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Supramolecular Conformational Control of Aliphatic Oligoketones by Rotaxane Formation

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ABSTRACT: Conformation control of aliphatic oligoketones bearing two 1,3-diketone subunits is achieved by molecular recognition with pillar[5]arene. Pillar[5]arene binds to aliphatic ketones, with association constants K of $\sim 10^4 \text{ M}^{-1}$, to form pseudo-rotaxanes. The pseudo-rotaxanes are locked by BF_3 -complexation at the 1,3-diketone sites through quasi-solid-state reactions. X-ray crystallography reveals linear conformations for the axis molecules. The effect of supramolecular conformational restriction is evaluated using an alkyl-linked dyad chromophore system that shows solvatochromism upon intramolecular aggregation.

Aliphatic polyketones are a class of indispensable precursors for the synthesis of natural products, pharmaceuticals, and functional materials.¹ Structural diversity of polyketone-related products is derived from the conformational flexibility of aliphatic chains as well as the reactivities of multiple carbonyl groups. Polyketones with oligomethylene chains can adopt numerous conformations in solution. In biological systems, conformations of flexible substrates are sophisticatedly controlled by enzymes for efficient chemical transformations.² Mimicking such systems, chemists have also developed various artificial hosts to control the conformations and orientations of structurally flexible substrates.³ However, substantial challenges still remain, especially for flexible substrates with many methylene units, because intermolecular interactions with

simple hydrocarbons are usually not sufficiently strong to fix their conformations in solution.

Pillar[5]arene **1** is a macrocyclic host that can bind various aliphatic guests.⁴ Owing to the multiple CH- π interactions within the tight cavity, host **1** preferentially incorporates guest compounds with oligomethylene units to form (pseudo) rotaxanes.⁵ Such rotaxane formation is expected to restrict the conformations of guest molecules to be linear rather than curled or bent. Given the guest binding properties of pillar[5]arene **1**, we examined the supramolecular conformational control of aliphatic oligoketones by rotaxane formation. In this work, we focused on aliphatic tetraketones **2–6** bearing various lengths of oligomethylene linkages between two 1,3-diketone subunits (Figure 1) as specific guests. As we have recently demonstrated with oligomers of acetylacetone derivatives, such

aliphatic polyketones have the potential to be converted to aromatic chains, π -conjugated chromophores, ion-conducting materials, and multidentate imine ligands.⁶ Here, we show the inducement and fixation of linear conformations of aliphatic oligoketones through harnessing molecular recognition by pillar[5]arene **1**. Although binding constants were rather small as compared with other hydrogen bonding guests, the induced conformations were locked by the non-pseudo rotaxane formation using BF_2 -complexation at the 1,3-diketone units. Furthermore, the effects of supramolecular conformational restriction were evaluated by the suppression of intramolecular aggregation in an alkyl-bridged dyad chromophore system.

Figure 1. Structures of pillar[5]arene **1** and guest ketones **2–6**.

Table 1. Association Constant K for Pillar[5]arene and Tetraketone Guests^a

guest	binding constant K [M^{-1}]
2a	17.0 ± 1.0
2b	–
3	5.5 ± 0.8
4	14.0 ± 0.8
5	8.1 ± 0.6
6	6.3 ± 0.3

^a Determined in CDCl_3 by ^1H NMR titration.

Guest compounds **2–6** were prepared by reactions of the corresponding terminal dihaloalkanes and acetylacetone in an analogous manner to the reported procedure (see Supporting Information(SI)).⁷ In CDCl_3 at a concentration of 10 mM, tetraketone **2a** existed as an equilibrated mixture of enol/keto = 85:15 for the 1,3-diketone units. When one equivalent of host **1** was added to the solution, the methylene protons of **2a** at the 6- and 7-positions upfield shifted from 1.65 ppm to 1.34 ppm in the ^1H NMR spectrum, which suggested a reversible formation of pseudo-rotaxane **1**⊃**2a**. The Job's plot obtained by NMR titration clearly indicated the 1:1 complexation of **1** and **2a** (Figure S1a). The association constant K between **1** and **2a**

was determined to be $17.0 \pm 1.0 \text{ M}^{-1}$ using the non-linear curve-fitting theorem.⁸ It should be noted that tetramethyl-substituted analogue **2b** showed no shift of signals in the ^1H NMR spectrum upon mixing with host **1**, which implied that the doubly methylated acetylacetone subunit was too bulky to pass through the cavity of **1** (see SI).

