

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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1. Introduction

1-1. Amidinium carboxylate salt bridges at construction of supramolecules

- Construction of supramolecular structure often relies on noncovalent interaction.
Ex) metal coordination, hydrogen-bonding-driven self-assembly, hydrophobic effect...
- Hydrogen bonding: powerful tool but still difficult to be applied in complicated structure.
=> The authors had succeeded in construction of several kinds of supramolecules with amidinium carboxylate salt bridges.

1-2-1. Previous work 1

- Construction of artificial double-helical assemblies (common structure in biomacromolecules) with amidine carboxylate salt bridge¹ (Figure 1)

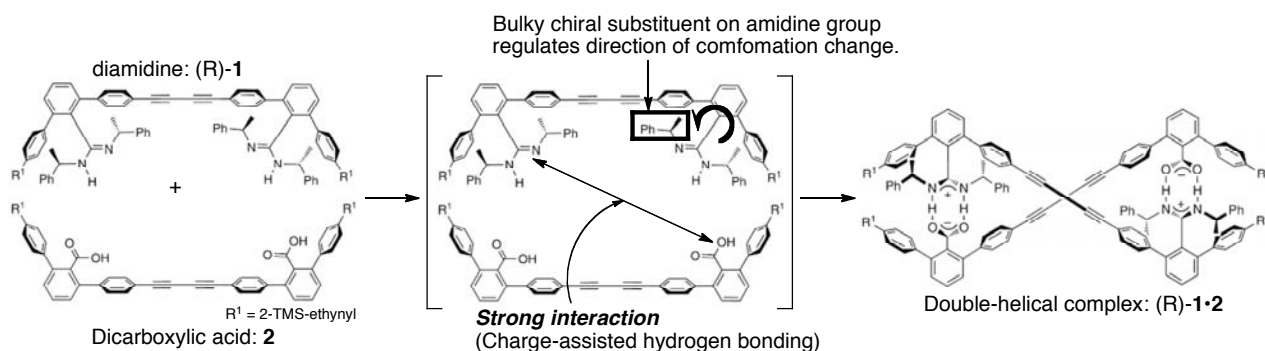


Figure 1. Formation of salt bridge between chiral diamidine and dicarboxylic acid leading intertwined compound

- Good points of amidinium carboxylate salt bridge: strong bonding assisted by charge, regulating the twist sense of the supramolecules by chirality of bulky substituents on the nitrogen atoms
- Characterization of (R)-1•2 by X-ray analysis (Figure 2)

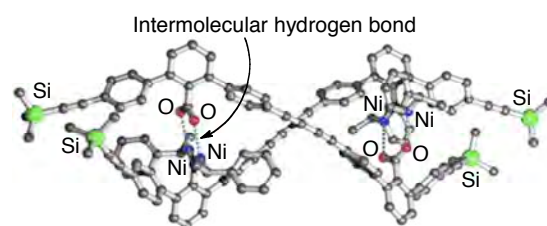


Figure 2. Crystal structure of (R)-1•2 (hydrogen atoms and solvent are omitted for clarity)

1-2-2. Previous work 2

- The modular with amidinium carboxylate salt bridge in previous work 1 could be

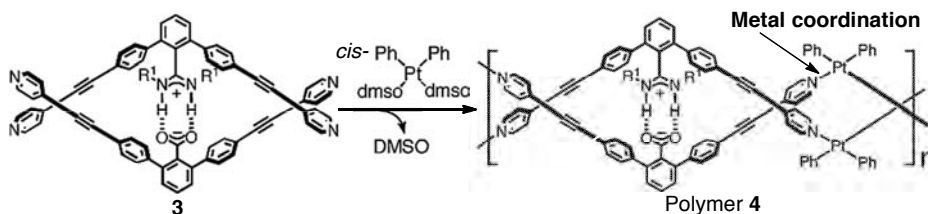


Figure 3. Synthesis of double-stranded metallosupramolecular helical polymers

- applied in construction of further helical structures, double-stranded polymers² (Figure 3).

- Formed double-stranded helical polymer which was constructed with salt bridge and metal coordination was stable and observable by AFM (Figure 4).

