Last Name	
First Name	
Legi-No.	
Program of Study	

Written Exam
Supramolecular Chemistry
Winter 2017

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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).

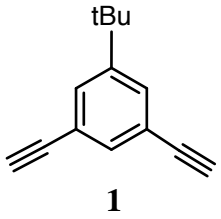
(1) Propose the synthesis of a [3]rotaxane (2 wheels, 1 axle), starting from the three components **1** (0.5 equiv), **2** (1 equiv), and **3** (1 equiv), using a Cu(I) salt. Suggest reaction conditions. Propose the mechanism of the high-yielding rotaxane formation. (7 points)

(2) How would you prepare macrocycle **3** starting from a 2,2'-bipyridyl and a benzene derivative? Suggest reagents and conditions. (7 points)

(3) Propose the preferred torsional angles (°) in free **3** around the bonds a, b, c, and d (shown in bold). What is the preferred conformation of free 2,2'-bipyridyl? (3 points)

(4) The bipyridine of each of the two wheels undergoes a distinct hydrogen-bonding interaction in the [3]rotaxane. Propose this interaction. (3 points)

(J. Am. Chem. Soc. DOI: 10.1021/jacs.6b08958)



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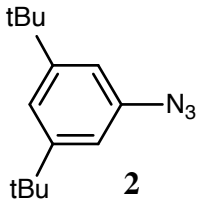

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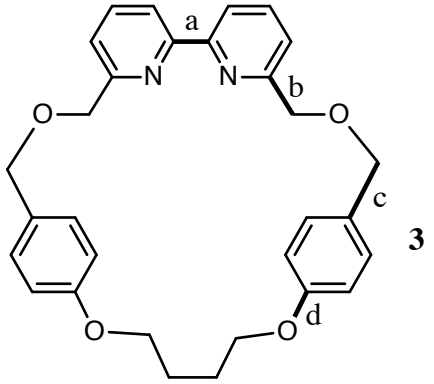


3

[3]Rotaxane

Problem 2 (20 points).

(1) Propose a synthesis of the hemispherand-strapped calix[4]pyrrole **4**. (10 points)

a) The hemispherand moiety is prepared starting from the boronate ester **5** and 6-bromopyridine-2-amine **6**. Suggest the synthesis including reaction conditions.

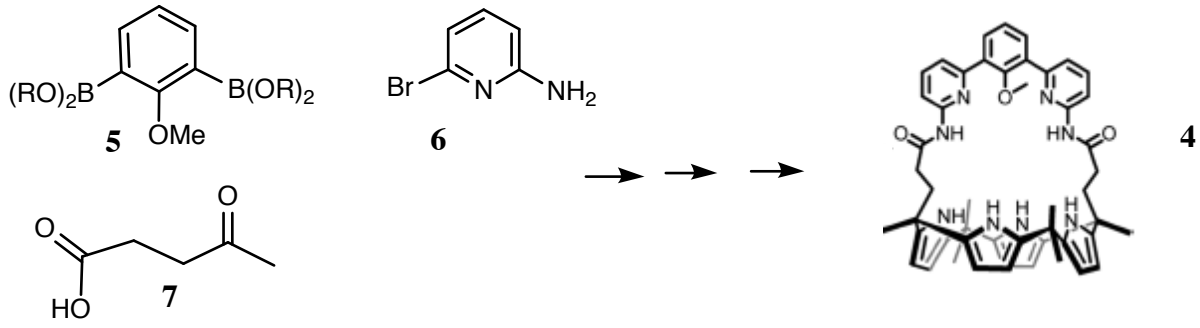
b) The calix[4]pyrrole is prepared from levulinic acid **7**. Suggest the synthesis and the reaction conditions.

c) Suggest the construction of the target compound **4** with reaction conditions.

(2) Compound **4** is a receptor and extracts salts such as LiCl, LiBr, $LiNO_2$ from the solid phase and binds them efficiently in CD_2Cl_2/CD_3OD. Suggest the 1:1 binding mode of the salts with the receptor and discuss the interactions that enable the complex formation. (5 points)

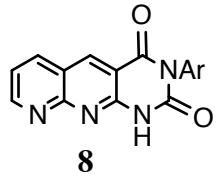
(3) While the formation of the complexes in the solid state is evident from X-ray analysis, distinct ^1H NMR shifts between free and bound **4** are also confirming complexation in CD_2Cl_2/CD_3OD 9:1. Suggest the main complexation-induced changes in chemical shift in the ^1H NMR spectrum of bound **4**, which support complexation in solution. (5 points)

(J. Am. Chem. Soc. 2016, 138, 9779-9782)



Problem 3 (10 points). The association constants for the three 1:1 complexes **8·9**, **10·11**, and **12·13** in $CDCl_3$ are given. Suggest the complex geometries and explain the observed differences in stability (Hint: consider that thermodynamics is a two-state function, in other words, consider also the conformational preference of free components).

(Org. Lett. **2004**, *6*, 1649-1653)



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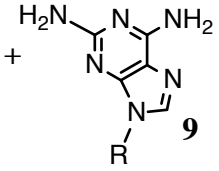

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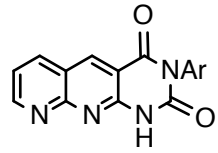
$K_a = 308\ M^{-1}$

Ar = aryl ring
R = protected ribose
(both not relevant for discussion)



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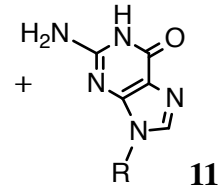

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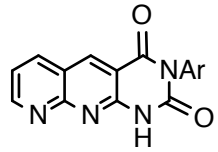
$K_a = 3200\ M^{-1}$



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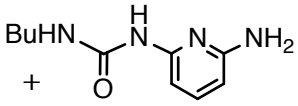

13

$K_a = 180\ M^{-1}$

Bu = n-Butyl

Problem 4 (10 points).

(1) Suggest the synthesis of **14** starting from azulene-1,3-dicarboxylic acid **15** and pyridine-2,6-dicarboxylic acid. Give all reagents and conditions. (7 points)

(2) Compound **14** complexes the tetra(*n*-butyl)ammonium salt of benzoic acid in the crystal and also in $(CD_3)_2SO/D_2O$ 95:5 (298 K, K_a = 3700 M^{-1}). Suggest the bonding interactions. (3 points)

(Chem. Eur. J. **2016**, *22*, 17673-17680)