Last Name	
First Name	
Legi-No.	
Program of Study	

Written Exam
Supramolecular Chemistry
Summer 2019

Y. Yamakoshi, Bartosz M. Lewandowski

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	

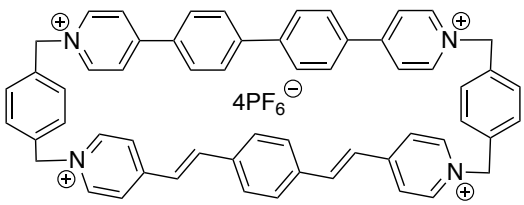
Grades

Written	
Oral	
Final	

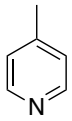
Problem 1 (15 points):
Stoddart, J. F. and co-workers, *J. Am. Chem. Soc.* **2019**, *141*, 1280 – 1289.

The constitution of compound **1** is based on the family of well-known "extended" viologen cyclophanes.

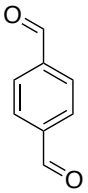
1. Propose a multistep synthesis of **1** starting from **2**, **3**, and **4**. Provide detailed conditions for each reaction step. (7 points)



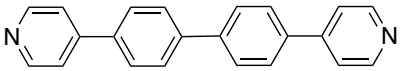
1



2



3



4

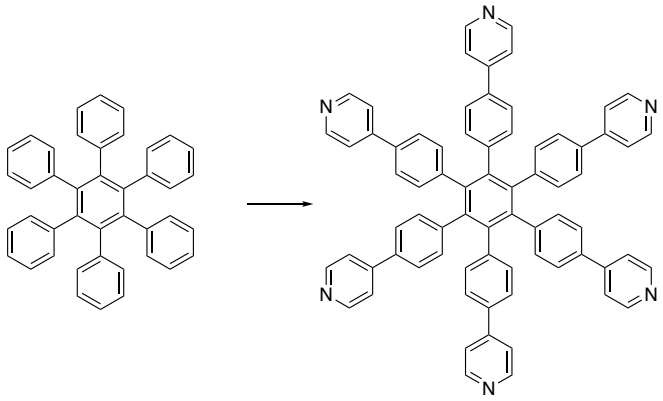
2. Irradiation of **1** leads to **5**, whereas the re-isomerization **5** → **1** occurs under thermal conditions. Suggest the structure of **5** and explain the isomerization process. Which spectroscopic methods would you use for monitoring of isomerization process and identify **1** and **5**? (4 points)

3. Compound **1** possesses high affinity for binding polycyclic aromatic hydrocarbon such as anthracene and anthraquinone. Suggest the structure of complex of **1** with anthracene. Explain the reasons of this binding and the photo- and thermal-controlled release and uptake of guest molecules. (4 points)

Problem 2 (17 points):

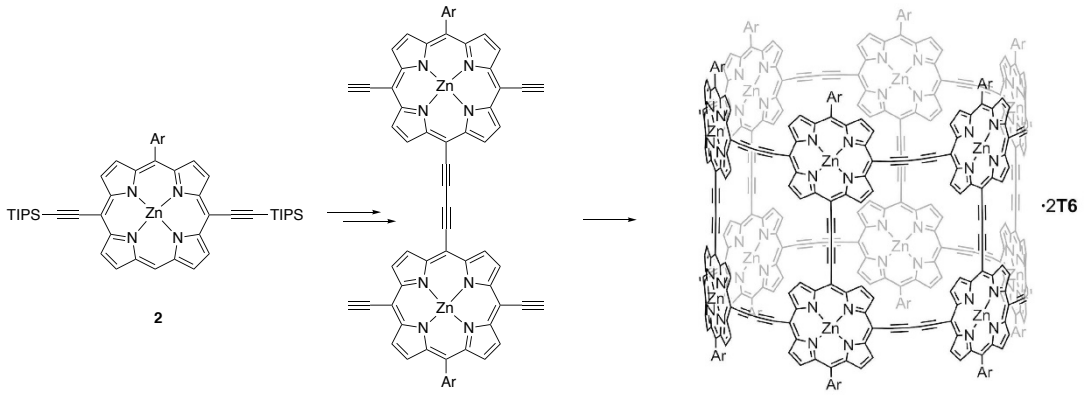
Anderson, H. and co-workers, *Helv. Chim. Acta* **2019**, *102,* e1800211; *J. Am. Chem. Soc.* **2011**, *133*, 17262-17273.

