$ = 71 kJ mol^{-1}).[16] The parallel and the antiparallel conformations of the diarylethenes having crown ether moieties can convert each other at ambient temperature.

2. Two-Phase Solvent Extraction of Alkali Metal Picrates with Diarylethenes Having Crown Ethers. Two-phase solvent extractions of alkali metal picrates with the open-ring forms **1**, **2**, **3**, or **4**, their photostationary state by irradiation with 313 nm light (PSS_{313}), and the reference crown ethers **10**, **11**, or **12** were carried out (*organic phase*, [**1**, **2**, **3**, or **4**] = 1.0 × 10^{-4} mol dm^{-3} or [**10**, **11**, or **12**] = 2.0 × 10^{-4} mol dm^{-3} in 5 mL of CH_2Cl_2: *aqueous phase*, [MOH] = 0.10 mol dm^{-3}, [picric acid] = 5.0 × 10^{-5} mol dm^{-3} in 5 mL of water, 20 °C). The decrease of absorbance of the aqueous phase at 357 nm was used to estimate the extractability of crown ethers for alkali metal picrates. The results of extractions are shown in Figure 4 and summarized in Table 1.

In the case of dithienylethene with benzo-15-crown-5 ether **2** (Figure 4b), a solution of open-ring form extracts KPic and RbPic to the organic phase. These results indicate that the large alkali metal ions such as K and Rb ion were captured with two crown ethers such as tweezers. Upon irradiation with 313 nm light, the percent of KPic and RbPic extrracted was dramatically decreased. The extractabilities of the PSS_{313} were similar to that of benzo-15-crown-5 ether **11** shown as a dotted line. Therefore, the metal ion tweezers **2a** changed to “single hand” benzo-crown ether by photoirradiation.

The dithienylethene with benzo-12-crown-4 ether **1a** in CH_2Cl_2 extracts NaPic and RbPic, while the extractability of **1** for NaPic and RbPic is much lower than that of **2**. The low extractabilities were further decreased by UV irradiation. The reduced extractabilities are similar to that of **10** (Figure 4a). Similarly, diarylethene **3** with benzo-18-crown-6 ether changed extractability for CsPic by photoirradiation as shown in Figure 4c.

The amide type **4** efficiently extracted KPic and CsPic from the aqueous phase as shown in Figure 4d. The high extractability for CsPic like **3a** indicated that a cesium ion was captured by two benzo-18-crown-6 ether moieties such as tweezers. Upon irradiation with 313 nm light, **4a** converts to **4b** in 55% yield. However, the extract-

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[17] Since the structures of the conformations are not same, the precise estimation of the energy barrier between two conformations should be carried out by line shape analysis of the coalesced signals. Two conformations of the obtained dithienylethenes exist nearly in the ratio of 1:1; therefore, $\Delta G_c^{\ddagger}$ was estimated approximately according to the literature: Calder, I. C.; Garratt, P. J. *J. Chem. Soc. (B)* **1967**, 660.

