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Highly Sensitive Detection of Anions by Soluble Chiral Bis-Urea Receptors

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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, in 2016 fiscal year, we have created an original chiral bisurea-type organic receptor that could realize the simultaneous detection of anion and chirality. In this study, we analyzed this method in detail, synthesized a chiral bisurea type receptor with soluble substituents, and examined the simultaneous detection of anion and chirality by fluorescence method.

Initially, the evaluation of the effect of complex concentration, the determination of separated signals by complexation, and the measurement of association constants were carried out by using three chiral bisureas, i.e., bis(phenylurea), bis(phenylthiourea), and bis(tosylurea), and tetrabutylammonium mandelate (TBAM) as a model substrate. As a result, it was revealed that the difference between the association constants of (*R*)-TBAM and (*S*)-TBAM during the formation of 1:2 complexes should account for the reason why the signals of both enantiomers of TBAM are well separated under the condition using 0.5 equivalents of bis(phenylurea) in acetone-d_6. On the other hand, chiral bisurea-based receptor with hexyl and pyrenyl groups as soluble and fluorescent substituents, respectively, was synthesized to create a receptor that has high solubility in organic solvents and can utilize highly sensitive fluorescence method. In addition, the chiral recognition of chiral anions by fluorescence method was realized by using a chiral bisurea type fluorescent molecule having a pyrenylpropyl group.

In summary, we revealed the mechanism of the simultaneous detection of anion and chirality by NMR method using the chiral bisurea-based receptors, and achieved the recognition of chirality of anions by fluorescent method using the fluorescent chiral anion receptor.