Functional Supramolecular Networks on Surfaces (FUNSURF)

1. Introduction and summary of project objectives:

Functional Supramolecular Networks on Surfaces (FUNSURF) is a multidisciplinary project which aims to use two-dimensional (2D) supramolecular self-assembly to produce functional molecular networks. These networks were studied using scanning probe microscopy (SPM) a technique which allows visualisation of structures with molecular resolution. The molecular building blocks used in this study were designed to have the ability to respond to external stimuli such as light irradiation or voltage pulses applied using an SPM tip. These responses include light induced structural changes (Fig. 1a) or controlled covalent reactions (Fig. 1b). The final objective was to implement an analysis method that combines the high spatial resolution of SPM with chemical sensitivity, tip-enhanced Raman spectroscopy (TERS).

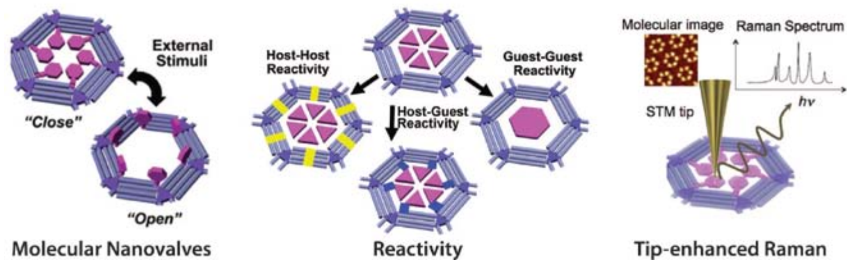

Figure 1: *The main objectives of the FUNSURF project.*

The self-assembly of simple molecules into complex structures is a ubiquitous process in nature. The self-assembly of molecules at surfaces into 2D molecular networks is promising areas of research. These structures can quickly and easily organise chemical groups across a surface with nanometre precision. Areas of particular interest are self-assembly at the liquid-solid interface and the formation of nanoporous networks. The molecular systems studied in FUNSURF are based on a previously studied system that is known to self-assemble at the liquid solid interface between graphite and organic solvents (see Fig. 2a), alkoxylated dehydrobenzo[12] annulenes (DBA). DBA molecules consist of a triangular annulene core decorated with six alkoxy chains. The DBA molecules interact with each other through the chain interdigitation (Fig. 2b). DBAs form two distinct network structures, a close packed *linear* phase and a hexagonal *porous* network (Fig. 2c). Which structure is formed depends on the length of the alkoxy chains, the solvent used and the concentration. DBA is an ideal system for functional networks as the alkoxy chains can be altered at the synthesis stage to include specific chemical groups.

2. Work carried out during the project:

Gaining a deeper understanding of which factors influence the self-assembly of DBA was a key step in producing functional networks. To this end STM experiments were carried out which investigated the effect of different substrate materials, different guest molecules, DBAs with different length alkoxy chains on a single molecule, chirality in DBA networks and the effect of temperature on self-assembly. In addition to these exploratory experiments two DBA derivatives were used which had specific target functionalities; azobenzene functionalised DBA to act as molecular nanovalves (Fig. 1a) and diacetylene functionalised DBAs to promote covalent stabilisation of networks (Fig. 1b). STM was again the main tool used to study these systems. Throughout the course of the project the implementation of TERS was pursued with the objective of using it to study these functional networks.

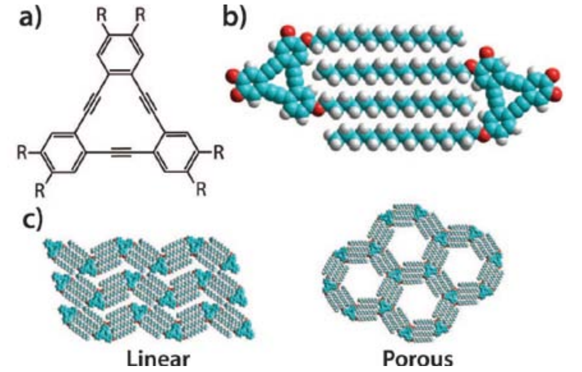

Figure 2: a) *Chemical structure of DBA.* **b)** *Interdigitation between DBAs.* **c)** *Linear and porous structures observed for the self-assembly of DBAs.*

3. Outline of the major results from the project:

Studies of the self-assembly of DBA derivatives highlighted the effect of; different substrate materials [Balandina et. al. *ACS Nano*, accepted 2012]; DBA molecules with asymmetric alkoxy chains [Adisoejoso et. al. *ACS Nano*, 2012, 6, pp.897-903]; and the chirality of porous DBA networks [Tahara et. al. *Nature Chem.*, 2011, 9, pp.714-719]. A key result from these experiments was the effect that temperature had on the self-assembly of DBAs. DBA systems which self-assembled into the linear phase were shown to undergo a reversible transition to the porous network with increasing temperature. A thermodynamic model was developed to model this transition which allowed parameters related to the enthalpy and entropy changes for individual molecules to be measured [Blunt et. al. *in preparation*].