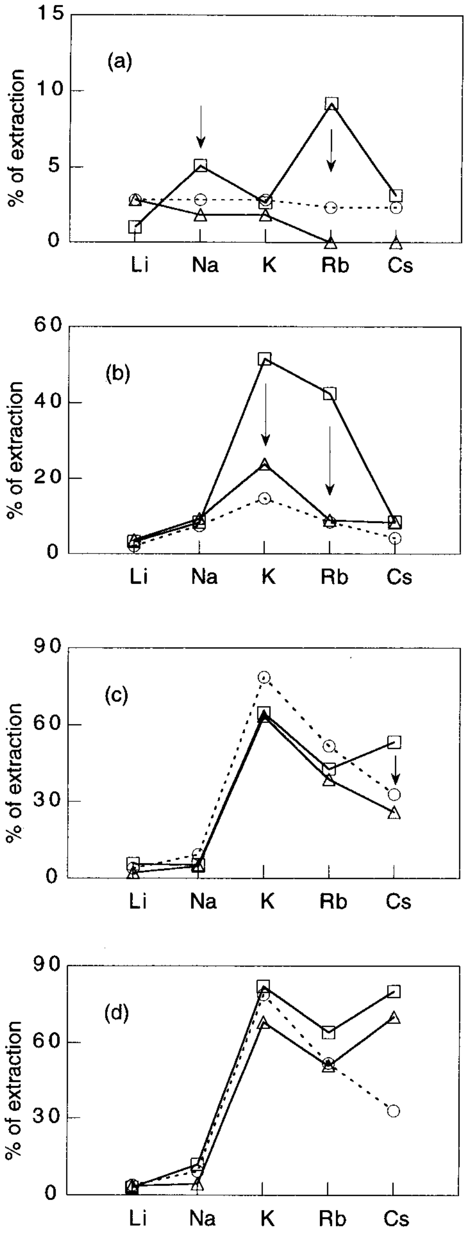

Figure 4. Percent extraction of two-phase solvent extraction of metal picrates with (a) cube: **1a**, triangle: PSS$_{313}$, circle: **10**; (b) cube: **2a**, triangle: PSS$_{313}$, circle: **11**; (c) cube: **3a**, triangle: PSS$_{313}$, circle: **12**; (d) cube: **4a**, triangle: PSS$_{313}$, circle: **12**.

ability of the mixture for CsPic did not change and was still higher than that for RbPic. The extractability of **4b** is similar to that of **4a**. Examination of CPK molecular modeling showed that the separation of two benzo-18-crown-6 ether moieties is not large enough to neglect the tweezers-type conformation because of the long and flexible amide chain between the switch and the binding sites of **4b**.

3. Solid–Liquid Extraction of Alkali Metal Picrates with Diarylethenes Having Crown Ethers. The solid–liquid extraction of NaPic, KPic, RbPic, and CsPic with a solution of **2a** (2.0 × 10^{-3} mol dm^{-3}) in a mixture of CDCl$_3$ and CD$_3$CN (5:1, 0.6 mL) was carried out at 20 °C, and the ^{1}H NMR spectra (600 MHz) of the solutions were measured. In all cases the phenyl protons of metal picrates were observed in the NMR spectra. In the case of NaPic and CsPic, no change in the ratio of parallel (p)/antiparallel (ap) conformations was observed (1:1), whereas the ratio of p/ap conformations changed from 1:1 (no metal) to approximately 10:1 in the presence of KPic or RbPic. Figure 5 shows ^{1}H NMR spectral change in the absence/presence of RbPic.

Table 1. Percent Extraction of Alkali Metal Picrates from Aqueous Phase to Organic Phase with Open-Ring Form and PSS$_{313}$ of Diarylethenes 1–4 and Mono-Benzocrown Ethers 10–12[a]

	LiPic	NaPic	KPic	RbPic	CsPic
1a	1.0	5.1	2.6	9.2	3.1
PSS$_{313}$[b]	2.8	1.8	1.8	<1	<1
10	2.8	2.8	2.8	2.3	2.3
2a	3.2	8.3	51.6	42.5	8.4
PSS$_{313}$[b]	3.7	9.3	24.0	8.9	8.3
11	2.1	7.4	14.7	8.4	4.2
3a	5.6	5.2	64.7	43.0	53.5
PSS$_{313}$[b]	2.2	4.7	63.5	38.8	25.9
12	3.9	9.3	78.7	52.0	32.9
4a	3.0	12.0	82.0	64.0	80.0
PSS$_{313}$[c]	3.6	4.4	68.0	51.0	70.0

[a] The two-phase solvent extraction. Conditions: *organic phase*, [**1**, **2**, **3**, or **4**] = 1.0 × 10^{-4} mol dm^{-3} or [**10**, **11**, or **12**] = 2.0 × 10^{-4} mol dm^{-3} in 5 mL of CH$_2$Cl$_2$: *aqueous phase*, [MOH] = 0.10 mol dm^{-3}, [picric acid] = 5.0 × 10^{-5} mol dm^{-3} in 5 mL of water, 20 °C. [b] **a**/**b** = 9:91. [c] **a**/**b** = 45:55.