Figure 2. X-ray crystal structures of pseudo-rotaxanes (a) **1**⊃**3** and (b) **1**⊃**4**, and locked rotaxane **1**⊃**8** (left: top view, right: side view). Host **1** and guests are drawn as line and ball-and-stick models, respectively. The major parts are shown for disordered guests.

An odd-even effect for the number of bridging methylene units was observed in the association constants of tetraketones **2–6** (Table 1). While the association constant of **2a** was approximately three times larger than that of pentamethylene-bridged **3**, hexamethylene-bridged **4** exhibited a similar binding constant to that of **2a**. The odd-even effect became trivial as the chain length increased. Eventually, the longer analogue **6** with 12 methylene units showed $K = 6.3 \pm 0.3 \text{ M}^{-1}$, which was comparable to that of the odd-number analogues. Although the association constants of tetraketones were on the order of 10^1 M^{-1} , these

values guaranteed almost 90% complexation at a concentration of 1.0 M for each component in chloroform.

The formation of pseudo-rotaxanes between host **1** and tetraketones **3** and **4** was unambiguously confirmed by single crystal X-ray diffraction analysis (Figure 2). When methanol was slowly diffused into a chloroform solution of **1** and **3** (molar ratio 1:3), colorless single crystals of pseudo-rotaxane **1**⊂**3** were formed. In the crystal structure, guest **3** penetrated into the cavity of pillar[5]arene **1**. Host **1** adopted a pseudo C_5 -symmetric conformation in which all the aromatic rings adopted the same planar chirality. The two 1,3-diketone units in guest **3** were observed in the planar enol forms with an apparent bond length alternation (see SI).

As axis molecule **3** did not show disorder in the crystal structure, the observed tautomer of **3** was determined as (3*Z*,11*Z*)-4,12-dihydroxytrideca-3,11-diene-2,10-dione (hereafter denoted as **3'**). Weak hydrogen bonds between oxygen atoms of **3'** and ethoxy groups of **1** were also proposed, owing to the short O⋯C distances (2.641 and 2.668 Å). The internal pentamethylene bridge of **3'** adopted an all *s*-trans conformation. As reported for analogous rotaxane systems,⁹ CH- π interactions were suggested by the distances of 2.999–3.431 Å between the guest methylene carbon and aromatic plane of **1**. The torsion angles of C3–C4–C5–C6 and C8–C9–C10–C11 were 5.4° and 84.4°, respectively, which rendered guest **3'** in a non-planar, twisted conformation.

While one 1,3-diketone unit of **4** was disordered because of keto-enol tautomerism, the other clearly showed a planar enol structure with bond length alternation. As seen in the crystal structure of **1**⊂**3**, the internal hexamethylene bridge adopted an all *s*-trans conformation so as to induce multiple CH- π interactions. The torsion angle of C3–C4–C5–C6 (non-disordered part) was 0.1°, which resulted in a roughly planar conformation of **4**. Because there was no significant difference in the host conformations between **1**⊂**3** and **1**⊂**4**, the difference in the association constant *K* was attributed to the conformational stability of the incorporated guests ketones inside the cavity of **1**.

To fix the conformation of tetraketones induced by pillar[5]arene **1**, we examined the introduction of BF₂-units at the 1,3-diketone sites of the axis molecule **4** as stoppers for rotaxane. We first synthesized the mono-BF₂-complex **7** by treatment of **4** with BF₃·OEt₂ and triethylamine. The association constant of **7** to host **1** was determined to be $K = 61 \pm 2.0 \text{ M}^{-1}$, which was *ca.* five times larger than that of **4**. Thus, we examined the direct synthesis of **1**⊂**8** by the reaction between **4** and BF₃·OEt₂ in the presence of host **1**. ¹H NMR analysis of the reaction solution indicated a new set of highly up-field shifted peaks assignable to 'locked' rotaxane **1**⊂**8** (see SI). Owing to the ring current effects of aromatic rings in **1**, the methylene protons at the 6- and 7-positions of **8** were observed at –0.102 and –2.35 ppm, respectively, in CDCl₃. However, rotaxane **1**⊂**8** was isolated in only 10% yield after chromatographic separation. We thus conducted a quasi-solid-state reaction⁹ using crystals of **1**⊂**4**. When crystals of **1**⊂**4** were ground with 30 equivalents of BF₃·OEt₂ and 10 equivalents of triethylamine in a mortar

