Supramolecular Chemistry

Tentamen 22-10-2014

Time: 3 hours

Name :
Student registration number :

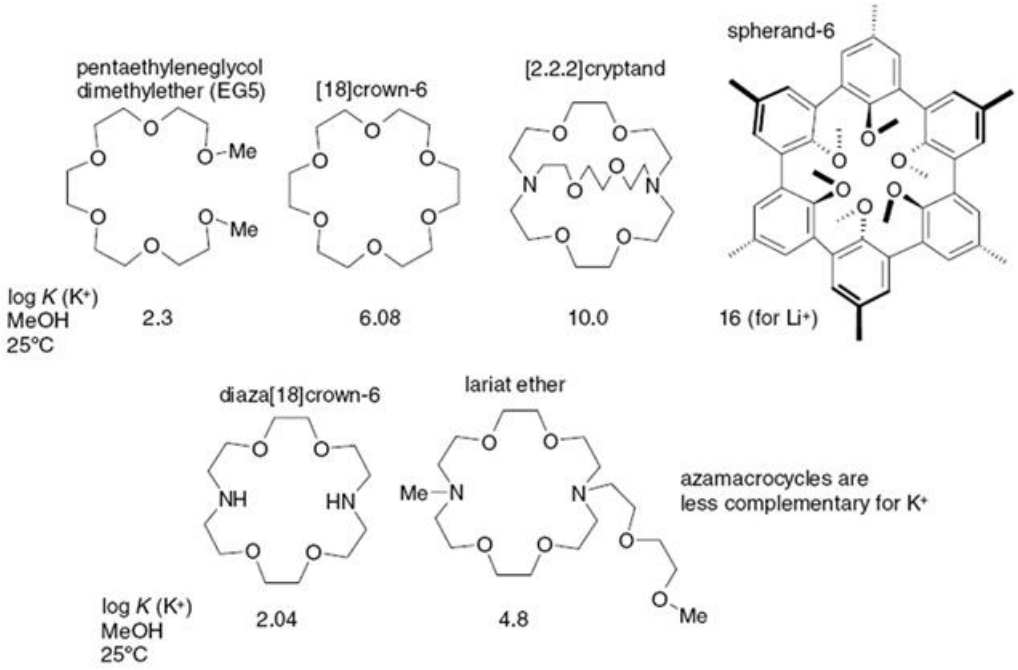
Always explain your answer

SCORE

Question	1	2	3	4	5	6	7	8	9		Totaal
Max score	15	10	10	15	10	10	10	10	10		100
Score											

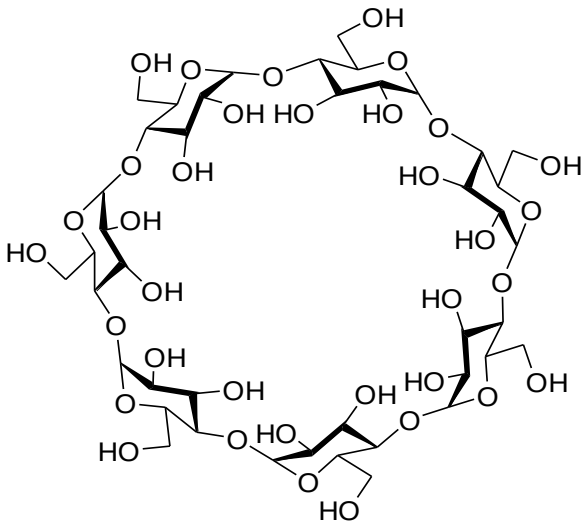
1a What is meant by negative cooperativity in a host-guest complex? Give a(n) (schematic) example

1b Explain the observed trend in the binding of potassium



2) What are the four commonly used approaches to synthesize DNA nanostructures? Compare and contrast the advantages and disadvantages of each method.

3a) Describe the driving forces for binding of toluene in beta-cyclodextrin in an aqueous solution. Explain the binding also in (qualitative) terms of entropy and enthalpy. What do you expect to be the sign of the free energy?