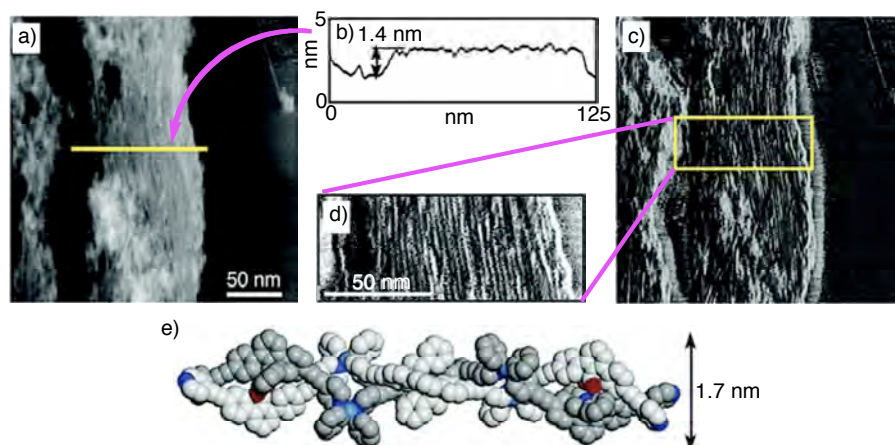


Figure 4. AFM a) height b) phase images of polymer 4 on HOPG e) calculated structure by MM calculation

1-3. Catenane

- Catenanes (Figure 5): a kind of interlocked molecules, candidates for nanomachines and nanodevices

<= Controllable relative motions and physical properties of macrocycles by stimuli

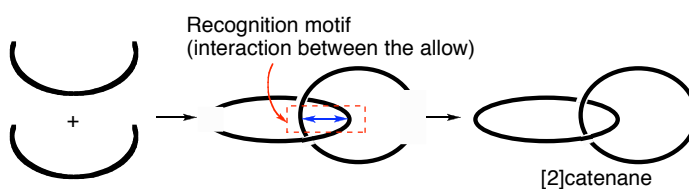


Figure 5. Schematic image of construction of [2]catenane

- Recognition motifs of catenane: important for synthesis of this structure and control of the relative motions of these macrocyclic components

=> Amidinium carboxylate salt bridge was applied as the recognition motif of [2]catenane in this study

1-4. This study

- Synthesis of novel [2]catenane (Figure 6) with the amidinium carboxylate salt bridge
- Control of the relative motion of its macrocyclic components by acid-base interactions and metal coordination

