

Last Name	
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Legi-No.	
Program of Study	

Written Exam Supramolecular Chemistry Winter 2020

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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

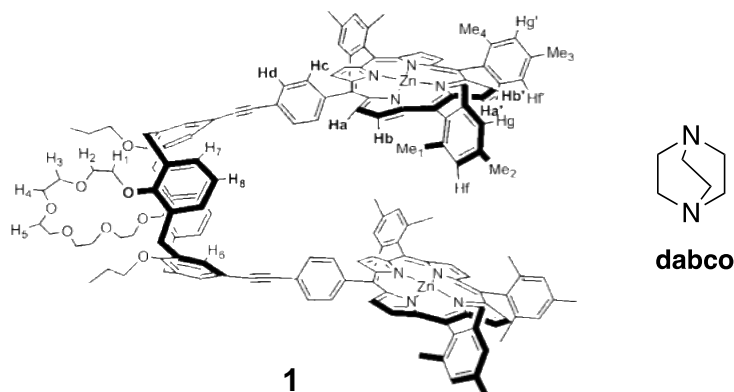
Problem 1	
Problem 2	
Problem 3	
Problem 4	
Total	

Grades

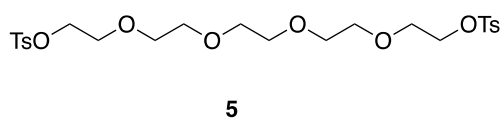
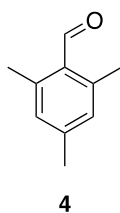
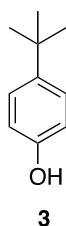
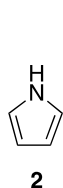
Written	
Oral	
Final	

Problem 1 (15 points): J. Weiss and co-workers, *Chem. Eur. J.* **2005**, *11*, 4199; *Org. Lett.* **2002**, *4*, 2129; J. Sessler *et. al.* *J. Am. Chem. Soc.* **2008**, *130*, 13162.

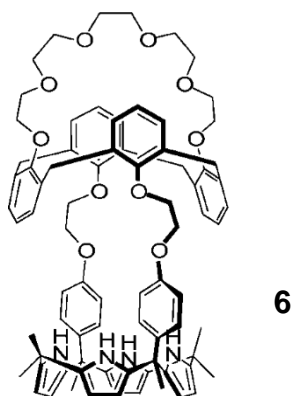
Compound **1** is a synthetic receptor for bidentate guests such as diazabicyclo[2,2,2]octane (dabco).



- (1) Please list the key structural features in this molecule and indicate which role they could play in the molecular recognition of guests. (3 points)
- (2) Propose the synthesis of compound **1** from commercially available compounds **2-5** below. Please note that these are not the only starting materials. Please describe the detailed conditions for each step. (7 points)

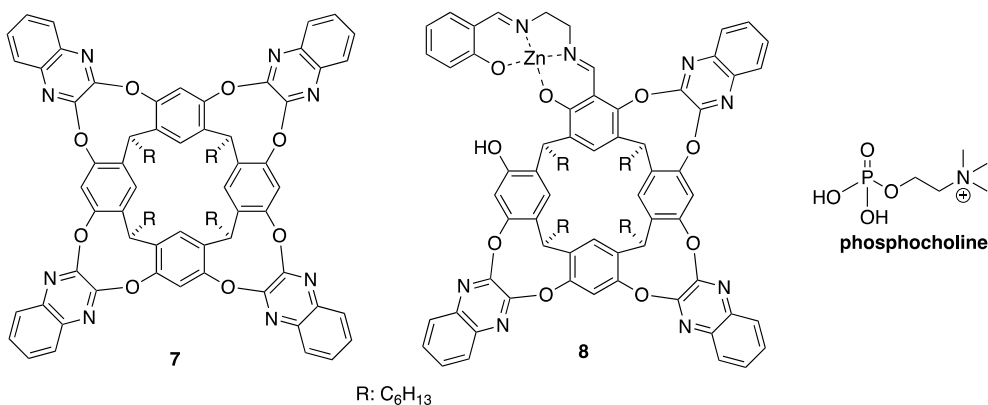


- (3) Please suggest two possible binding modes between receptor **1** and dabco. Please explain how you would differentiate between the suggested binding modes. (3 points)
- (4) Using similar starting materials, Sessler and co-workers synthesized compound **6** shown below. Please describe the key structural difference between this building block and compound **1**. Please suggest what type of guests are particularly well-suited to form host-guest complexes with **6**. (2 points)



Problem 2 (15 points): G. T. Sfrassetto and co-workers, *Chem. Commun.* **2020**, 56, 539.

