Supramolecular Polymers by Self-Assembling Cyclic Peptides as Linkers

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Supramolecular polymers are structures with reversible secondary interactions between repeating units. These non-covalent interactions give rise to novel and useful properties. For example, materials that can be stimuli-responsive and/or self-healing. The versatility and functionality (in particular, directed H-bonding) of peptides have been increasingly exploited in supramolecular chemistry.

Thoroughly explored in the 1990s by Ghadiri et al. and Lorenzi et al. cyclic peptides made from alternating L and D residues were found to self-assemble into cylindrical beta-sheets (i.e. tubes). Although there has been interest in the ability for these cyclic peptides to self-assemble into tubular structures as a template for complex nanostructures, by selectively sequencing N-methylated residues, cyclic peptides can be designed to restrict self-assembly to one face.

Using microwave assisted copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) ‘click’ chemistry we have synthesised cyclic peptide / polymer conjugates in which each polymer is conjugated to either one or two N-methylated cyclic peptide(s) at their chain-end(s) (Fig. 1a). The cyclic peptides with one face N-methylated are then used as linkers to form supramolecular polymers, either as dimers from the mono-conjugated polymer (Fig. 1b), or as multimers from the di-conjugated polymers.

Figure 1. (a) Synthesis of cyclic peptide / polymer mono-conjugate. (b) Self-assembled dimer (2 CH\textsubscript{3} groups and 4 CH\textsubscript{2}Phenyl groups have been omitted from each cyclic peptide for clarity).

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