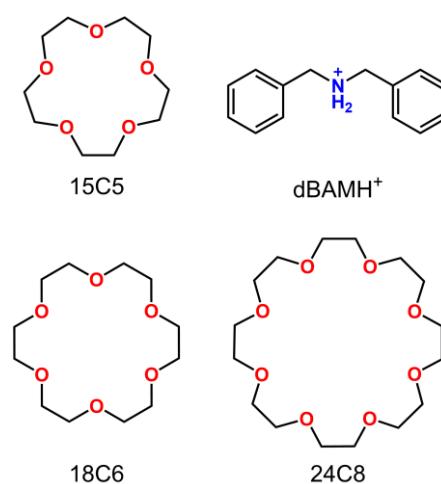


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Rotaxanes, which are composed of macrocycles threaded by dumbbell-shaped molecules, have attracted a great interest due to their potential use in molecular machines, such as molecular switches and molecular shuttles[1]. It is known that macrocycles with 24 or more atoms, such as dibenzo-24-crown-8 (DB24C8), were frequently used to form rotaxanes with dialkylammonium ions[2]. In this study, we observe UV spectra of protonated dibenzylamine (dBAMH⁺) and its complexes with 15-crown-5 (dBAMH⁺–15C5), 18-crown-6 (dBAMH⁺–18C6), and 24-crown-8 (dBAMH⁺–24C8) (Scheme) under cold gas phase conditions by UV photodissociation (UVPD) and UV–UV hole-burning (HB) spectroscopy. We also perform quantum chemical calculations for these ions to examine the structure and energetics.



Scheme

Figure 1 displays the UVPD spectra of the dBAMH⁺–15C5, dBAMH⁺–18C6, dBAMH⁺–24C8 complexes[3]. Spectral features are quite different among the complexes, though the chromophore is dBAMH⁺ for all the complexes. The UVPD spectrum of the dBAMH⁺–15C5 complex shows an extensive low-frequency progression (Figure 1a), which originates from a unique conformation of the dBAMH⁺ part with benzene rings facing closely to each other, while UVPD and calculation results suggest open conformations of the dBAMH⁺ part for dBAMH⁺–18C6 and dBAMH⁺–24C8. Results of UV–UV HB spectroscopy indicate that the dBAMH⁺–24C8 complex has at least two conformers, whereas the dBAMH⁺–15C5 and dBAMH⁺–18C6 complexes have one dominant conformer each. The presence of multiple isomers for the dBAMH⁺–24C8 complex contributes to high stability of pseudorotaxanes with dBAMH⁺ and 24C8 because of “conformational” entropic effect. In this talk, we will discuss the structure and energetics of the dBAMH⁺ complexes in details.

[1] Bissell *et al. Nature* **369**, 133 (1994).

[2] Ashton *et al. Angew. Chem.* **34**, 1865 (1995).

[3] Kida *et al. Phys. Chem. Chem. Phys.* **20**, 18678 (2018).

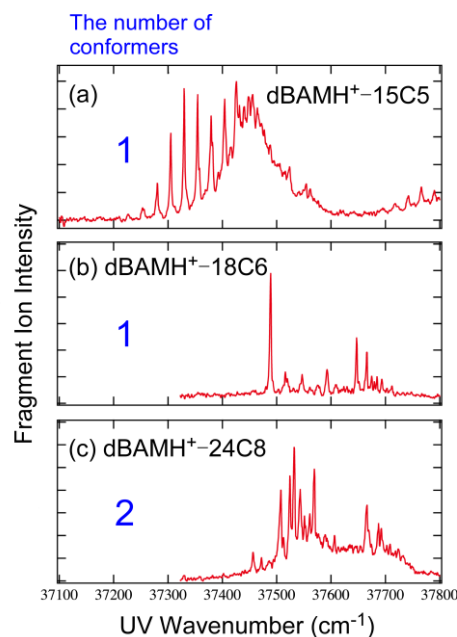


Figure 1 UVPD spectra of the dBAMH⁺ complexes