

Supramolecular Chemistry Investigated by Cold, Gas-Phase Spectroscopy

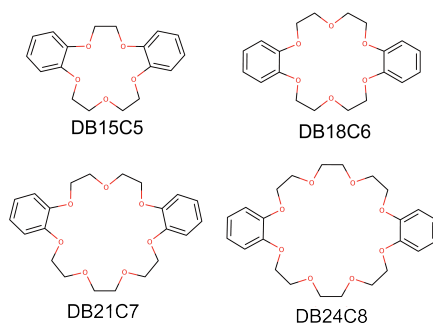
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【Abstract】 We examine the geometric and electronic structures of dibenzo-crown ether (CE) complexes with alkali metal ions by UV photodissociation (UVPD), UV-UV hole-burning, and IR-UV double resonance spectroscopy under cold gas-phase conditions. UV spectral features are strongly dependent on the ring size, or relative position of the benzene chromophores in the dibenzo-CEs. Results of gas-phase spectroscopy, quantum chemical calculations, and fluorescence spectroscopy in solution indicate that dibenzo-24-crown-8 (DB24C8) complex with K^+ ion ($K^+ \cdot DB24C8$) forms “intramolecular” excimer upon UV excitation. DB24C8 can emit strong “intramolecular” excimer fluorescence only with K^+ among alkali metal ions, suggesting that DB24C8 can be used as a sensitive, background-free, selective probe for K^+ in solution.

【Introduction】 Cooling of large functional molecules in the gas phase can suppress congestion in their spectra, which enables ones to explore their intrinsic natures in detail and sometimes to discover new functions that have never been known in condensed-phase studies. We have been investigating host-guest complexes of crown ethers (CEs), calixarenes, and other host molecules by cold, gas-phase spectroscopy. In this talk, we present our recent results on dibenzo-CE complexes with alkali metal ions, in particular with K^+ ion.

【Experimental and Computational Methods】 In UV photodissociation (UVPD) spectroscopy, ion complexes are produced by electrospraying methanol solutions of metal salts and CEs (Scheme 1). Ions are cooled in a cold (~ 4 K) Paul-type quadrupole ion trap and irradiated by a UV laser. Resulting fragment ions are mass-analyzed and detected with a home-made time-of-flight mass spectrometer. UVPD spectra are obtained by plotting yields of the fragment ions against the UV wavenumber. We employ UV-UV hole-burning and IR-UV double-resonance spectroscopy to identify vibronic bands of a single isomer and to obtain conformer-specific IR spectra. We also perform quantum chemical calculations of the complexes by using the CONFLEX, GAUSSIAN 09, and TURBOMOLE program packages to explain the experimental results and determine the geometric and electronic structures of the complexes.



Scheme 1. CEs used in this study.

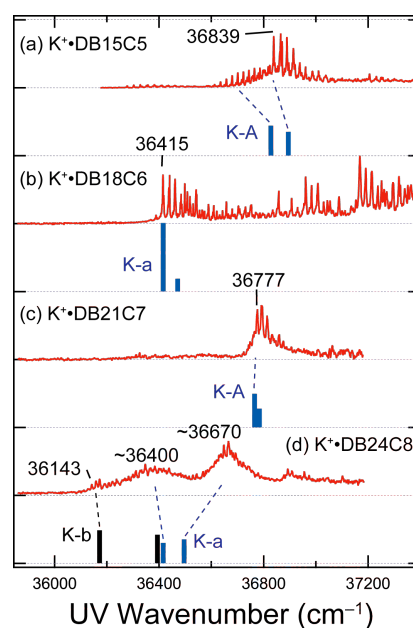


Fig. 1. UVPD spectra.