1. Propose a synthesis, detailing the reaction conditions, reagents and solvents, for the preparation of the **T6** from compound **1**. (5 points)



1 **T6**

2. Propose a multistep synthesis, detailing the reaction conditions, reagents and solvents, for the preparation of the porphyrin nanotube **4** starting from **2** clearly indicating the role of **T6**. (12 points)

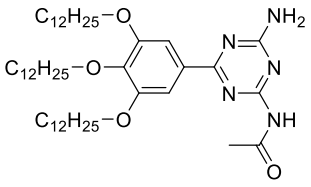


2 **3** **4**

Problem 3 (12 points):

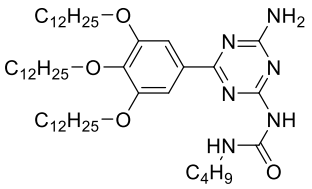
Meijer, E. W. and co-workers, *Angew. Chem. Int. Ed.* **1998**, 37, 75-78

Compounds **1-4** all form dimers in $CDCl_3$. The association constants for the four dimers in $CDCl_3$ at 298 K are given. Suggest the complex geometries, show all intra- and intermolecular interactions and explain the observed differences in stability. (12 points)



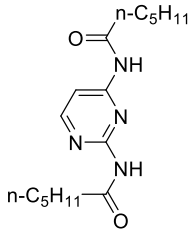
1

$K_{dim} = 530\ [M^{-1}]$



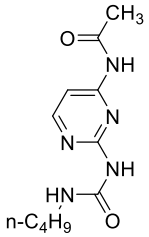
2

$K_{dim} = 2x10^4\ [M^{-1}]$



3

$K_{dim} = 170\ [M^{-1}]$



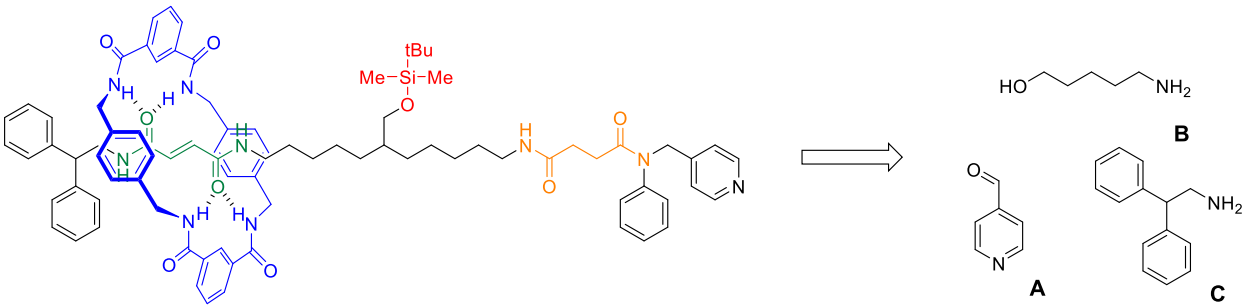
4

$K_{dim} = 2x10^5\ [M^{-1}]$

Problem 4 (16 points):

Leigh, D. A. and co-workers, *J. Am. Chem. Soc.* **2006**, *128*, 4058-4073.

Below you can see the structure of a rotaxane-based molecular switch:



1. Propose conditions required to achieve switching of the macrocycle between the fumaramide and succinamide binding sites in the rotaxane. Provide the underlying reasons for the switching to occur. (6 points)
2. Propose a synthesis of the rotaxane from starting materials **A**, **B**, **C** and other commercially available small molecule building blocks (indicate reagents and reaction conditions for each step). (7 points)
3. What is the main requirement for a synthetic supramolecular system to be considered as a molecular machine? Does the above-described molecule fulfill this requirement? If yes, which Brownian ratchet mechanism does it follow? (3 points)