Conformational Control of Aliphatic Oligoketones by Pillar[5]arene and its Application

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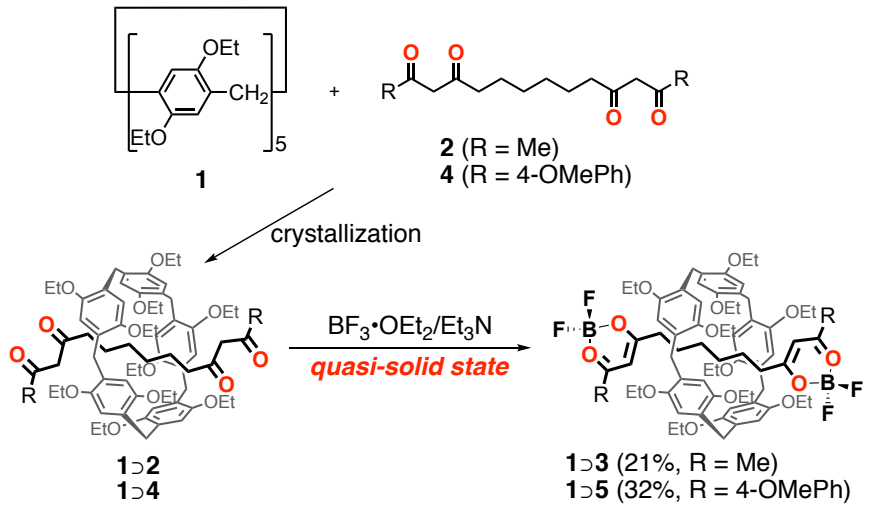
Control of specific conformations in flexible chain molecules is a key for controlling their reactivities and properties. Herein, we show induction and fixation of linear conformation of aliphatic oligoketones, which combine structural flexibility of aliphatic chains and reactivities of carbonyl groups, by host-guest complexation with pillar[5]arene **1**.[1]

Conformationally flexible tetraketone **2** was reversibly incorporated into pillar[5]arene **1** with an association constant of $K = 14\ M^{-1}$ in chloroform. The linear conformation of **2** induced by host-guest complexation was locked by BF_2-complexiation at the 1,3-diketone sites; when pseudo-rotaxane **1**⊃**2** was treated with BF_3•OEt_2 and Et_3N in quasi-solid state reaction conditions, rotaxane **1**⊃**3** was obtained in 21% yield (Scheme 1). Single crystal X-ray structure of rotaxane **1**⊃**3** revealed the linear conformation of axis molecule **3** was retained after BF_2-complexiation, and both ends of axis molecule **3** was 12.4 Å apart from each other.

Similar conformational control was applied to alkyl-linked flexible chromophore dyad **5**. Rotaxane **1**⊃**5** was similarly obtained in 32% yield from pseudo-rotaxane **1**⊃**4** (Scheme 1). The UV-vis spectra of conformationally flexible dyad **5** showed solvatochromic behavior in CH_2Cl_2, THF and 1,4-dioxane while the solvatochromism was not observed in rotaxane **1**⊃**5** due to the conformational restriction of intramolecular aggregation of axis molecule **5**.



Scheme 1. Synthesis of rotaxane **1**⊃**3** and **1**⊃**5** under quasi-solid state reaction conditions.

[1] Y. Manabe, K. Wada, Y. Baba, T. Yoneda, T. Ogoshi, Y. Inokuma, *Org. Lett.*, **2020**, *22*, 3224–3228.