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| **Relation** | |
Selective Probing of Potassium Ion in Solution by Intramolecular Excimer Fluorescence of Dibenzo-Crown Ethers

Motoki Kida, Mayuko Kubo, Tomoyuki Ujihira, Takayuki Ebata, Manabu Abe, and Yoshiya Inokuchi*

Abstract: Observation of an excimer fluorescence in solution is proposed for detecting the encapsulation of potassium ion as opposed to other alkali ions by dibenzo-crown ethers. The scheme has been validated by ultraviolet photodissociation (UVPD) spectroscopy of dibenzo-21-crown-7 and dibenzo-24-crown-8 complexes with potassium ion, K⁺DB21C7 and K⁺DB24C8, performed under cold (~10 K) conditions in the gas phase and by quantum chemical calculations of the geometry and electronic structures of the complexes. Calculations suggest formation of a closely spaced excimer structure of benzene rings only for the K⁺DB24C8. Interaction of the rings may lead to lifetime broadening in UV absorption, which is experimentally observed in the gas phase, indeed, only for this cold complex. Consistently, intramolecular excimer fluorescence of DB24C8 in solution is observed only for K⁺DB24C8. The excimer fluorescence is not observed with other alkali metal ions. The detection of such intramolecular excimer fluorescence therefore can, potentially, serve as a simple, background-free, selective probe of potassium ion in solution.

Crown ethers (CEs) can encapsulate guest species efficiently and selectively.[1] Their ability of encapsulation is related to the conformation; the structure of host-guest complexes has been determined by X-ray diffraction of crystals.[1] However, stable crystals cannot be always obtained for all the host-guest systems. Our primary approach to host-guest species is gas-phase spectroscopy under cold conditions.[2] Cooling of molecules and ions in the gas phase makes it possible to observe their absorption spectra free from congestion or broadening due to solvent and thermal effects, and this spectroscopy provides new physical-chemical insights into host-guest chemistry.[3] Here we focus our attention on the electronic interaction between aromatic chromophores in dibenzo-CE complexes with metal ions. Metal salts of dibenzo-18-crown-6 (DB18C6) were ones of CE complexes that Pedersen firstly reported in 1967,[4] and aromatic rings in macromolecules often play indispensable roles in intermolecular/intramolecular interaction.[5] The electronic interaction in the excited states strongly affects the functionality of organic devices such as dye-sensitized solar cells.[5] In the present study, we investigate the geometric and electronic structures of dibenzo-21-crown-7 and dibenzo-24-crown-8 complexes with potassium ion, K⁺DB21C7 and K⁺DB24C8. We measure UV spectra of the complexes under cold (~10 K) gas-phase conditions, and compare the results with those of K⁺dibenzo-15-crown-5 (K⁺DB15C5) and K⁺DB18C6 complexes, which were previously reported.[6] We examine the effects of the crown size and conformation on the electronic interaction for these complexes. Figure S1 of the Supporting Information shows UV absorption spectra of KBr complexes of (a) DB15C5, (b) DB18C6, (c) DB21C7, and (d) DB24C8 in methanol at room temperature, which are reproduced from a previous study.[16] These spectra show only broad features, providing almost no information on the conformation or the electronic structure of the complexes.

Figure 1. UVPD spectra (red curves) and oscillator strengths (blue and black bars) of the K⁺DB15C5, K⁺DB18C6, K⁺DB21C7, and K⁺DB24C8 complexes calculated at the M05-2X/6-31+G(d) level.

Supporting information for this article is given via a link at the end of the document.

