

# Photoresponsive Cesium Ion Tweezers with a Photochromic Dithienylethene

Michinori Takeshita\* and Masahiro Irie

Department of Chemistry and Biochemistry, Graduate School of Engineering,  
Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-81, Japan

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**Abstract:** Novel molecular tweezers having two 18-crown-6 moieties as recognition sites and dithienylethene as a photoswitch reversibly changed the affinity for cesium ion by photoirradiation.  
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Recognition of the cesium ion has been extensively studied since it is one of the main metal ions in radioactive wastes generated in the atomic power stations.<sup>1</sup> Therefore, various types of receptors for cesium ions have been synthesized and their affinities for the cesium ion have been examined.<sup>2</sup> Crown ethers with a large ring such as 21-crown-7<sup>3</sup> and calixarenes with a polyether bridge<sup>4,5</sup> are typical cesium ion receptors. Another class of receptors for the cesium ion is a tweezers-type molecule which is composed of two crown ether moieties.<sup>6</sup>

Switching of host-guest events by photoirradiation potentially enables us to carry out active transportation of guest molecules. Photochromic compounds, such as thioindigo,<sup>7</sup> azobenzene,<sup>8</sup> and anthracene,<sup>9</sup> have been widely used as switching moieties. We have already reported a bis(benzothienyl)ethene receptor bearing two boronic acid moieties changes the affinity for glucose by photoirradiation.<sup>10</sup> The dithienylethene undergoes a thermally irreversible and fatigue-resistant photochromic reaction.<sup>11</sup> The open-ring form of dithienylethene has

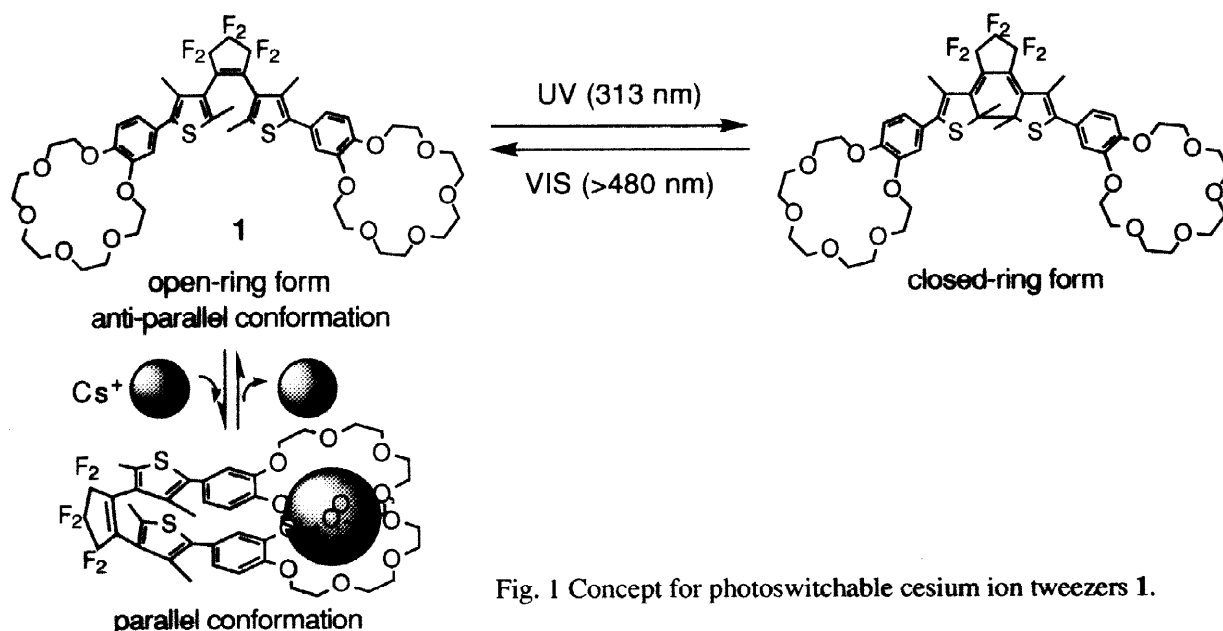


Fig. 1 Concept for photoswitchable cesium ion tweezers 1.

