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The Use of Molecular Dynamics to Predict the Stability of Squaraine Rotaxanes

Ruth Nelson

Concordia University - Portland

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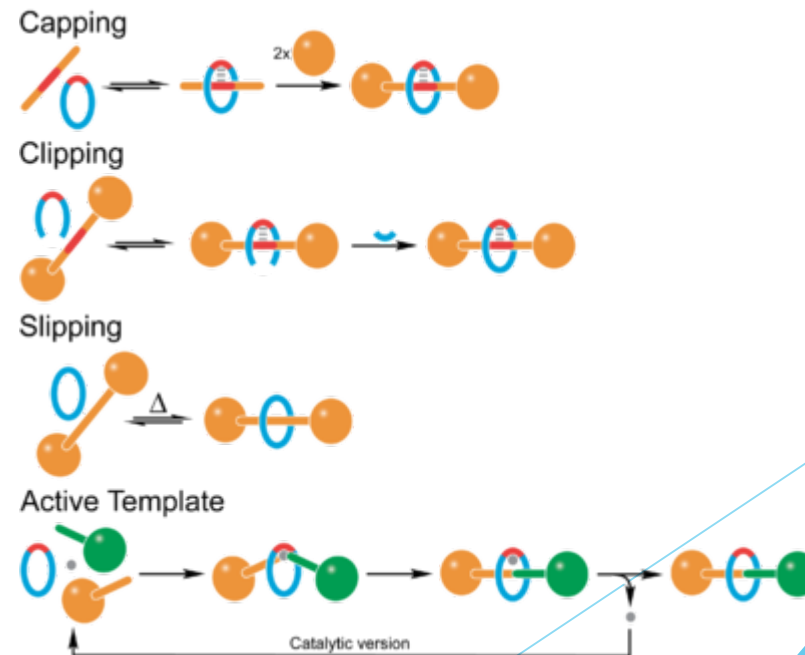
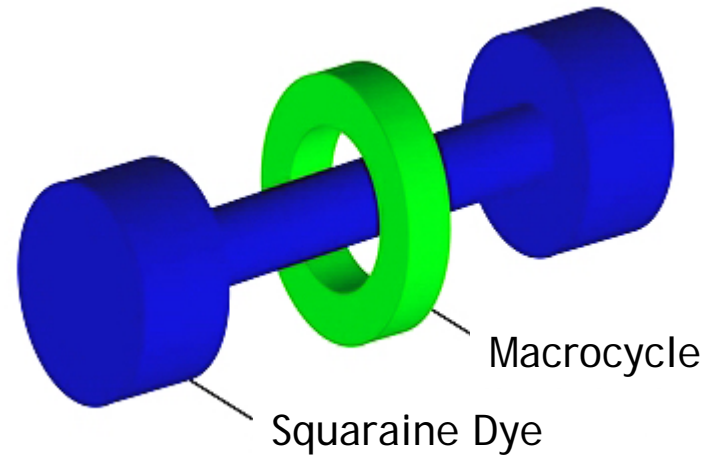
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The Use of Molecular Dynamics to Predict the Stability of Squaraine Rotaxanes

Ruth Nelson

What is a Rotaxane?

- ▶ Generic shape
- ▶ Mechanically interlocked
 - ▶ Hydrogen bonds between squaraine dye and macrocycle
 - ▶ Size of endcaps prevents slipping
- ▶ Four main methods for synthesis
 - ▶ Capping
 - ▶ Clipping
 - ▶ Slipping
 - ▶ Active template
 - ▶ a.k.a. Leigh-type templating reaction