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progression around 36700 cm$^{-1}$, and the other has a strong band at 36839 cm$^{-1}$ followed by several vibronic bands on the high frequency side.[6] We assigned these progressions to the S$_0$–S$_1$ and S$_1$–S$_2$ transitions of a single conformer.[6] In the UVPD spectrum of the K$^+$•DB18C6 complex, a strong origin band is found at 36415 cm$^{-1}$, and vibronic bands show an exciton splitting with an interval of ~2.7 cm$^{-1}$, which indicates that a weak electronic interaction occurs between the two benzene chromophores.[3a] Figures 2a and 2b show the structure with the highest occupied molecular orbital (HOMO) and second highest occupied molecular orbital (HOMO-1) of the K$^+$•DB15C5 (K-A) and K$^+$•DB18C6 (K-a) complexes determined in the previous studies.[3a, 5] Molecular orbitals (MOs) that contribute the most to the S$_0$–S$_1$ and S$_1$–S$_2$ transitions are shown in the Supporting Information. Numbers in Figure 2 represent the contribution (%) of each benzene part to the MOs. The crown cavity of DB15C5 is too small to encapsulate K$^+$ ion, and the K$^+$•DB15C5 complex has a C$_1$ structure. In the K$^+$•DB18C6 complex, the crown opens the cavity the most, and the K$^+$ ion is located at the center of the cavity, providing a boat-type, C$_{2v}$ form.

The UVPD spectra of the K$^+$•DB21C7 and K$^+$•DB24C8 complexes (Figures 1c and 1d) show different features from those of K$^+$•DB15C5 and K$^+$•DB18C6. The K$^+$•DB21C7 complex exhibits several sharp bands on the high frequency side of ~36777 cm$^{-1}$. In sharp contrast, the K$^+$•DB24C8 complex shows very broad features with maxima at ~36400 and ~36670 cm$^{-1}$, accompanied by very weak, sharp bands around 36143 cm$^{-1}$. We determine the most probable structure of the K$^+$•DB21C7 and K$^+$•DB24C8 complexes on the basis of quantum chemical calculations. Figures 2c and 2d depict the most stable form of the K$^+$•DB21C7 and K$^+$•DB24C8 complexes with the HOMO and HOMO-1. Vertical electronic transition energies obtained by the time-dependent density functional theory (TD-DFT) calculations are shown in Figure S2 of the Supporting Information. Numbers in Figure 2d, isomer K-a of K$^+$•DB24C8 has a highly folded conformation for the encapsulation of K$^+$ ion, different from the case of K$^+$•DB15C5, K$^+$•DB18C6, and K$^+$•DB21C7. As a result, the distance between the benzene rings is very short (< 4 Å). The UV band positions obtained by TD-DFT calculations agree well with those of experimental UVPD spectra with an accuracy of ~50 cm$^{-1}$ using a scaling factor of 0.8340 (see the Experimental Section), in the case that benzo-CE complexes have a small structural change between the ground and excited states and thus show a strong origin band in UVPD spectra.[5a, 7] The relatively poor agreement between the UVPD maxima and calculated transition energies for K$^+$•DB24C8 (Figure 1d) suggests a large structural change upon the electronic excitation.

In the calculations of the K$^+$•DB24C8 complex, the total energy of the second most stable isomer (K-b in Figure 2e) is only 1.0 kJ/mol higher than that of K-a, which implies contribution of K-b to the UVPD spectrum. The calculated S$_1$–S$_0$ transition energy of K-b well coincides with the positions of the weak UVPD band at 36143 cm$^{-1}$ (Figure 1d). Hence, this weak, sharp band can be assigned to K-b. This assignment indicates that the broad features of K-a are due not to insufficient cooling of ions in the ion trap but to intrinsic natures of the excited state of K-a.

The difference in the features of the UVPD spectra originates from the electronic structures of these complexes. As
seen in Figures 2a and 2c, the MOs are distributed mainly in one of the benzene rings in the K⁺·DB15C5 and K⁺·DB21C7 complexes; the TD-DFT calculations predict that the S₁→S₂ and S₃→S₄ transitions are localized in one of the benzene rings (see Figures S4 and S6 of the Supporting Information). In contrast, the MOs are equally delocalized over the two benzene rings for the K⁺·DB18C6 complex (K-a, Figure 2b) and the dominant conformer of K⁺·DB24C8 (K-a, Figure 2d). In particular, the K⁺·DB24C8 complex has a substantial overlap of MOs between the benzene rings. The structure and MOs characteristic of K⁺·DB24C8 shown in Figure 2d can remind us of the possibility of an "intramolecular" excimer in the excited state.

