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Amidinium Carboxylate Salt Bridges as a Recognition Motif for Mechanically Interlocked Molecules: Synthesis of an Optically Active [2]Catenane and Control of Its Structure**

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Catenanes and related mechanically interlocked molecules[1] have been regarded as intriguing candidates to serve as indispensable components for nanomachines and nanodevices, since control over the relative motion of the components is possible by external stimuli, such as heat and light, which lead to changes in the catenanes' physical properties, such as conductivity, fluorescence, and circular dichroism (CD).[2] The past three decades have witnessed substantial progress in recognition motifs for the synthesis of mechanically interlocked molecules, most of which rely on noncovalent interactions,[3–7] such as metal coordination,[3] hydrogen bonding,[4] hydrophobic effects,[5] and charge transfer interactions,[6] which arrange their synthetic intermediates in the correct orientation favorable for the formation of interlocked molecules. The noncovalent interactions used for the directed synthesis of the interlocked molecules are not only of significant importance for the synthesis, but they are often utilized for control over the relative location or motion of the components, which can be changed by external stimuli.[2] Consequently, the development of new recognition motifs is very important for advances in this emerging research area.

We recently reported the rational design and synthesis of artificial double helical supramolecules and polymers consisting of complementary molecular strands by utilizing amidinium carboxylate salt bridges, which exhibit high association constants even in polar solvents, have a well-defined geometry by the nature of the double hydrogen bonding interactions, and can be controlled by acid–base interactions.[8,9] Therefore, the amidinium carboxylate salt bridges can be regarded as promising candidates for a recognition motif for a variety of mechanically interlocked molecules. Moreover, the salt bridges can accommodate chiral substituents on the nitrogen atoms that could regulate the twist sense of the salt-bridge-based supramolecules.[8–10] We have designed a new optically active [2]catenane utilizing the amidinium carboxylate salt bridges. This catenane is prepared from a chiral amidine strand and an achiral carboxylic acid strand, both of which bear a crescent-shaped *m*-terphenyl ligand with a terminal olefin at each end (Figure 1). The two complementary molecules form a precatenane through the salt bridge, which is converted to the [2]catenane by the ring-closing metathesis (RCM) reaction.[11] Herein, we describe the synthesis of the optically active [2]catenane based on the amidinium carboxylate salt bridges as a new recognition motif and the control of the relative motion of its macrocyclic components by acid–base interactions together with metal coordination.

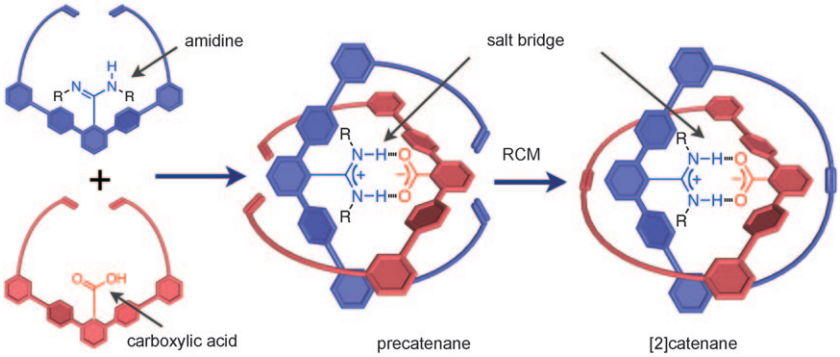

Figure 1. Schematic illustration of the synthesis of [2]catenanes that relies on the amidinium carboxylate salt bridges during the RCM reaction.

The synthesis of the [2]catenane was carried out according to Scheme 1 (see also the Supporting Information). The optically active amidine with two arms bearing vinyl groups (**1a**) was synthesized by Sonogashira coupling between the *m*-terphenyl amidine with two acetylene groups (**4a**)[9b] and the *m*-iodobenzoate derivative with vinyl-group-terminated oligo(ethylene oxide) side chains (**5**). The *m*-terphenyl-bound carboxylic acid with vinyl-terminated oligo(ethylene oxide) side chains (**1b**) was prepared in a similar manner. The ^{1}H NMR spectrum ($CDCl_3$) of an equimolar mixture of **1a** and **1b** showed a downfield signal for the NH protons ($H_{a,a'}$)

