http://dx.doi.org/10.5012/bkcs.2012.33.8.2793

Development of [2]-Catenane with Orthogonal Binding Chloride Template

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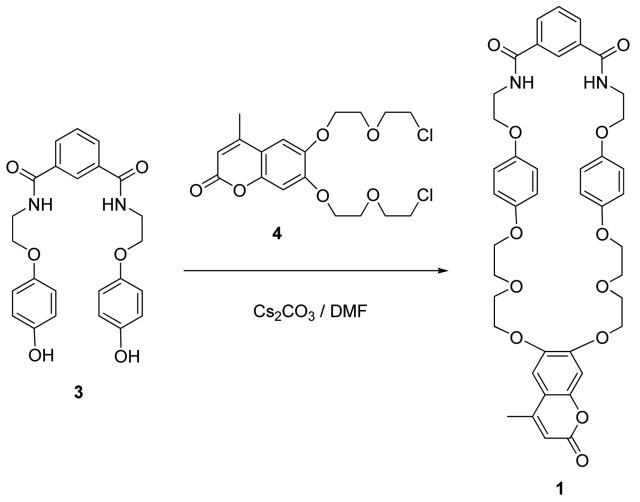
Received March 14, 2012, Accepted May 16, 2012

Key Words : Catenane, Anion template, Hydrogen bonding, Supramolecule

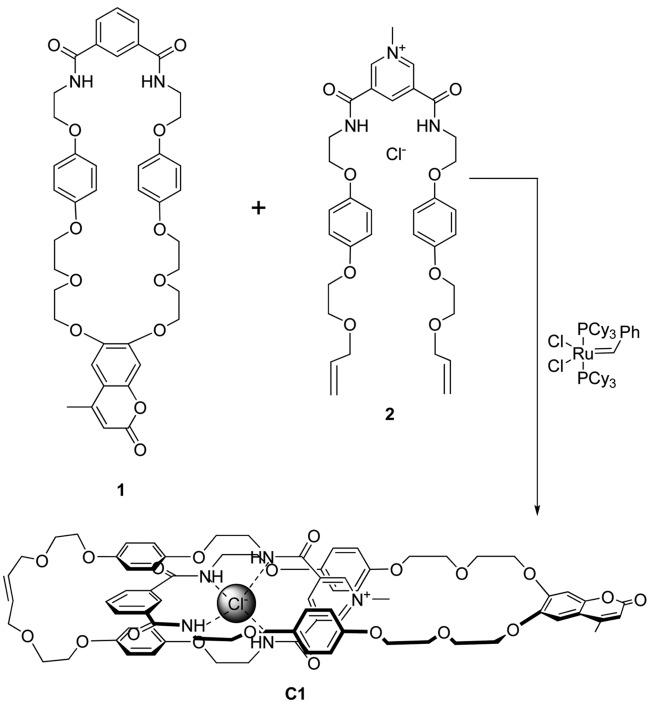
Developing a multi ion acceptor such as catenane, rotaxane and pseudorotaxane was carried out in an effort to overcome the number of binding sites in an ionic receptors that is composed of a single molecule.[1-3] More than two supramolecules can form molecular complex through self-assembly by coordination.[4] When the anion binding sites in each supramolecules form orthogonal complex, the binding sites provide three dimensional spaces. Anions of spherical, linear, triogonal planar and tetrahedral shapes can selectively form complex in such binding sites. Quite often the catenane and rotaxane were not obtained through a planned strategy. They were obtained as byproducts while synthesizing some other compounds.[5] Since the structures of catenane and rotaxane are similar to DNA, they are drawing much attention in the study of biochemical structure. They can be utilized in the newly emerging field of controlling molecules in nano-scale such as molecular electronics, molecular mechanics and molecular self-assembly.[6] But, due to the difficulties in their synthetic work, no much progress has been accomplished until recently. Anionic substrates have received little attention as potential templates in the formation of interlocked molecules, due to their varying geometries, low charge/radius ratios and pH dependence. Recently complexes with orthogonal ion binding sites were synthesized by coordinating derivatives of pyridinium chloride and isophthalamide[7] from the fact that isophthalamide derivatives can recognize chloride. This study showed that rotaxanes and catenanes can be synthesized using anion templates. Beer and co-workers reported more advanced design of the anion template from the fact which the electron deficient and electron rich components are arranged so that π-π stacking is possible.[8-10] Although catenanes were synthesized using other types of anion templates, still more research needs to be developed.[11-13] Herein, we are reporting [2]-catenane using anion template and RCM reaction. The anion templation forms a pseudorotaxane assembly and a subsequent clipping reaction using RCM affords the catenane structure.