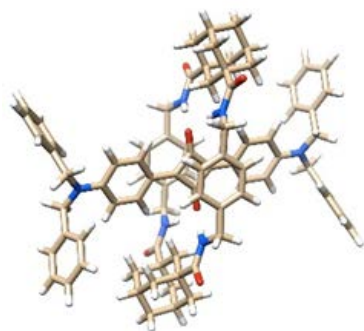


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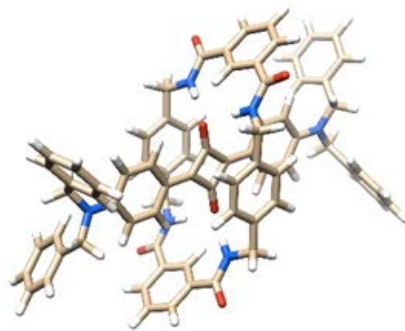
- ▶ Fluorescent dye
 - ▶ Can stain cancer cells, bacterial cells, etc.
- ▶ Absorbs near-infrared radiation
 - ▶ Can easily penetrate skin and tissue
- ▶ Washes out of samples easily if needed
- ▶ Can be used as molecular machine
 - ▶ Shuttles, switches, etc.

Previous Studies

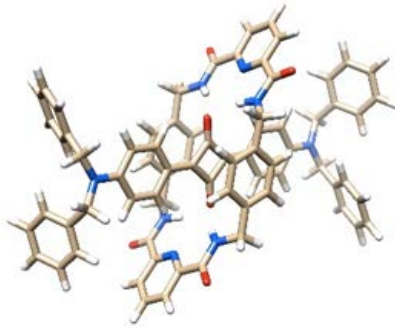
- ▶ Smith Group at the University of Notre Dame