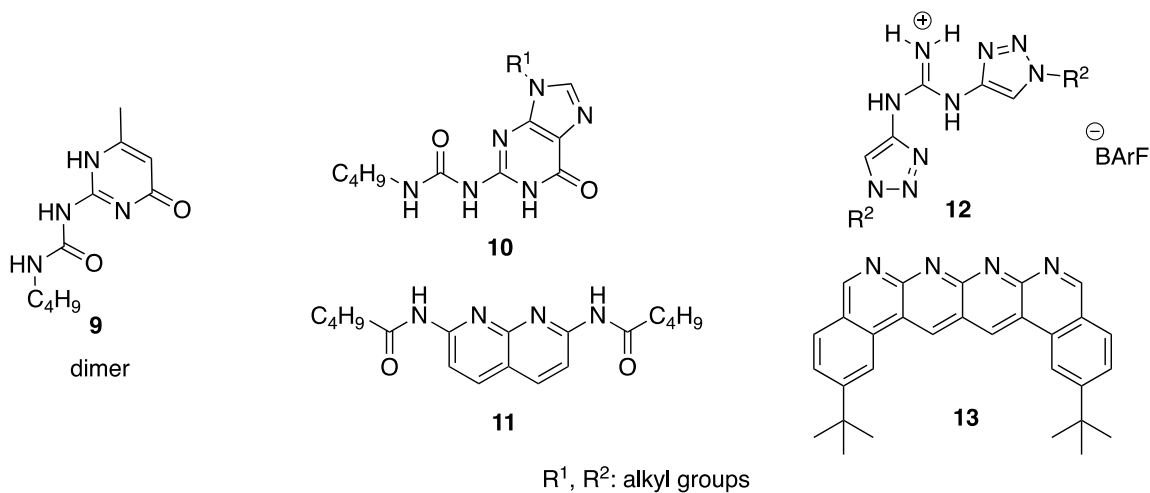
Compounds **7** and **8** below contain within their structures one of the most important building blocks in supramolecular chemistry.



- (1) How is this building block called? (1 point)
- (2) Please provide two important functions for which these types of compounds are typically utilised. How can you monitor such processes? (4 points)
- (3) Compound **8** is a variation of compound **7** and forms a supramolecular complex with phosphocholine. Please explain what is the complexation mode between phosphocholine and **8**. (3 points)
- (4) Please suggest the synthesis of **8** from commercially available compounds. Please describe the detailed reaction conditions for each step. (7 points)

Problem 3 (15 points): D. A. Leigh and co-workers, *J. Am. Chem. Soc.* **2013**, *135*, 9939.

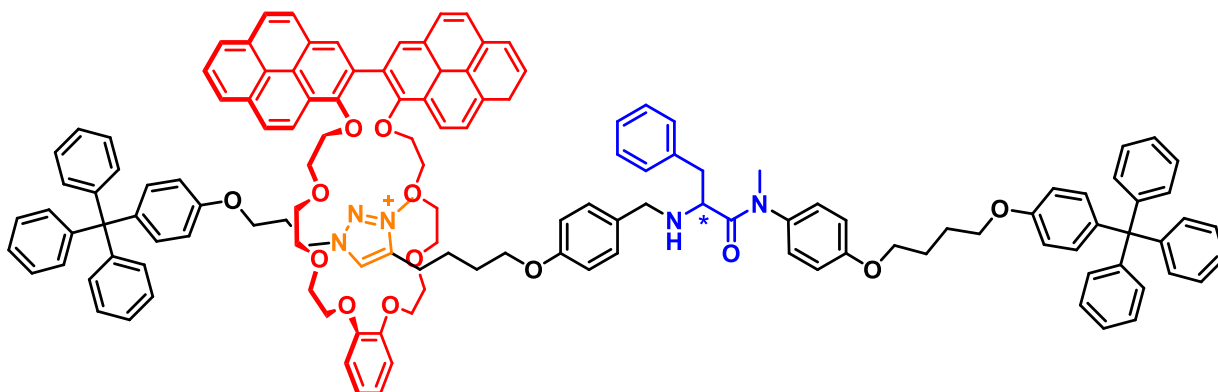
Compounds **9** – **13** below form supramolecular complexes through quadruple hydrogen-bond arrays.



(1) Please show the structures of hydrogen bond arrays in the following bimolecular complexes: **9** – **9** dimer, **10** – **11** complex, and **12** – **13** complex. (9 points)

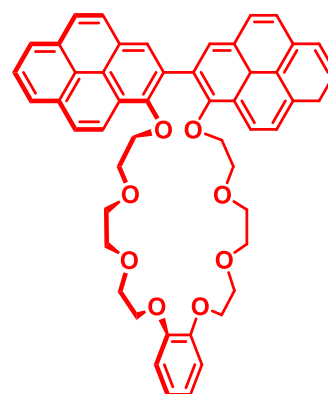
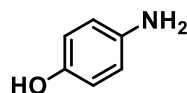
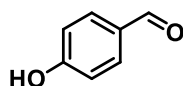
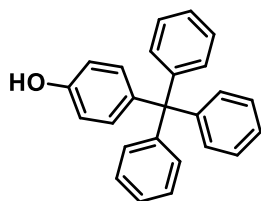
(2) The above complexes have association constants of 6.0×10^7 (in CH₂Cl₂), 3.0×10^8 (in CHCl₃) and 3.4×10^{12} (in CH₂Cl₂) M⁻¹, respectively. Please explain the reasons for the observed differences in K_a . (6 points)

Problem 4 (15 points): A. H. G. David, R. Casares, J. M. Cuerva, A. G. Campaña, V. Blanco *J. Am. Chem. Soc.* **2019**, *141*, 18064-18074



Above you see the structure of a rotaxane-based bistable molecular switch.

- (1) Propose conditions to achieve switching of the macrocycle between the two stations in the rotaxane. Explain why the switching occurs in the conditions you proposed. (3 points)
- (2) Provide two analytical techniques which you could use to monitor the switching process. (2 points)
- (3) Provide a synthetic route to access this rotaxane from the compounds below and other simple, small molecule building blocks. (6 points)



- (4) The configuration of the chiral center of the amino-acid plays an important role in inducing structural changes in a certain part of this interlocked molecule. Which part and what is the resulting structural alteration? This alteration also implies a specific physical phenomenon displayed by the above rotaxane. Please recognize this effect and name an analytical technique which you could use to demonstrate it. (4 points)