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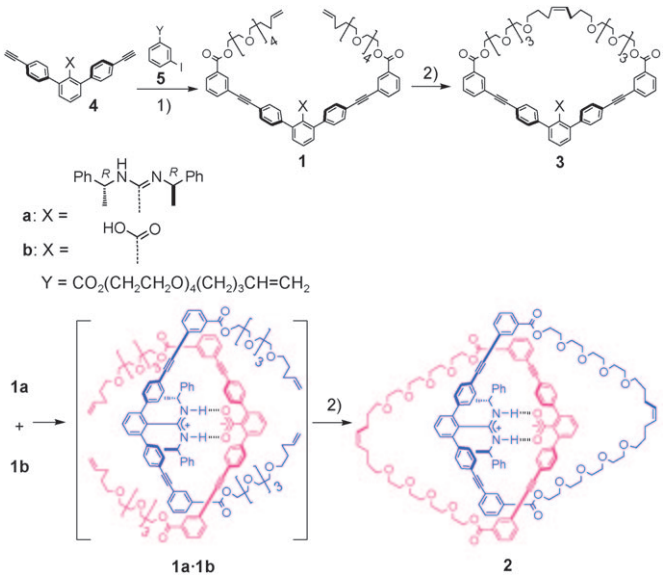

Scheme 1. Synthesis of the [2]catenane **2**. 1) $[PdCl_2(PPh_3)_2]$, CuI, Et_3N/THF, RT; 2) Grubbs catalyst (first generation), toluene, RT.

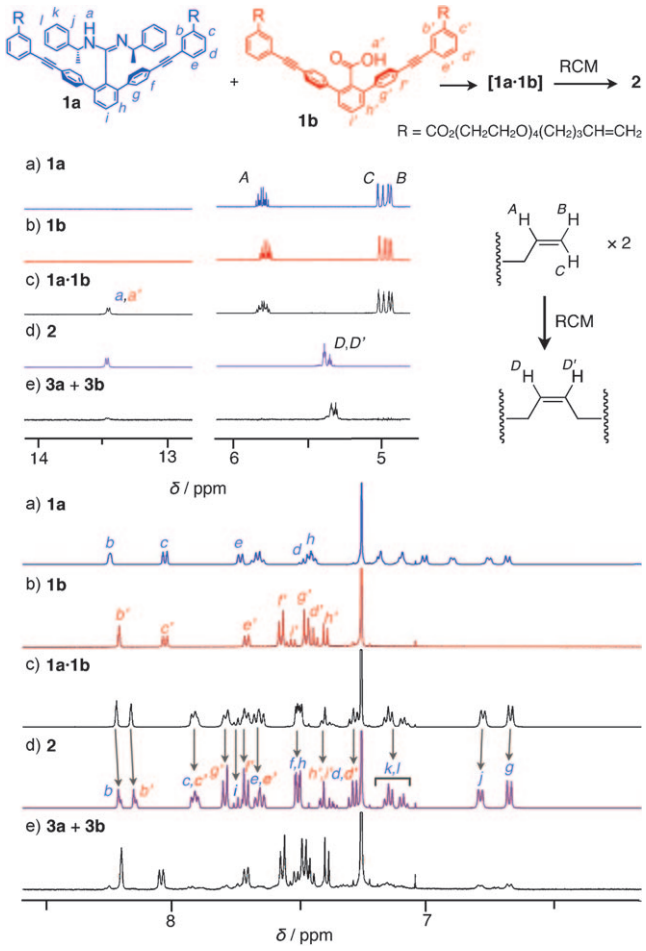

Figure 2. Partial ^1H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of a) the amidine (**1a**), b) the carboxylic acid (**1b**), c) the precatenane (**1a·1b**), d) the [2]catenane (**2**), and e) an equimolar mixture of the macrocycles (**3a** and **3b**).

at $\delta = 13.45$ ppm, which indicated the formation of the precatenane (**1a·1b**) through the salt bridge (Figure 2). The precatenane in chloroform was treated with a catalytic amount of the first-generation Grubbs catalyst to afford the [2]catenane (**2**) in 27% yield after chromatographic purification; the yield was improved to 68% using toluene as the solvent instead of chloroform. The individual macrocyclic amidine and carboxylic acid (**3a** and **3b**) were prepared by the RCM reaction of **1a** and **1b**, respectively. The structure of **2** was first investigated by ^1H NMR spectroscopy (Figure 2). The RCM resulted in disappearance of the signals of the terminal methylene groups and detection of the methine protons of the internal olefin group. The resonance of the NH protons was observed at $\delta = 13.46$ ppm, and the chemical shifts of the aromatic protons were close to those of the precatenane, thus indicating that **2** retained the intertwined structure bound together by the salt bridge as in the precatenane structure. The formation of **2** was also suggested by electrospray ionization mass spectrometry (ESI-MS); the ESI mass spectrum of a $CHCl_3$/MeOH (1:1, v/v) solution of **2** showed signals for the mono- and dicationic species ($[2+Na]^+$ and $[2+2Na]^{2+}$) at m/z 2274.10 and 1148.52, respectively, of which the isotopic patterns were in good agreement with the simulated ones (Figure S5 in the Supporting Information).

