

Synthesis and dynamics study of [7]catenane

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Introduction

Mechanical Interlocked Molecules (MIM) like catenanes are topologically nontrivial compounds. Due to this, lots of intriguing large amplitude motions which cannot be done by architecturally simple molecules are possible. For example swinging¹ and gliding², which leads to molecular machinery. Rotaxanes and catenanes also have lots of potential applications like polymer³ and molecular electronics⁴. Catenane is a molecule in this project, a [7]catenane using β -cyclodextrin (β -CD)(Figure.1) and cucurbit[6]uril (CB[6])(Figure.2) is synthesized and the motion of β -cyclodextrin in the [7]catenane was studied briefly.

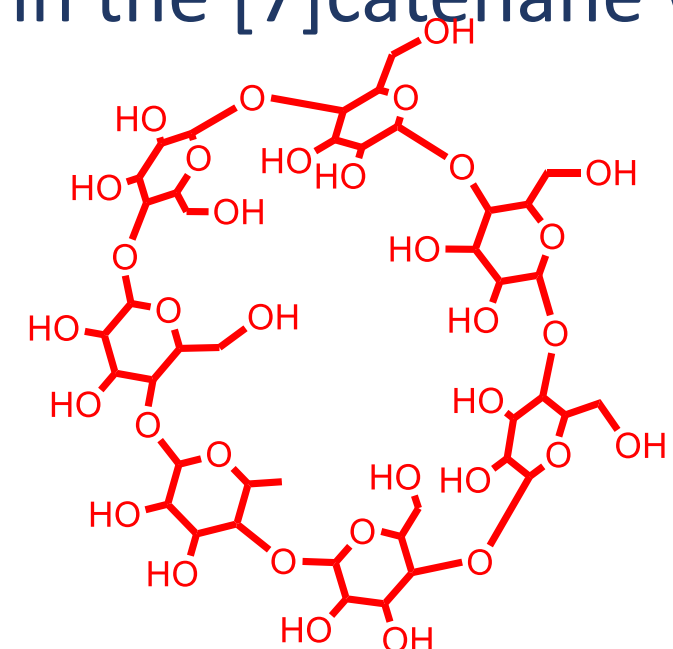


Figure.1 Chemical structure of β -CD

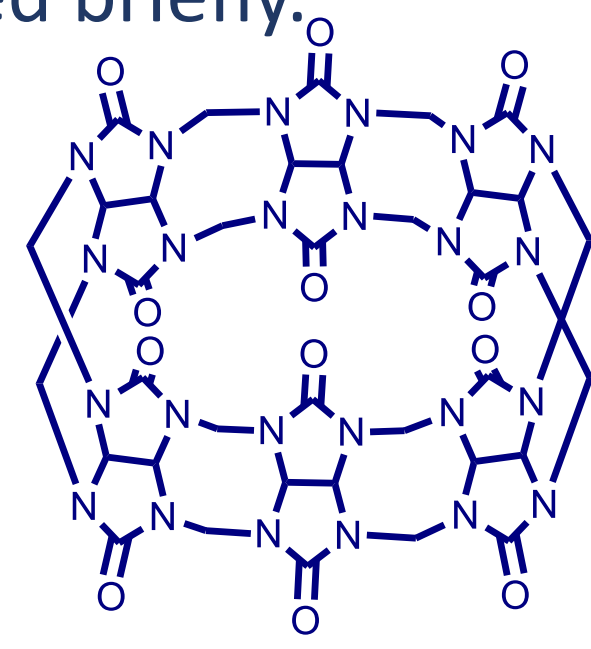


Figure.2 Chemical structure of CB[6]

[7]Catenane

For the [7] catenane the starting materials are commercially available reagents. Through multiple steps synthesis, a building block with R group where R is an alkyne or an azide group is synthesized. Then the [7]catenane is assembled according to the assembly scheme. The macrocycles are first heated separately with the building blocks to thread the macrocycles inside. Then two building blocks are mixed to close the ring via cucurbituril mediated alkyne-azide cycloaddition(CBAAC). β -CD will tend to be at the biphenyl groups as they are attracted by hydrophobic effect, CB[6] will be attracted to the amino group.