As shown in Figure 5, the methyl protons at 2.05, 2.08, 2.33, and 2.35 ppm in the absence of metal picrate shifted to 1.61 (p), 2.10 (ap), 2.41 (ap), and 2.50 (p). These signals were assigned with the aid of EXSY spectra; the exchange was observed between methyl protons at 1.61 and 2.10 ppm and between those at 2.41 and 2.50 ppm. The phenyl protons assigned to parallel conformation also changed from multiplets at 6.87–6.89 ppm to a singlet at 6.25 ppm and a set of doublets at 6.84 and 6.98 ppm with 8.4 Hz coupling constants in the presence of RbPic. The large high-field shift of one of the aromatic protons indicates that the thiophene and phenyl rings of parallel conformation are close to the rubidium ion. These results confirm that the potassium and rubidium ions were captured by the two intramolecular crown ether moieties of **2a** like tweezers as shown in Figure 6.

Similarly, a solution of **3a** (2.0 × 10^{-3} mol dm^{-3}) in a mixture of CDCl$_3$ and CD$_3$CN (5:1, 0.6 mL) extracted solid alkali metal picrates. In all cases the phenyl protons of metal picrates were observed in the NMR spectra. The ratio of p/ap conformational and ^{1}H NMR spectral change was observed only when CsPic was added. The p/ap ratio changed from 1:1 to 5:2 by the extraction of CsPic. The methyl protons at 2.04, 2.07, 2.34, and 2.32 ppm in the absence of metal picrate shifted to 1.70 (p), 2.10 (ap), 2.40 (ap), and 2.48 (p). Some aromatic protons also shifted from 6.85 to 6.42 ppm in the presence of CsPic. The open-form **3a** captures cesium ion like tweezers. On the contrary, the complexation with KPic and RbPic did not affect both the p/ap ratio. These results indicate that **3a** cannot capture potassium and rubidium ions like tweezers.

4. Repeated Change in Concentration of Metal Ions in Aqueous Phase by Alternate Photoirradiation. As described above, diarylethene receptors change the concentration of alkali metal ions by photoirradiation. Figure 7a shows the change in concentration of KPic and RbPic in the aqueous phase of a stirring mixture of **1b** (1.0 × 10^{-4} mol dm^{-3}) in CH$_2$Cl$_2$, and KOH or RbOH (0.10 mol dm^{-3}) and picric acid (5.0 × 10^{-5} mol dm^{-3}) in water

