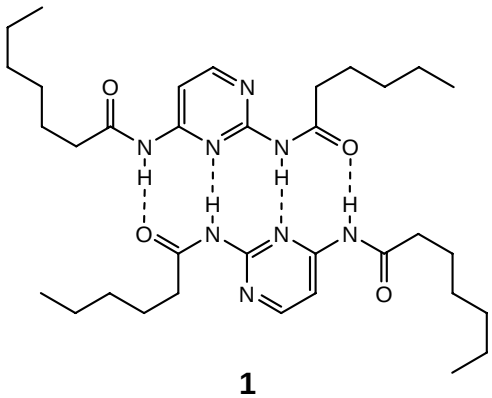
Chemistry 4011/8011 Wednesday, September 20

Workshop 3

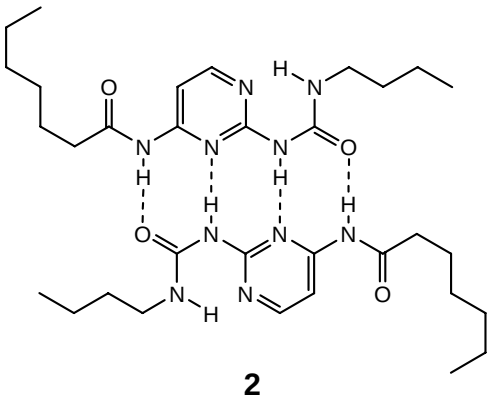
1. Sijbesma, Meijer and coworkers have investigated the use of hydrogen bonding motifs in the assembly of "supramolecular polymers"—polymer chains that are formed from the noncovalent rather than covalent association of monomer units.[1] The monomers are flexible chains terminated with complementary units that interact via multiple hydrogen bonds.

   a) When Sijbesma's group began this project, they needed to develop pairs of molecules that would interact very strongly with each other through hydrogen bonding only. Initially, they examined the self-complementary pair **1** below in $CHCl_3$, and found that dimerization was not as favored as they had hoped. They found, however, that pair **2** had a substantially higher dimerization constant K_{dim}, even though the number of H-bonds between the units was the same.



1

K_{dim} = 890 M^{-1}



2

K_{dim} = 2 x 10^5 M^{-1}

   What is the difference in ΔG_{dim} ($\Delta\Delta G_{dim}$, you might call it) between these two hydrogen-bonded pairs? Is it a hydrogen bond's worth (in $CHCl_3$), or more or less?

   b) What else, other than *inter*molecular hydrogen bonding, might be responsible for the energetic difference between these pairs?

   c) The next goal of this group was to construct polymers from these hydrogen bonded pairs.

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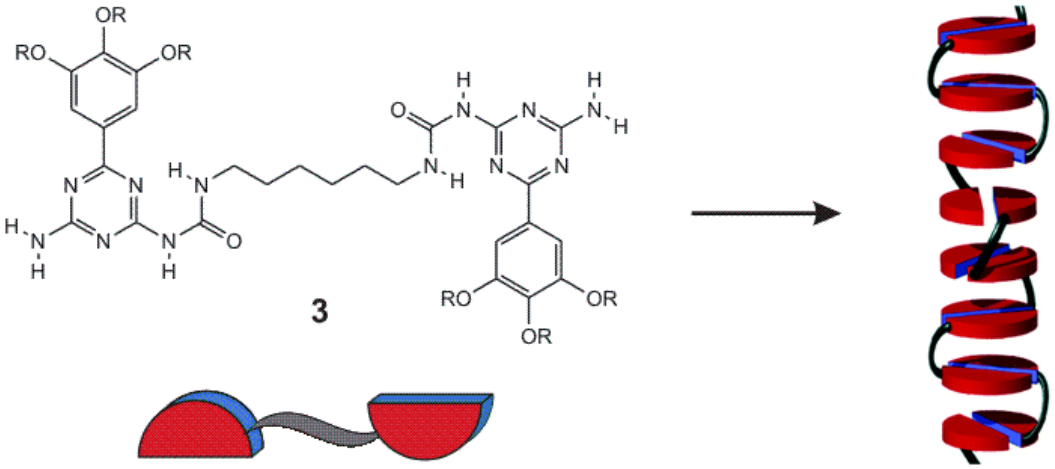
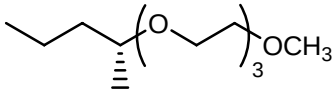
[1] Sijbesma, R. P.; Meijer, E. W. *Chem. Commun.* **2003**, 5-16. Sijbesma and Bert Meijer also started a company, SupraPolix BV, to commercialize the materials they developed. The company website (http://www.suprapolix.com) has a neat movie that shows stretching of one of their supramolecular elastomers.