two conformations, parallel and anti-parallel (Fig. 1). Two crown ether moieties of the open-ring form in the parallel conformation can cooperatively bind with a large metal ion such as the cesium ion like tweezers, while in the photogenerated closed-ring form the crown ether moieties are separated from each other and can not capture the metal ion like tweezers.

The synthesis of **1** is shown in Scheme 1. The coupling reaction of thiophene-boronic acid **3** and iodobenzo-18-crown-6 **5**, which was prepared by treatment of benzo-18-crown-6 **4** with benzyltrimethylammonium dichloriodate<sup>12</sup> was carried out in the presence of Pd(0). The coupling reaction of **6** and perfluorocyclopentene afforded **1**.<sup>13</sup> Compound **1** was isolated by recycle preparative GPC and reversed phase HPLC (eluent: methanol). <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> indicated that compound **1** is an inseparable 1:1 mixture of parallel and anti-parallel conformations at 20 °C.

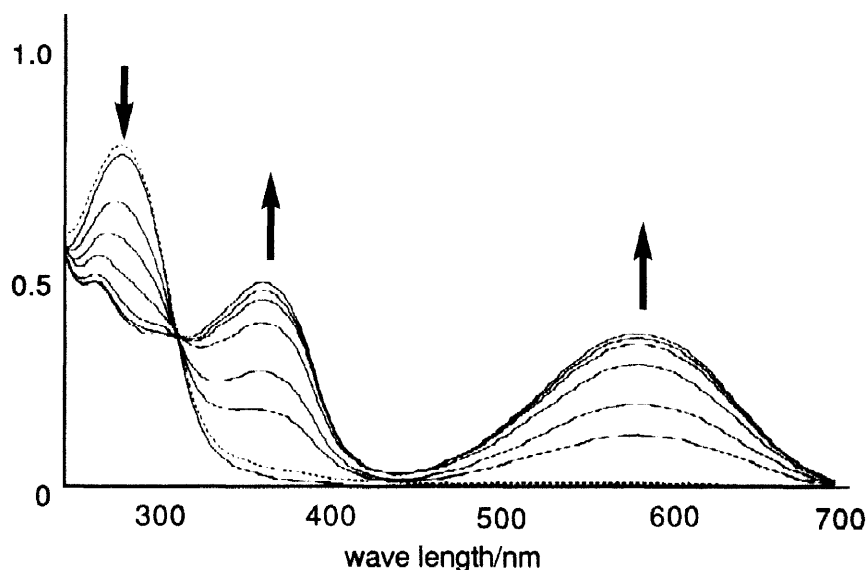
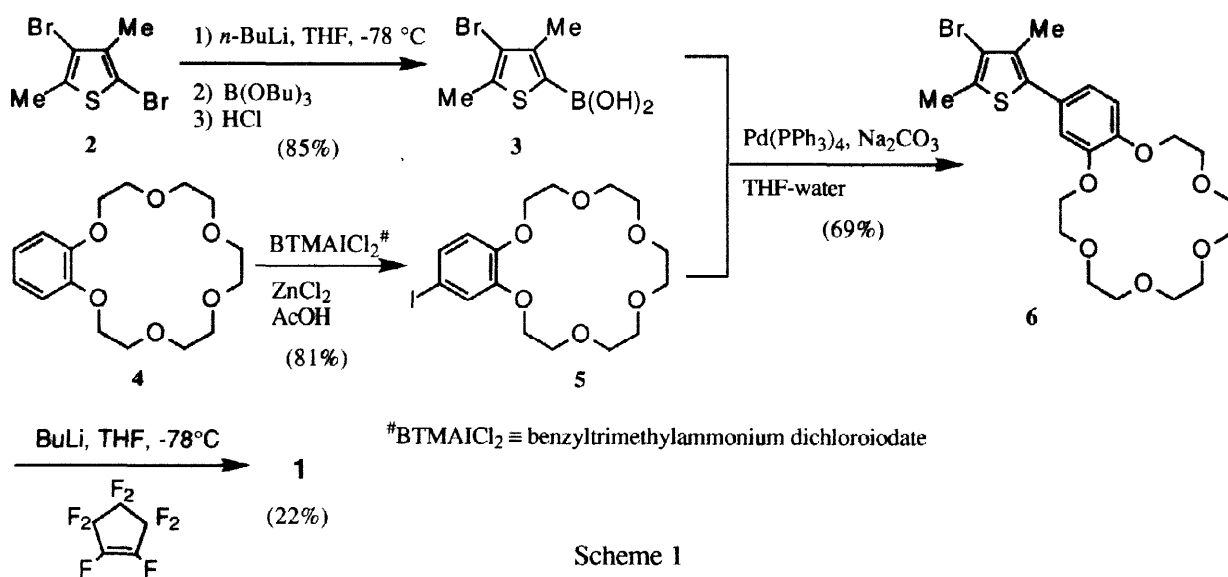