Results and Discussion

Compound **1** was prepared by bridging of compound **3**[14] with **4**[15] in the presence of Cs_2CO_3 in DMF (Scheme 1). Compound **1** provides one marcrocyclic unit of the target catenane, incorporating an amide cleft for anion recognition. The pyridinium chloride thread component **2**[16] has been designed to complement the binding sites of the macrocycle; pyridinium chloride tight ion-pair where the chloride anion's coordination sphere can be satisfied by the macrocycle's amide cleft, the presence of an electron-deficient aromatic ring capable of favorable secondsphere π-π stack-



Scheme 1. Synthetic routes to macrocycle compound **1**.



Scheme 2. Synthetic route of [2]-catenane with **1** and **2**.

Figure 1. Anion templated [2]-catenane.

ing to the hydroquinone moieties of the macrocycle. In addition, functionalization of the thread with terminal allylic groups enables a RCM reaction to be carried out. Mixing components **1** and **2** in dichloromethane followed by addition of 10 wt % Grubb's catalyst and stirring overnight allows the metathesis reaction to proceed. Separation of the reaction mixture on preparative TLC afforded the isolation of the [2]-catenane, in 19% yield.

Catenane formation can be progressed from two step process. First, **1** and **2** form a complex with chloride ions like a pseudorotaxane and then followed by RCM reaction provide a catenane as shown in Figure 1.

Analysis of the ^{1}H NMR spectra of catenane **C1** reveals the interlocked structure of the components **1** and **2**. When components **1** and **2** complexed with the chloride ion, amide protons of **1** at δ 6.99 shifted downfield at δ 7.31 by hydrogen bonding and inclusion of the pyridinium ring within the supramolecule **2** generates π-π stacking-induced upfield shifts of the protons. Also, the NH protons shifted upfield because two anion binding moieties are competing for one chloride in the catenane **C1**. Finally, two allylic end groups of the **2** appeared a single peak at **C1** due to ring closing methathesis as shown in Figure 2.

In conclusion, we have developed anion template synthesis of [2]-catenane *via* a novel anion directed interweaving strategy which assembles two similar anion recognizing motifs into an orthogonal structure. Catenane formation resulting from a RCM reaction is critically dependent on the molar equivalence of chloride anion template present. ^{1}H NMR analysis provides evidence for the formation of the catenane.

Experimental

Courmarine Macrocycle 1. A solution of compound **3** (0.50 g, 1.14 mmol) and **4** (0.56 g, 1.14 mmol) in DMF (100 mL) was heated at 60 °C for 24 h with Cs_2CO_3 (0.74 g). After removing the solvent the resulting oil was extracted with hot chloroform (2 × 100 mL), which was purified by column chromatography (eluent: ethyl acetate) to give **1** as a white solid (0.13 g, 15%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (m, 3H, ArH), 7.57 (t, 1H, ArH, J = 7.8 Hz), 7.26 (s, 1H, ArH), 7.04 (s, 1H, ArH), 6.99 (br s, 2H, NH), 6.58-6.72 (m, 8H, ArH), 5.99 (s, 1H, CH), 3.8-4.3 (m, 24H, -CH_2CH_2-), 2.26 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.7, 161.9, 153.1, 153.0, 152.8, 152.7, 152.6, 149.4, 145.6, 134.4, 134.3, 131.2, 129.3, 123.6, 115.8, 115.5, 115.4, 115.2, 112.9, 112.1, 109.7, 101.7, 70.4, 70.3, 70.1, 69.9, 69.5, 69.0, 68.4, 68.2, 67.2, 67.1, 39.7, 39.6, 18.7.

[2]-Catenane C1. Courmarine macrocycle **1** (50 mg) and 3,5-bis-(2-(4-2-allyloxy-ethoxy)-phenoxy)-ethylcarbamomyl)-1-methyl-pyridinium chloride **2** (64 mg) in 50 mL dichloromethane was treated with Grubbs' catalyst (12 mg, 10% by weight) overnight. The solvent was removed to give the crude solids which were purified by prep TLC using dichloromethane:methanol (95:5) as eluent to give **C1** (18

