Last Name	
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Legi-No.	
Program of Study	

Written Exam
Supramolecular Chemistry
Winter 2018

F. Diederich, Y. Yamakoshi

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: Supramolecular Chemistry (20 points)
(D. A. Leight, A, R, Thompson, *Tetrahedron* **2008**, *64*, 8411-8416)

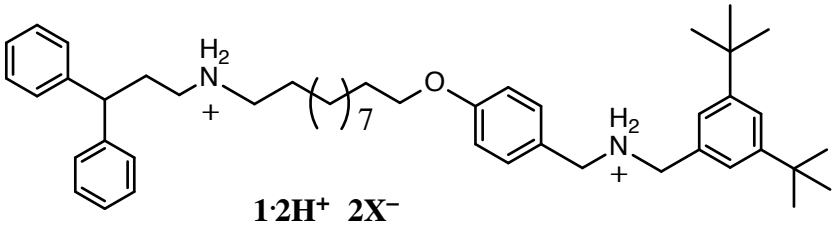
(a) Propose a synthesis of **1·2H$^+$ 2 X$^-$** starting from **2** and **3** (indicate reaction conditions; the counterions in the investigation were $2SBF_6^-$ obtained by ion exchange. They do not need to be further considered). (6 points)

(b) Also, propose a synthesis of **4** starting from catechol (**5**). (3 points)

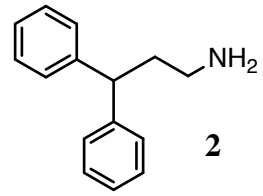
(c) When the backbone of **1·2H$^+$** is assembled in the presence of **4**, an interlocked structure **1·2H$^+$·4** forms. Propose this structure (can be drawn schematically). In this structure, **4** prefers two distinct positions. Suggest which ones (schematic structures acceptable). (6 points)

(d) Exchange of **4** between the two positions in **1·2H$^+$·4** is slow on the NMR time scale, so the ratio of the two isomers can be determined by ^{1}H NMR (CD_2Cl_2, 298 K). Suggest NMR signals that could be useful in this determination. (3 points)

(e) Which type of isomerism is present in the doubly protonated interlocked structure **1·2H$^+$·4**? (2 points)



1·2H$^+$ 2X$^-$



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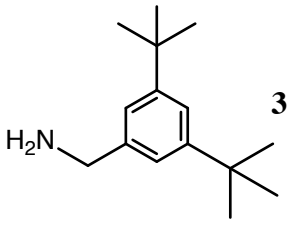

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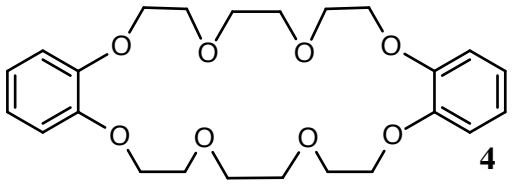

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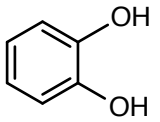

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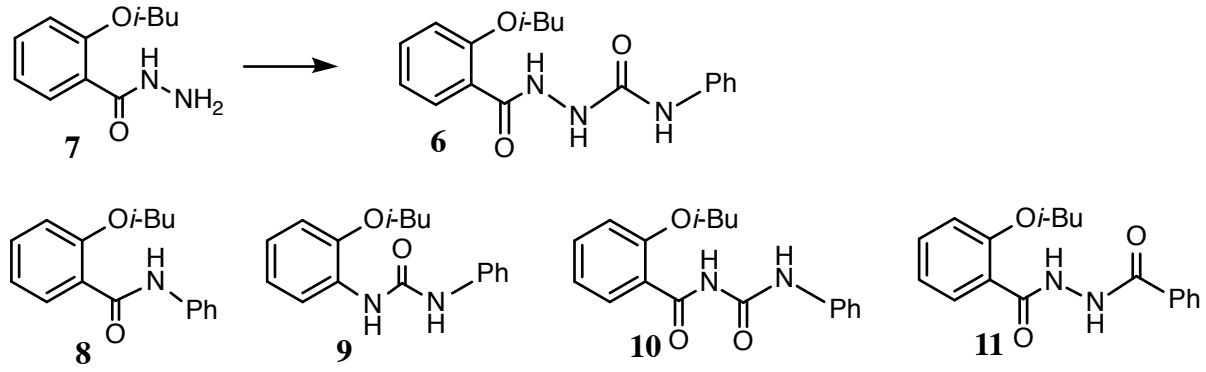
Problem 2: Hydrogen Bonding Arrays (15 points).
(Chu et al., *Org. Lett.* **2010**, *12*, 3156-3159)

(a) Propose a synthesis of **6,** starting from **7**, showing reagents and conditions. (2 points)

(b) Compound **6** forms a supramolecular dimer in $CDCl_3$. Propose its structure showing all interactions. Which characteristic signal changes are observed in the ^1H NMR spectrum ($CDCl_3$, 298 K) upon dimerization? (4 points)

