INCREASING THE STRENGTH OF SUPRAMOLECULAR HEALABLE MATERIALS THROUGH THE USE OF MULTIPLE COOPERATIVE p-p STACKING INTERACTIONS

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ABSTRACT

Supramolecular polymers are typically comprised of relatively low molecular weight oligomers which form higher ordered structures by the reversible assembly of designed receptor units. The resulting supramolecular structure behaves in a similar manner to a high molecular weight polymer in both the solution and the solid state. A key advantage of supramolecular polymers over covalent polymers is that the strength of the supramolecular interactions between the components can be reversibly changed by application of a suitable stimulus such as heat or light. On application of the stimulus, receptors within the supramolecular polymer disengage, and the previously tough material reverts to the properties of the low molecular weight components from which it was assembled. The adaptive nature of supramolecular materials has seen them become the basis for the fabrication of a range novel healable materials.[i]

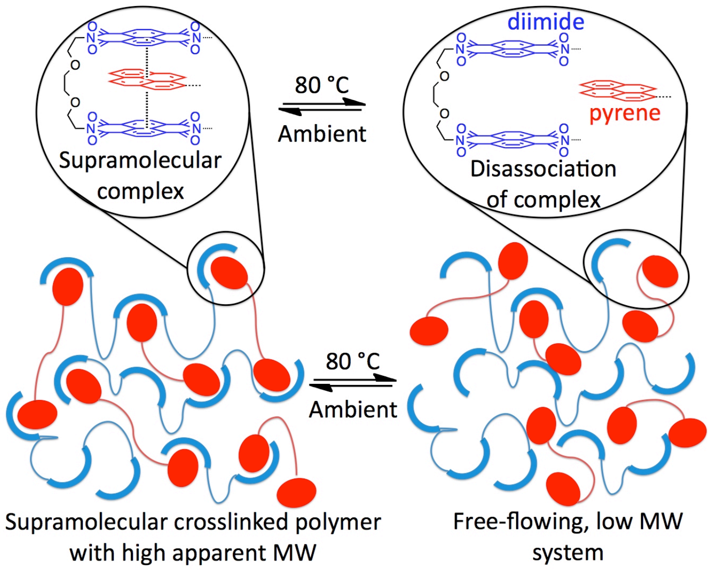
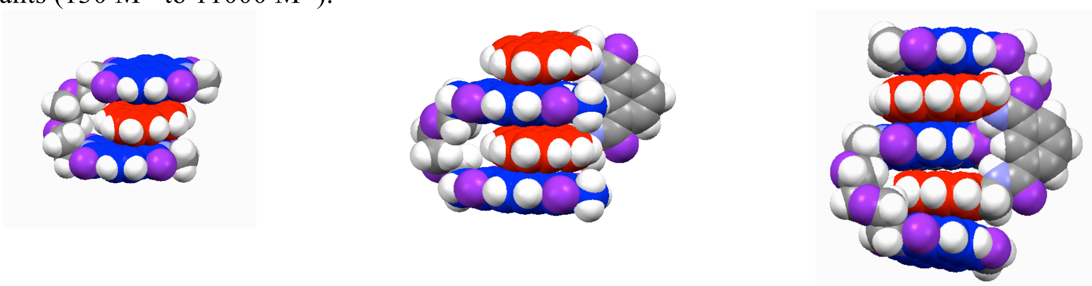


Figure 1 – Chemical structures of the supramolecular p- p-stacked complex at ambient temperature and 80 °C. Schematic of the incorporation of this complex into a supramolecular polymer: crosslinks are formed by the p- p-stacked complex and are broken during fracture or by increasing the temperature, but re-form at ambient temperature.

We will present the molecular level design, synthesis and evaluation of supramolecular materials made from two distinct oligomers that show healing characteristics when blended.[ii,iii] These materials harness the well-known interactions between p-electron deficient diimide species and p-electron rich pyrenyl residues. [iv] One of the components within the blend is a simple oligo(amide) which contains pyrenyl endgroups (red, Figure 1). The second component contains multiple diimide residues within the oligomer backbone where the diimides are separated by a carefully designed diethyleneoxy spacing unit (blue, Figure 1). The spacing unit allows the diimide residue to attain a chain-folded conformation – ideally positioning them to bind pyrenyl endgroups through the formation of a highly ordered p-stacked complex. The combination of multiple, weak non-covalent crosslinks between the two components of the blend produces a self-supporting material which has improved mechanical properties than either of the two starting oligomers.

Our novel supramolecular materials are found to be extremely thermally sensitive, exhibiting a large variation in viscosity over relatively narrow yet easily accessable temperature ranges (20 to 80 ºC). This temperature sensitivity is attributed to the partial disengagement of the supramolecular crosslinks above ambient temperature permitting the material to behave like the low molecular weight oligomers from which it is composed. Healing tests were carried out by cutting the material, overlapping the edges and heating briefly (50 ºC for 5 minutes). The material was found to regain over 95% of the tensile modulus of the pristine, undamaged material within this time. In addition, the material could undergo up to 5 break and heal cycles without exhibiting any loss of healing efficiency.

Through the rational optimisation of receptor design it is possible to increase the number of p - p stacking interactions between the components from 2 to 4 complementary interactions (Figure 2, complexes **1** to **3**, respectively) with the resulting complexes having progressively higher binding constants (130 M^{-1} to 11000 M^{-1}).



130 M^{-1} **1** | 3500 M^{-1} **2** | 11000 M^{-1} **3**

Figure 2 – Energy minimized space filling models and binding constants [iv] of complexes between pyrene (red) and diimide (blue) containing molecules with increasing numbers of complementary face-to-face p - p stacking interactions.

Synthesising new oligomers that can form stronger complexes in the solid state increases the cohesive energy between the components in the supramolecular polymer blend.[v] The resulting materials are correspondingly tougher, allowing the rational design of healable polymeric materials with targeted mechanical properties. The talk will highlight how molecular level design can lead to *de novo* synthesis of healable materials with targeted properties.

REFERENCES

[i] S. Burattini, B. W. Greenland, D. Chappell, H. M. Colquhoun and W. Hayes, Healing Polymeric Materials: A Tutorial Review. *Chem. Soc. Rev.*, **39**, 2010, pp. 1973-1985.

[ii] S. Burattini, H. M. Colquhoun, B. W. Greenland and W. Hayes, A Novel Self-Healing Polymer System. *Faraday Disc*. **143,** 2009, pp. 251-264.

[iii] S. Burattini, H. M. Colquhoun, J. D. Fox, D. Freidmann, B. W. Greenland, P. J. F. Harris, W. Hayes, M. E. Mackay and S. J. Rowan, A Self-Repairing, Supramolecular Polymeric System: Healablity as a Consequence of Donor-Acceptor *p- p* -Stacking Interactions. *Chem. Commun.* 2009, pp. 6717-6719.

[iv] B. W. Greenland, S. Burattini, W. Hayes, and H. M. Colquhoun, Design, Synthesis and Computational Modeling of Aromatic Tweezer-Molecules as Models for Chain-Folding Polymer Blend. *Tetrahedron*, **64**, 2008, pp. 8346-8354.

[v] S. Burattini, B. W. Greenland, W. Hayes, M. E. Mackay, S. J. Rowan and H. M. Colquhoun. A Supramolecular Polymer Based on Tweezer-Type π-π-Stacking Interactions: Molecular Design for Healability and Enhanced Toughness. *Chem. Mater.* **23**, 2011, pp. 6-8.