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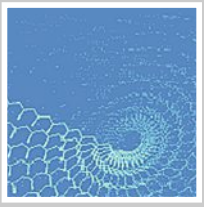

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Temporal Control of Soft Materials with Chemical Clocks

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Materials are normally designed for stability. However, there are a few intriguing examples of materials that are designed to vary over time.[1] For example, certain polymeric materials have been designed to degrade, releasing drugs slowly over time.[2] In that case, the temporal response is built into the material's building blocks. A more general approach, inspired by the self-regulation ability of living systems, is to embed materials with networks of chemical reactions that regulate the properties of the building blocks. A beautiful example of this approach is the mechanical beating of a hydrogel embedded with the Belousov-Zhabotinski (BZ) chemical oscillator.[3] While this suggests tantalizing possibilities for materials design, there is a limited toolkit of chemical systems available to control material properties in the time domain.

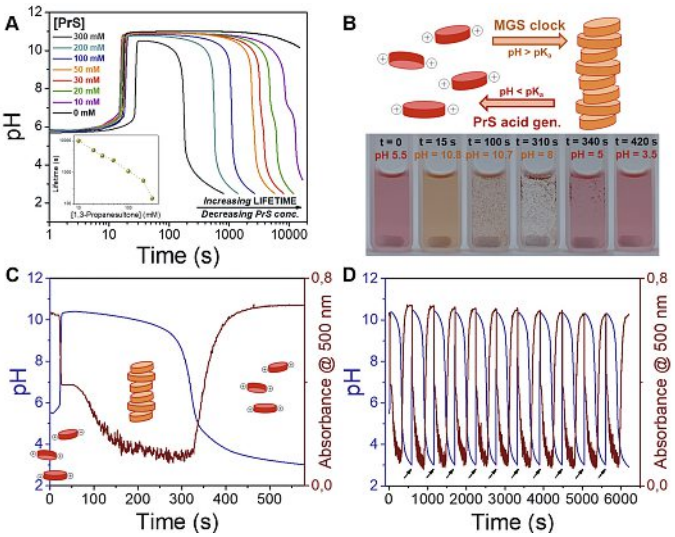

Fig. 1 A. pH-Time evolution for the MGS-PrS system showing its programmable lifetime. B: The MGS-PrS system is coupled with a pH-responsive perylene-based supramolecular building block (disks), enabling its reversible assembly (high pH) and disassembly (low pH). Demonstration of (C) one and (D) repeated cycles of assembly-disassembly. Adapted from ref. [9].

We recently introduced the use of clock reactions as *in situ* generators of chemical (*e.g.* pH, redox) stimuli for the control of self-assembly and disassembly of a variety of building blocks. Clock reactions are chemical systems with a sudden variation in composition after a programmable induction time, usually as a result of autocatalytic mechanisms.[4] We focused on the acid-to-alkali methylene glycol-sulfite (MGS) reaction, or 'formaldehyde clock', which generates a sudden and intense pH change after a programmable delay.

The formaldehyde clock can be used for the controlled precipitation of polymers. Consider chitosan, which precipitates in basic solutions. When the pH is adjusted by the addition of external base, the pH change is heterogeneous, resulting in a macroscopic precipitate. However, when the pH change occurs suddenly *in situ*, as is the case when using the formaldehyde clock, stable suspensions of chitosan particles are produced.[5] Furthermore, the size distribution of the particles could be controlled by tuning the clock parameters. Similar results were obtained for the coacervation of poly(allylamine hydrochloride) (PAH), another pH-responsive polyelectrolyte.[6]

Chemical clocks can also serve as the basis for reversible self-assembly. Lagzi *et al.*[7] demonstrated that lactones, functioning as slow acid-generators, could be coupled to pH-clocks to produce a transient change in pH. We extended this approach through the introduction of sultones, such as propanesultone (PrS), as slow acid generators. With their slower hydrolysis and lower pK_a of the acid product, they enable (i) tuning of the lifetime of the pH change by almost three orders of magnitude, and (ii) repeatable semi-batch cycles of pH change. We applied this system to control transient and cyclic assembly of perylene-based pH-responsive supramolecular building blocks[8,9] (Fig. 1).

As a next step, chemical clocks will be applied to other soft materials, such as gels. In the long term, efforts should focus on the development of stimuli-responsive chemical networks.

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