**Programming the self-assembly of polymers, gels and other functional systems**

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**Introduction.** Our work is driven by understanding and learning from nature how its chemistry works so we synthesise new systems and materials that do complex tasks but outside the boundaries that life puts on those task. In our case, we are particularly interested in how molecules interact – which is Supramolecular Chemistry – and to understand how structure and property are linked together – which is the classical approach in Physical Organic Chemistry.

**Aims.** The aim of our work is therefore to develop novel ways to ***program*** the formation of complex self-assembled polymers, gels and other functional system. We aim to create bio-mimetic functional structures combining some of latest advances in supramolecular and physical organic chemistry with modern efficient synthetic methods for creating elaborative polymer and peptide structures.

**Results and Discussion.** To illustrate our ability to program functional systems, we will discuss here three recent examples for our work.

1. Using strong aromatic interaction for shape control in self-assembled polymer systems. This work hinges on the underutilised fact that aromatic-aromatic interactions are not only directional, they amongst the strongest forms of hydrophobic interactions known. This is allows us to create kinetically trapped non-spherical structures such as ellipsoidal micelles and vesicles1 as well as faceted (tessellated) self-assembled polymersomes.2 These systems are not only remarkable in terms of their structures but also in terms of their biodistributions and ability to penetrate tumour models in animals.

2. We report here on our progress in this field including the design and creation of a transient programmable supramolecular peptide-gel system. This new transient hydrogel system uses orthogonal methods for activation and deactivation, *i.e.*, the competition between the gelation of the oxidised cystine form of *N*,*N*’-dibenzyol-L-cystine (DBC) gelator and its reduction to the soluble cysteine by a chemical reducing agent; tri(2-carboxyethyl) phosphine (TCEP).3 Detailed kinetic analysis of the system allowed the authors to program the lifetime of these gels with good accuracy down to 15 min. Furthermore, we are able to generate multiple transient hydrogel cycles (sol↔gel oscillation), simply by periodically adding more of the DBC gelator to a TCEP “bath”. The general concept outlined here relies on kinetic control over self-assembly and is applicable to not only redox-active systems but other stimuli –responsive systems – which should aid the design of next-generation of spatiotemporal hydrogel peptide materials.

**References**

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