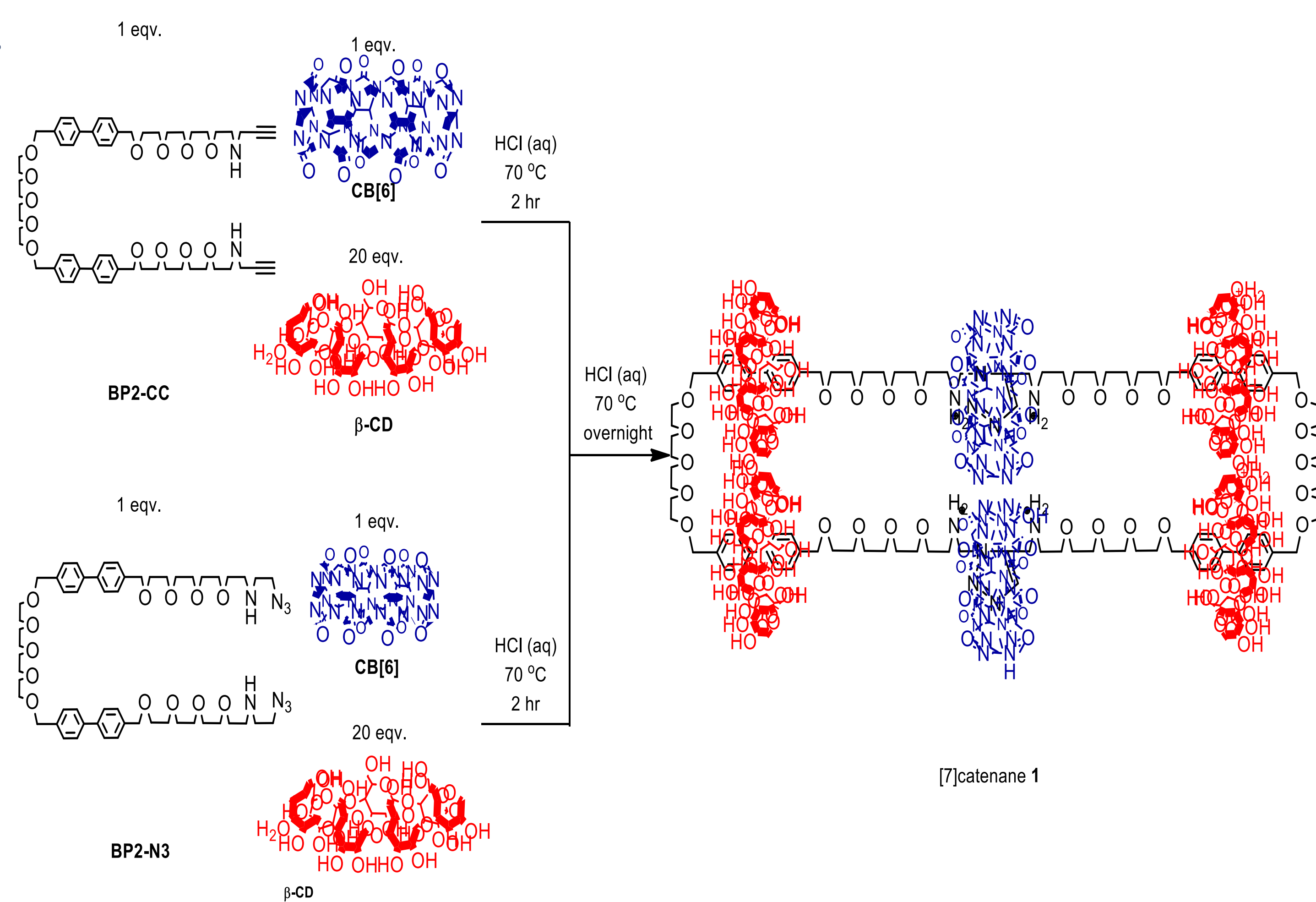