【Results and Discussion】 Figure 1 displays the UVPD spectra of the DB15C5, DB18C6, DB21C8, and DB24C8 complexes with K^+ ion. Thanks to the cooling of the complexes, the UVPD spectra of the K^+ •DB15C5, K^+ •DB18C6, and K^+ •DB21C8 complexes show sharp vibronic bands; results of UV-UV, IR-UV, and quantum chemical calculations suggest that these complexes each have a single isomer [1, 2]. In contrast, the K^+ •DB24C8 complex shows broad spectral features with maxima around 36400 and 36670 cm^{-1} , accompanied by weak but sharp bands around $\sim 36143 cm^{-1}$. Figure 2 shows the HOMO and HOMO-1 of the stable isomers. The crown cavity of DB15C5 is too small to fully encapsulate K^+ ion, giving a C_1 structure. The MOs and the electronic transitions of the K^+ •DB15C5 complex are almost localized in one of the two benzene chromophores. 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 MOs are delocalized over the two benzene rings due to high symmetry, but the interaction is not so strong, providing an exciton splitting of $\sim 2.7 cm^{-1}$ in the UVPD spectrum [1]. For the K^+ •DB21C7 complex, the MOs are localized, similar to those of the K^+ •DB15C5 complex. In the case of the K^+ •DB24C8 complex, the most stable isomer (K-a, Fig. 2d) has a highly folded conformation for the encapsulation of K^+ ion with C_2 symmetry. As a result, the distance between the benzene rings is very short ($< 4 \text{ \AA}$) [3]. This unique structure reminds us of “intramolecular” excimer formation, which should be related to broad features in the UVPD spectrum. In order to demonstrate the excimer formation after the UV excitation of the K^+ •DB24C8 complex, we observe fluorescence spectra of the K^+ •DB24C8 complex in solution [4]. As seen in Fig. 3b, the K^+ •DB24C8 complex shows strong, red-shifted fluorescence around 350 nm. This can be assigned to the fluorescence of “intramolecular” excimer, induced by the encapsulation of K^+ ion. One interesting finding in fluorescence spectroscopy in solution is that this excimer fluorescence is observed only with K^+ ion among alkali ions (Figs. 3b–e), which suggests that DB24C8 can be used as a sensitive, background-free, selective probe for K^+ ion in solution [3].

【References】

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 [3] M. Kida *et al.* *ChemPhysChem* **19**, 1331 (2018).
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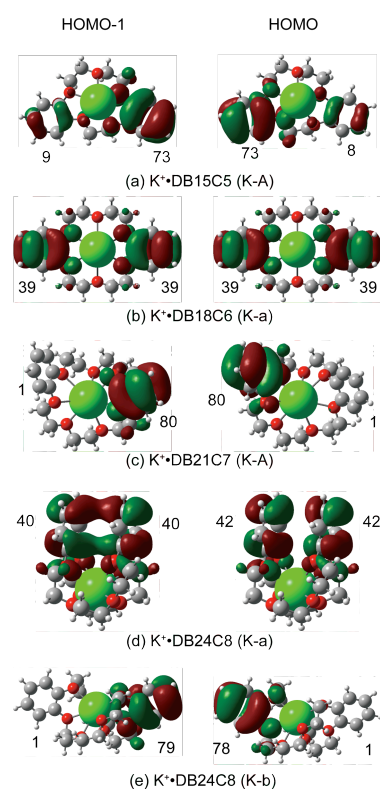


Fig. 2. HOMO and HOMO-1 of the complexes.

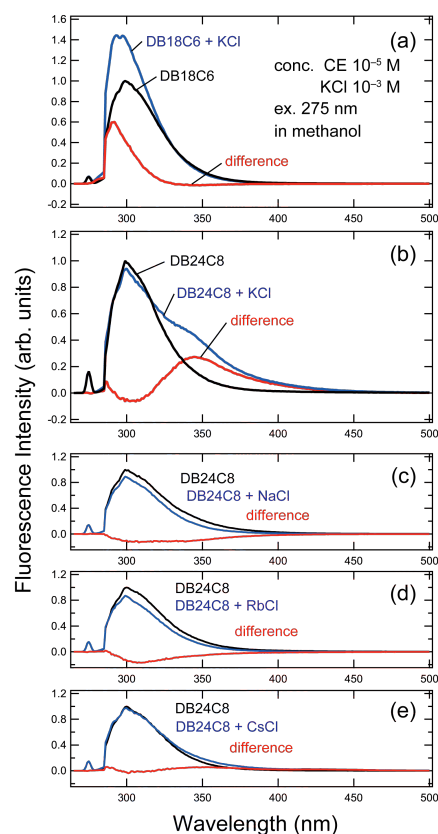


Fig. 3. Fluorescence spectra in methanol.