



# Monocationic ionophores capable of ion-responsive intramolecular charge transfer absorption variation



Tetsuo Kuwabara<sup>a,\*</sup>, Xuanyi Tao<sup>a</sup>, Haocheng Guo<sup>a</sup>, Masayo Katsumata<sup>b</sup>, Hideki Kurokawa<sup>c</sup>

<sup>a</sup> Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4 Takeda, Kofu 400-8511, Japan

<sup>b</sup> Center for Instrumental Analysis, Center for Creative Technology, University of Yamanashi, 4 Takeda, Kofu 400-8511, Japan

<sup>c</sup> Graduate School Science and Engineering, Saitama University, 225, Shimo-Okubo, Sakura, Saitama 338-8570, Japan

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## ABSTRACT

In this study, two monocationic hosts, **1** and **2**, were prepared. They are structural isomers of phenylpyridinium compounds conjugated benzocrown ether, in which a phenyl group is substituted at the four- and 3-positions on the pyridinium unit, respectively. Both compounds showed intramolecular charge transfer (ICT) absorptions at around 340 nm, which shifted the blue side by the presence of alkali and alkaline earth metal ions due to the formation of a 1:1 host-guest inclusion complex. Compounds **3** and **4**, which are analogs of **1** and **2** with a non-crown ether structure, exhibited ICT absorptions similar to those exhibited by **1** and **2**, but did not show guest-induced absorption variations. The guest-induced absorption variations of **1** and **2** could be used for alkali and alkaline metal ion sensing. Both **1** and **2** detected Mg<sup>2+</sup> with high sensitivity and showed a similar preference to smaller ions for both alkali earth metal ions and alkali metal ions. For comparison, compounds **5** and **6** were also used for ion sensing, whose structures are similar to that of **1**, but different in the substituent of a hydrogen atom and the pyridyl group instead of phenyl group of **1**, respectively. All monocationic hosts showed similar sensing patterns that are roughly parallel to their binding constants.

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## 1. Introduction

Conjugated compounds in which  $\pi$ -electron donor and acceptor units are connected through a  $\pi$ -conjugated system, have received considerable attention. These compounds exhibit intramolecular charge transfer (ICT) absorptions, which are applicable to various fields such as sensors and nonlinear optics.<sup>1</sup> In particular, quaternized pyridinium derivatives have attracted interest as an acceptor because they are readily synthesized, highly stable, and structurally simple.<sup>2</sup> When pyridinium derivatives are connected to functional  $\pi$ -electron-donating components, the conjugated compounds are expected to show ICT absorption in the visible region and exhibit certain unique properties in addition to their original properties. Our objective is to design and develop chemosensors that undergo optical variations that are remarkable as possible when binding with chemical species.<sup>3</sup> Such chemosensors could facilitate the development of a prompt and convenient sensing system. A number of chemosensors, particularly for metal ions, have been

prepared for the detection of chemical species, by absorption and fluorescence changes induced by the host-guest complex formation.<sup>4</sup> Such supramolecular systems are based on crown ethers, calixarenes, and so on because of easy modification with functional groups and appropriate chromophores. In past decades, there are many reports on supramolecular chemosensors exhibiting ICT variations in response to metal ions in solutions. The majority of these systems are based on ICT fluorescence variations induced by host-guest complexation.<sup>5</sup> There is a few reports on sensing systems using fluorescent chromophore and bipyridinium acting as the fluorescent probe for the analyte and its quencher, respectively.<sup>6</sup> These involved a face-to-face  $\pi$ - $\pi$  packing structure for the probe and its quencher and/or for the intermolecular CT absorption complex in the system. Recently, we have reported ion sensing systems utilizing dicationic compounds, in which the bipyridinium unit was directly connected to the benzocrown ether without a methylene spacer.<sup>7</sup> These compounds with the  $\pi$ -conjugated structure exhibited ICT absorption in the visible region in response to the presence of guest ions, which could be applied to ion sensing systems. Furthermore, we found that the monocationic pyridinium benzocrown ether conjugate **5**, which unlike the bipyridinium benzocrown conjugates, lacked the pyridinium

\* Corresponding author. Tel./fax: +81 55 220 8548; e-mail address: [kuwabara@yamanashi.ac.jp](mailto:kuwabara@yamanashi.ac.jp) (T. Kuwabara).

substituent, exhibited the ICT absorption and showed the different ICT absorption and ion sensing ability.<sup>8</sup> The substituent unit on the pyridinium benzocrown conjugate would affect both ICT absorption and ion sensing properties.

In the course of our investigation, we wish to report the synthesis and guest-responsive ICT absorption variations of two novel pyridinium-benzocrown ether conjugates, **1** and **2**, which possess a phenyl group at the four- and 3-positions on the pyridinium ring, respectively, together with their non-crown ether analogs, **3** and **4**. These conjugates have advantages for easy synthesis with only two-step reaction from commercially available reagents, although other chemosensors are needed a multistep reaction for synthesis. Furthermore, these conjugates would show unique ICT absorptions, depending on the position and the kind of the substitution on the pyridinium ring, in response to the ions and interesting ion sensing abilities when compared to **5** and **6**, which possess a hydrogen atom and a pyridyl group rather than the phenyl group of **1**, respectively.<sup>8,9</sup> Because of the simple structure, they would provide information about the mechanism of the guest-induced spectral variations and would elucidate its role in the conjugated unit and the substituent effect in the molecule as well as the sensing abilities of the monocationic host. The positive charge in the molecule would also affect the selectivity and affinity for ion sensing (Chart 1).

