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Evaluation and Applications of Highly Chloride-Selective Cyclic Amide Compounds

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Summary

Recognition of chloride anion is one of the important topics in molecular recognition chemistry since chloride anion plays crucial roles in living cells and environment. Cyclic bisurea derivatives **2** were designed for construction of a highly chloride-selective artificial anon receptor. Receptor **2a** can be obtained by the reaction of a diamine **3** and a diisocyanate **4** in the presence of TBACl as a template. Guest free **2a** was successfully prepared from **2a**·Cl^- with silver nitrate in DMSO. The solubility of **2a** in common organic solvent is very low, however **2a** can be soluble in DMSO. The structure of **2a** was identified by NMR spectroscopies including 2D NMR techniques. In the ^{1}H NMR spectrum of **2a**, large upfield shifts of N-H and 1 C-H groups were observed comparing with those of **2a**·Cl^- complex indicating that chloride anion was hydrogen bonded by these groups. This result is strongly supported by X-ray crystallographic analysis.

UV-vis spectroscopic titrations of **2a** with anions were performed in 18% DMSO-MeCN (v/v). Small bathochromic shift at 320 nm of **2a** was observed upon the addition of chloride anion. The association constant of **2a** with Cl^- was calculated to be $1.57 \pm 0.09 \times 10^5$ $mol^{-1}dm^3$ by a non-linear curve fitting program and the value was 2.73-fold larger than that with AcO^-. However, the association constants of acyclic analog **1a** with these anions were one order of magnitude smaller than those of **2a**. These results suggest that receptor **2a** is highly selective for chloride anion.

An introduction of bulky substitutions of **2a** was performed to increase the solubility of **2a**. During course of the study, the introduction of t-butyl group to naphthyl moiety was achieved to give a cyclic bisurea derivative **2b** as a novel receptor.