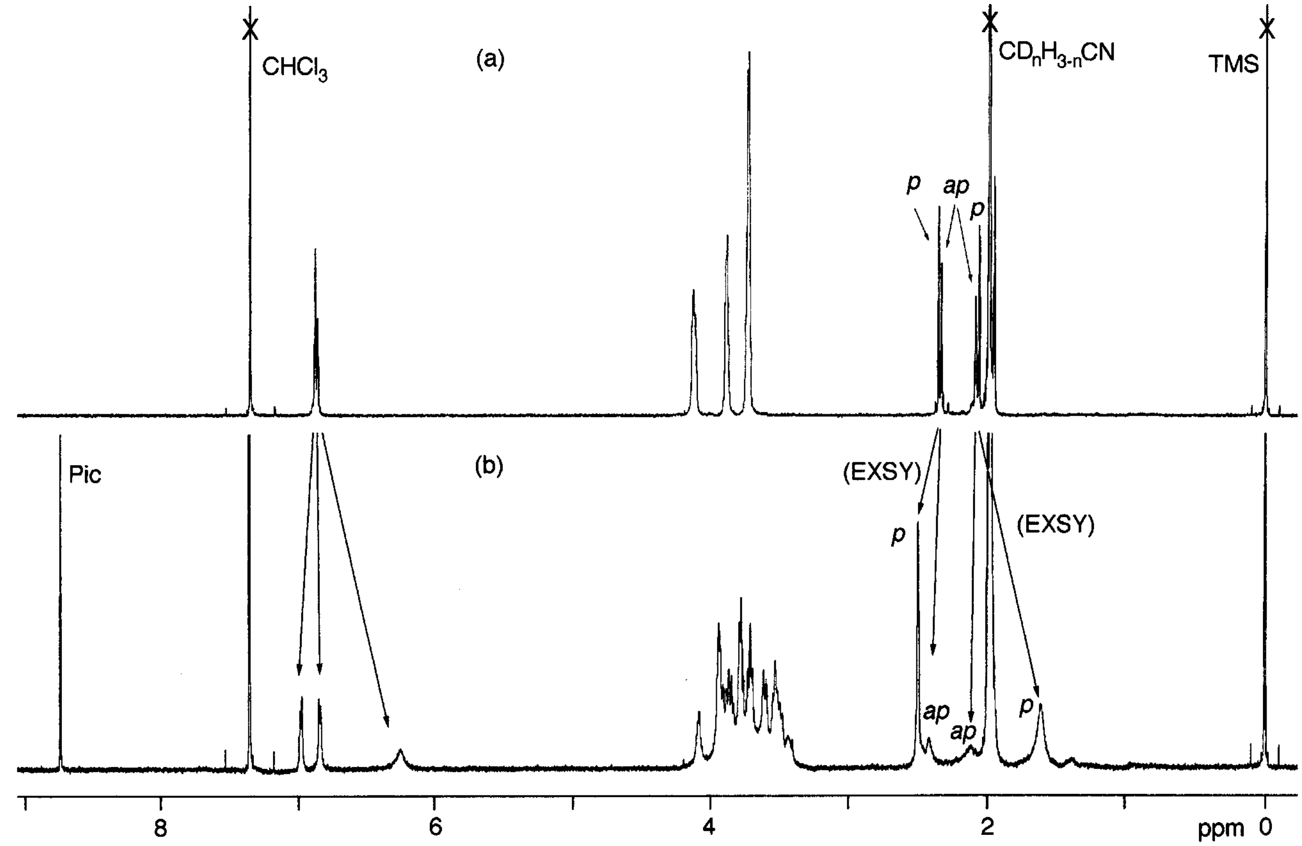

Figure 5. ^{1}H NMR spectrum (600 MHz, 20 °C) of (a) a solution of **2a** (2.0×10^{-3} mol dm^{-3}) in 0.6 mL of CDCl$_3$/CD$_3$CN (5:1); (b) a mixture of (a) and solid RbPic.

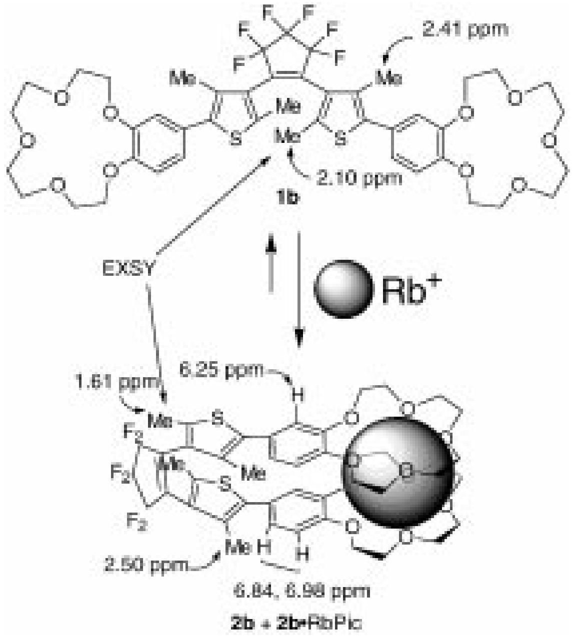

Figure 6. Conceivable structure and assignment of ^{1}H NMR spectrum (600 MHz, 20 °C) of **2a**·RbPic complex.

at 20 °C, by alternative irradiation with 330 ± 70 nm (3 min) and >480 nm light (2 min). The concentration of MPic was estimated from the absorbance at 357 nm. The alternate irradiation of UV light and visible light reversibly changes the concentration of potassium and rubidium ion in aqueous phase. The reversible change of concentration of cesium picrate in aqueous phase by alternate irradiation (UV: 3 min, vis: 3 min, 20 °C) was also observed by use of **3** as shown in Figure 7b.[8] In both cases good reversibility without any photodestruction was observed.