Adamantyl
Rotaxane



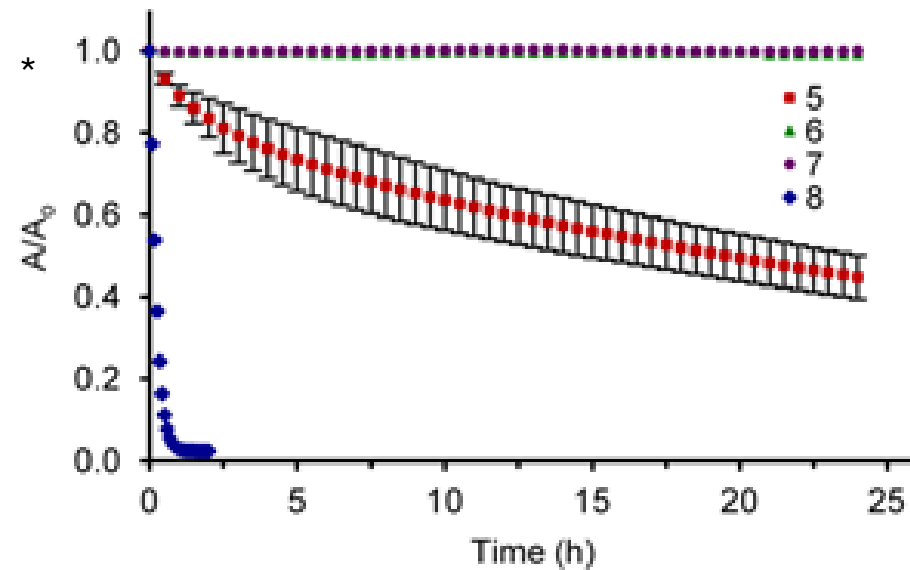
Isophthalamidyl
Rotaxane



Pyridinyl
Rotaxane



◆ = free squaraine dye



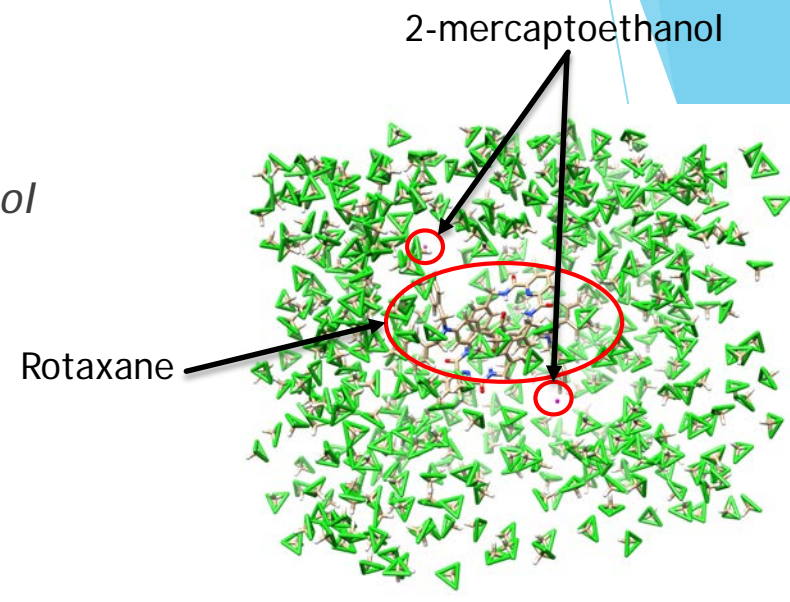
* Collins, C. G.; Johnson, A.; Connell, R. D.; Nelson, R.; Murgu, I.; Oliver, A. G.; Smith, B. (Unpublished work).

Methods

- ▶ Minimize the structure of each rotaxane
- ▶ Implicit solvent
 - ▶ Proof of concept study
 - ▶ Born implicit solvation model, dielectric constant of chloroform used ($\epsilon = 4.81$)
 - ▶ Cutoff = 20 Å
 - ▶ 100 ns molecular dynamics (MD) trajectories
 - ▶ 1 fs timestep
 - ▶ Create histograms

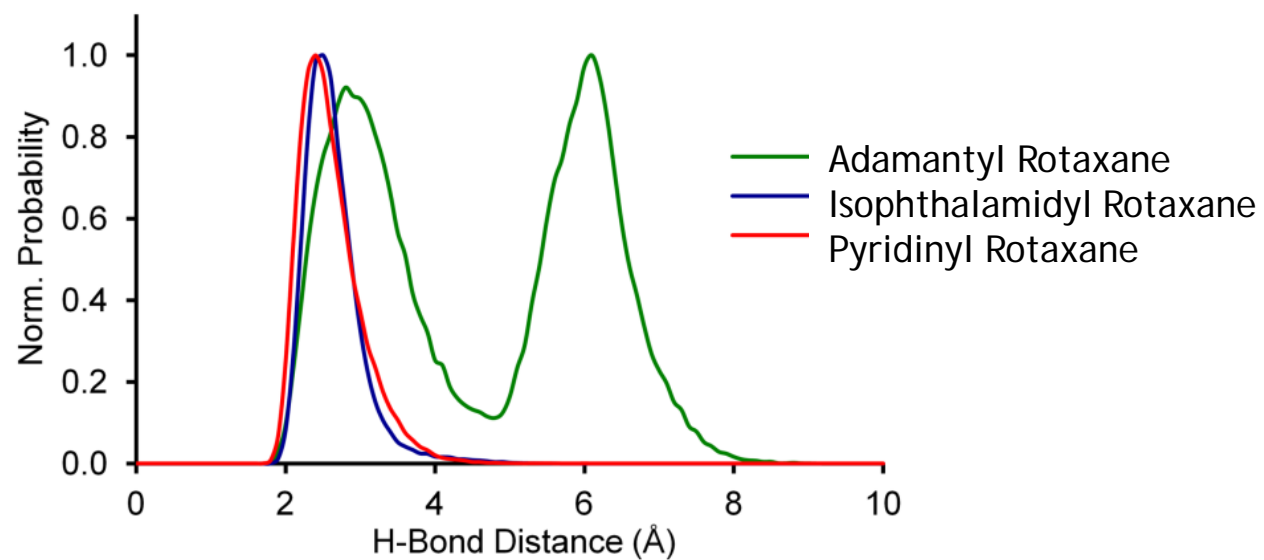
Methods

- ▶ Explicit solvent
 - ▶ Solvate each rotaxane in box of chloroform using *Packmol*
 - ▶ 2 molecules of 2-mercaptoethanol added
 - ▶ 5 μ M concentration
 - ▶ Minimized solvent while constraining solute
 - ▶ Unconstrained minimization
 - ▶ Heat to 300 K while constraining solute
 - ▶ All constraints released, 200 ns MD trajectories
 - ▶ Create histograms

