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Cooperative Recognition of Alkaline Metal and Bromide Ions by Ditopic Receptors

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Summary

Bromine is versatile for a component of various synthetic intermediates and fire retardants. Bromine is separated and purified from natural salt-water and salt-lake. Sea water contains bromine in 0.0065%, however, purification methods of bromine from sea water have not been established. In this work, we studied design and synthesis of bromine-selective receptors based on our previous anion recognition chemistry. We designed two independent receptors bearing urea moieties as recognition sites using carbazole (receptor **3a**) and 1,3-bisnaphthyl-1,2,3-triazole (receptor **4a**) as spacer groups. These spacer groups separate two urea groups away to recognize larger bromide than that of 2,2'-binaphtyl-based receptors for chloride-selective receptors as previously reported. Receptors **3a** and **4a** have been successfully prepared by multi-step organic synthesis and identified by several spectroscopic methods. The binding abilities of these receptors for anions including bromide were evaluated by UV-vis spectral titrations. The original UV-vis spectra of receptors showed drastic shift upon the addition of guest anions through isosbestic points suggesting host:guest = 1:1 stoichiometry. The association constants of **3a** and **4a** for bromide were determined by non-linear curve fitting analysis to be $5.00\pm0.57\times10^3$ and 1.74×10^5 $mol^{-1}dm^3$, respectively and selectivities of **3a** and **4a** for bromide to chloride ($K_{11,Br}/K_{11,Cl}$) were calculated to be 0.19 and 0.34, respectively. These selectivities were significantly larger than that of chloride-selective receptors (for instance, 0.0022 for **1**). These results strongly suggest that suitable alignment of two urea groups makes improvement of bromide-selectivity. We now study introduction of azacrown ether moieties as cation recognition site for construction of ditopic receptors for selective separation of alkaline bromide.