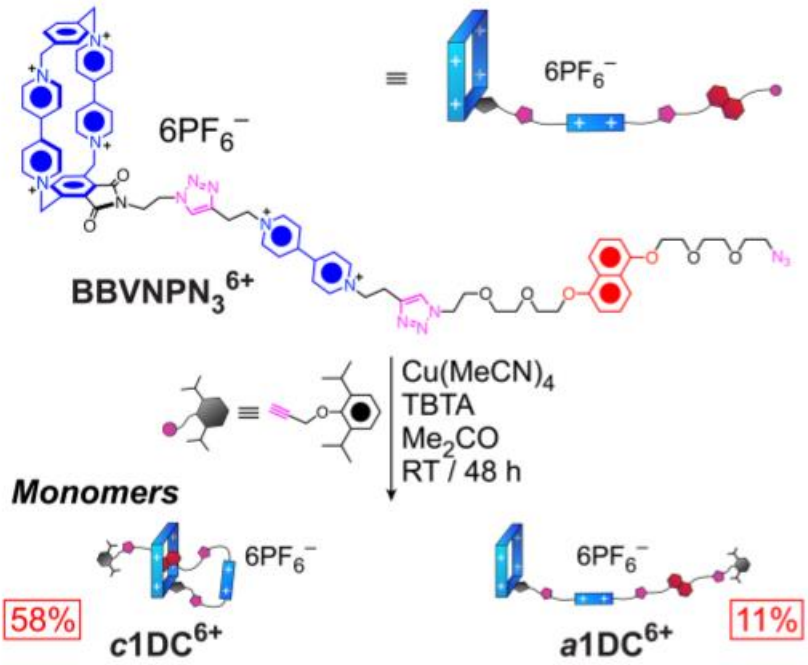
b) What is the meaning of the Hammett relation?

Hammett relation: $\log \frac{K_a}{K_0} = \sigma \times \rho$

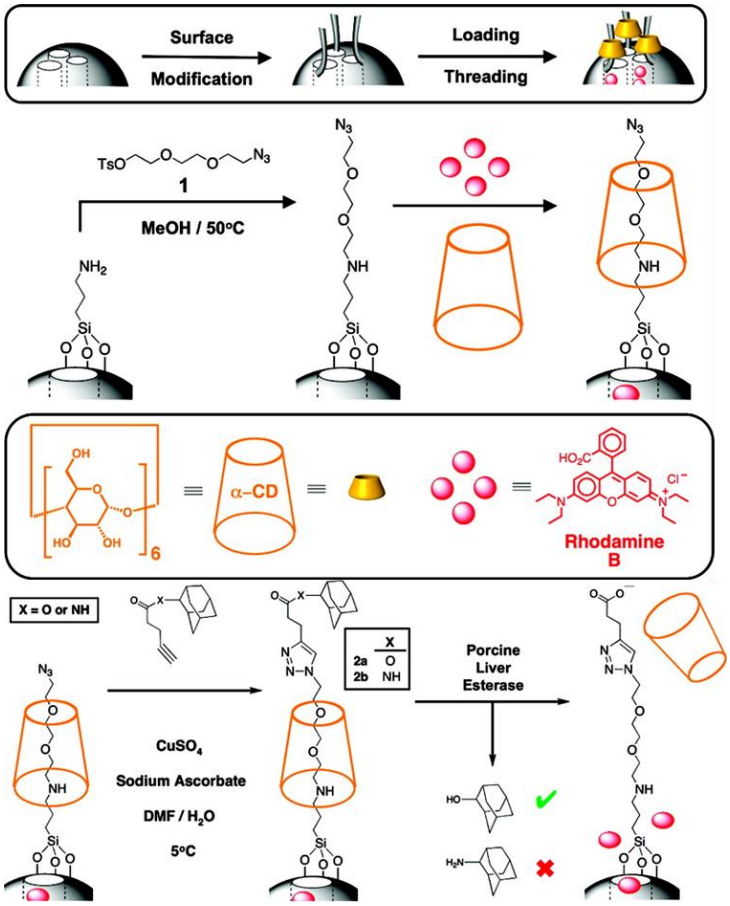
4) How would you synthesize of a nanosized map of South America using DNA? Explain both your design process and preparation method. What experimental technique(s) would you use to investigate its formation?

5a)

Explain the observed yields in the following reaction:

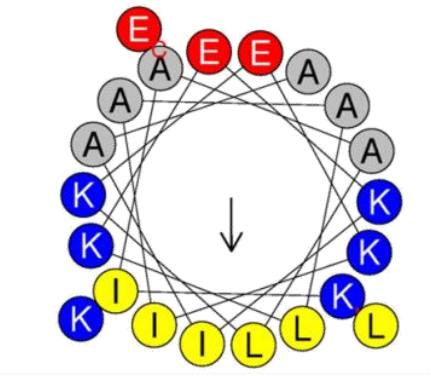


5b) Jeff Zink pioneered the field of enzyme-controlled snap tops on mesoporous silica nanoparticles (MSN). During the preparation of the MSN, all steps have to occur in one-pot to ensure the proper loading and capping of the pores. Why is this?

