

Last Name	
First Name	
Legi-No.	
Program of Study	

**Written Exam**  
**Supramolecular Chemistry**  
**Summer 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	
<b>Total</b>	

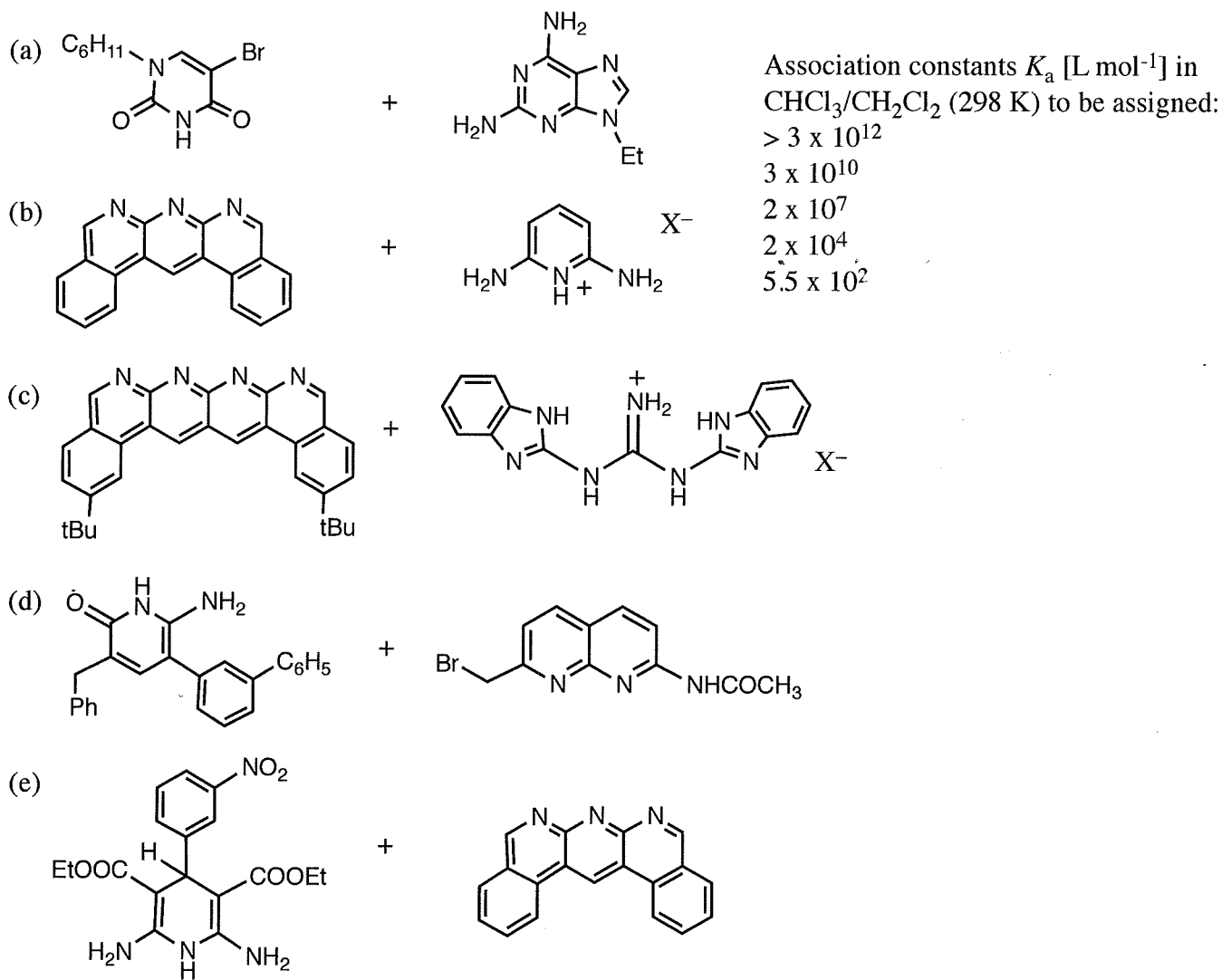
**Grades**

Written	
Oral	
<b>Final</b>	

**Problem 1** (15 points). Shown are five sets (a) to (e) of pairwise interacting molecules. The two molecules in a pair undergo multiple H-bonding 1:1 complexation in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ . Very large differences in complexation strength are observed.

(i) Suggest geometries for the five 1:1 complexes formed in these solvents, specifying all stabilizing intermolecular and intramolecular interactions.

(ii) Assign the association constants to the various complexes and explain the very large differences in the measured  $K_a$  values. The anion  $\text{X}^-$  is not involved. (*Nature Chemistry*, 2011, 3, 244.)



**Problem 2.** (20 points). Rotaxane **1** is prepared by pre-forming the quaternized ammonium thread (the axle). The axle subsequently templates the formation of the macrocycle (wheel) under formation of the interlocked structure.

