Last Name	
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Legi-No.	
Program of Study	

Written Exam
Supramolecular Chemistry
Winter 2016

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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.

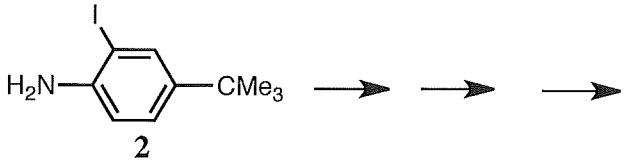
Points

Problem 1	
Problem 2	
Problem 3	
Problem 4	
Total	

Grades

Written	
Oral	
Final	

Problem 1 (15 points).



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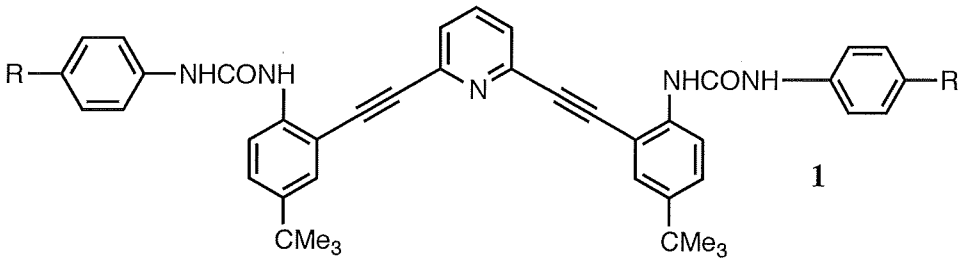


1

(a) Propose a synthesis of the receptor **1** (R = H) starting from iodoaniline **2**, providing detailed conditions for each reaction step (8 points).

(b) Compound **1** binds Cl^- anions from Bu_4NCl in $CHCl_3$ at room temperature with $K_a = 2100\ M^{-1}$ for the formed 1:1 complex. Suggest the geometry of the complex (3 points).

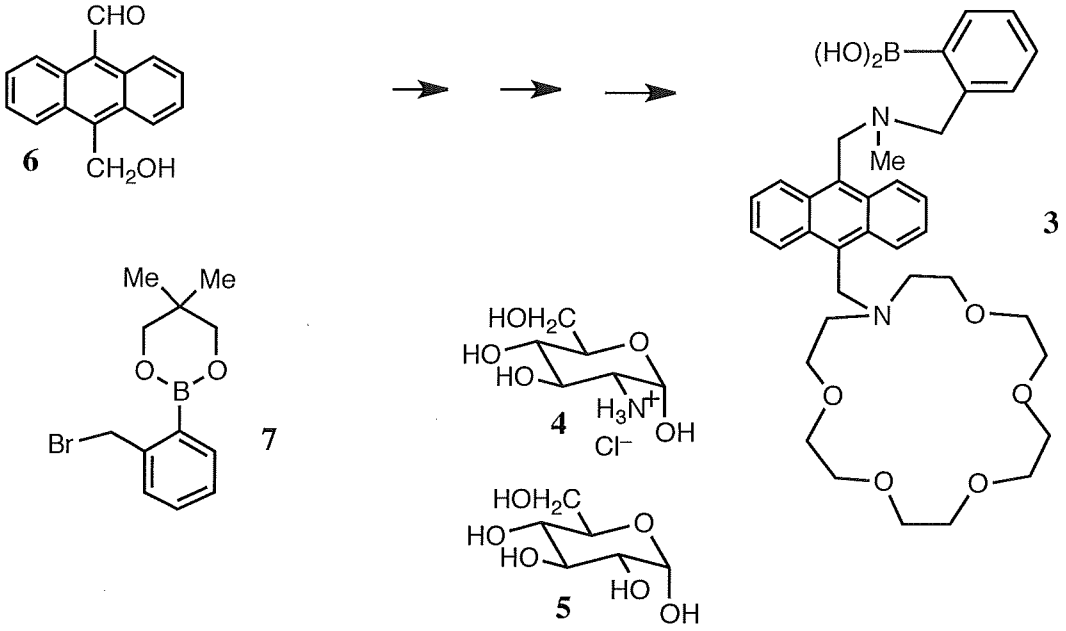
(c) Upon addition of $F_3C–COOH$, the binding affinity for Cl^- is strongly increased to $K_a = 42700\ M^{-1}$. Explain the increase and suggest the 1:1 binding mode, which was proven by X-ray analysis (3 points).

(d) Which substituents R ≠ H further enhance the binding affinity (1 point)?

(*Chem. Commun.* 2009, 2520-2522)

Problem 2 (20 points).

Compound **3** is a fluorescent sensor for D-glucosamine hydrochloride **4** but not for D-glucose **5** in EtOH/H_2O 1:2, pH 7.2.



(a) Suggest the synthesis of **3**, starting from **6**, using compound **7** in one of the final steps, providing reagents and conditions for each step (10 points).

(b) Upon binding of D-glucosamine·HCl (**4**), fluorescence becomes strongly increased as sensoric readout. Suggest in schematic drawings a 1:1 binding mode, indicating the major host-guest interactions (4 points).

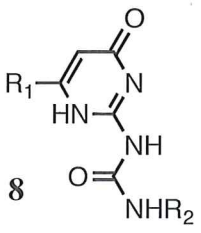
(c) Explain the mechanism for fluorescence recovery upon binding D-glucosamine·HCl (**4**) (8 points).