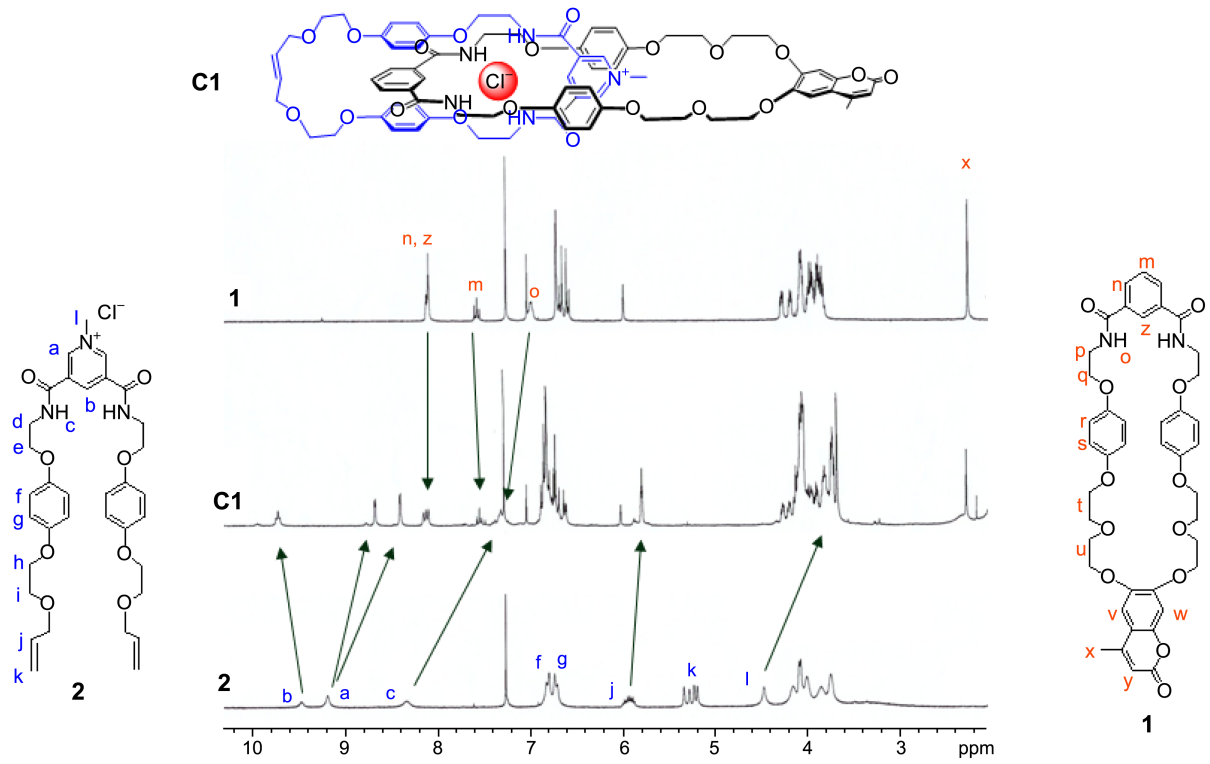


Figure 2. ^{1}H NMR spectra of **1**, **2** and **C1** in $CDCl_3$ at 293 K.

mg, 19%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (s, 1H, ArH-Cl^-), 8.68 (s, 1H, Ar N+CH), 8.40 (s, 1H, Ar N+CH), 8.11 (br m, 3H, ArH), 7.54 (t, 1H, ArH, J = 8.7 Hz), 7.31 (br s, 4H, NH), 7.04 (s, 1H, ArH), 6.93-6.60 (m, 17H, ArH), 6.02 (s, 1H, ArH), 5.79 (s, 2H, HC=CH), 4.28-3.68 (m, 47H, -CH_2CH_2-, N^+ CH_3), 2.28 (s, 3H, $ArCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.9, 163.6, 163.1, 162.1, 161.7, 153.3, 153.1, 153.0, 152.8, 152.7, 152.5, 149.5, 145.6, 144.8, 139.3, 134.4, 131.1, 129.2, 129.1, 128.4, 126.4, 119.4, 115.9, 115.8, 115.7, 115.6, 115.4, 115.3, 115.2, 112.9, 112.8, 112.1, 101.6, 71.0, 70.9, 70.2, 70.1, 70.0, 69.5, 69.0, 68.5, 68.3, 68.2, 67.2, 66.9, 39.7, 39.6, 39.1, 38.7, 35.5, 35.0, 26.9, 26.8, 26.2, 26.0.

Acknowledgments. NMR spectra were taken at the Korea Basic Science Institute, Kwangju, Korea. "This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2010-0003415)".

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