In order to verify the presence of the intramolecular excimer of the K⁺·DB24C8 complex, we perform geometry optimization of K⁺·DB24C8 in the first excited state. Figure 3 displays optimized structures of the K⁺·DB24C8 complex in the ground (S₀) and first excited (S₁) states. The benzene parts in the S₀ state are slightly displaced to each other. In the S₁ state, the benzene rings are fully overlapped, and the distance between the benzene rings becomes substantially shorter from S₀ (~3.5 Å) to S₁ (~3.0 Å). These theoretical results indicate that the intramolecular excimer form will be stable in the S₁ state of the K⁺·DB24C8 complex.

Furthermore, we try to observe the fluorescence of the excimer in solution, because excimers of aromatic molecules emit largely Stokes-shifted fluorescence by UV irradiation.⁹⁻¹² Figures 4a and 4b depict fluorescence spectra of DB18C6 and DB24C8 in methanol at room temperature measured with and without KCl salt. For DB18C6 (Figure 4a), addition of KCl increases the fluorescence intensity and shifts the maximum position from ~300 to ~292 nm, but the spectral pattern is essentially the same as that with no KCl. In sharp contrast, the K⁺·DB24C8 complex exhibits largely red-shifted fluorescence around 350 nm (Figure 4b). This spectral feature is quite similar to that of excimers of benzene and benzene derivatives observed in condensed phase.¹³ Based on the theoretical and experimental verification described above, we conclude that the K⁺·DB24C8 complex forms the intramolecular excimer after the UV excitation. In addition, the intramolecular excimer fluorescence is not strongly observed for other alkali metal ions (Figures 4c–e). Hence, DB24C8 can form the intramolecular excimer only with K⁺ among alkali metal ions.

A schematic drawing of potential energy surfaces for K⁺·DB24C8 is displayed in Figure S8a of the Supporting Information. In addition, Figure S8b depicts energy levels of K⁺·DB24C8 structures optimized in the S₀ and S₁ states. As suggested in Figure 3, the K⁺·DB24C8 complex has a stable, intramolecular excimer form in the first excited state. Hence, the potential energy surface of the first excited state accessible from the potential minimum of the ground state will have a repulsive nature or a shallow well. This is probably one reason for the broad spectral features in the UVFD spectrum of the K⁺·DB24C8 complex. In addition, the excimer formation following the UV absorption will decrease the lifetime of the excited state, which will also make the UV spectrum broad. In isomer K-b of K⁺·DB24C8 (Figure 2e), the distance between the benzene rings is substantially longer than that of K-a (Figure 2d). The MOs of
K-b are almost localized on one of the benzene rings (Figure 2e). These results of the structure and the MOs suggest that the formation of an intramolecular excimer hardly occurs for isomer K-b, which therefore provides the sharp spectral features at 36143 cm\(^{-1}\) in the UVPD spectrum. Hence, the broad spectral features of K*•DB24C8 are reasonably ascribed to the intramolecular excimer formation after the UV excitation of isomer K-a (Figure 2d). Similar detection schemes of metal ions using excimer fluorescence were reported previously by a few groups.\(^{[9]}\) In these studies, new molecules consisting of a host and a fluorescent part separately had to be synthesized, while in our case DB24C8 is easily available commercially. Hence, DB24C8 can be used as a very simple, easily available probe of potassium in solution. Moreover, background-free, high-sensitive detection of potassium ion could be achieved with DB24C8 by the observation of the excimer fluorescence at a wavelength free from the fluorescence of bare DB24C8, such as at 400 nm, using photon counting systems. Detailed characterizations of detection ability such as guest sensitivity and selectivity are now in progress.