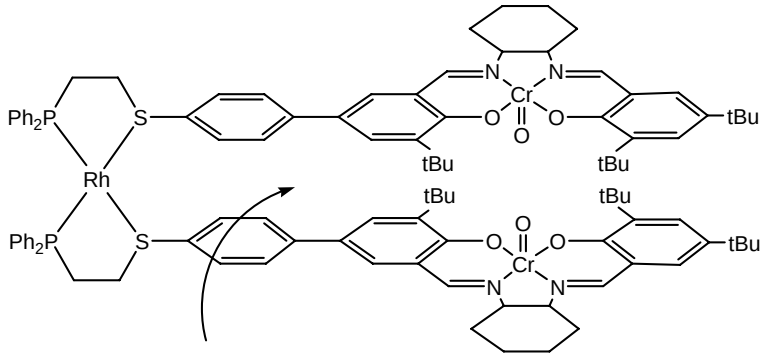


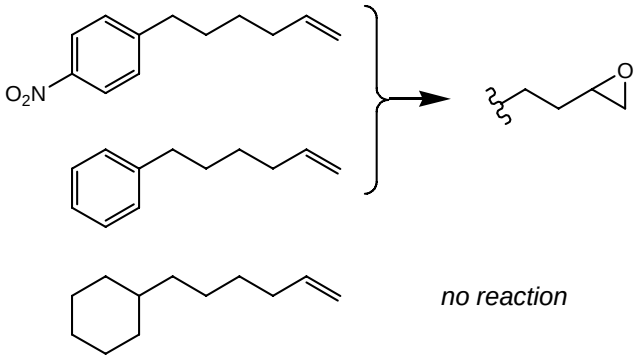
3a R = $C_{12}H_{25}$ *hydrophobic*

3b R =  *water-solubilizing*

Both **3a** and **3b** assembled into polymeric stacks in $CHCl_3$, but not in dimethylformamide (DMF). Interestingly, **3b** re-assembled into stacks again in H_2O. (**3a** was completely insoluble in H_2O.) What weak interactions are involved in the assembly and disassembly of **3a** and **3b**? Why does **3b** assemble, then disassemble, and then re-assemble as solvent is changed from $CHCl_3$ to DMF to H_2O?

2. Mirkin and coworkers have developed a number of organometallic reagents with adjacent binding pockets that are intended to target specific starting materials. For example, the chromium(V)-oxo species shown below converts alkenes to epoxides in chloroform, but only if the alkene is attached to an aromatic group.





In these reactions, the epoxide oxygen comes from the Cr=O group of the reagent, and selective binding of substrates to the binding pocket is responsible for substrate specificity.

a) What types of interactions are responsible for selective binding of substrates to the reagent binding pocket?

b) Putting your three-dimensional thinking cap on, how might the substrates be oriented/positioned in the pocket to maximize the interactions you described above?

c) Let's say you wanted to improve selectivity further, such that only the nitrophenyl-substituted substrate was epoxidized. What structural changes might you make to the oxidizing agent? (The nitro group makes the nitrophenyl ring *electron poor*.)