No. 1705

Cooperative Recognition of Alkaline Metal and Bromide Ions by Ditopic Receptors

Shin-ichi Kondo

Faculty of Science, Yamagata University

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 a ditopic receptor **6** based on a 2,2'-binaphthalene skeleton bearing benzo-15-crown-5 ethers via urea functionalities. Receptors **6** has been successfully prepared from the corresponding diisocyanate and amines and identified by several spectroscopic methods. ESI-MS revealed that receptor **6** formed complexes with K^+ and Cl^-, respectively. The binding abilities of receptor **6** for cations and anions were evaluated by UV-vis spectral titrations. Receptor **6** showed 1:2 complexation with Na^+, whereas 1:1 complexation with K^+ by cooperative binding of two crown ether moieties. The binding ability of receptor **6** for anions were fairly similar to those of original receptor **1** suggesting no inhibition by peripheral crown ether moieties. The binding constants of receptor **6** were enhanced in the presence of Na^+ and K^+ suggesting cooperative binding of both anion and cation by two binding sites and positive allosteric effect has been observed. In particular the binding ability of receptor **6** for Br^- in the presence of K^+ was 100 times larger than that in the absence of alkaline metal cations resulting in the selectivity ($K_{11,Br}/ K_{11,Cl}$) reached 0.41. (In the absence of K^+, $K_{11,Br}/ K_{11,Cl} = 0.041$) Liquid-liquid extractions of KCl and KBr from water to chloroform phase have been achieved by the addition of receptor **6**. These results strongly suggest that suitable alignment of two urea groups and cation recognition sites makes improvement of bromide-selectivity.