

# Peptide-Based Supramolecular Constructs

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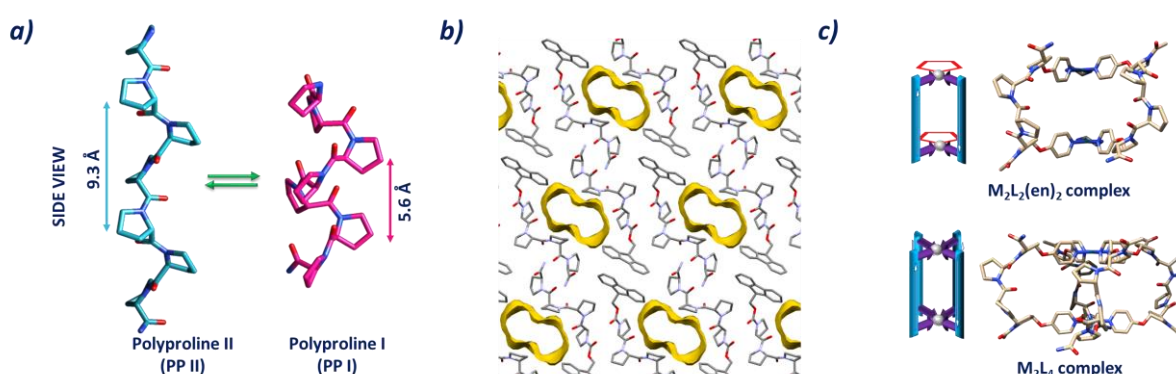
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The rational design of supramolecular constructs using bio-inspired building blocks is an ever-growing research field. In this talk, I will introduce a class of peptides, polyproline helices, that can be used as supramolecular building blocks to rationally design supramolecular responsive frameworks as well as discrete supramolecular nano-constructs.

Polyproline helices are secondary structures which appear in most proteins. They have a similar occurrence in nature to  $3(10)$  and  $\alpha$  helices. These helices present a high proportion of proline amino acids in their primary structure. This type of biopolymer can interconvert between two different secondary conformations as a function of the environment it is exposed to *i.e.* temperature, solvent polarity and pH (Figure 1a, polyproline II, left-handed helix with all trans conformations of the amide bonds and polyproline I, right-handed helix with all cis conformations of the amide bonds). Moreover, polyproline helices, have been shown to be extraordinarily tolerant to different functionalities [1,2].

We have recently demonstrated how this class of peptides, can self-assemble into a peptide framework capable of thermal activation, guest-induced dynamic porosity and enantioselective guest inclusion [3]. Based on these results, we were able to show how oligoproline tetramers can be specifically designed and functionalised, allowing predictable tuning of supramolecular interactions, to engineer the formation of supramolecular peptide frameworks with varying properties [4] (Figure 1b).

Finally, applying the knowledge acquired about these peptides, I will demonstrate how polyproline resilience to functionalities and periodicity, can be used to translate the design principles developed for classical metallo-organic systems to peptide-based ligands, in order to rationally synthesise the first examples of chiral, metallo-peptide cavities (Figure 1c).



**Figure 1** a) Polyproline helices I & II; b) Crystal structure of **PP<sub>4</sub>(-SPF)**, 50 % ellipsoids (Mercury), view along the *b* axis; c) Polyproline functionalised with two monodentate pyridine coordinating functional groups *CFG* to form two metallo-peptide complexes (homoleptic and heteroleptic).

## References

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