Thermoresponsive polymers and host-guest chemistry: a win-win combination

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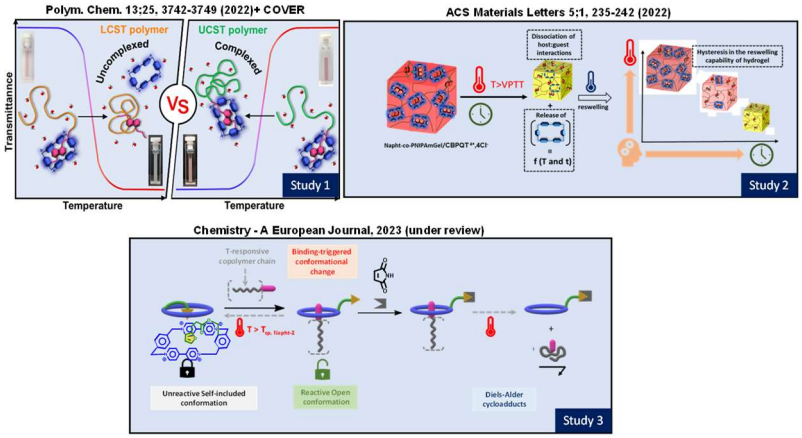
Abstract:

The combination of heat-sensitivepolymers and supramolecular chemistry has recently led to the development of fascinating adaptive materials. In this context, most studies have focused on exploiting host-guest interactions to control the physicochemical properties of polymeric materials.[1] This approach has notably enabled the creation of materials with programmable thermosensitivity and sensor properties.[2] In contrast, the exploitation of polymer thermoresponsiveness to control the recognition properties of host-guest systems at the molecular level is much less developed, and a perfect understanding of the mechanisms triggering thermo-induced decomplexation or complexation is still elusive.

In this communication, we will illustrate through three studies how the host-guest chemistry and the thermo-induced phase separation mechanisms can "talk together" to synergistically tune the coil↔globule transition and the complexation state of polymeric systems. The first example[3] concerns a comparative analysis of the behaviour of complexes formed from different naphthalene end-functionalized LCST or UCST polymers and the electron-deficient cyclobis(paraquat-p-phenylene) tetrachloride (**$CBPQT^{4+}$, $4Cl^-$**)[3] host when subjected to heat treatment. This study provided an understanding of the mechanisms triggering the thermo-induced (de)complexation of such complexes. The second study reports a supramolecular approach for developing an intelligent thermoresponsive polymeric hydrogel featuring a dual temperature and time memory function based on a kinetic control of the material's (de)complexation and (re) swelling behaviours. The last study illustrates how a thermo-induced phase separation mechanism can regulate on demand the Diels-alder reactivity of a synthetic self-complexing host-guest molecular switch **$CBPQT^{4+}$-Fu**, consisting of an electron-rich furan unit covalently attached to the electron-deficient $CBPQT^{4+}$host, with maleimide in water. Thanks to a supramolecular control over the topology of **$CBPQT^{4+}$-Fu** combined with a thermoresponsive supramolecular regulator, we reported a rare example of decreased reactivity upon increasing temperature.



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