Last Name	
First Name	
Legi-No.	
Program of Study	

Written Exam
Supramolecular Chemistry
Winter 2015

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Please check:
This exam paper includes 4 printed pages (4 questions) in addition to the cover.

Please note:
- All problems have to be solved.
- Unreadable texts or drawings will not yield any points.
- If you use additional sheets, make sure to mark them with your name and to attach them to this paper.

Points

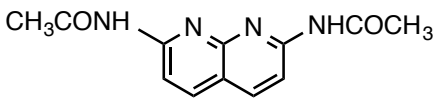
Problem 1	
Problem 2	
Problem 3	
Problem 4	
Total	

Grades

Written	
Oral	
Final	

Problem 1 (20 points). Multiple hydrogen bonding interactions

a) Suggest the structure of the 1:1 complex formed between **1** and **2** in $CHCl_3$ solution and discuss the major interactions in the complex (Org. Lett. 2013, 15, 3506) (5 pt)



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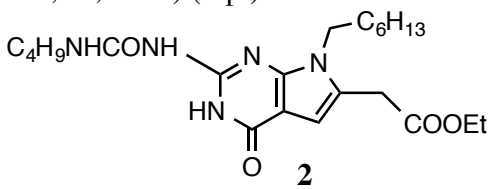

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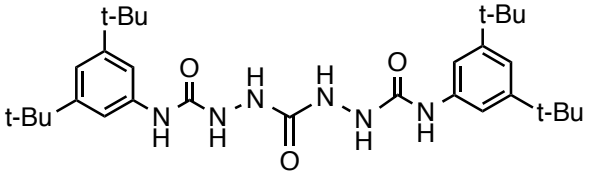
b) Trisurea **3** self-assembles in the solid state. Note, that the ureas are connected by hydrazine-type bonds. The conformation about hydrazin N–N bonds is nearly perpendicular, with a substantional rotational barrier. Suggest the assembly of **3** taking this conformational information into account. The crystals also contain one equivalent of DMSO (Me_2SO). Suggest how the solvent molecule additionally binds and stabilizes the assembly of **3**. Describe the interactions that drive the self-association of **3** and the solvation by DMSO. How would you suggest synthesizing **3** from two starting materials in one step? (Chem. Eur. J. 2013, 19, 8814) (8 pt)



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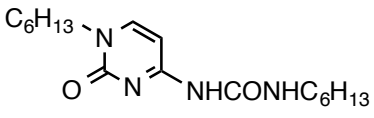
c) Compound **4** undergoes stable H-bonding self-association in the solid state as well as in $CDCl_3$. Suggest the structure of the dimer **4·4** and indicate the major interactions that stabilize the assembly. When compounds **4** and **5** are mixed together in $CDCl_3$, they compete for self-association and a nearly 1:1:1 mixture of **4·4**, **4·5**, and **5·5**, is observed by ^1H NMR. The complexes are at slow exchange. Suggest the structures of **4·5** and **5·5**. Why are **4·4**, **4·5**, and **5·5** of similar stability? What is the practical interest into such strong multiple H-bonding arrays? (J. Am. Chem. Soc. 2006, 128, 6544) (7 pt)



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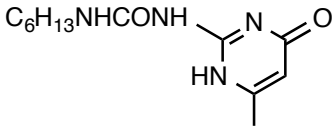

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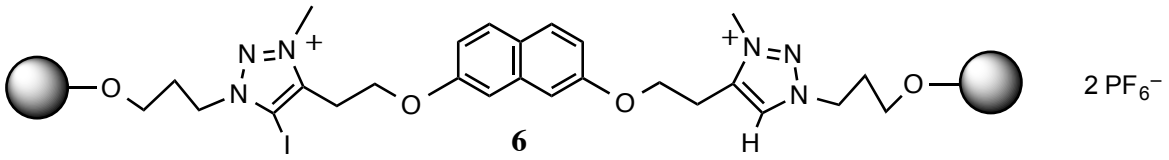
Problem 2 (20 points). Rotaxane synthesis, binding properties, and binding-induced shuttling (Angew. Chem. Int. Ed., 2014, 53, 11854)



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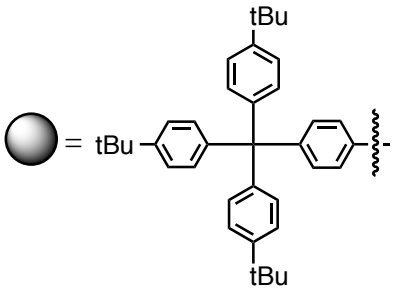
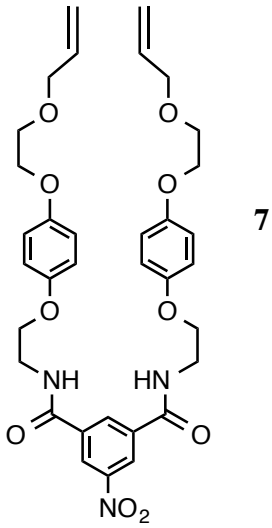




