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

Professor Steven Brown (s.p.brown@warwick.ac.uk)[b]
Dr Andrew Marsh (a.marsh@warwick.ac.uk)[a]
Professor Mark Rodger (p.m.rodger@warwick.ac.uk)[a,c]

Departments of Chemistry[a] and Physics[b] and Centre for Scientific Computing,[c]
University of Warwick

Aim: use a molecular-level simulation method to correlate supramolecular structure for a construction set which has available experimental solution (Diffusion Ordered Spectroscopy) and solid state (Double Quantum Coherence) NMR data.

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 molecular dynamics methods (DL_POLY, NAMD: **Rodger**) in order to better understand and develop models for experimental data (DOSY solution NMR measurements and isothermal titration calorimetry, solid state NMR) generated at Warwick (**Brown**, **Marsh**). In particular we have a need to implement improved methods with which to correlate existing DOSY datasets with putative assembled structures and better understand how these translate into the solid state.

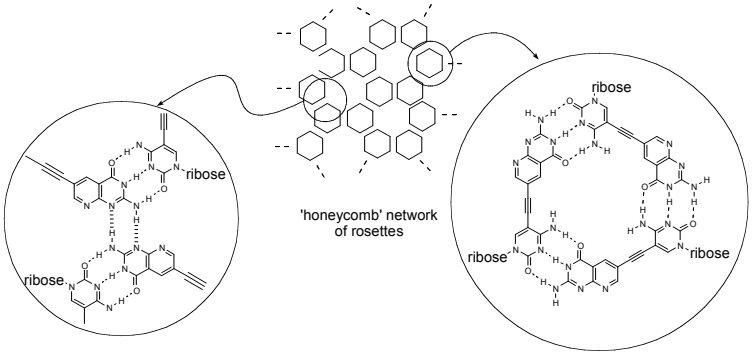

Figure 1 Self-assembly into 'rosettes' and higher-order honeycomb

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. Solid state NMR provides crucial insight to intermolecular positioning at high resolution and potentially allows inference of structure in the absence of X-ray data. This project will allow the student to assess which method(s) 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 these being used to create non-biological structures with technological potential. [4]

1. J. M. Lehn, *Science*, 2002, **295**, 2400.
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.