(d) Explain why D-glucose **5** does not give a fluorescent readout, despite also binding to **3** (2 points).

(*Chem. Commun.* **1997,** 1419-1420)

Problem 3 (15 points). Intermolecular interactions.

(a) The keto and enol tautomers **8** and **9** each form homo-dimers, one with $K_{dim} = 9 \times 10^5$ M^{-1} and the other with $K_{dim} = 6 \times 10^7$ M^{-1}. Suggest the structures of the homo-dimers and assign the K_{dim} to the two dimerization processes. Explain your reasoning (5 points). (*J. Am. Chem. Soc.* 1998, *120*, 6761)



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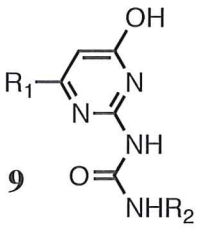
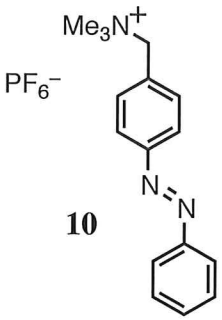
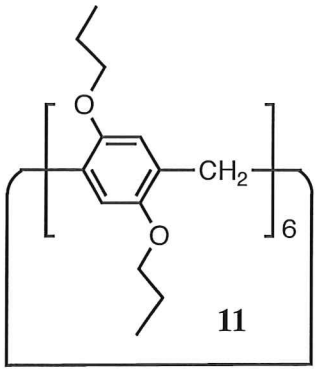


9

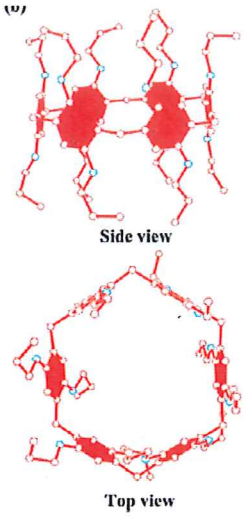
(b) Guest **10** binds to pillar[6]arene **11** (X-ray crystal structure of **11** shown in red), forming a 1:1 inclusion complex in $CDCl_3/CD_3CN$ ($K_a = 2 \times 10^3$ M^{-1}).



10



11

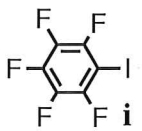


(b-1) Suggest the binding mode and propose complexation-induced shifts of ^{1}H NMR signals of **10** that support the binding mode (3 points).

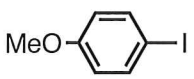
(b-2) Upon UV-irradiation, the guest changes its configuration and a different binding mode with $K_a = 2 \times 10^3$ M^{-1} is measured (upon Vis-irradiation, the initial complex is re-established; this switching can be repeated reversibly many times). Suggest the new guest configuration after UV-irradiation, the new binding geometry, and identify protons of the guest that now feature distinct shift changes in the ^{1}H NMR spectrum (3 points). (*J. Am. Chem. Soc.* 2012, *134*, 8711)

(c) Define halogen bonding and describe the geometric and electronic requirements for this interactions (2 points).

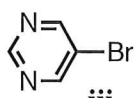
(d) Rank the three compounds **i-iii** in their ability to form halogen bonds (1 point):



i



ii

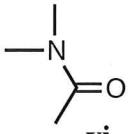


iii

(e) Rank the three compounds **iv-vi** in their ability to form halogen bonds (1 point):

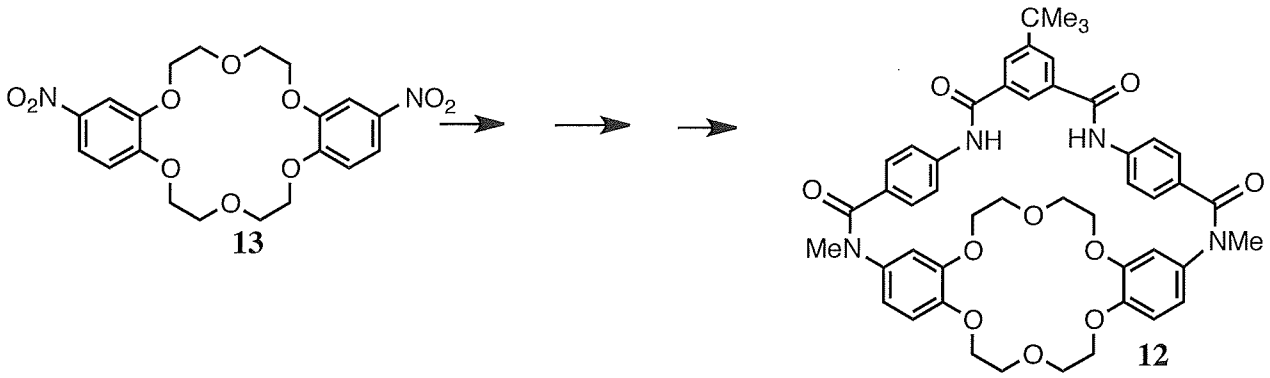
iv

v



vi

Problem 4 (10 points).



(a) Propose a synthesis of receptor **12** starting from **13** (8 points).

(b) Compound **12** is an ion-pair receptor. Propose the structure of the complex formed with ammonium chloride (2 points).

(*J. Am. Chem. Soc.* 2000, *122*, 6201).