Last Name	
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Program of Study	

Written Exam
Supramolecular Chemistry
Summer 2012

F. Diederich, C. Thilgen

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

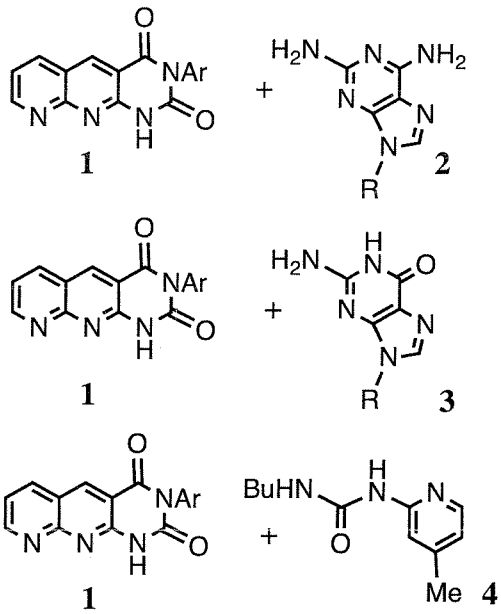
Problem 1	
Problem 2	
Problem 3	
Problem 4	
Total	

Grades

Written	
Oral	
Final	

Problem 1 (20 points). The association constants for the three 1:1 complexes **1·2**, **1·3**, and **1·4** in $CDCl_3$ are given. Suggest the complex geometries and explain the observed differences in stability (hint: consider that binding free enthalpy is a two-state function, in other words, consider also the conformational preference of free components).

Show all attractive (——) and repulsive (- - - -) interactions in the suggested complex geometries.



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

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

$K_a = 406\ M^{-1}$

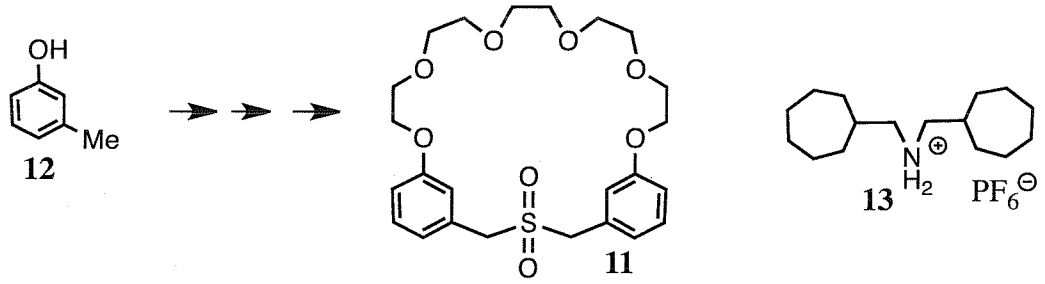
Ar = aryl residue
R = protected ribose
(both not relevant for the discussion)

Bu = *n*-butyl

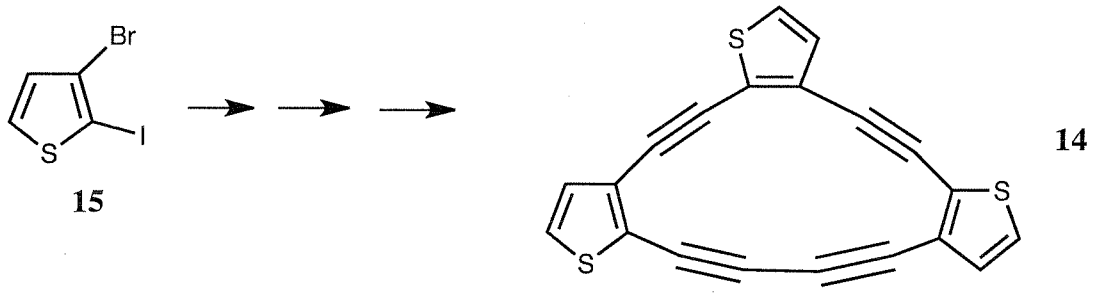
Problem 2 (20 points). **a**) Suggest a synthesis for macrocycle **11** starting from *m*-cresol **12**. Give reagents and conditions for each step.

b) Macrocycle **11** forms a rotaxane with **13** in $CDCl_3/CD_3CN$ (9:1). Suggest the structure of the rotaxane and the bonding interactions stabilizing the structure. The exchange kinetics is slow on the ^1H NMR time scale at 298 K. How is this reflected in the spectra? Suggest characteristic ^1H NMR signal shifts you would expect for the supramolecular complex as compared to the free components.

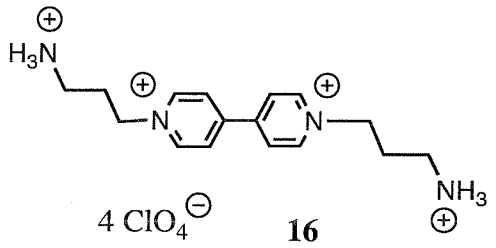
c) The rotaxane can even be made tighter, upon irradiation (we have seen this process that takes place under pyrolysis conditions). Suggest the reaction of macrocycle **11** occurring upon irradiation and the structure of the new macrocycle and of the rotaxane formed with **13**.



Problem 3 (10 points). Suggest a synthesis for **14** starting from thiophene **15**. Show reagents and key reaction conditions.



Problem 4 (10 points). The two components **16** and **17** form a highly stable (log $K_a = 9.15$) 1:1 complex in MeCN. Suggest its geometry and discuss in detail the various intermolecular interactions stabilizing the complex. An X-ray crystal structure of the complex was obtained. Which characteristic spectral features do you expect to be indicative of complexation in the ^{1}H NMR and UV/Vis spectra?



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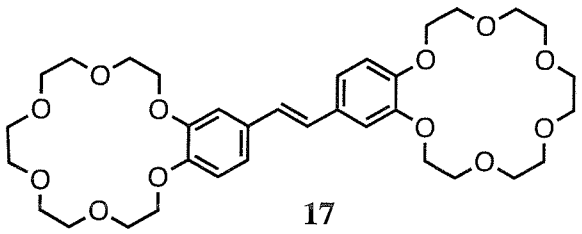

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