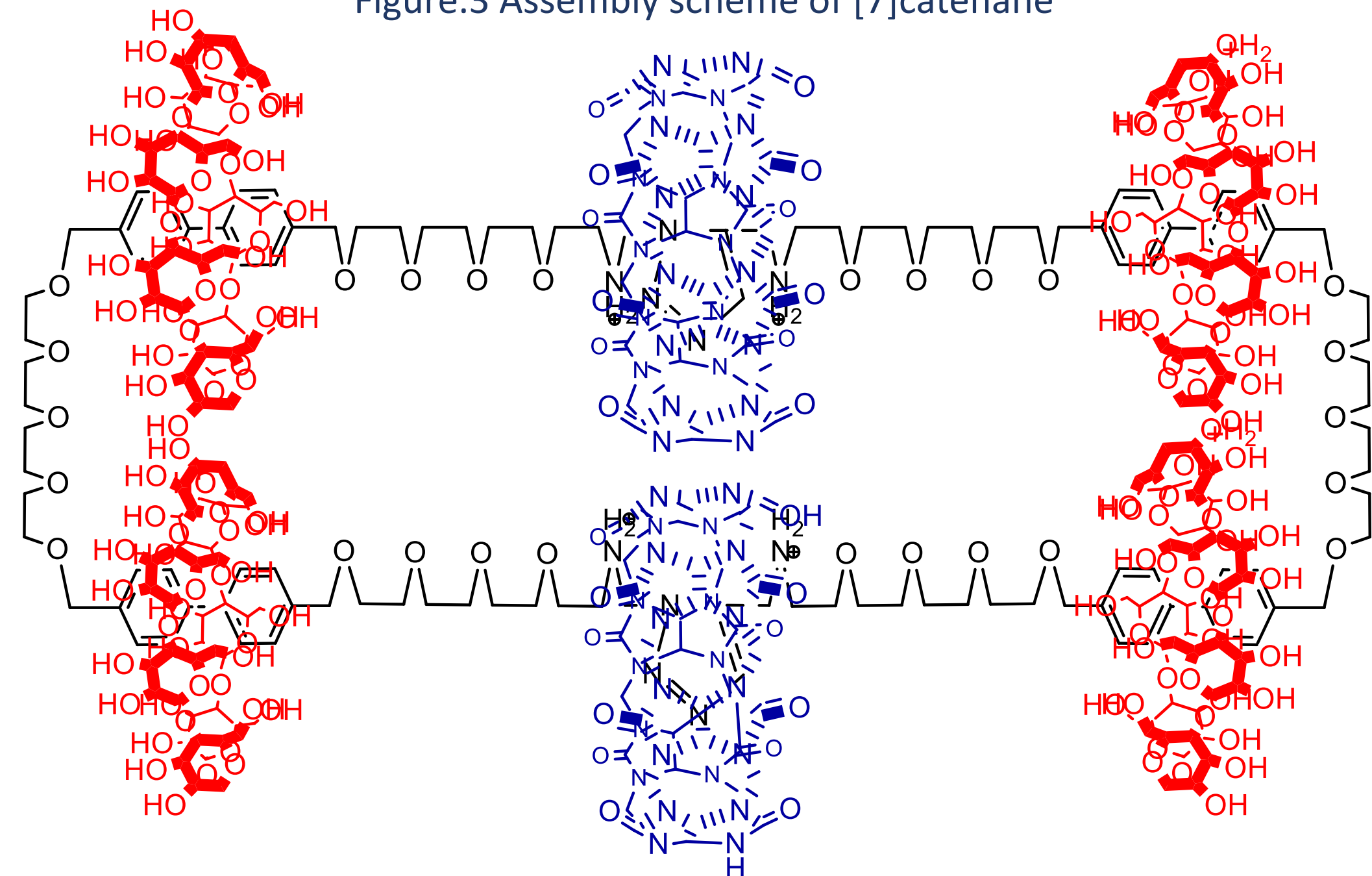