Fig. 2 Absorption spectra change of **1** in CH<sub>2</sub>Cl<sub>2</sub> (2.5×10<sup>-5</sup> mol dm<sup>-3</sup>); solid line, 313 nm irradiation; dotted >480 nm irradiation.

Figure 2 shows photochromic reaction of **1**. Upon irradiation with 313 nm light, absorption maxima appeared at 583 and 375 nm. The spectrum returned to the initial one by irradiation with >480 nm light.  $^1\text{H}$  NMR as well as absorption spectra indicated that at the photostationary state (PSS; irradiation wavelength: 313 nm) 91% of **1** converted to the closed-ring form.

The two-phase solvent extraction of alkali metal picrates (Mpic) with receptor **1** was carried out and the results are summarized in Fig. 3 (organic phase,  $[\mathbf{1}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$  in 5 ml of  $\text{CH}_2\text{Cl}_2$ ; aqueous phase,

$[\text{MOH}] = 0.10 \text{ mol dm}^{-3}$ , [picric acid] =  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$  in 5 ml of water;  $20^\circ\text{C}$ ). The decrease of absorbance of picrates in aqueous phase at 357 nm was used to estimate the affinity of **1** for metal ions. The open-ring form of **1** efficiently extracts KPic, CsPic and RbPic to an organic phase. LiPic and NaPic were scarcely extracted. The larger affinity of **1** for CsPic than RbPic suggests that the opening form behaves like tweezers when it captures the cesium ion.

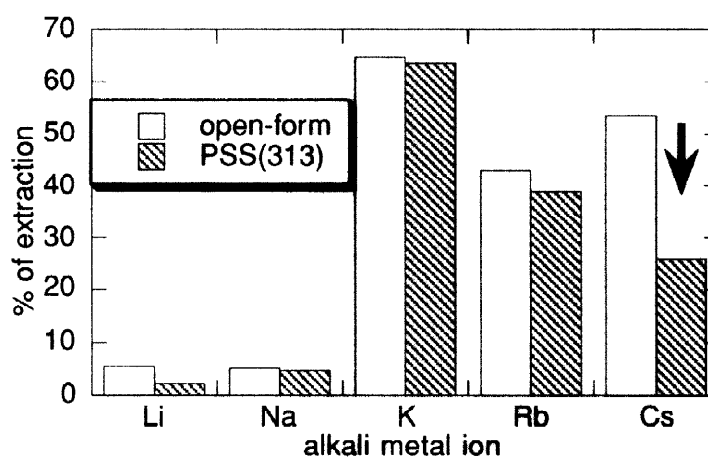


Fig. 3 Two-phase extraction of alkali metal picrates with photoswitchable metal ion tweezers **1**.

