

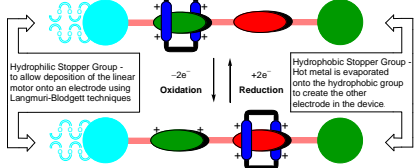


Making Linear Molecular Machines

Jan O. Jeppesen,^[a,b] Kent A. Nielsen,^[a,b] Julie Perkins,^[a] Jan Becher,^[a] and J. Fraser Stoddart^[a]

[a] Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA). E-mail: stoddart@chem.ucla.edu
[b] Department of Chemistry, Odense University (University of Southern Denmark), Campusvej 55, 5230 Odense M (Denmark). E-mail: kan@chem.sdu.dk, jo@chem.sdu.dk

A [2]Rotaxane as a Molecular Machine



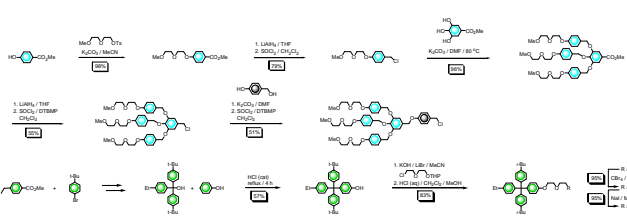
A [2]rotaxane is a molecule composed of a macrocyclic and a dumbbell-shaped component.^[1] The macrocycle encircles the linear rodlike portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. Thus, the two components cannot dissociate from one another.

If the dumbbell components contains two different recognition sites (green and red) for the macrocycle (blue), it's assumed that the macrocycle resides preferentially around the stronger recognition site (green) until a stimulus (oxidation) is applied that switches off the stronger of the two recognition sites, thus inducing the macrocycle to move to the second weaker recognition site (red). By applying a new stimulus (reduction) the stronger recognition site (green) can again be switched on and the macrocycle moves back to the stronger recognition site.

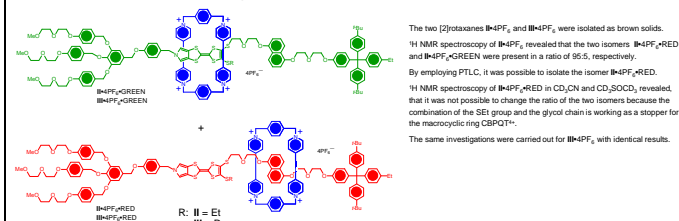
Here, we report the synthesis of four amphiphilic bistable [2]rotaxanes (I, II, III and IV) in which the ring component is cyclobis(paraquat-p-phenylene) (CBPQT⁴⁺) and the dumbbell-shaped component-containing a monopyrrolo-tetrahydrofullerene^[2] (TTF) unit and a 1,5-dioxynaphthalene (DNP) ring system within its rodlike portion-terminated by a hydrophilic dendritic stopper at one end and a hydrophobic tetraarylmethane stopper at the other end.

Furthermore, we demonstrate (1) the separation of two possible translational isomers (red and green) for the [2]rotaxane I, (2) the slow interconversion of the two isomers (red and green) for the [2]rotaxane II, (3) the structure of [2]rotaxanes III and IV, and (4) the fast interconversion of the two isomers (red and green) for the [2]rotaxane IV.

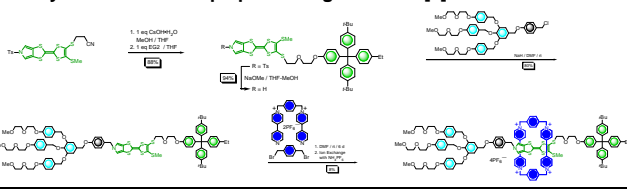
1. Synthesis of the Hydrophilic and Hydrophobic Stoppers^[3]



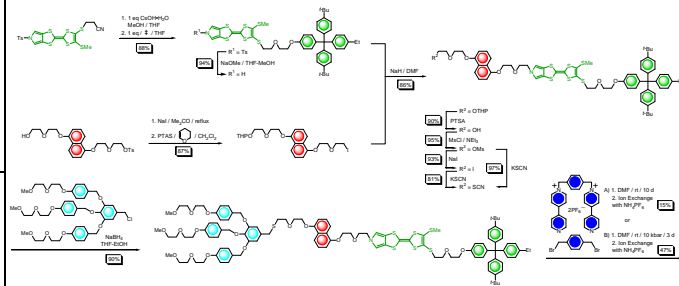
5. Prevention of Shuttling in an Amphiphilic Bistable [2]Rotaxanes



