Correlation of H-bond mediated self-assembly with experimental datasets

Dr Andrew Marsh (a.marsh@warwick.ac.uk)
Professor Mark Rodger (p.m.rodger@warwick.ac.uk)
Dr Alessandro Troisi. (a.troisi@warwick.ac.uk)

Department of Chemistry, University of Warwick

Aim: use a molecular-level simulation method to predict supramolecular structure from a construction set with well-defined hydrogen bonds for which experimental data is available.

Self-assembling systems depend upon the information encoded within molecular structures being expressed in a specified environment, thereby forming supramolecular architecture.[1] The resultant properties are however not readily predicted, in part because the methods used to simulate these systems must take account of a large number of interactions that can affect subsequent assembly steps, leading to hierarchies of order. This project aims to use either molecular dynamics methods (DL_POLY: **Rodger**) and/or an agent based approach (**Troisi**) in order to better understand and develop models for experimental solution data (NMR titration, diffusionally order spectroscopy (DOSY) measurements and isothermal titration calorimetry) generated at Warwick (**Marsh**). In particular we have a need to implement improved methods with which to correlate existing DOSY datasets with putative assembled structures.

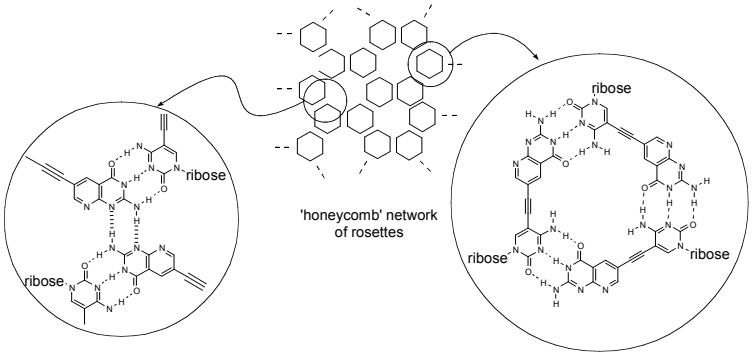

Figure 1 Self-assembly into 'rosettes' and higher-order honeycomb

The ultimate goal of this work is to provide a hierarchical assembly set comprising a series of construction units, for example those shown in Figure 1, enabling a more rational approach to be taken to understanding and making functional objects on 'the nanoscale'. We have prepared[2] a number of self-assembling systems that add unique functionality (redox activity, fluorescence, molecular recognition) to the natural oligonucleotide palette and are readily incorporated into self-assembling structures. Most recently we have focussed on rosette structures such as **Figure 1** and gathered datasets including diffusion measurements and association constants that would map well onto quantities that can be generated by simulation, allowing for their parameterisation. This project will allow the student to assess which method(s) to use for the simulations that facilitate best use of available data for the generation of plausible models. Striking examples of nanostructured objects prepared from oligonucleotides[3] demonstrate the versatility of molecules we associate with cellular function being used to create non-biological structures with technological potential. [4]

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2. A. Marsh, N. W. Alcock, W. Errington, and R. Sagar, *Tetrahedron* 2003, **59**, 5595; A. Likhitsup, R. J. Deeth, S. Otto, A. Marsh *Org. Biomol. Chem.* **2009**, DOI: 10.1039/B812969j.
3. P. W. K. Rothemund, *Nature*, 2006, **440**, 297.
4. G. P. Spada and G. Gottarelli, *Synlett*, 2004, 596.