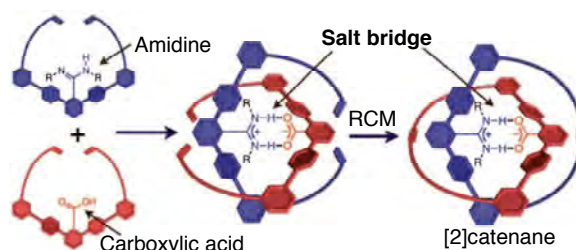


Figure 6. Schematic image of this work

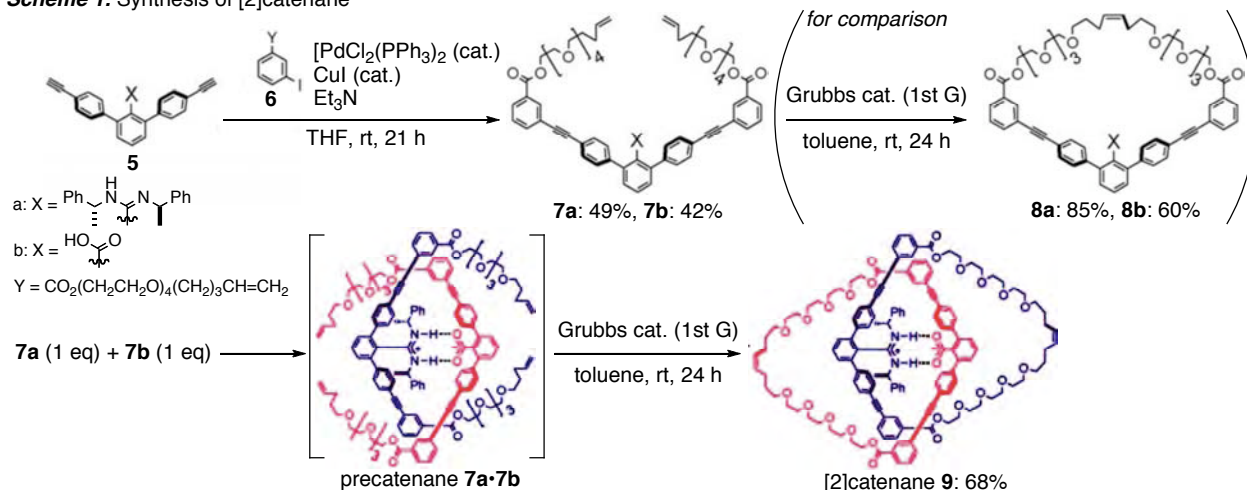
2. Results and discussion

2-1. Synthesis and characterization of the [2]catenane with amidinium carboxylate salt bridge

2-1-1. Synthesis

- Synthesis of the [2]catenane was achieved via Sonogashira coupling and ring closing metathesis (RCM) (Scheme 1).

Scheme 1. Synthesis of [2]catenane



2-2-2. Characterization of [2]catenane 9

- Characterization of [2]catenane 9 itself was mainly done by ^1H NMR (1D and 2D), ESI-MS.
- There are three possible passes to form macrocyclic compound when RCM reaction proceed on the monomer 7a and 7b (Figure 7).

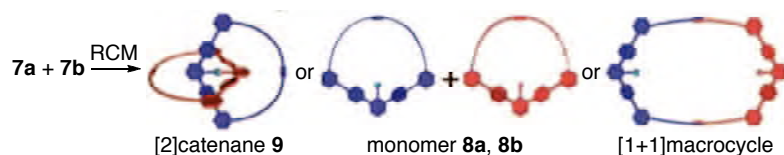


Figure 7. Schematic image of possible products from RCM reaction of the mixture of 7a and 7b

- Difference between 7, 8, 9 was distinguished by ^1H NMR (Figure 7) and ESI-MS

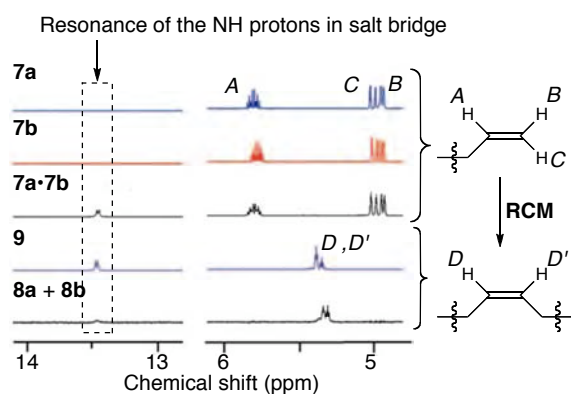


Figure 7. Partial ^1H NMR spectra (500 MHz, CDCl_3 , rt)

- Peak at $\delta = 13.45$ ppm of 7a·7b and 9: resonance of the NH protons \Rightarrow formation of salt bridge
- Peak of the proton on terminal alkene of 7 was different from 9 and (8a + 8b) \Rightarrow RCM reaction
- Absence of [1+1]macrocycles was demonstrated by ESI-MS of the fragments which gave by alcoholysis of the ester groups of the resulting product.

2-2. Control over on/off switching of the salt bridge

2-2-1. Control of relative motion of [2]catenane 9 by addition of TFA

- This [2]catenane 9 was controlled its relative motion through controlling the state "locked" or "unlocked" acid-base interaction (Figure 8). \Rightarrow Change in ^1H NMR spectrum and CD spectrum (Figure 9)

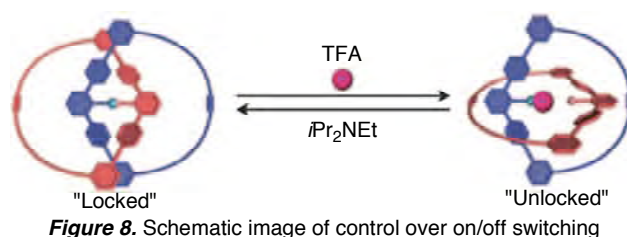


Figure 8. Schematic image of control over on/off switching

- CD spectrum of only **9** => two *m*-terphenyl groups bound together by the salt bridge were twisted in one direction as monomer (**8a** + TFA).
- Addition of TFA led decrease of chirality of [2]catenane **9**.
=> TFA “unlocked” the catenane **9** to free relative rotation.
- Chirality could be recovered by addition of *i*Pr₂NEt.