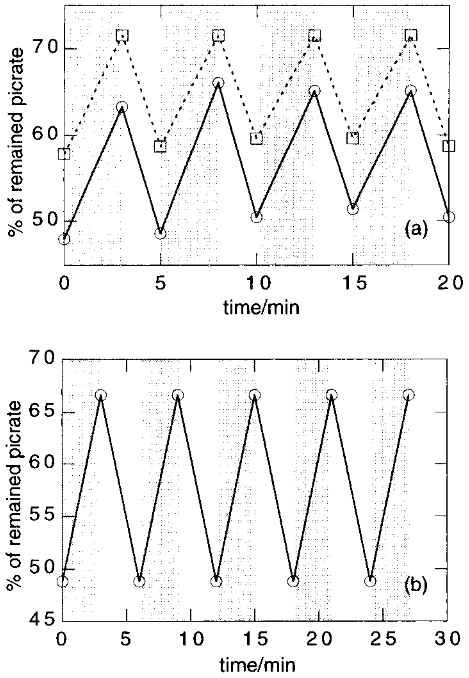

Figure 7. Control of concentration of (a) KPic (solid line) and RbPic (dotted line) in aqueous phase with **2** in CH$_2$Cl$_2$ and (b) CsPic with **3** by alternate irradiation with 330 ± 70 nm (gray) and >480 nm light.

Conclusions

The dithienylethene receptors having two benzo-crown ethers in the molecule changed the extractability for various alkali picrates whose ionic radii were larger than the ring sizes of crown ethers. The ^{1}H NMR spectra of the solution of the solid−liquid extractions indicated that such larger metal ions are captured with two intramolecular crown ethers like tweezers.

Experimental Section

General Remarks. ^{1}H NMR spectra were recorded at 200 MHz unless otherwise noted and at 600 MHz only for Figures 5 and 6. TMS was used as reference. Melting points are not corrected. Merck silica gel 60 (230−400 mesh) was used for column chromatography. HPLC was performed with Kanto Chemical Mightysil RP-18, and methanol was used as eluent. Recycling preparative GPC was performed by a Japan Analytical Industry LC-908. Spectrograde solvents were used for absorption spectra. A mercury lamp (Ushio 1 kW) was used as a light source. Monochromic light was obtained by passing light through a Toshiba band-pass filter (UVD-33S), cutoff filter (Y-48), or Jobin Yvon monochromator.

Materials. 2,4-Dibromo-3,5-dimethylthiophene (**5**),[18] 4-iodobenzo-12-crown-4 ether (**7**),[12] 4-iodobenzo-15-crown-5 ether (**8**),[12] and 4-iodobenzo-18-crown-6 ether (**9**),[13] and 3-(2-(6-carboxy-2-methylbenzo[*b*]thiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2-methylbenzo[*b*]thiophene-6-carboxylic acid (**13**)[19] were prepared according to the manner described in the literatures. 4-Aminobenzo-18-crown-6 ether sesquihydrate hydrochloride (**14**) was purchased from ACROS.

4-Bromo-3,5-dimethylthiophene-2-boronic Acid (6). To a stirred solution of **5** (15.0 g, 55.5 mmol) in 300 mL of diethyl ether at −70 °C was added dropwise 1.6 N *n*-BuLi in hexane (40 mL, 64 mmol), and the reaction mixture was stirred for 30 min at −70 °C. To the reaction mixture was added 10 mL of tributyl borate (81 mmol), and the mixture was stirred for 2 h and was allowed to stand to room temperature. To the mixture was added 100 mL of 4% HCl, and the organic phase was separated. The organic phase was extracted with 100 mL of 4% NaOH aqueous solution two times. The aqueous phase was separated and acidified with 10% HCl. The white precipitate was collected by filtration and washed with water. Drying of the white powder in vacuo afforded 10.3 g of **6** in 80% yield. Boronic acid **6** was so labile that **6** was used without further purification: ^{1}H NMR (DMSO) δ 2.32 (s, 3H), 2.37 (s, 3H).