Figure.3 Assembly scheme of [7]catenane



[7]catenane 1
Chromatographic yield: 96%

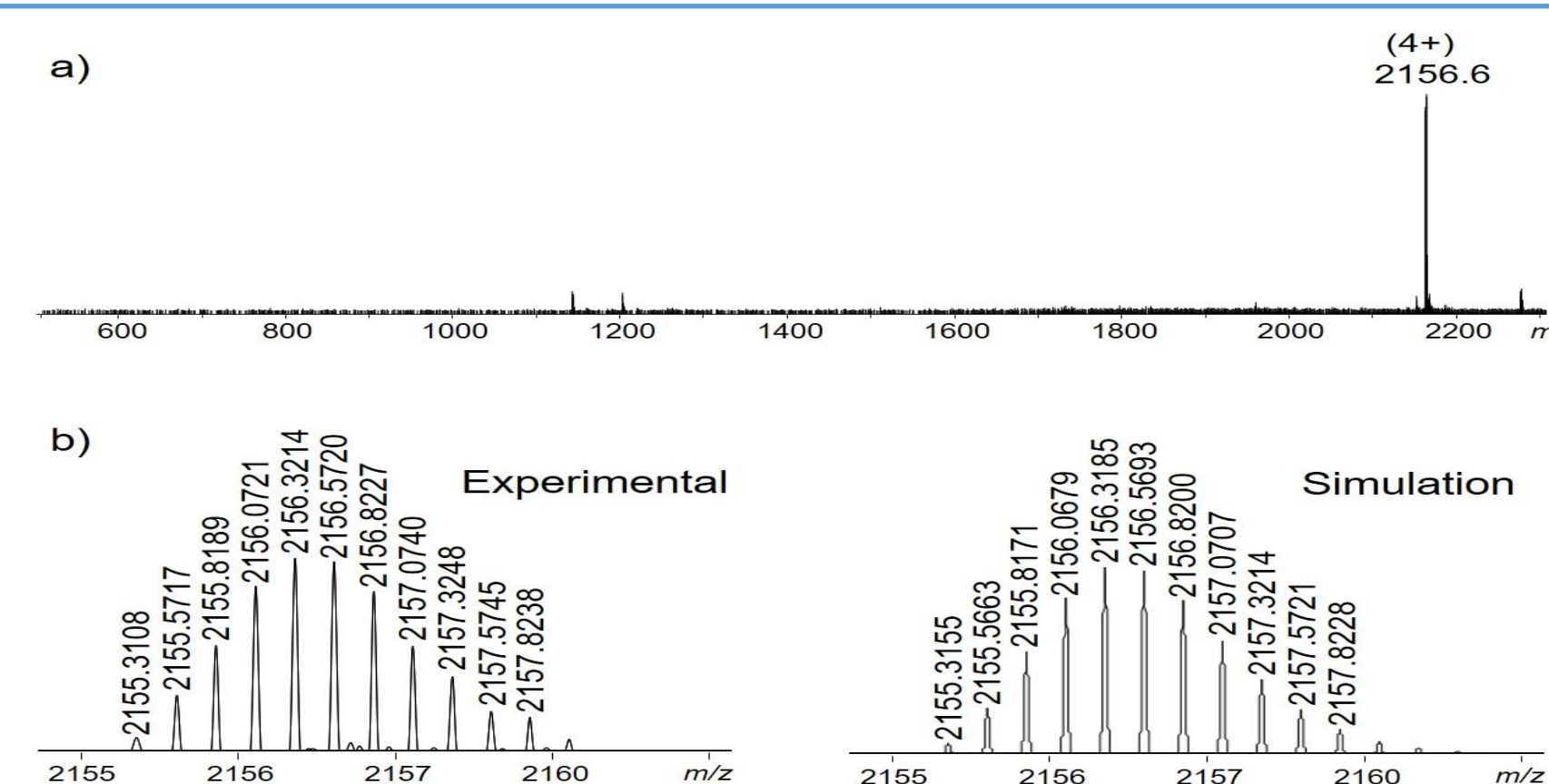
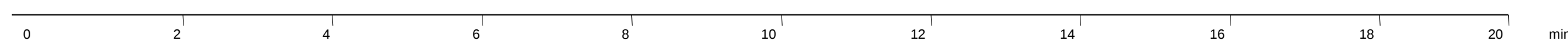