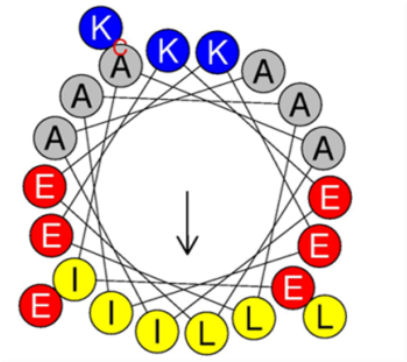

Surface
Modification
Loading
Threading
TsO
N3
1
MeOH / 50°C
NH2
NH
Si
α–CD
Rhodamine
B
X = O or NH
CuSO4
Sodium Ascorbate
DMF / H2O
5°C
X
2a O
2b NH
Porcine
Liver
Esterase

6) What are the key differences between cooperative and isodesmic supramolecular polymerizations? Imagine you have prepared a new supramolecular polymer, what experiment(s) can you propose to be able to distinguish between these two mechanistic possibilities?

7a) Peptide K (helical wheel shown) has been classified as an amphiphilic class A peptide which are known to interact with membranes in a so-called snorkeling mode; what are the attractive forces occurring in this mode?



7b) If you want to design a peptide-K mutant which does not interact with a membrane, yet still is able to adopt an helical conformation or a a coiled coil with peptide E (helical wheel shown), which modification(s) would you make in the amino acid sequence ?



8a)

A Chinese applicant recently showed me his MSc work on the self-assembly of peptides, see below. Why does it take so long to form fibers for peptide GAGAGAGS?

We synthesised two silk peptides (GAGAGAGS and GAGAGAGY) based on silk

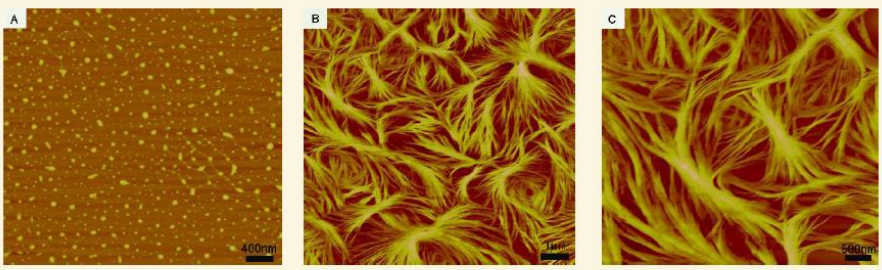


Fig. 1 Time-dependent AFM images for the structures of GAGAGAGS peptide aqueous solution with concentration of 0.2 mg/ml on fleshly cleaved mica surface. (A) After 1 day, (B) and (C) After 15 days.

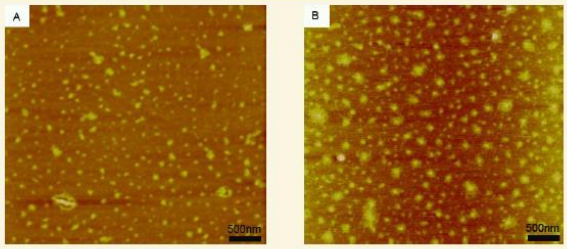


Fig. 2 Time-dependent AFM images for the structures of GAGAGAGY peptide aqueous solution with concentration 0.2 mg/ml on fleshly cleaved mica surface. (A) After 1 day, (B) After 15 days.

While GAGAGAY did not form fibers, it lipidated version did. Explain this difference in behavior. The addition of Calcium ions enhances the tendency to form fibers, give a possible explanantion

2. Silk peptide amphiphile (C_{12}-GAGAGAGY)

In previous work, we found silk fibroin-derived peptide amphiphile (C_{12}-GAGAGAGY) tended to assemble into parallel nanofiber bundles at pH=7.2-7.4, whose surface exposed COO^- from the tyrosine residue.[1]

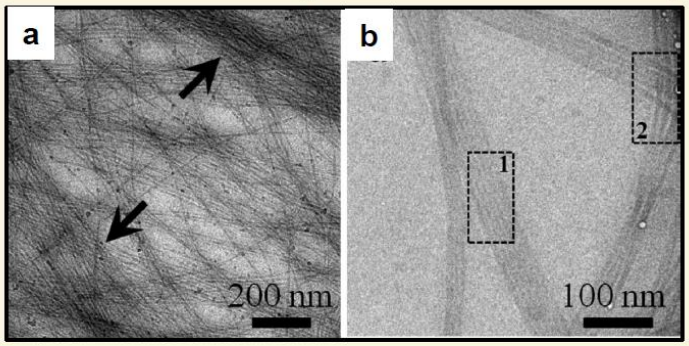


Fig. 1 Cryo-TEM images of C_{12}-GAGAGAGY assembly and aggregates at pH= 7.2-7.4. The concentration was 1 wt %.

9) From these two supramolecular motifs below, which would you anticipate to be more strongly associated and why? Based on your rationale, if you were to design a new motif, what would you propose as an important design consideration?