Cyclic Oligopyrroles as Sensors for Absolute Configuration Determination of Carboxylic Acids

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Introduction

Understanding the role of chirality in medicine, technology and nature requires facile methods for the absolute configuration determination. Chiral carboxylic acids, amino acids among them, are of great importance in development of new therapeutic drugs and other precursors for next generation materials. Cyclic oligo- and polypropyroles (pyrrole,\textsuperscript{7}) have been found to have excellent physicochemical properties such as \(\lambda_{\text{abs}}\) at 400-650 nm with high absorption coefficient, metal guest insertion (one or more) in their cavity, and flexibility.

Among \((1,0,0)\) type cyclic propyroles, the number of the pyrrole subunit has been found to control the macrocyclic backbone conformation and with the numbers 8, 12, and 16 the macrocycle adopts a figure eight type helical shape. Various factors affect to the basicity of the pyrrole subunit, and rate and energy barrier of the chirality interconversion in these flexible macrocycles. Thus, using the properties what these polypropyroles possess, we have found that some of them can sense the chirality of carboxylic acids at low concentrations at room temperature.

Results and Discussion

We employed circular dichroism (CD) exciton chirality method\textsuperscript{4} and found that a variety of carboxylic acids upon forming a host-guest complex with \((1,0,0,0,0,0)\) oligopyrroles (Figure 1) induce CD spectra at macrocyclic absorption region and in which the sign of the \(i^\text{th}\) Cotton effect is determined solely by the absolute configuration of the carboxylic acid (Figure 2).\textsuperscript{2}

![Figure 1. The cyclic pyrroles used in this study as chirality sensors for carboxylic acids. Pyrrole \(\beta\)-ethyl and \(\alpha\)-phenyl substituents are omitted for clarity.](image)

The addition of the chiral carboxylic acid to the present oligopyrroles caused clear bathochromic shifts in the UV-vis spectra due to the formation of an oligopyrrole host-guest complex (Figure 1). The CD spectra are silent for the both oligopyrroles but the addition of the chiral carboxylic acid causes bisignate CD signal band formation most likely due to the chiral carbohydrate binding into the cavity of OP1 and OP2.

![Figure 2. a) UV-vis spectra and b) CD spectra of OP1 in the absence (black) and presence of (S)-(+) hexahydromandelic acid (red) or (R)-(−) hexahydromandelic acid (blue) and OP2 in the absence (magenta) and presence of N-BOC-L-Asp-4-OBz (green) or N-BOC-D-Asp-4-OBz (cyan) in CH\textsubscript{3}Cl/McOH at 298 K.](image)

Figure 3. Chirality induction in octaplyrin OP1 upon binding of chiral carboxylic acids. Coupling of the electronic transitions (s and y) of two dipyrrolmethene subunits yields positive 1st Cotton effect. The pyrrole \(\beta\)-ethyl and \(\alpha\)-phenyl substituents have been omitted for clarity.

Conclusions

Absolute configuration of various synthetic and natural chiral carboxylic acids can be determined easily based on the idea of supramolecular chirogenesis. Two examples show that the cavity size of the cyclic oligopyrrole host molecule plays crucial role upon binding of large guest molecules.

References