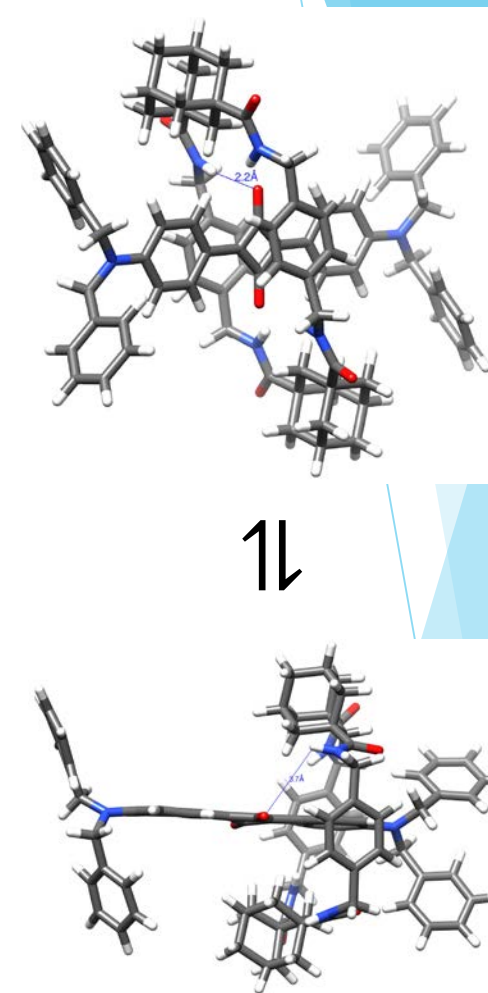


| Rotaxane | Dimensions (Å) | Number of 2-mercaptoethanol molecules | Number of chloroform molecules |
|-----------------|----------------|---------------------------------------|--------------------------------|
| Adamantyl | 47x43x36 | 2 | 538 |
| Isophthalamidyl | 47x39x35 | 2 | 481 |
| Pyridinyl | 47x40x35 | 2 | 491 |

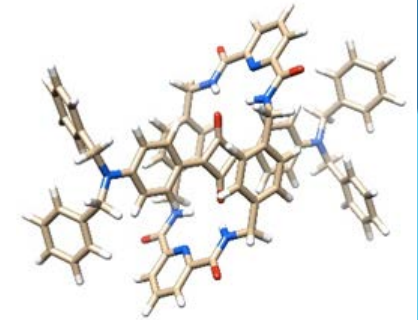
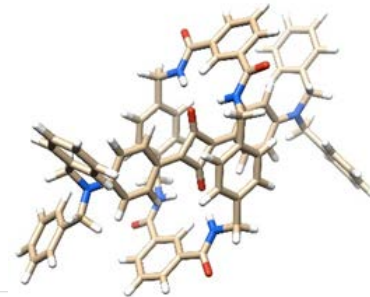
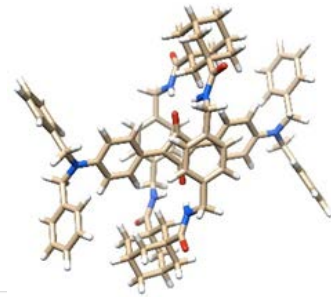
Results