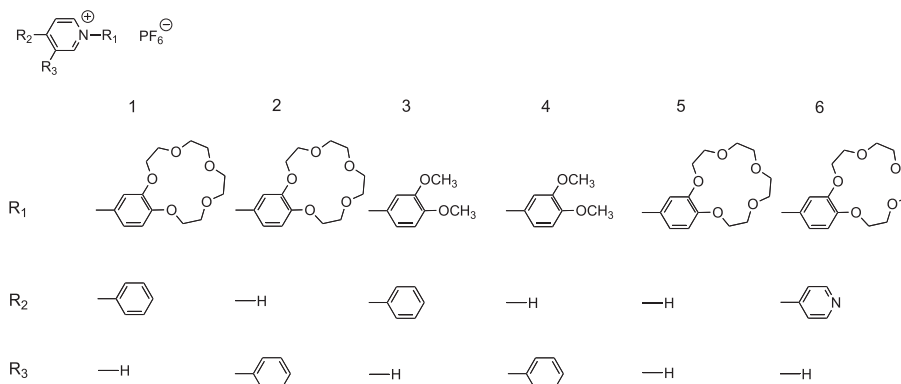


Chart 1. Structure of monocationic hosts and their analogs.

## 2. Results and discussions

### 2.1. Absorption spectra

Fig. 1 shows the absorption spectra of **1**, **2**, **3**, and **4** together with **5** and **6** (0.02 mM) in acetonitrile. Compound **1** showed two absorption bands at 305 and 342 nm, although the latter band was observed as a shoulder band of the former band broadly, whereas compound **3**, as an analog of **1** with the non-crown ether structure, showed absorption bands at 304 and 344 nm, which was similar to **1**. Similar absorption spectra of **1** and **3** indicate a similar  $\pi$ -electron distribution character. Compound **2** also showed absorption spectrum similar to that of **4**. Absorption peaks were observed at 234 and 260 nm for **2** and at 232 and 260 nm for **4**. These peaks are split and shifted to blue side compared with the band at around 300 nm for **1** and **3**. The broad bands observed above 340 nm for **2** and **4** were small compared with those for **1** and **3**, even through there was no wavelength shift. The positional difference of the substituent phenyl group between **1** and **3** and/or **2** and **4** may affect the intensity of the band observed at both longer and shorter

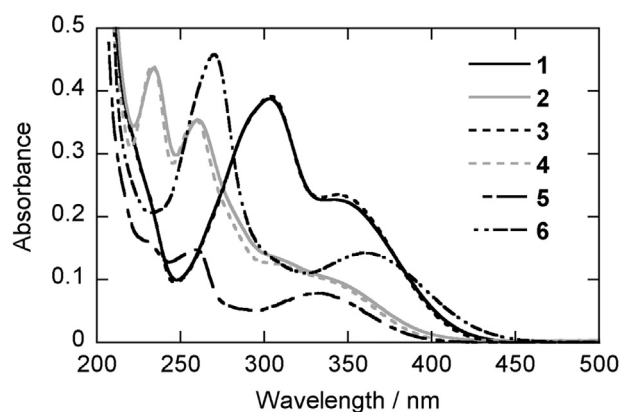


Fig. 1. Absorption spectra of **1**, **2**, **3**, and **4** together with **5** and **6** in acetonitrile. The concentrations were 0.02 mM.

wavelength sides rather than the wavelength. The bands observed above 340 nm for **1**, **2**, **3**, and **4** are characteristic because absorption is not observed above 340 nm for *N*-propyl-4-phenyl-pyridinium (**7**) and *N*-propyl-3-phenyl-pyridinium (**8**) (Fig. 1S). The bands are associated with the conjugated structure of the benzocrown ether and pyridinium units, which are  $\pi$ -electron-rich and  $\pi$ -electron-deficient, respectively. The direct conjugation of these units through the  $\sigma$ -bond should result in charge transfer absorption. Since **1** and **2** possess a positive charge in pyridinium and the crown

ether is attracted to the positive charge in a molecule, we have investigated the possibility of intermolecular interaction. The concentration dependencies of the molecular extinction coefficients at 305 and 340 nm for **1** and those at 260 and 340 nm for **2** were not observed in concentrations ranging from 5  $\mu$ M to 0.1 mM. Furthermore, the spectral shapes of **1** and **2** did not change under lower and higher concentration conditions. These results indicate that their charge transfer absorptions occur intramolecularly but not intermolecularly.

On the other hand, compound **5**, which lacks of the phenyl group, clearly exhibited an ICT absorption band at approximately 330 nm.<sup>8</sup> The ICT absorption band of **5** was observed at a wavelength similar to those of **1** and **2**. Compound **6**, bearing a pyridyl group rather than the phenyl group in **1** at the *para*-position on the pyridinium unit, exhibited ICT absorption at 360 nm, which is observed at the longer wavelength side by approximately 20–30 nm compared with **1**, **2**, and **5**. This is associated with the acceptor character of the pyridinium unit. The acceptor character of the pyridinium unit is enhanced when the pyridyl unit is incorporated onto the pyridinium ring at the *para*-position as the substituent

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