

Compactness of Linear Aggregation Controlled by Molecular Selective Binding of Bridged Bis(β -cyclodextrin)s

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(Received June 18, 2003; CL-030549)

Studies on linear aggregation prepared by inclusion complexation of bridged bis(β -cyclodextrin)s and calix[4]arene derivatives provide a simple method to control linear aggregation compactness by molecular recognition.

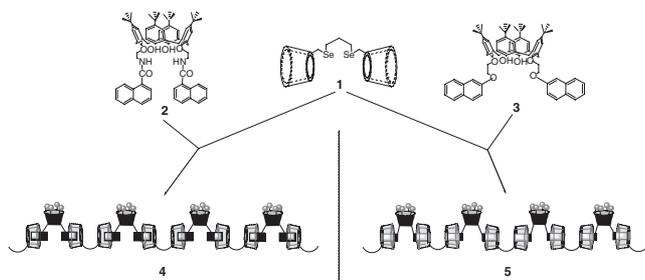
The developing process of supramolecular chemistry has focused on constructing controlled well-defined supramolecular architectures through noncovalent intermolecular interactions showing unexpected functions.¹⁻³ Recently, we reported that the bis(pseudo-polyrotaxane)s possessing copper(II) ions could be prepared from different polymer chains with bis(β -CD)s.⁴ Especially, the organoselenium bridged bis(β -CD)s can form the nanometer aggregates by the inclusion complexation with calix[4]arene derivatives.⁵ In the present letter, we wish to report a novel linear aggregation constructed by the intermolecular interactions between bis(β -CD)s and calix[4]arene derivatives. It is of our particular interest to examine whether the molecular recognition by CD can control the linear aggregation compactness. The results obtained indicate that the different binding ability of bis(β -CD)s with two calix[4]arene derivatives leads to two different density linear aggregations.

Two nanostructure aggregations were prepared according to the procedure shown in Scheme 1. The organoselenium-bridged bis(β -CD)s **1** was synthesized by mono-[6-*O*-(*p*-toluenesulfonyl)]- β -CD and 1,2-diselenacylopentane. Linear aggregation **4** was prepared by the reaction of **1** and **2**.⁵ In order to compare the connect effect of **2** contained α -naphthalene residue, compound **3** tethered by β -naphthalene residue as a linear aggregation linker was obtained by the following procedure: A sample of 5,11,17,23-tetra-*tert*-butyl-26,28-bis-(2-bromoethoxy)-25,27-dihydroxycalix[4]arene⁶ was added to a mixture of 2-naphthol in the presence of K_2CO_3 to give pure white powder **3**.⁷ Furthermore, we adopted an analogical method preparing **4** to obtain a novel nanometer size supramolecular assembly **5** through the host-guest inclusion complexation.

Fluorescence spectroscopy titrations were performed to

give stability constants for the intermolecular interaction between calix[4]arene derivatives and natural β -CD or dimer **1**. The calix[4]arene derivatives possessing naphthyl groups show strong fluorescence emission peak at 364 nm. Upon gradual addition of **1** into a water and acetonitrile mixed solution of **3**, a new broad emission appears at 422 nm and the fluorescence intensity gradually increases. In sharp contrast, on addition of bis(β -CD)s **1** into **2** the fluorescence intensity remarkably decreases at the shorter wavelength and the tail band slightly increases at the longer wavelength with an isosbestic point appearing at 458 nm (Figure 1). It is interestingly noted that the opposite fluorescence behavior reflects the complex stability formed by dimer **1** and the two calix[4]arene derivatives. From the Table 1, it can be seen clearly that the effective binding constant ($\log K_{e\beta} = 4.67$) obtained from a nonlinear least-squares method for **3** is nearly 100 times higher than for **2** ($\log K_{e\alpha} = 2.69$).

In the present investigation, nanosecond time-resolved fluorescence experiments were performed with calix[4]arene derivative **3** in acetonitrile and water mixture (1:9/V:V) in the presence or the absence of natural β -CD or bridged bis(β -CD)s in order to assess the microenvironmental polarity around the included naphthalene residue. Correspondingly, the fluorescence lifetimes (τ) and relative quantum yields (Φ) for **3** are measured. It is significant to note that **3** ($7.4 \mu\text{mol}\cdot\text{dm}^{-3}$) in the mixed solution gives two different fluorescence lifetimes,⁸ indicating the presence of two independent fluorescing species in the solution. The shorter lifetime (τ_S) is 3.2 ns with a relative quantum yield (Φ_S) of 63.2%, while the longer lifetime (τ_L) is 9.0 ns with a relative quantum yield (Φ_L) of 36.8%. Judging from the two independent lifetimes (τ_S and τ_L), the short and long-lived fluorescing species are most likely assigned to the calixarene framework and naphthalene groups of **3**, in which long lifetime species (naphthalene) give prolonged lifetimes (from 9.0 to 10.0 and 10.3 ns), whereas the lifetimes of short-lived species do not show any significant change (from 3.2 to



Scheme 1.