with a pestle, rotaxane **1**⊂**8** was formed in a yield of 21%. The axis molecule **8** in rotaxane **1**⊂**8** did not dissociate even in a refluxing toluene solution, which indicated that the BF₂-unit had enough stability and bulkiness to maintain the interlocked structure.

Scheme 1. Synthesis of rotaxane **1**⊂**8**

Figure 3. Structures of axis molecule **9**, dyad chromophore **10**, rotaxane **1**⊂**10**, and monomer **11**.

Single crystal X-ray analysis of **1**⊂**8** revealed that the almost linear conformation of the axis molecule induced by pillar[5]arene **1** was still preserved after BF₂-complexation (Figure 2c). While the hexamethylene bridges displayed positional disorder, the linear conformation of **8** rendered two boron atoms located at a distance of 12.4 Å. These observations guarantee that supramolecular control by

rotaxane formation can restrict the conformations of structurally flexible axis molecules so that both ends cannot contact each other even in solution.

To evaluate the effect of the supramolecular conformational restriction, we synthesized an alkyl-bridged dyad chromophore **10** as an axis molecule by BF₂-complexation of 4-methoxyphenyl-substituted tetraketone **9**. The dyad **10** exhibited a sharp absorption band at 362 nm in dichloromethane that was almost identical to that of monomer **11** (Figure 4(a) and SI). The absorption band was broadened in tetrahydrofuran (THF), and a new peak appeared at 349 nm in 1,4-dioxane. These spectral changes occurred almost independently with concentrations of chromophore **10** in the measurement range of UV-Vis absorption spectra (10⁻⁹–10⁻⁶ M). The solvatochromic behavior of **10** was attributed to the formation of an intramolecular aggregate¹⁰ in which the hexamethylene-bridge adopted a curved conformation. Therefore, the dyad system can be used as a probe for the conformational control of flexible oligomethylene bridges in solution.

Figure 4. UV-vis absorption spectra of (a) axis molecule **10** and (b) rotaxane **10** in CH₂Cl₂ (black), THF (blue), and 1,4-dioxane (red).

Rotaxane **10** was synthesized by a quasi-solid-state reaction with a yield of 32% in a similar fashion to **8**. Single crystal X-ray analysis revealed that the five H₂C–CH₂ bonds in the hexamethylene bridge of **10** adopted (from end-to-end) antiperiplanar, gauche, antiperiplanar, gauche, and antiperiplanar conformations in an almost similar fashion to **8** (Figure 5). As a result, the axis molecule **10** adopted a rather linear conformation, which rendered the two boron centers to be well-separated with a distance of 12.5 Å.

Unlike pure compound **10**, rotaxane **10** showed virtually no solvatochromism. The absorption spectral shape of **10** did not change in various solvents including dichloromethane, THF, and 1,4-dioxane (Figure 4(b)). In every solvent, the spectral shapes were almost identical to

that of monomer **11** (SI).¹¹ These results indicated that intramolecular aggregation of **10** was totally suppressed by supramolecular conformational control by rotaxane formation.

Figure 5. Crystal structure of rotaxane **10**.

In conclusion, conformations of structurally flexible aliphatic oligoketones were controlled to be linear by inclusion into the cavity of pillar[5]arene. Despite the rather low association constants, pseudo-rotaxanes were efficiently locked by BF₂-complexation at the 1,3-diketone subunits through quasi-solid-state reactions. The supramolecular conformational restriction was confirmed by solvatochromism of chromophore **10** in solution. Such a supramolecular approach will contribute to the efficient chemical conversion of aliphatic oligo- and polyketones in a conformationally-controlled fashion. In this sense, pillar[5]arenes can also be used as a molecular reactor for the conversion of aliphatic ketones into organic chromophores and other functional molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and spectral data for all new compounds (PDF)

Single crystal X-ray diffraction data (CIF)

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