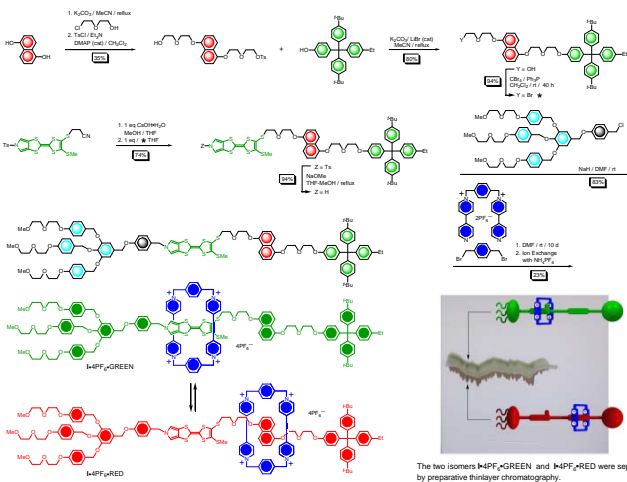
2. Synthesis of an Amphiphilic Single-Station [2]Rotaxane^[3]



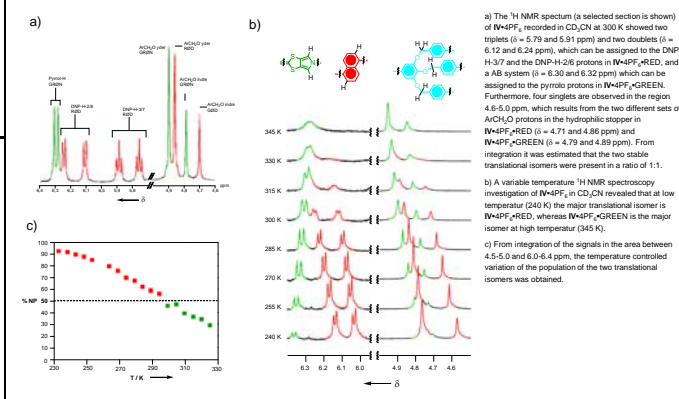
6. Synthesis of a Fast Bistable [2]Rotaxane



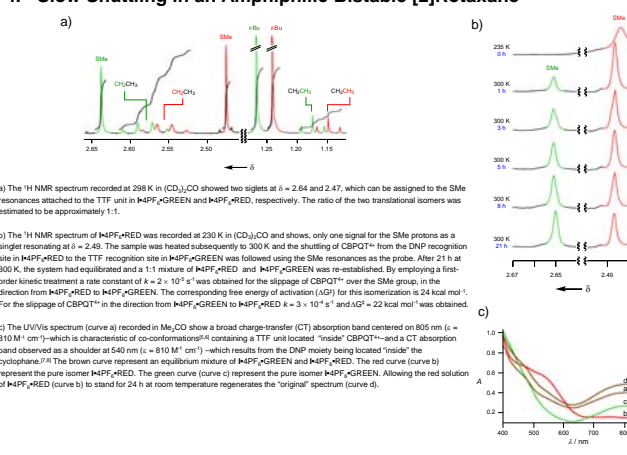
3. Synthesis of a Slow Bistable [2]Rotaxane^[4]



7. Fast Shuttling in an Amphiphilic Bistable [2]Rotaxane



4. Slow Shuttling in an Amphiphilic Bistable [2]Rotaxane



8. Conclusions

- 1) We have devised and completed the syntheses of one amphiphilic [2]rotaxane and four amphiphilic bistable [2]rotaxanes, comprising two different recognition sites – a monopyrrolo-TTF unit and a DNP ring system – for CBPQT⁴⁺.
- 2) The steric hindrance exhibited from the SME group situated between the two recognition sites in the slow molecular shuttle M^{PF_6} has made it possible to isolate the translational isomers M^{PF_6} -RED and M^{PF_6} -GREEN and to study the kinetics of the shuttling of the tetraaromatic cyclophane between the two recognition sites.
- 3) The steric hindrance exhibited from the SEI and SP₂ groups situated between the two recognition sites in the [2]rotaxanes M^{PF_6} and M^{PF_6} prevented shuttling of the tetraaromatic cyclophane between the two recognition sites.
- 4) In the fast molecular shuttle M^{PF_6} , the steric hindrance between the two recognition sites has been decreased by insertion of a planar pyrrolo moiety, instead of a bulky SME (or SEI, SP₂) as in M^{PF_6} between the DNP and TTF recognition sites. This interchange results in a considerably faster shuttling of CBPQT⁴⁺ between the two recognition sites, making the separation of the two isomers impossible. The shuttling of CBPQT⁴⁺ can be induced by heat stimuli and followed using ¹H NMR spectroscopy. At low temperature (255 K) the major isomer is M^{PF_6} -RED, whereas at higher temperature (330 K) the major isomer is M^{PF_6} -GREEN.
- 5) The switching of the new amphiphilic [2]rotaxanes by electrochemical stimuli (i.e. oxidation of the TTF unit) is currently being assessed, together with their ability to self-organize into monolayers as a prelude to their introduction into devices.

Acknowledgment and References

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