## Controlling chitosan precipitation in the time domain by the formaldehyde clock

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Clock reactions are fascinating chemical systems, in which the formation of a product occurs abruptly after a certain time depending on the starting conditions. For this reason they have great potential for materials science applications, especially for programming the self-assembly of polymers and colloids in the time-domain.

Here we demonstrate that the formaldehyde-sulfite clock reaction, best known as "formaldehyde clock", allows the time-controlled precipitation of chitosan, a biopolymer with broad technological applications. Chitosan exhibits a pH-dependent solubility in water (pK<sub>a</sub>  $\approx$  6.5) and the formaldehyde clock exhibits an abrupt pH change from acidic (pH  $\approx$  5.5) to basic pH ( $\approx$  10.5). By performing the formaldehyde clock in presence of chitosan, the latter is precipitated in the form of nanoparticles as soon as the "alarm" sets off *i.e.* the solution becomes alkaline.

Moreover, we show that the chemical structure of chitosan is not significantly affected by the reaction itself. Apart from demonstrating the suitability of the formaldehyde clock reaction for applications concerning biopolymers, our results may open up new possibilities for the production of chitosan particles for, e.g. controlled delivery applications.