A simple equimolar mixture of **3a** and **3b** and a larger [1+1]macrocycle can be regarded as other possible structures, as illustrated in Figure 3. Despite our efforts, we could not obtain single crystals suitable for X-ray analysis. Final confirmation of the interlocked nature of **2** was provided by a ^1H NMR spectroscopy comparison and chemical derivatization of **2** in combination with ESI-MS. We first recorded the ^1H NMR spectrum of an equimolar mixture of macrocycles **3a** and **3b**, which was almost identical to the sum spectrum of those of **3a** and **3b** and was different from that of **2** (Figure 2). In addition, the ESI mass spectrum (positive mode) of the

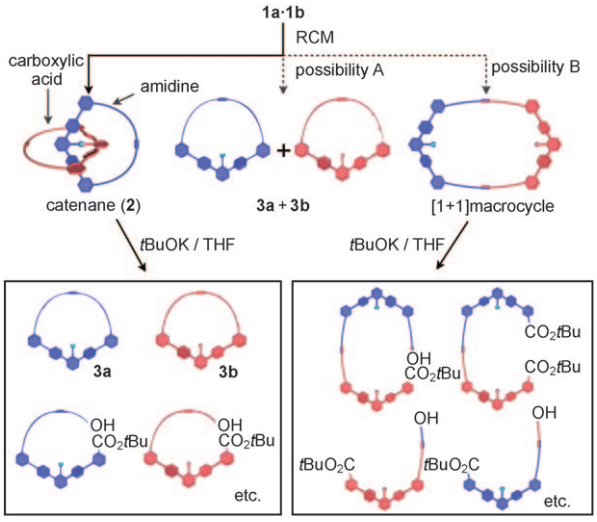

Figure 3. Schematic illustration of possible products from RCM reaction of the precatenane (**1a·1b**) and subsequent degradation reaction of the [2]catenane (**2**) and the [1+1]macrocycle through the ester exchange reaction using *t*BuOK.

mixture of **3a** and **3b** showed only signals attributable to the macrocyclic species $[\mathbf{3a}+H]^+$ and $[\mathbf{3b}+Na]^+$ (Figure S6 in the Supporting Information). Both the ^{1}H NMR spectroscopy and ESI-MS results unambiguously excluded the possibility of an equimolar mixture of the macrocycles for the RCM product. We also investigated the possible formation of the [1+1]macrocycle. The treatment of **2** with a slight excess of *t*BuOK in refluxing THF for 12 h afforded a mixture of cleaved products through alcoholysis of the ester groups, and this mixture was subjected to ESI-MS measurements. The positive-mode ESI mass spectrum of the product mixture did not exhibit any signals of products from the [1+1]macrocycle, but rather showed those of the esters and the macrocyclic amidine (**3a**), the last of which unambiguously indicates the catenated structure of **2** (Figure S7 in the Supporting Information).

The CD spectrum of a solution of **2** in chloroform showed first negative and second positive distinct Cotton effects for the absorption of the *m*-terphenyl ligands around 300 nm, thus indicating that the two *m*-terphenyl groups bound together by the salt bridge were twisted in one direction by the optically active (*R*)-phenylethyl substituents on the amidine groups[9a] (Figure 4b and Figure S8 in the Supporting Information). Upon the addition of one equivalent trifluoroacetic acid (TFA), the CD intensities were reduced by nearly two thirds. After the addition of two equivalents TFA, the CD spectrum became the same as that of the TFA salt of the amidine macrocycle **3a** and remained the same after the addition of ten equivalents TFA, thus suggesting that the salt bridge between the two macrocyclic components was "unlocked" by TFA and that the two macrocyclic components underwent a virtually free relative rotation around each other. The ^{1}H NMR spectrum of **2** changed upon the addition of TFA and reached equilibrium with two equivalents TFA, as is the case for the CD spectrum (Figure S9 in the Supporting Information). In the ^{1}H NMR spectrum of the TFA salt of **2**, the signals for macrocyclic components with amidine and carboxylic acid were almost the same as those for the TFA salts of **3a** and **3b**, respectively, supporting the deduction from the CD results that the two macrocyclic components were "unlocked" by TFA, undergoing free relative rotation. The neutralization by the further addition of an equal amount of diisopropylethylamine (*i*Pr$_2$NEt) completely restored both CD and ^{1}H NMR spectra, thus indicating that the macrocyclic components were again "locked" in the twisted arrangement as a result of the restoration of the salt bridge (Figure 4 and Figure S9 in the Supporting Information).