3-Bromo-2,4-dimethyl-5-(2,5,8,11-tetraoxabicyclo[10.4.0]hexadeca-1(12),13,15-trien-14-yl)thiophene (10). To a stirred solution of **6** (1.76 g, 7.5 mmol), 4-iodobenzo-12-crown-4 ether (1.97 g, 5.0 mmol), and Pd(PPh$_3$)$_4$ (500 mg, 0.43 mmol) in 30 mL of THF was added an aqueous solution of Na_2CO_3 (2 N, 15 mL). The mixture was stirred and refluxed for 8 h and allowed to cool to room temperature. The organic phase was separated, washed with brine, and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was subjected to silica gel column chromatography (eluent: $CHCl_3$/MeOH (20:1)). Concentration of second eluate and recrystallization of the residue from hexane afforded 1.34 g (65%) of **10** as colorless plates: mp 104.5−107.0 °C. ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 2.42 (s, 3H), 3.80 (s, 4H), 3.82−3.93 (m, 4H), 4.16−4.23 (m, 4H), 6.98−7.01 (m, 3H). MS m/z = 412, 414 (M$^+$). Anal. Calcd for $C_{18}H_{21}BrO_4S$: C, 52.30; H, 5.12. Found: C, 52.77; H, 5.17.

3-Bromo-2,4-dimethyl-5-(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-1(15),16,18-trien-17-yl)thiophene (11). Compound **11** was obtained from **6** and **8** by a manner similar to that described above: colorless prisms (hexane), mp 93.5−94.5 °C. ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 2.40 (s, 3H), 3.76 (s, 8H), 3.82−3.94 (m, 4H), 4.12−4.18 (m, 4H), 6.86−6.92 (m, 3H). MS m/z = 456, 458 (M$^+$). Anal. Calcd for $C_{20}H_{25}BrO_5S$: C, 52.52; H, 5.51. Found: C, 52.98; H, 5.52.

3-Bromo-5-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)-2,4-dimethylthiophene (12). Compound **12** was obtained from **6** and **9** by a manner similar to that described above: colorless prisms (hexane), mp 65.2−67.7 °C. ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 2.40 (s, 3H), 3.68 (s, 4H), 3.70−3.78 (m, 8H), 3.91−3.95 (m, 4H), 4.14−4.20 (m, 4H), 6.87−6.91 (m, 3H). MS m/z = 500, 502 (M$^+$). Calcd for $C_{22}H_{29}BrO_6S$: C, 52.70; H, 5.83. Found: C, 52.69; H, 5.86.

3-(2-(2,4-Dimethyl-5-(2,5,8,11-tetraoxabicyclo[10.4.0]hexadeca-1(12),13,15-trien-14-yl)(3-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2,4-dimethyl-5-(2,5,8,11-tetraoxabicyclo[10.4.0]hexadeca-1(12),13,15-trien-14-yl)thiophene (1a). To a solution of **10** (1.0 g, 2.4 mmol) in 15 mL of THF was added dropwise a solution of 1.6 N *n*-BuLi (2.0 mmol, 3.2 mmol) in hexane at −70 °C, and the reaction mixture was stirred for 30 min at this temperature. To the mixture, was added octafluorocyclopentene (0.1 mL, ca. 1.2 mmol) dropwise two times, and the mixture was stirred for 2 h at −70 °C. The mixture was allowed to stand to room temperature, and water was added. The organic phase was separated, washed with brine, and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was subjected to column chromatography (eluent: chloroform/methanol = 20:1). The second eluent was concentrated, and the residue was subjected to preparative GPC (eluent: $CHCl_3$). The first eluate was concentrated, and the residue was subjected to reversed phase HPLC (eluent: MeOH). Concentration of the first eluate and recrystallization of the residue from hexane afforded 140 mg (14%) of **1a** as colorless prisms: mp 178.5−179.8 °C. ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H), 2.06 (s, 3H), 2.31 (s, 3H), 2.33 (s, 3H), 3.79 (s, 8H), 3.83−3.86 (m, 8H), 4.16−4.20 (m, 8H), 6.94−6.95 (m, 6H). MS m/z = 840 (M$^+$). Anal. Calcd for $C_{41}H_{42}F_6O_8S_2$: C, 58.50; H, 5.03. Found: C, 58.55; H, 5.17.