7

Give reaction conditions and reagents for the individual steps in a)-c)

a) Suggest how you would synthesize axle **6** of the rotaxane starting from naphthalene-2,7-diol. (5pt)

b) Suggest how you would prepare **7** starting from 5-nitro-isophthalic acid. (3 pt)

c) Propose how you assemble the rotaxane. (3 pt)

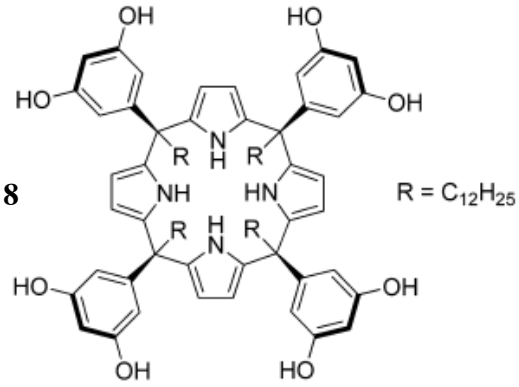
d) The wheel in the rotaxane has a distinct preference to be positioned on the axle **6**. Suggest where the macrocycle resides and which intermolecular interactions are at the origin of this preferential positioning. (4 pt)

e) However, if an excess of iodide salt is added, the I^- anions induce translation to an another site where the wheel resides preferentially. Suggest this site and explain the driving force for the translational switching and the interactions involved. With Ag^+ salts, the translation and switching can be reversed. Explain. What changes in the ^1H NMR spectrum do you expect to be characteristic for the two translational isomers? (5 pt)

Problem 3 (10 points). Cavitand Synthesis, Dynamics, and Binding (J. Org. Chem. 2014, 79, 5545)

a) Suggest a preparation of **8** starting from 3,5-dimethoxybenzaldehyde. The last step is the macrocyclization and only gives 19% yield. Suggest why. (5 pt)

8



$R = C_{12}H_{25}$

b) Starting from **8**, compounds **9** and **10** are prepared in one step. Please provide the reaction conditions for each transformation. (3 pt)

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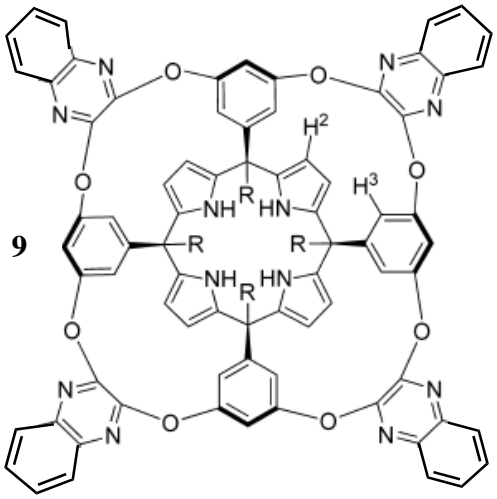

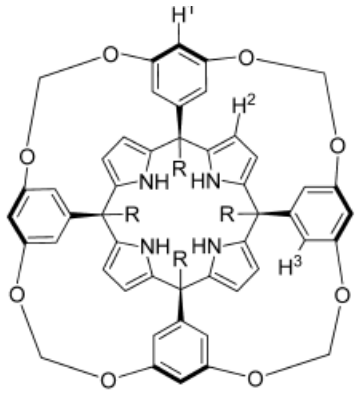

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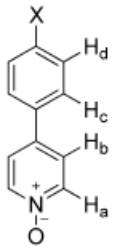
$R = C_{12}H_{25}$

c) We have seen analogous systems to **9** in class, that can be switched from a vase to a kite. Show schematically the vase-kite switching for **9**. Receptor **9** complexes guest **11** in the vase form. Suggest which way the polar guest orients in the cavity and which interactions are responsible for this orientation. (2 pt)

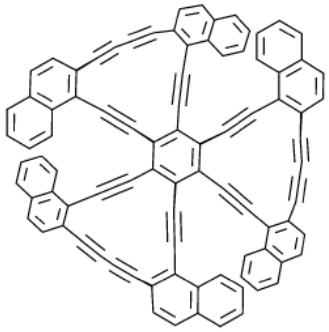


11 X = H

Problem 4 (10 points). Acetylenic macrocycle synthesis (Chem. Eur. J. 2012, 18, 12814-12824)

a) Suggest how you would prepare compound **12**, starting from hexabromobenzene. Please give reagents and conditions. (8 pt)

b) What is the structural interest in compound **12**, as verified by X-ray analysis? (2 pt)



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