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Development of Chiral Bis-Urea Receptors for Use in the Highly Sensitive Detection of Anions

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Summary

Many of currently marketed pharmaceuticals are chiral drugs that consist of one isomer of right- or left-handed molecules. These are formulated as salts to improve the solubility and stability. For the detection of such ionic compounds, organic molecules have advantages as artificial ion receptors over inorganic compounds in terms of their low cost and toxicity. Although excellent organic artificial ion receptors have been developed for cations, anion receptors are under development and hence the simultaneous detection of anions and chirality still remains a challenging task. On the other hand, we have recently developed a chiral bisurea-type organic receptor that exhibits remarkable anion recognition ability. In this study, the simultaneous detection of anion and chirality was investigated by using chiral bisurea-type receptors.

Initially, three chiral bisureas, i.e., bis(phenylurea), bis(phenylthiourea), and bis(tosylurea), were synthesized by the reaction of isocyanates with a chiral diamine previously reported by us. The enantiomeric NMR signals of racemic tetrabutylammonium mandelate (DL-TBAM) were efficiently separated by the addition of 0.5 molar amounts of bis(phenylurea) in d_8-acetone. Based on the association constants for the 1:1 and 1:2 complexes of three chiral bisureas and (*R*)- and (*S*)-TBAM, the formation of 1:2 complexes was found to play an important role for the effective enantiomeric signal separation by bis(phenylurea). In addition, it was suggested that the preferential formation of a 1:2 complex with (*R*)-TBAM should also be a key factor for the separation of both enantiomers. Meanwhile, aiming at the application to highly sensitive detection of chiral anions by the fluorescence method, a chiral bisurea with pyrenyl groups was synthesized from the chiral diamine and an isocyanate with a fluorescent pyrenyl group. A significant decrease in fluorescence intensity was observed by the addition of a chiral anion to a solution of the fluorescent chiral bisurea.

In summary, we achieved the simultaneous detection of the anion and chirality by the chiral bisurea-based receptor and created the fluorescent chiral anion receptor.