

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

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## Abstract:

The combination of heat-sensitive polymers 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.<sup>1</sup> This approach has notably enabled the creation of materials with programmable thermosensitivity and sensor properties.<sup>2</sup> 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<sup>3</sup> will concern 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<sup>4+</sup>**, **4Cl<sup>-</sup>**)<sup>3</sup> 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 will report 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 will illustrate 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<sup>4+</sup>-Fu**, consisting of an electron-rich furan unit covalently attached to the electron-deficient **CBPQT<sup>4+</sup>** host, with maleimide in water. Thanks to a supramolecular

control over the topology of **CBPQT<sup>4+</sup>-Fu** combined with a thermoresponsive supramolecular regulator, we reported a rare example of decreased reactivity upon increasing temperature.

## References :

- 1) V. R. de la Rosa and coll., Mater. Today, 2016, 19, 44-55; 2) N. Herzer and coll. J. Am. Chem. Soc. 2012, 134, 7608–7611; 3) H. Guo and coll. Polym. Chem. 2022, 13;25, 3742-3749, 4) P. R. Ashton and coll. Angew. Chem., 1988, 27, 1550-1553; 5) L. De Smet and coll. ACS Materials Letters, 2022,5;1, 235-242; 6) C. Ribeiro and coll. submitted

