

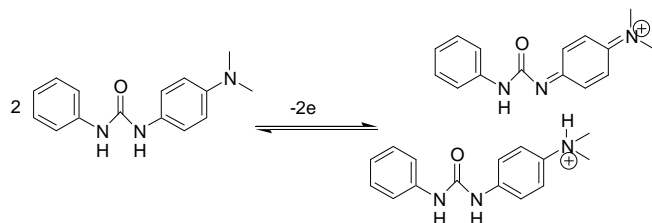
Preparation and Characterization of an Electroactive Ureidopyrimidinone Derivative, A Four Hydrogen Bond Array Containing a Dimethylaminophenylurea

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Electron transfer reactions can be used to perturb the strength of hydrogen bonding interactions between organic molecules. When a molecular redox center is integrated onto hydrogen bond arrays, this combination can become a powerful tool for controlling binding strength in supramolecular complexes. Whether used for sensing devices, molecular machines or self-assembly, the strength of a hydrogen bond can also be enhanced simply by arrangement of hydrogen donor interactions (D) versus hydrogen acceptor interactions (A). Indeed, because of secondary interactions, dimerization constants of the DDAA 4 H-Bond array typically exceed that of the DADA 4 H-Bond array.¹ By combining a DDAA 4 H-bond array such as Meijer's ureidopyrimidinone¹ with an electroactive center such as the dimethylaminophenylurea, the strength of hydrogen bonding becomes tunable.

Cyclic voltammetry investigation, in nonaqueous solvents, of dimethylaminophenylurea (UHH), a DD 2H-bond array, show that without a guest present, there is one reversible oxidation wave in methylene chloride of one electron height. CV Digital simulations as well as UV-vis spectroelectrochemistry indicate a proton transfer from the radical species to the reduced U(H)H, followed by another electron transfer due to potential inversion to give the quinoidal cation, Scheme 1. With the integration of the dimethylphenylamino redox center, this mechanism would certainly complicate the dimerization of Meijer's DDAA array.



Scheme 1. Proposed oxidation mechanism of UHH undergoing an overall one electron transfer due to proton transfer.

Due to the acidity of the urea NH that is part of the electroactive center, proton transfer could also occur as part of the electrochemistry associated with the DDAA dimer. We hypothesize that depending on the ratio of arrays substituted with an electroactive center versus those without, the DDAA sequence could change to a DDAD array. With all arrays containing an electroactive center the hydrogen bonding array would form an ADDA homodimer.

This presentation will cover cyclic voltammetry studies that includes concentration and scan rate dependence investigations on Meijer's DDAA dimer equipped with a dimethylphenylurea electroactive center. Digital CV simulations and spectroelectrochemistry will be used to

analyze experimental CV 's.

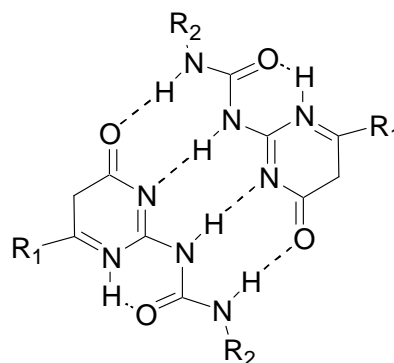


Figure 1. Meijer's ureidopyrimidinone (Upy) 4 H-bond system without redox functionality as a DDAA homodimer .

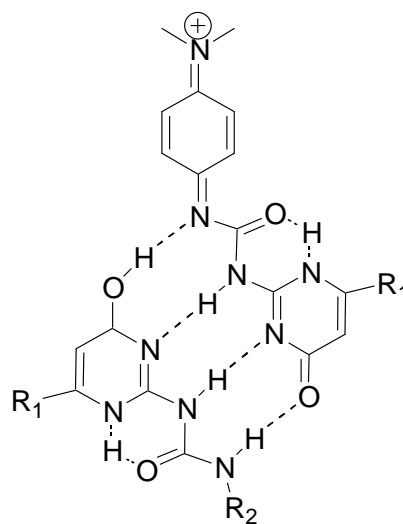


Figure 2. Structure of the proposed heterodimer, DDAD array, as a result of half the concentration with an electroactive center and the other half without.

References

1. Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W., Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding. *Journal of the American Chemical Society* **1998**, 120, (27), 6761-6769.