DBA molecules functionalised with light responsive azo-benzene groups were investigated as potential molecular nanovalves. Azo-benzene groups were attached to alternate chains on a DBA core. Azo-benzene groups can undergo a *trans-to-cis* isomerisation on irradiation with UV light. This causes them to change structure from a planar, to a bent conformation. These molecules self-assemble into porous structures with six azo-benzene groups in each hexagonal nano-pore. The chemical nature of the azo-benzene groups were tuned to produce a network in which the six groups in each nano-pore interact via hydrogen bonds to form an adsorption location for a guest molecule, namely coronene. With the azo-benzene groups in the *trans* conformation the adsorption location can only accommodate a single coronene guest. Following irradiation of the network with UV light several examples of multiple coronene guests adsorbed within a nano-pore were observed. This demonstrated the *on-surface opening* of this *molecular nano-valve*. This is the first reported example of a functional molecular network which responds to external stimuli to perform a specific task [Tahara et. al. *in preparation*].

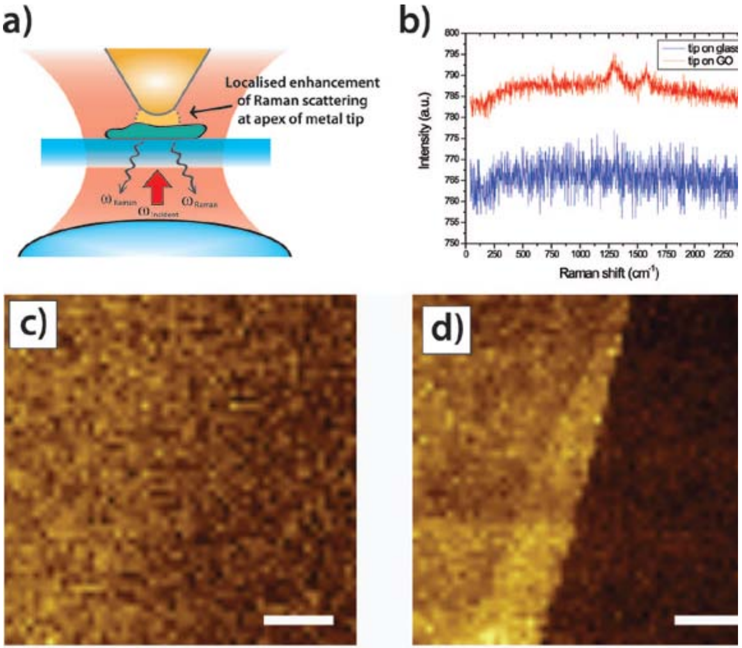

Figure 3: *Implementation of TERS.* ***a)*** *Schematic of setup for TERS measurements.* ***b)*** *Example spectra for a monolayer graphene oxide sheet with (red) and without (blue) TERS tip.* ***c)*** *and* ***d)*** *Comparison between standard confocal Raman map and TERS map for a monolayer flake of graphene oxide.*

The possibility of producing covalently stabilised networks was investigated using DBAs which contained diacetylene groups within the alkoxy chains. The diacetylene groups were positioned so that following self-assembly groups from different molecules were aligned next to each other. It was hoped that UV irradiation would cause these diacetylene groups to polymerise. This process proved to be impossible to realise as following UV irradiation network structures were no longer visible. Changes in the relative position of alkoxy chains following polymerisation may lead to excessive tension in the network causing it to de-stabilise and desorb from the surface.

The implementation of TERS has been a challenging aspect of the FUNSURF project. A combined optical spectroscopy and SPM system was designed and constructed during the project. In addition, large quantities of work investigated different modes of SPM for use with TERS and different methods to fabricate metallic tips suitable for TERS. The culmination of this work resulted in TERS measurements of test samples consisting of graphene oxide monolayers (Fig. 3). These results show the increased spatial resolution available to TERS in comparison to confocal Raman mapping. While it was not possible to use TERS to directly map the chemical make-up functional networks important steps were taken in the construction of the systems and in the development of fabrication protocols needed to produce effective TERS tips.

4. Final results and their potential impact:

FUNSURF has successfully investigated an array of 2D self-assembled systems using SPM as well as implementing an analysis technique which combines SPM and optical spectroscopy. These experiments have provided a deeper understanding of the self-assembly process and how we can hope control it to produce structures with desired morphologies and thus functionalities. The key results of the project being a detailed understanding of the effect of temperature on the self-assembly of 2D systems and the formation of a network which can act as externally activated molecular nano-valve.

2D supramolecular self-assembly represents an easy and highly controllable method for organising matter on the nano-scale, this is an important requirement for the future development of nanotechnology. The 2D self-assembly studies reported here will have an important impact on future research in this area. They will provide scientists with structural and environmental tools with which to control the structures formed during self-assembly, control which is vital if these structures are to form useful devices. In particular, the formation of a molecular nano-valve device has demonstrated one of the first examples of a nanoscale functional supramolecular machine. This will have implications for the future development of nano-functional surfaces for applications such as molecular electronics and targeted sensors for medical diagnosis. These are areas of areas of nanotechnology which could have profound social and economic implications.