Last Name	
First Name	
Legi-No.	
Program of Study	

Written Exam
Supramolecular Chemistry
Summer 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 a synthesis, detailing the reaction conditions, reagents and solvents, for the preparation of **1** starting from **2** (10 points).

(2) Compound **1** upon irradiation can be reversibly switched into an isomeric form and back to **1**, depending on the wavelength of the light used. Suggest the structure of this isomeric form (2 points).

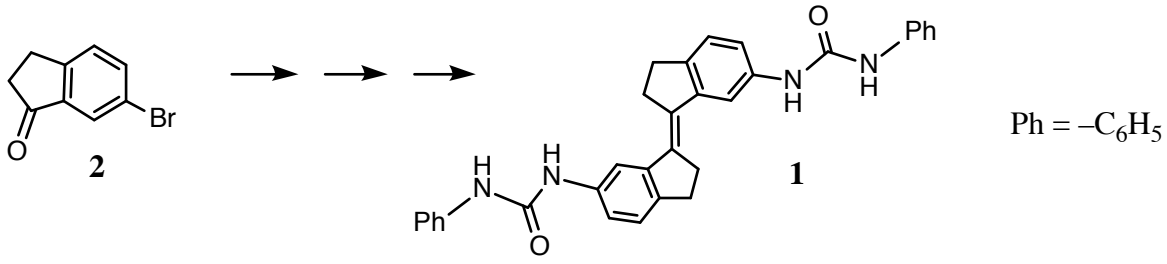
(3) One of the two forms binds anions such as dihydrogenphosphate, in Me_2SO/0.5% H_2O. Propose the binding geometry for $[(HO)_2PO_2]^-$ $[N\textit{n}Bu_4]^+$ (2 points).

(4) By which method would you monitor complexation in binding titrations and what would be the observable quantity, indicative of complexation (2 points)?

(5) While $[(HO)_2PO_2]^-$ $[N\textit{n}Bu_4]^+$ forms a 1:1 complex, $[Cl]^-$ $[N\textit{n}Bu_4]^+$ forms a 1:2 host-guest complex. By which analysis method would you determine the stoichiometry? (1 points).

(6) Show schematically the graphs that are indicative for the 1:1 and 1:2 complexation modes. (2 points).

(*Org. Lett.* DOI: 10.1021/acs.orglett.6b03423).

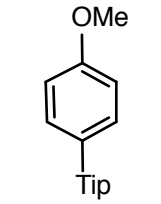


Problem 2 (20 points).
(1) Propose a multi-step synthesis, detailing the reaction conditions, reagents and solvents, for the preparation of **3** starting from **4** and **5** (14 points).

(2) The shape-persistent macrocycle complexes glucosides such as octyl-β-D-glucoside (Oct-β-Glc) very strongly in their interior cavity in 1,2-dichloroethane (K_a (298 K) for Oct-β-Glc: 4 x 10^6 M^{-1}). Since such high binding constants cannot be accurately determined by NMR titrations, other methods were applied to measure them. Make suggestions (2 points).

(3) One interesting binding motif, **6**, is found three times in the structure of **3**. Suggest in a drawing, how this motif interacts with sugar functional groups and makes a particularly important contribution to complexation and give your reasoning (4 points).

(*Chem. Eur. J.* **2016**, *22*, 18944).



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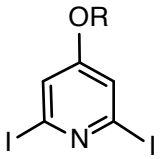

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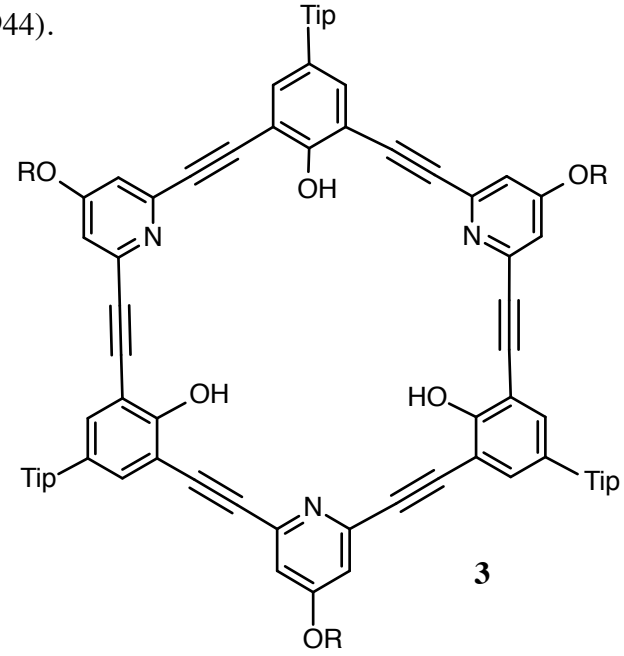

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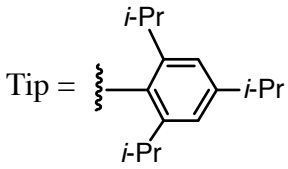
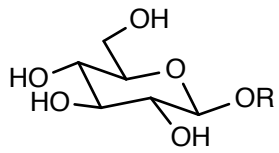
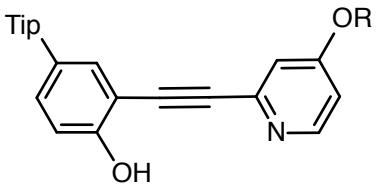