Upon irradiation with 313 nm light,

the percentage of extraction for CsPic decreased from 54% to 26%. The decrease is due to the structural change of **1** to the closed-ring form which is unable to capture cesium ion. The remaining small affinity of the closed ring form of **1** for CsPic indicates that intermolecular binding with cesium ion coexists or benzo-18-crown-6 weakly binds with cesium ion solely. It is worthwhile to note that the photoresponsive effect was observed only for CsPic and the affinity for other ions does not change by photoirradiation.

The solid-liquid extraction of KPic, RbPic and CsPic with a solution of **1** ( $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) in a mixture of  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$  (5:1, 0.6 ml) was also carried out at  $20^\circ\text{C}$  and the  $^1\text{H}$  NMR spectra of the solutions were measured. In all cases the phenyl protons of metal picrates were observed in the NMR spectra. In the case of KPic and RbPic, no change in the ratio of parallel (p)/anti-parallel (ap) conformations was observed (1:1), whereas the ratio of p/ap conformations changed from 1:1 (no metal) to 5:2 in the presence of CsPic. Furthermore, 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 shifts of the methyl protons and phenyl protons are due to the effect of the opposite aromatic ring. These results imply that only the cesium ion was captured by intermolecular two crown ether moieties like tweezers.

Figure 4 shows the change in extracted CsPic in the organic phase of a stirred mixture of **1** ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2$ , and CsOH ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ ) and picric acid ( $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) in water at  $20^\circ\text{C}$  by alternate irradiation with  $330 \pm 70 \text{ nm}$  and  $>480 \text{ nm}$  light. The alternate irradiation of UV and visible light reversibly changes the concentration of the cesium ion in aqueous phase.

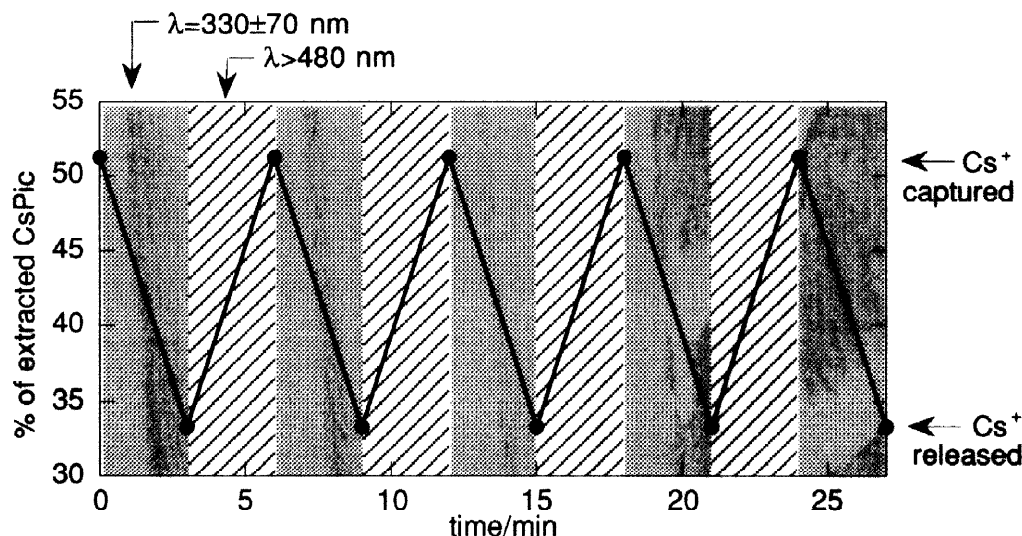


Fig. 4 Control of extraction of cesium picrate by alternate photoirradiation.

In conclusion, the photochromic molecular tweezers composed of two 18-crown-6 moieties and a photochromic dithienylethene changed the affinity for the cesium ion by photoirradiation.

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