Figure.4 HRMS Spectrum

Dynamics of β -cyclodextrin

Position of β -cyclodextrin on the [7]catenane is not fixed because the interaction between β -cyclodextrin and biphenyl group is not very strong. By changing the ionic strength and temperature, the interaction of β -cyclodextrin will be variable. We are interested in how the dynamics of β -cyclodextrin will change in different condition, which can be represented by signals of biphenyl groups in NMR.

NMR Spectrum

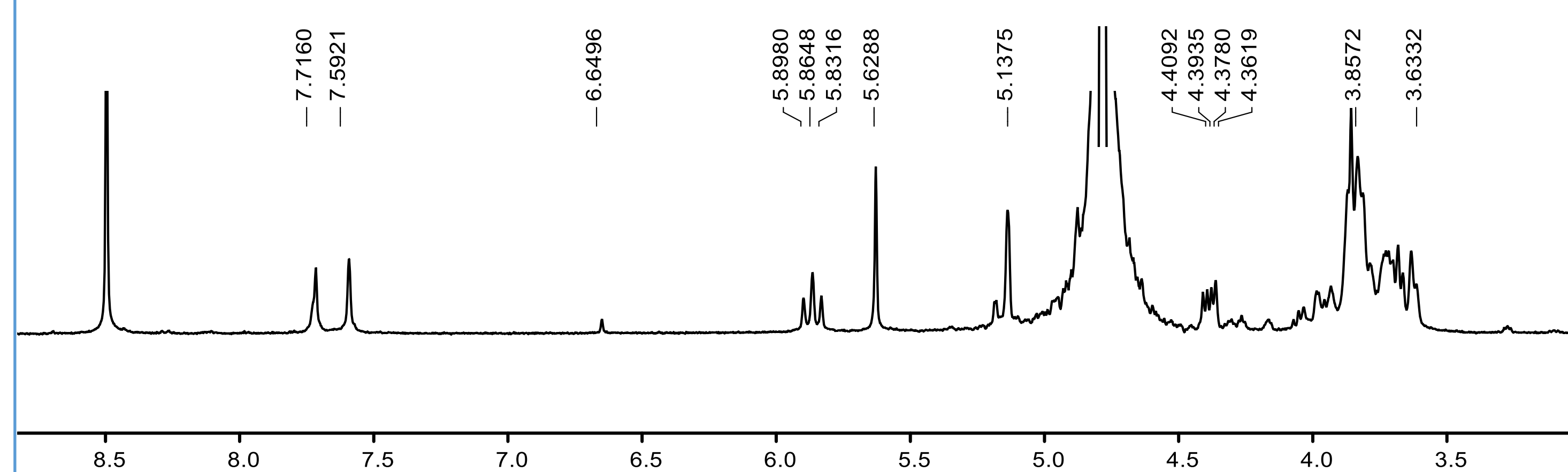


Figure.5 500MHz ¹H NMR in pure D₂O at 298K

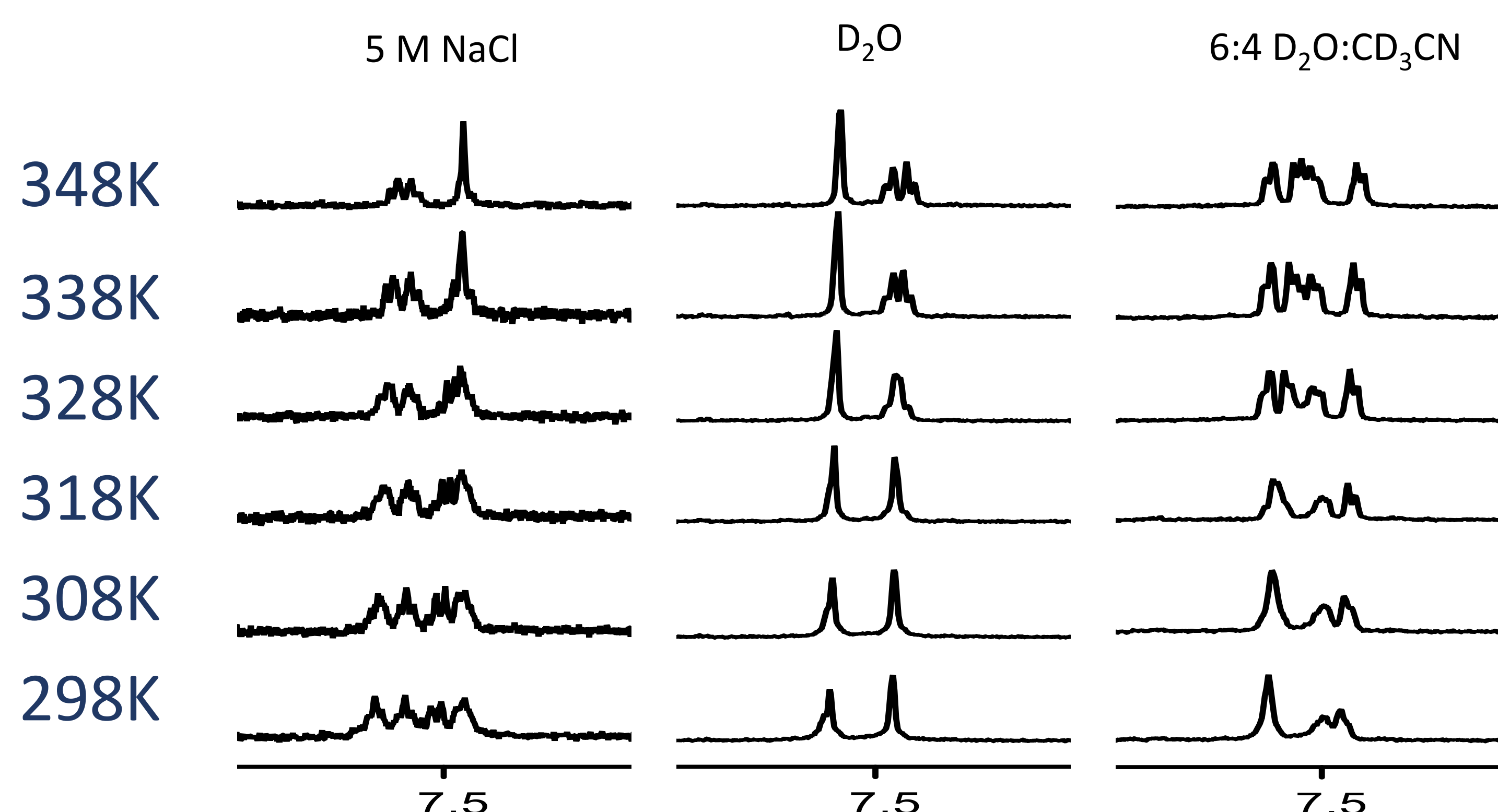


Figure.6 Biphenyl signals of 500MHz VT-¹H NMR in various solvent system

Results & Discussion

Because of the unsymmetrical nature of β -CD there will be different chemical shifts for protons of biphenyl groups and we will expect multiple doublets to appear. In the 298K D₂O solution two broad singlets are observed this is because the motion of β -CD is at a comparable rate to the NMR timescale. To resolve the biphenyl signals, two approach were taken to quicken and slow down the rate of motion. In the 6:4 D₂O:CD₃CN solution the solution is less polar which makes the biphenyl bind more loosely, the biphenyl signals are more resolved because the motion of β -CD is faster. On the other hand if the solvent is 5M NaCl, the ionic strength of the solution increases, the hydrophobic effect also increase at the end the β -CD are bind to biphenyl groups more tightly. This leads to a slower exchange rate and a more resolved spectrum.

Reference and acknowledgement

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