R = n-C_8H_{17}



Oct-β-Glc



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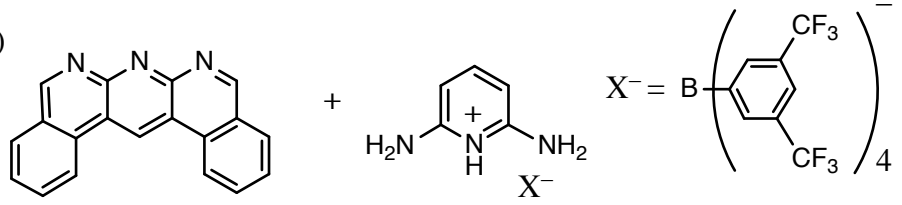
Problem 3 (10 points).
(1) Shown are four sets of pairwise interacting molecules a)–d). The two molecules shown in each set form a supramolecular 1:1 complex in CH_2Cl_2 or $CDCl_3$. Suggest geometries for these complexes, specifying all inter- and intramolecular interactions (8 points).

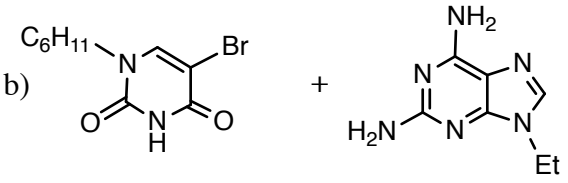
(2)Assign the association constants shown (in the box below) to the various complexes and explain the differences in the measured association constants (2 points).

Note that the anion X^- is not involved in the association. (*Nature Chem*. **2011**, *3*, 244)

a)

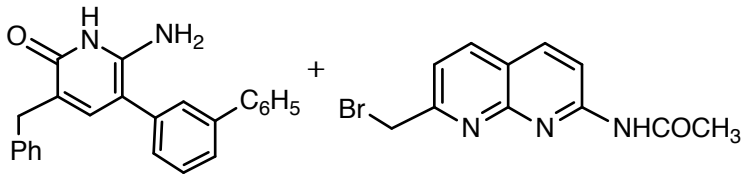


b)

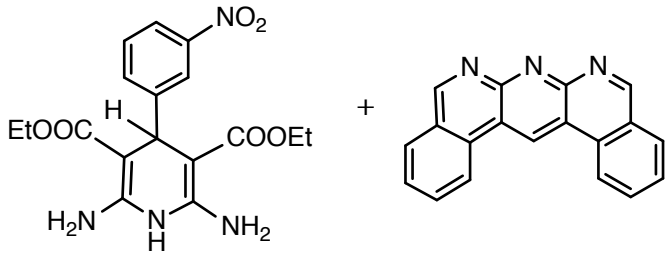


Association constants K_a [M^{-1}] (298 K) to be assigned:
2 x 10^7
3 x 10^{10}
5.5 x 10^2
2 x 10^4

c)



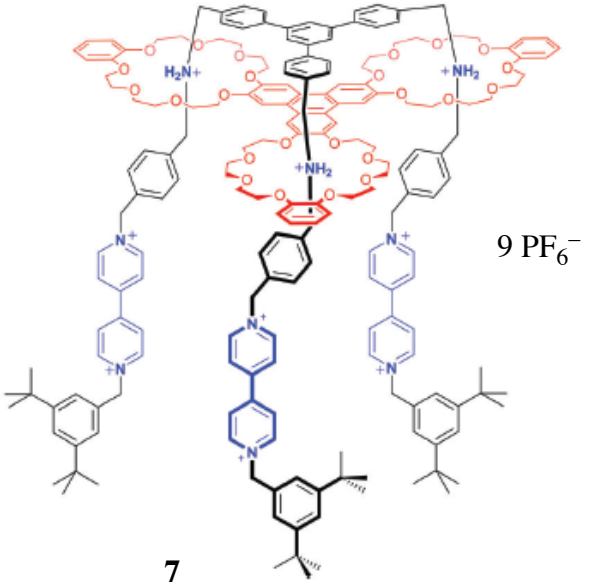
d)



Problem 4 (10 points).
(1) Shown is the artificial molecular machine **7**. Propose its synthesis starting from **8** and **9**. It is sufficient to show the synthesis only for one of the three interlocked subunits. Note that in this problem, the correct outline of the construction strategy is important, not the specific conditions of the individual transformations (6 points).

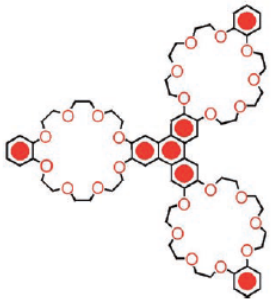
(2) Compound **7** can be switched to a greatly different geometry by a reversible switching mechanism. Propose by which mechanism this reversible geometric switching would be achieved and show schematically, which structural change takes place.

(*Science* **2004**, *303*, 1845)



9 PF_6^-

7



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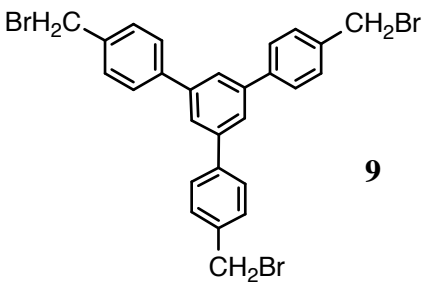

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