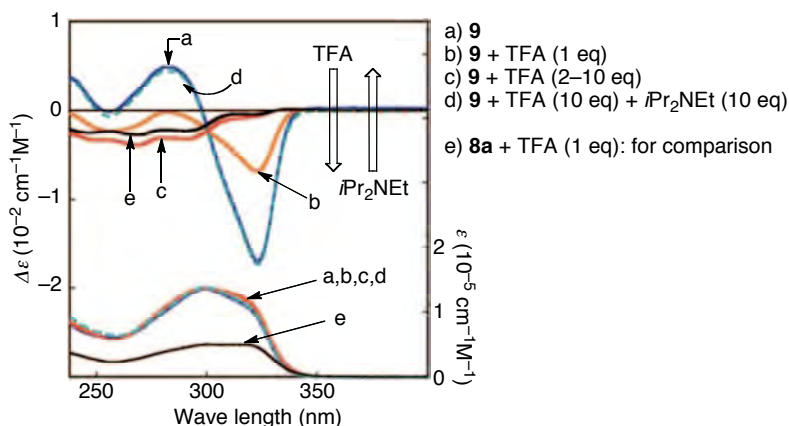


Figure 9. CD and absorption spectra (CDCl₃, rt, 0.1 mM of **9** or **8a**)

2-2-2. Control of relative motion by addition of metal

- The switch between the “locked” and “unlocked” states (Figure 8) was also achieved by Zn ion.
- [2]catenane **9** has conjugated *m*-terphenyl unit: FL (EX 300 nm, EM 440 nm)
=> Control of movement of this macrocyclic components by addition of Zn(ClO₄)₂ was demonstrated with change in FL (Figure 10).

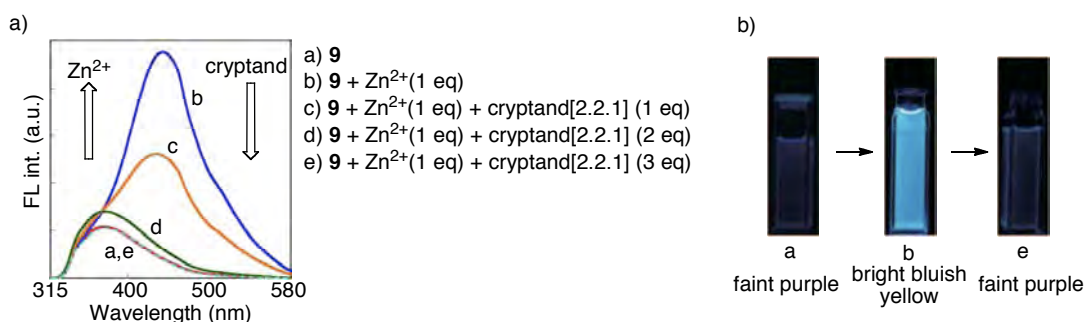


Figure 10. a) Fluorescence spectra (CH₂Cl₂/THF (10:1, v/v), rt, 0.01 mM of **9**) b) Photographs of the solutions (EX: 254 nm)

- Addition of Zn²⁺ ions caused a significant enhancement of FL and red shift.
- <= Zn²⁺ was coordinated to amidine residue and distance between two *m*-terphenyl unit increased.
- Removal of Zn²⁺ ion by addition of cryptand restored FL intensity, “locked” state.

Conclusion

The authors succeeded in applying versatile hydrogen bonding, amidinium carboxylate salt bridge in construction of a novel optically active [2]catenane. This salt bridge was good recognition motif in the aspect of controlling relative motion of the macrocycles via acid–base interaction and metal coordination.

References

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- 2) Ikeda, M.; Tanaka, Y.; Hasegawa, T.; Furusho, Y.; Yashima, E.* *J. Am. Chem. Soc.* **2006**, *128*, 6086–6807.