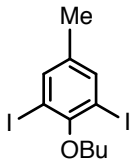
(c) How does the association strength change when the solvent is changed from $Me_2SO/CDCl_3$ 20:80 to $Me_2SO/CDCl_3$ 1:99? Suggest an explanation. (1 point)

(d) How does the strength of the dimerization by self-association change in the series **6**, **8**, **9**, **10**, **11** ? Explain your assignment by showing the most plausible dimers, with interactions, of each compound. (8 points)



Problem 3: Acetylenic Scaffolding (15 points)
(S. Höger and co-workers, *J. Am. Chem. Soc.* **2004**, *126*, 214-222)

Propose a multi-step synthesis of the shape-persistent phenylacetylenic macrocycle **12**, starting from **13** and **14** and using as further building blocks also **15** and **16**. Please give reaction conditions (reagents, solvent).
Abbreviations: TIPS = $(i\text{-Pr})_3Si$; TMS = Me_3Si; THP = 2-tetrahydropyranyl)



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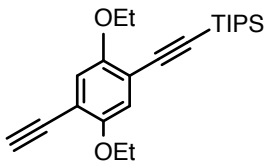

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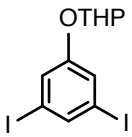

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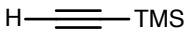

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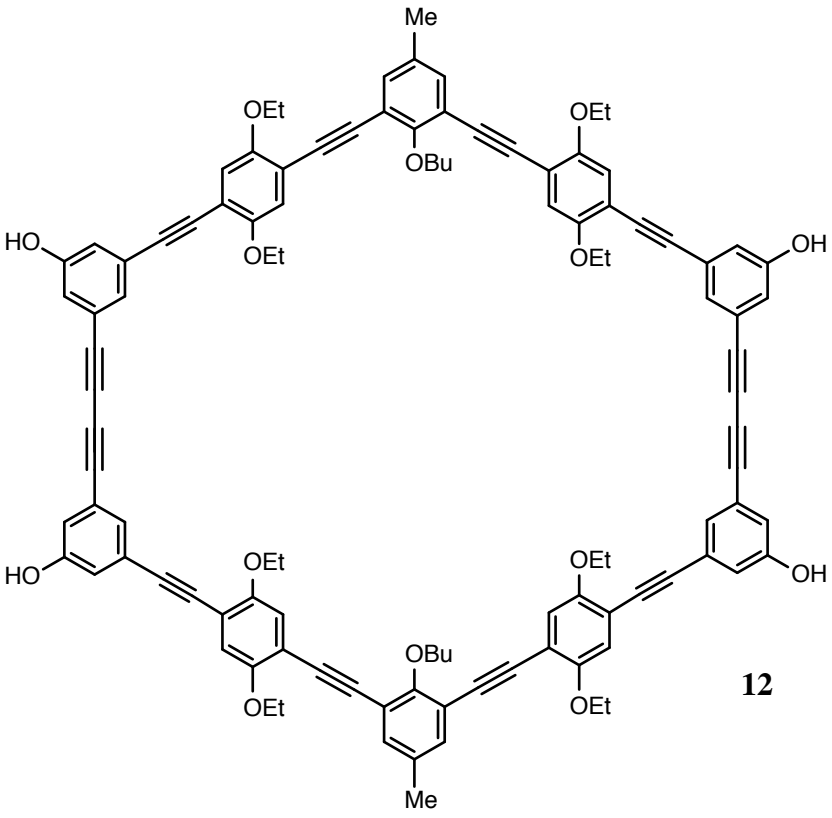

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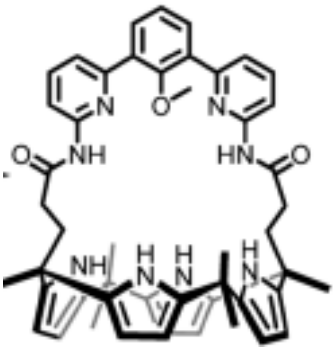
Problem 4: Molecular Recognition (10 points)
(J. L. Sessler and co-workers, *J. Am. Chem. Soc.* **2016**, *138*, 9779-9782 and *Angew. Chem. Int Ed.* **2017**, *56*, 13396-13400)

(a) Propose a multi-step synthesis of receptor **17** using the four components **18**-**21** (indicate reaction conditions). (8 points)

(b) Receptor **17** binds Cs_2CO_3 under formation of the complex **17**·$\mathbf{Cs_2CO_3}$ which was characterized by X-ray analysis. Suggest a possible binding mode for the two Cs^+ cations and the CO_3^{2-} dianion. (3 points)



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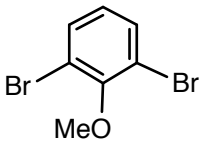

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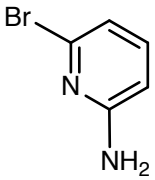

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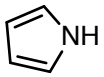

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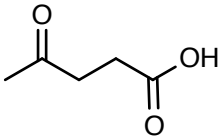

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