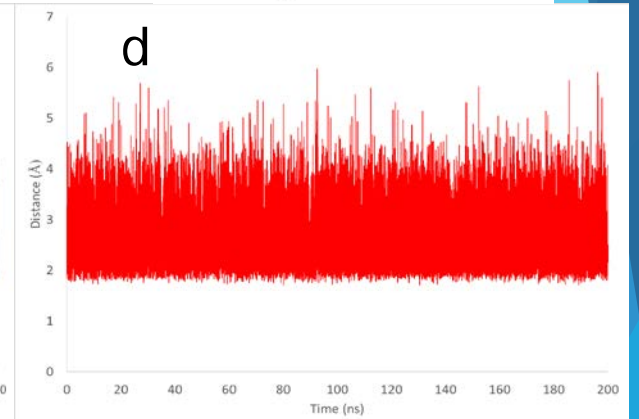
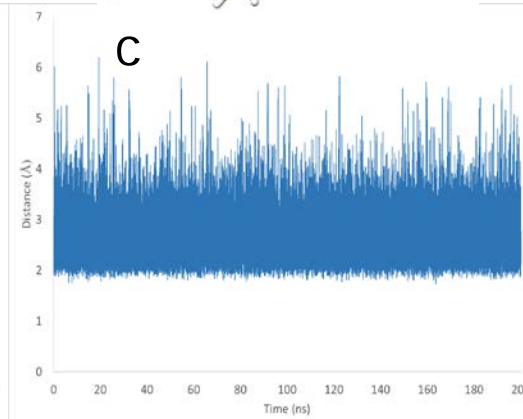
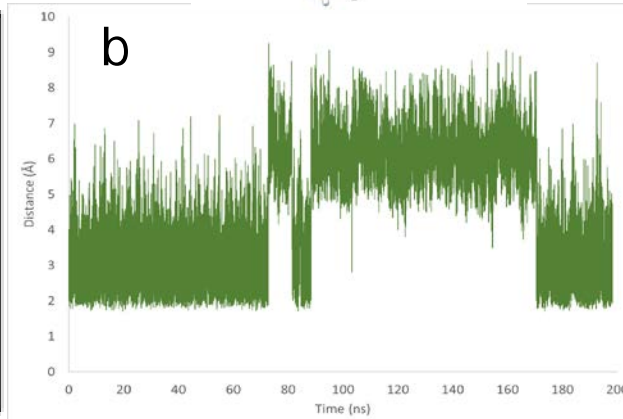
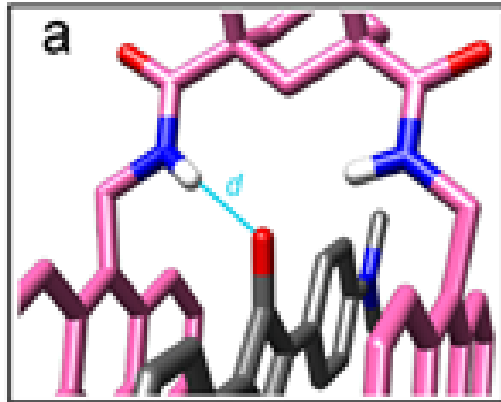
Normalized histogram of the hydrogen bond distances for each rotaxane