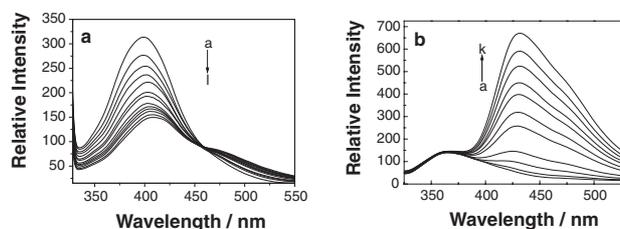


Figure 1. Fluorescence spectral changes of calix[4]arene derivative (a) **2** (1.6×10^{-6} M) (b) **3** (1.4×10^{-6} M) upon addition of **1** ($0-2.3 \times 10^{-3}$ M) in 0.8% CH_3CN aqueous solution. Excitation wavelength was 285 nm.

Table 1. Effective binding constant (K_{es}) and Gibbs free energy change ($-\Delta G^\circ$) for inclusion complexation of **2/3** with β -CD/**1** in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (0.8:100, V:V) mixed solution at 25 °C

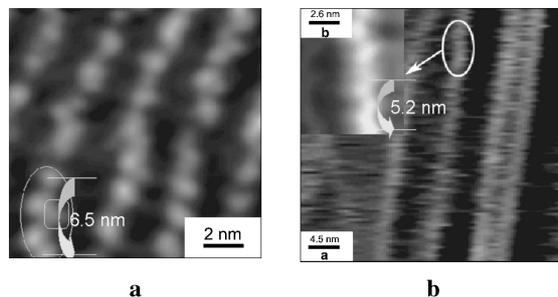
	C[4]A	K_{es}	$\log K_{es}$	$-\Delta G^\circ/\text{kJ}\cdot\text{mol}^{-1}$
β -CD	2	270 ± 20	2.43	13.8
1	2	430 ± 30	2.63	15.0
β -CD	3	1500 ± 75	3.16	18.1
1	3	46700 ± 1200	4.67	26.7

3.2 and 3.3 ns) on addition of the β -CD and dimer, respectively. It is deduced from the results obtained above that only naphthalene moieties penetrate into the CD cavity.

To further obtain the information about inclusion mode, 2D-NOESY spectrum was performed in the mixture of CD_3CN and D_2O (1:1, V:V). The cross-peaks were observed between H-5 and H-3 of CD and the H-1, H-4, H-5, and H-8 of naphthalene moiety of host **3**, and the NOE intensity between H-3 of CD and H-1 of naphthalene was stronger than that of H-5 and H-1, indicating that the naphthalene rings are longitudinally included into the cavity from the secondary side of CD. On the other hand, examinations with CPK models also validate that β -substitutional naphthalene is embedded deeply into the cavity of β -CD in the longitudinal direction, while α -substitutional naphthalene only shallowly penetrating into the cavity.

Furthermore, the scanning tunneling microscopy (STM) was measured to observe the formed aggregation compactness. In the experiment, the water-acetonitrile (1:1, V:V) solution with equimolar mixture of **3** and bis(β -CD)s **1** (1.0×10^{-5} M each) was dropped onto a highly ordered pyrolytic graphite surface, followed by evaporating the liquid at least 2 h in vacuum (Sample bias voltage +300 mV, tunneling current 2.10 nA and a W tip). Compared with the image of **4** (Figure 2a), **5** shown in Figure 2b(a) clearly displays more straight linear arrays, which may be attributed to the strong binding between the calix[4]arene unit and the β -CD cavity. To investigate the precise structural difference of the two assemblies, a sectional picture was shown in Figure 2b(b). Interestingly, although each unit (one calix[4]arene and two CD dimers) of **4** and **5** display a similar "W" shape, the lengths of unit are quite different, i.e., the relative length of one unit is contracted from ca. 6.5 nm in **4** to ca. 5.2 nm in **5**. The heights of the rodlike supramolecular structures **4** and **5** are ca. 2 nm, which is close to the diameter of CD.

Transmission electron microscopy (TEM) has been performed to further provide an insight into the shape and length

**Figure 2.** STM images of linear aggregation **4** (a) and **5** (b).

of supramolecular aggregates. There exist lots of linear structures with the length in a range of 1000–4000 nm, which are joined together through about 190–760 units of inclusion complex with a calixarene **3** and a β -CD dimer **1**. Compared with linear aggregation **4**, the compact array of linear aggregation **5** leads to the longer and tighter linear aggregation.

This work was supported by NNSFC (No. 29992590-8 and 20272028), and Foundation of Ministry of Education.

References and Notes

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- 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(β -naphthoyl)ethoxy]-26,28-dihydroxycalix[4]arene (**3**): yield, 78%; mp 201–203 °C; $^1\text{H-NMR}$ δ 7.72–7.20 (m, 14H, ArH), 7.03 (s, 4H, ArH), 6.90 (s, 4H, ArH), 4.43 (d, 4H, $J = 12.0$ Hz, ArCH_2Ar), 4.31 (t, 4H, $J = 3.0$ Hz, OCH_2), 4.26 (t, 4H, $J = 3.0$ Hz, OCH_2), 3.32 (d, 4H, $J = 12.0$ Hz, ArCH_2Ar), 1.26 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.05 (s, 18H, $\text{C}(\text{CH}_3)_3$); Anal. Calcd for $\text{C}_{68}\text{H}_{76}\text{O}_6$: C, 80.71; H, 6.90%; Found: C, 80.96; H, 7.02%.
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