In summary, we have investigated the electronic interaction in the complexes of DB15C5, DB18C6, DB21C7, and DB24C8 with potassium ion by UVPD spectroscopy under cold (\(-10\) K) conditions in the gas phase. The K*•DB24C8 complex shows very broad absorption even under cold gas-phase conditions. The geometric and electronic structures of the complexes are determined on the basis of the UVPD spectra with the aid of quantum chemical calculations. The S\(_1\)--S\(_o\) and S\(_o\)--S\(_2\) electronic excitations of the K*•DB15C5 and K*•DB21C7 complexes are almost localized in one of the benzene rings. In contrast, the K*•DB18C6 and K*•DB24C8 complexes have a delocalized nature. Since the K*•DB24C8 complex has a very short distance between the benzene rings, a strong electronic interaction occurs in the complex. The conformation and MOs characteristic of K*•DB24C8 can result in the formation of an intramolecular excimer and provide the broad nature of the UVPD spectrum. We have observed red-shifted excimer fluorescence of K*•DB24C8 in methanol by UV irradiation. Since this intramolecular excimer fluorescence of DB24C8 is detected only with K\(^+\) ion among alkali metal ions, it will be possible to utilize DB24C8 as a simple, background-free, high-sensitive, selective probe of potassium ion by detecting the excimer fluorescence.

**Experimental Section**

Details of the experiment for UVPD spectroscopy have been described in our previous report.\(^{[10]}\) Briefly, the K*•DB21C7 and K*•DB24C8 complexes are produced by electrospraying methanol solutions of KCl salt and DB21C7 or DB24C8 with a concentration of \(~100\) \(\mu\)M each. Ions are bunched with a repetition rate of 10 Hz and introduced into a cold, Paul-type quadrupole ion trap (QIT) with octopole ion guides. The QIT is cooled to \(-4\) K by a He cryostat, and He buffer gas is continuously introduced into the QIT. The ions are stored in the QIT for \(~50\) ms and cooled translationally and internally by the collision with the cold He buffer gas. We estimated the vibrational temperature of trapped ions as \(~10\) K from the intensity of a hot band in a UVPD spectrum of K*•[benzo-(18-crown-6)] complex.\(^{[11]}\) Ions other than parent ions of interest can be removed from the QIT by an RF potential applied to the entrance end cap.\(^{[11]}\) The trapped ions are then irradiated by a UV laser, and resulting fragment K\(^+\) ions are mass-analyzed and detected with a home-made time-of-flight mass spectrometer.\(^{[12]}\) UVPD spectra are obtained by plotting yields of the fragment ions against the wavenumber of the UV laser. Fluorescence spectra of DB18C6 and DB24C8 with NaCl, KCl, RbCl, and CsCl are observed using a commercial fluorescence spectrometer (HORIBA Fluoromax-4).

We also perform quantum chemical calculations of the K*•DB21C7 and K*•DB24C8 complexes. The initial conformation search is performed with the CON Flex High Performance Conformation Analysis program with the MMFF94s force field.\(^{[13]}\) The structure obtained by the initial search is further optimized with the GAUSSIAN 09 program package at the M05-2X/6-31+G(\(d\)) level of theory.\(^{[14]}\) The vibrational analysis is also performed at the same calculation level. The electronic transition energy and oscillator strength are obtained by TDDFT calculations at the M05-2X/6-31+G(\(d\)) level. For comparison of calculated UV spectra with UVPD spectra, a scaling factor of 0.8340 is employed for the calculated transition energy. This factor was determined so as to reproduce the transition energy of the K*•DB18C6 complex,\(^{[15]}\) and it was applicable very well to alkali metal ion complexes of benzo-CEs.\(^{[16]}\) We estimate the contribution of each benzene ring to the MOs using the Gaussian sum ver. 3.0 written by O’Boyle et al.\(^{[17]}\) We also perform geometry optimization of the K*•DB24C8 complex using the TURBOMOLE program package.\(^{[18]}\) The calculations are carried out at the MP2/def2-SVP and ADC(2)/def2-SVP levels in the S\(_0\) and S\(_1\) state, respectively, with the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals.

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**Keywords:** crown ethers • fluorescence • photodissociation spectroscopy • metal ions • excimer

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Ultraviolet spectroscopy of dibenzo-24-crown-8 complex with K⁺ ion (K⁺•DB24C8) in the gas phase suggests that the conformation of DB24C8 is highly folded by the encapsulation of K⁺ ion, with a very short distance (< 4 Å) between the benzene rings. This can cause the formation of an “intramolecular” excimer by the UV irradiation, which emits red-shifted excimer fluorescence in solution.