The switch between the "locked" and "unlocked" states of the two macrocyclic components was also achieved by the sequential addition of $Zn(ClO_4)_2$ and [2.2.1]cryptand,[12] resulting in a similar change in the CD spectra (Figure S10 in the Supporting Information). The CD spectrum of **2** became identical to that of the Zn^{2+} complex with **3a** after the addition of one equivalent of the Zn^{2+} ion, thus suggesting that the salt bridge was "unlocked" by the formation of the Zn^{2+} complex through coordination to the amidine residue. The addition of the Zn^{II} ion caused a significant change in the ^{1}H NMR spectrum of **2**, in which the chemical shifts of the signals for the macrocyclic components with carboxy groups

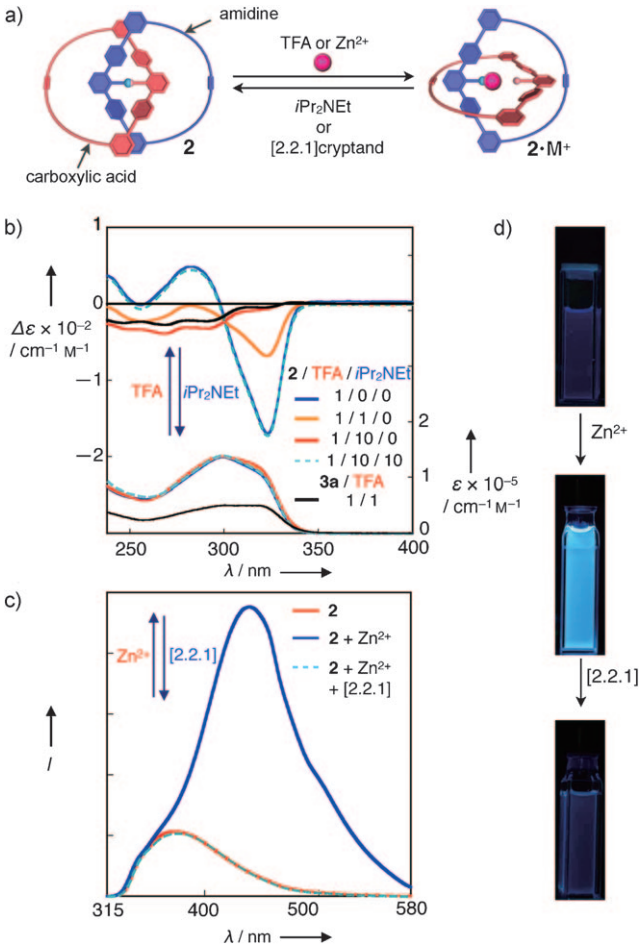

Figure 4. a) Schematic illustration of control over on/off switching of the salt bridge between the two macrocyclic components using an acid/base or Zn^{2+}/[2.2.1]cryptand system. b) CD and absorption spectra ($CDCl_3$, 0.1 mM, ca. 20 °C) of the [2]catenane (**2**) before (blue) and after the addition of TFA (1 equiv (orange), 10 equiv (red), and further neutralization with 10 equiv of *i*Pr$_2$NEt (dashed light blue). CD and absorption spectra of the TFA salt of **3a** are also shown (black). c) Fluorescence spectra (CH_2Cl_2/THF (10:1, v/v), 0.01 mM, ca. 20 °C) of **2** before (red) and after the addition of $Zn(ClO_4)_2$ (blue), with subsequent removal of Zn^{2+} ion with [2.2.1]cryptand (dashed light blue). d) Photographs of a solution of **2** in CH_2Cl_2/THF (10:1, v/v) under irradiation at 254 nm.

became similar to those for free **3b**, whereas those for the macrocyclic components with amidine groups were totally different from those of free **3a** (Figure S11 in the Supporting Information). The ^{1}H NMR spectral change also supported the switching between the "locked" and "unlocked" states. The [2]catenane **2** has conjugated *m*-terphenyl units, which emit light centered at 440 nm when irradiated at 300 nm (Figure 4c). Interestingly, the addition of Zn^{2+} ions caused a significant enhancement and red shift of this fluorescence, leading to a change in color from faint purple to bright bluish yellow (Figure 4c,d). The CD and fluorescent spectra were restored after the addition of [2.2.1]cryptand, which trapped the Zn^{2+} ion from **2**, thus indicating that the salt bridge lock was restored (Figure 4c and Figures S10 and S11 in the Supporting Information).

In summary, we have designed and synthesized a new optically active [2]catenane utilizing amidinium carboxylate salt bridges as a new recognition motif and have successfully controlled the relative motion of the two macrocyclic components by acid–base interactions and metal coordination. Changes could be detected by CD spectra and fluorescence color. This methodology utilizing salt bridges may allow access to a wide variety of mechanically interlocked molecules owing to the complementarity of the salt bridges as well as their compatibility with various functional groups.

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