Results



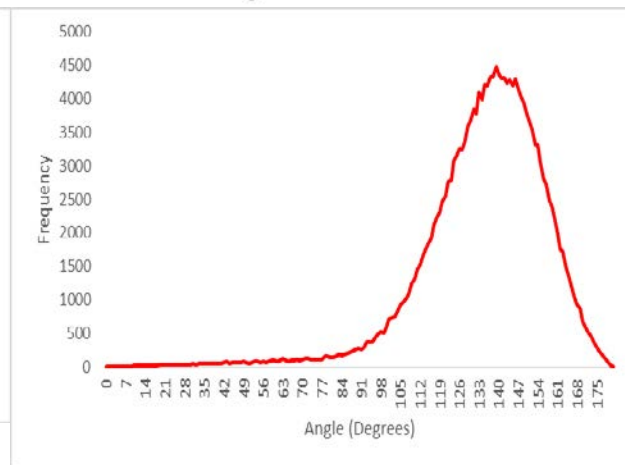
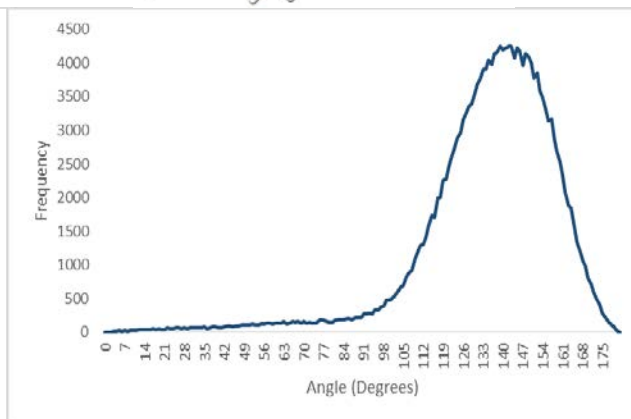
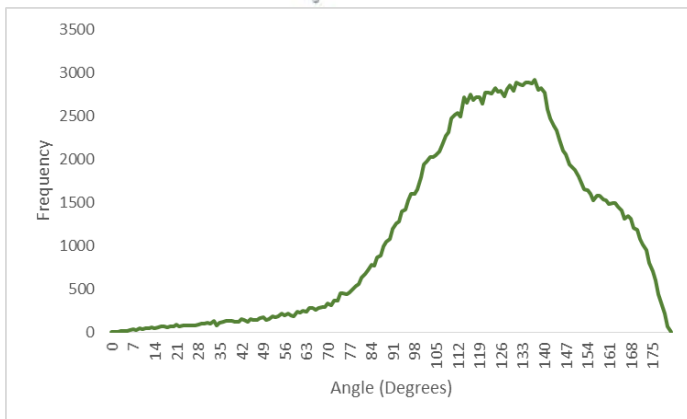
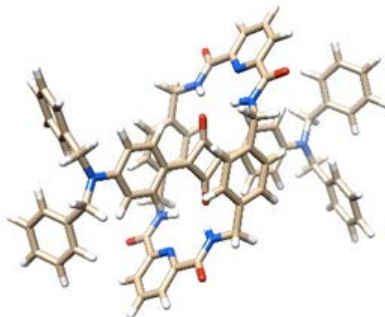
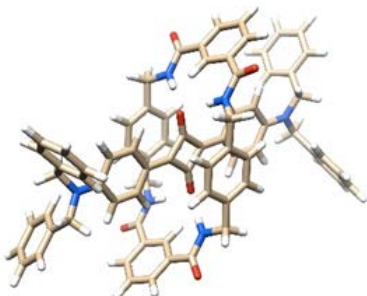
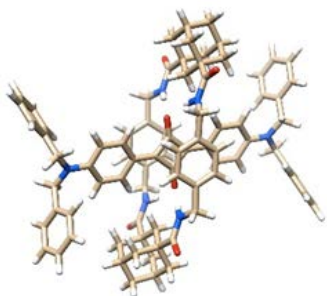
*



- (a) Hydrogen bond distance measured for each rotaxane
- (b) Adamantyl hydrogen bond distance vs. time
- (c) Isophthalamidyl hydrogen bond distance vs. time
- (d) Pyridinyl hydrogen bond distance vs. time