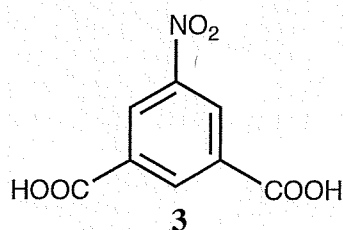
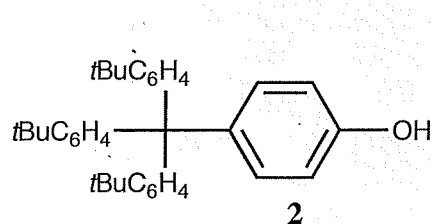
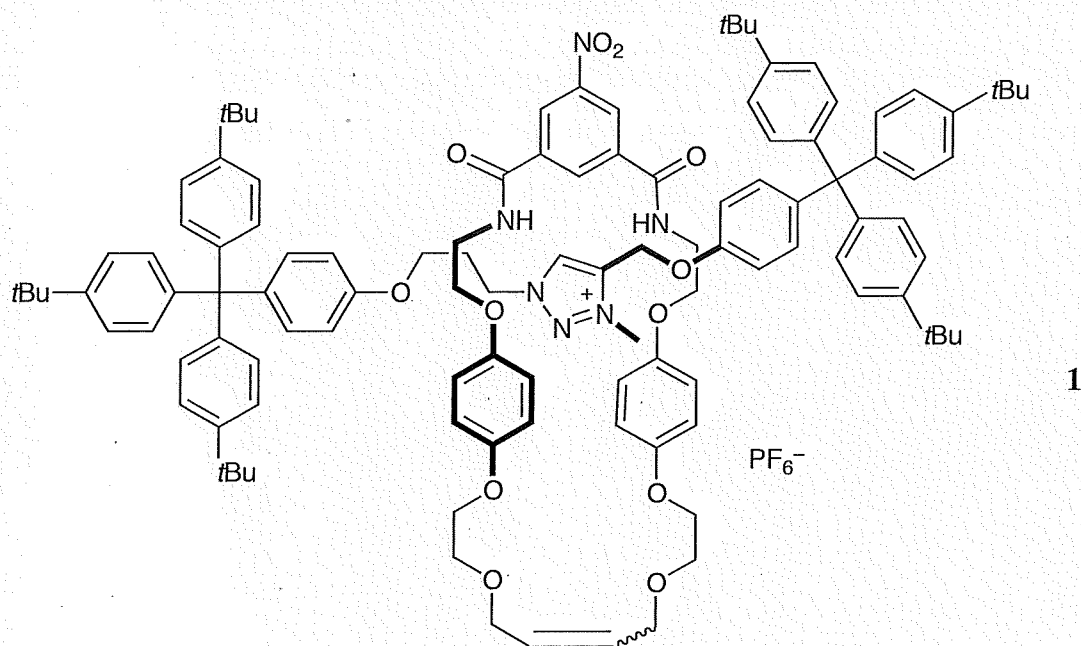
(i) Propose how you would prepare the thread starting from **2**. Give reagents and conditions (6 pts).

(ii) Propose how you would prepare the wheel, forming the rotaxane, starting from **3**. Give reagents and conditions. (6 pts).

(iii) Which templating mechanism is effective in the rotaxane-forming step? (4 pts).

(iv) This rotaxane shows anion recognition in  $(\text{CD}_3)_2\text{CO}$ , with a selectivity for  $\text{Cl}^-$  and  $\text{Br}^-$  ( $K_a \approx 1100 \text{ M}^{-1}$ ) over the larger anions  $\text{H}_2\text{PO}_4^-$  or  $\text{I}^-$  ( $K_a \approx 100\text{-}200 \text{ M}^{-1}$ ). Propose a binding mode for the halide ion recognition, which could explain the observed selectivity (4 pts).

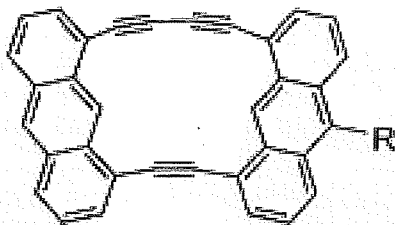
(*Angew. Chem. Int. Ed.* **2009**, *48*, 4781-4784.)



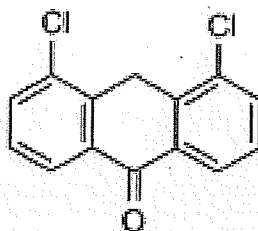
**Problem 3.** (15 points). The dianthracene macrocycle **4** with unsymmetrical acetylenic bridges and a long alkyl chain forms self-assembled monolayers on graphite, which were investigated by scanning tunneling microscopy (STM).

The multi-step synthesis of **4** starts from 4,5-dichloro-9-anthrone **5**. Propose a route to **4** starting from **5**. Propose reagents and conditions for each individual step.

(*Chem. Eur. J.* 2015 (DOI: 10.1002/chem.201405638).)



**4** R = (CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>



**5**

