Title: Realizing fully photo-responsive amphiphilic polymers through azo dye functionalization of polyacrylamides

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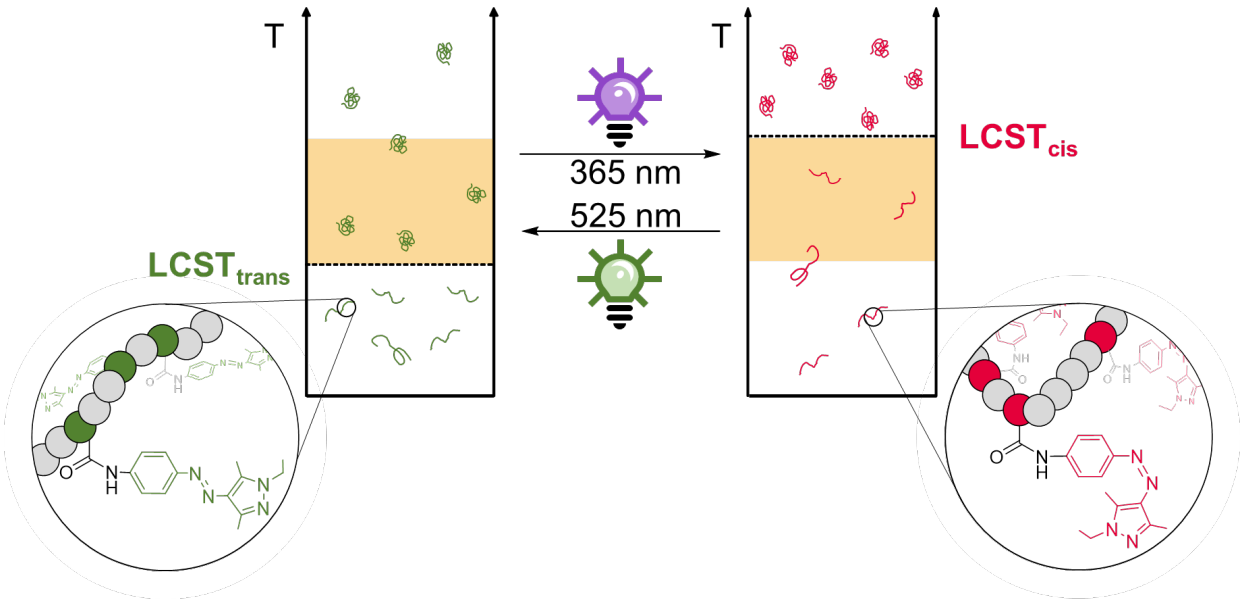
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We combine thermo-responsive polyacrylamides that show a lower critical solution temperature (LCST) transition with photo-responsive azo dyes to build long-time stable, water-soluble, and multi-responsive polymers. On top of their versatile switching options, such systems have the advantage that both temperature and light are non-invasive and independent triggers. Furthermore, such stimuli are fast and easy to apply, enabling quick back and forth switching, in contrast to commonly used triggers such as changes of the pH or salt concentration.

The reversible, light induced E-Z (trans-cis) isomerization increases the dipole moment of the chromophore, thus decreasing its hydrophobicity and a priori, increasing the phase transition temperature of the polymers. The usually incorporated azobenzene moiety induces typically rather small shifts of the phase transition temperature of around 5 K. Yet, by replacing azobenzene with aryl azopyrazoles (AAP) that have emerged recently as advanced azophoto-switches, we can boost this effect up to almost 25 K, while incorporating less than 10 mol-% of the dye-bearing monomer into the copolymer. Moreover, in contrast to classical azobenzenes, AAP azoheteroarenes allow for reversible and nearly quantitative photo-switching with UV- and green light between the two isomeric states by virtue of their well-resolved absorption spectra, and excel also by the long-liveness of their Z-state. They also show no sign of fatigue over multiple cycles of irradiation with UV- and green light.

In our contribution, we shall present the synthesis and characterization of new multi-responsive AAP functionalized copolymers, and their UV- and green light modulated switching behavior in water using methods such as temperature resolved NMR and EPR as well as turbidimetry to investigate this phase transition from the molecular up to the macroscopic level.



Caption: Photo-modulation of the LCST transition temperature of aryl azopyrazole bearing acrylamide copolymers in aqueous solution with UV- and green light. The temperature window between $LCST_{trans}$ and $LCST_{cis}$ allows for fully photo-responsive switching between soluble and insoluble.