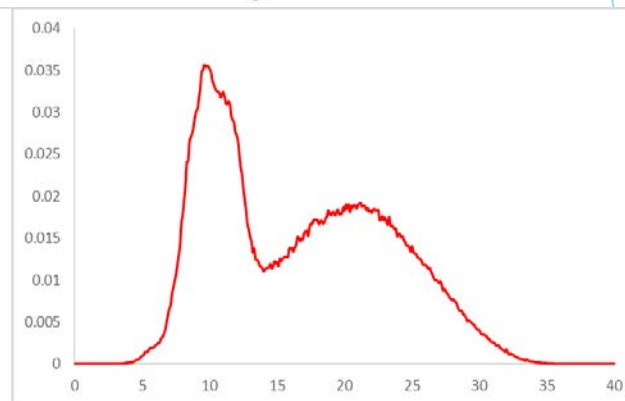
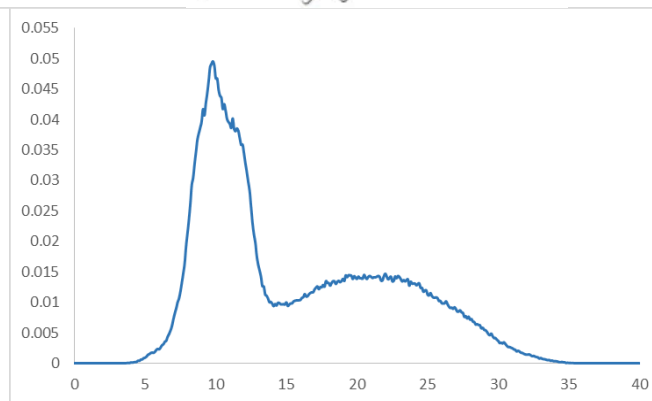
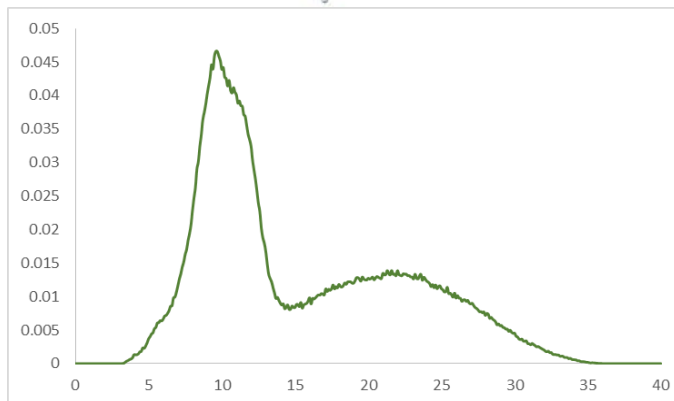
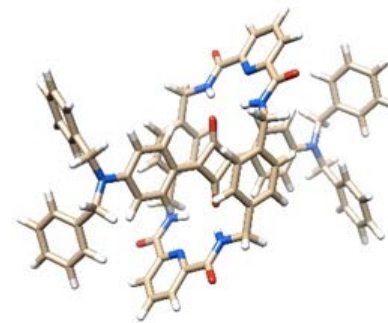
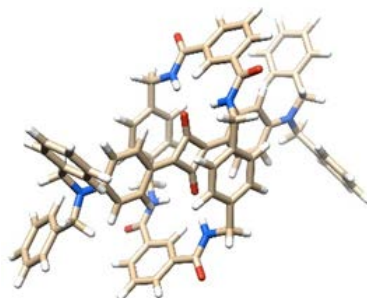
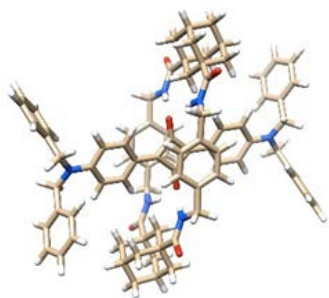
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Results



Squaraine-macrocycle angle vs. time for each rotaxane

Results



Sulfur-carbon distance vs. time

Conclusions

- ▶ Along with previous studies, our results show that isophthalamidyl and pyridinyl macrocycles can effectively protect squaraine dyes from nucleophilic attack
 - ▶ MD simulations show that squaraine does not slip out of these macrocycles
- ▶ Isophthalamidyl and pyridinyl macrocycles have many double bonds and are therefore conjugated
 - ▶ Higher rigidity does not allow squaraine dye to slip out
- ▶ Adamantyl macrocycle has fewer double bonds and is therefore not conjugated
 - ▶ Lower rigidity allows bond angles to rotate enough to let the squaraine slip through
- ▶ These methods can be used in the future to help design new rotaxanes
 - ▶ Future of biomedical imaging probes?

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