3-(2-(2,4-Dimethyl-5-(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-1(15),16,18-trien-17-yl)(3-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2,4-dimethyl-5-(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-1(15),16,18-trien-17-yl)thiophene (2a). Compound **2a** was obtained from **11** by a manner similar to that described above: colorless prisms (hexane), mp 137.0−138.0 °C. ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3H), 2.08 (s, 3H), 2.33 (s, 3H), 2.35 (s, 3H), 3.76 (s, 16H), 3.89−3.92 (m, 8H), 4.12−4.16 (m, 8H), 6.86−6.87 (m, 6H). MS m/z = 928 (M$^+$). Anal. Calcd for $C_{45}H_{50}F_6O_{10}S_2$: C, 58.18; H, 5.42. Found: C, 58.38; H, 5.49.

3-(3,3,4,4,5,5-Hexafluoro-2-(5-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)-2,4-dimethyl(3-thienyl))cyclopent-1-enyl)-5-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-tiren-20-yl)-2,4-dimethylthiophene (3a). Compound **3a** was obtained from **12** by a manner similar to that described above: colorless viscous oil. ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3H), 2.07 (s, 3H), 2.31 (s, 3H), 2.33 (s, 3H), 3.70 (s, 16H), 3.72−3.80 (m, 8H), 3.85−3.98 (m, 8H), 4.12−4.18 (m, 8H), 6.86 (s, 3H). MS m/z = 1175 (M$^+$). Anal. Calcd for $C_{49}H_{58}F_6O_{12}S_2$: C, 57.86; H, 5.75. Found: C, 58.10; H, 5.93.

4,14-Bis(2,5,8,11-tetraoxabicyclo[10.4.0]hexadeca-1(12),13,15-trien-14-yl)-8,8,9,9,10,10-hexafluoro-1,2,5,13-tetramethyl-3,15-dithiatetracyclo[10.3.0.0^{2,6}.0^{7,11}]pentadeca-4,6(7),11(12),13-tetraene (1b). Irradiation of a solution of **1a** in $CDCl_3$ with 313 nm light afforded a mixture of **1a** and **1b** (9:91) at photostationary state. **1b**: ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 6H), 2.23 (s, 6H), 3.80 (s, 8H), 3.82−3.88 (m, 8H), 4.18−4.24 (m, 8H), 6.99 (s, 2H), 7.05 (s, 4H).

4,14-Bis(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-1(15),16,18-trien-17-yl)-8,8,9,9,10,10-hexafluoro-1,2,5,13-tetramethyl-3,15-dithiatetracyclo[10.3.0.0^{2,6}.0^{7,11}]pentadeca-4,6(7),11(12),13-tetraene (2b). Irradiation of a

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solution of **2a** in $CDCl_3$ with 313 nm light afforded a mixture of **2a** and **2b** (9:91) at photostationary state. **2b**: ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 6H), 2.24 (s, 6H), 3.76 (s, 16H), 3.85−3.92 (m, 8H), 4.12−4.20 (m, 8H), 6.85−6.98 (m, 6H).

4,14-Bis(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)-8,8,9,9,10,10-hexafluoro-1,2,5,13-tetramethyl-3,15-dithiatetracyclo[10.3.0.0^{2,6}.0^{7,11}]-pentadeca-4,6(7),11(12),13-tetraene (3b). Irradiation of a solution of **3a** in $CDCl_3$ with 313 nm light afforded a mixture of **3a** and **3b** (9:91) at photostationary state. **3b**: ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 6H), 2.23 (s, 6H), 3.68 (s, 8H), 3.66−3.78 (m, 16H), 3.90−3.96 (m, 8H), 4.15−4.21 (m, 8H), 6.89 (s, 2H), 6.84−6.98 (m, 6H).

(3-(3,3,4,4,5,5-Hexafluoro-2-(6-(*N*-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-triene-20-yl)-carbamoyl)-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-enyl)-2-methylbenzo[*b*]thiophen-6-yl)-*N*-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)formamide (4a). To a stirred solution of 56 mg of dicarboxylic acid (**13**) (0.10 mmol), 30 mg of 1-hydroxybenzotriazole (0.20 mmol), and 80 mg of 4-aminobenzo-18-crown-6 ether sesquihydrate hydrochloride (**14**) (0.20 mmol) in 25 mL of THF−DMF (4:1) were added 51 mg of dicyclohexylcarbodiimide (0.25 mmol) and 0.2 mL of triethylamine at room temperature, and the mixture was stirred for 4 h. To the reaction mixture, 50 mL of brine was added, and products were extracted with 50 mL of $CHCl_3$. The extracts were washed with brine, dried over $MgSO_4$, and evaporated. The residue was subjected to preparative GPC. Concentration of the first eluate and recrystallization of the residue from hexane−acetone afforded 50 mg (43%) of **9** as colorless needles: mp 177.5−180.5 °C. ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 2.6H), 2.48 (s, 3.4H), 3.70 (s, 8H), 3.65−4.02 (m, 28H), 4.13−4.15 (m, 4H), 6.60−8.24 (m, 12H), 8.78 (br s, 2H). MS $m/z = 1175$ (M^+). Anal. Calcd for $C_{57}H_{60}F_6N_2O_{14}S_2 \cdot H_2O$: C, 57.38; H, 5.24; N, 2.35. Found: C, 57.30; H, 5.03; N, 2.36.

(3,3,4,4,5,5-Hexafluoro-20-(*N*-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)carbamoyl)-15,16-dimethyl-14,17-dithiahexacyclo[14.7.0.0^{2,6}.0^{7,15},0^{8,13},0^{18,23}]tricosa-1(2),6(7),8(9),10,12,18(19),20,22-octaen-11-yl)-*N*-(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)formamide (4b). Irradiation of a solution of **4a** in $CDCl_3$ with 313 nm light afforded a mixture of **4a** and **4b** (45:55) at photostationary state. **4a**: ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 6H), 3.70 (s, 8H), 3.65−4.02 (m, 28H), 4.13−4.15 (m, 4H), 6.60−8.24 (m, 12H).

Two-Phase Solvent Extraction of Alkali Metal Picrates. In the dark a 5 mL solution of diarylethene having crown ethers **1a**, **2a**, **3a**, and **4a** (1.0×10^{-4} mol dm^{-3}), or their photostationary state (313 nm), or monomeric crown ether **10**, **11**, and **12** (2.0×10^{-4} mol dm^{-3}) in CH_2Cl_2 and a 5 mL aqueous solution of metal hydroxide (0.10 mol dm^{-3}) and picric acid (5.0×10^{-5} mol dm^{-3}) were mixed, and the mixture was shaken vigorously for 2 min at 20 °C. The aliquot of upper aqueous solution was withdrawn, and the absorption spectrum was recorded. The extractabilities of the crown ethers were determined by decrease of the absorbance at 357 nm which is the absorption maxima of metal picrates in aqueous solution.

Solid−Liquid Extraction of Alkali Metal Picrates. In the dark to a solution of **2a** or **3a** (1.2×10^{-6} mol) in a mixed solvent of $CDCl_3/CD_3CN$ (5:1) 0.6 mL was added alkali metal picrates (1.0×10^{-5} mol), and the mixture was shaken vigorously for 10 min at 20 °C. The ^{1}H NMR spectrum of the mixture was recorded at 20 °C.

Repeated Change in Concentration of Metal Ions in Aqueous Phase by Alternate Photoirradiation. In the dark a mixture of a 5 mL solution of **2a** or **3a** (1.0×10^{-4} mol dm^{-3}) in CH_2Cl_2 and a 5 mL aqueous solution of metal hydroxide (0.10 mol dm^{-3}) and picric acid (5.0×10^{-5} mol dm^{-3}) was vigorously stirred by magnetic stirrer for 3 min, and the absorption spectra of aqueous phase was recorded (0 min). The mixture was irradiated with 330 ± 70 nm light for 3 min with vigorous stirring, and the spectrum was recorded. Then the mixture was irradiated with >480 nm light for 3 min (for **2**) or 2 min (for **3**) with vigorous stirring at 20 °C, and the spectrum was recorded. The alternate irradiation and measurement of the spectrum were repeated 4−5 times. The percent of metal picrate remaining in aqueous phase was determined by the change of the absorbance at 357 nm.

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