Title:	Stimuli-responsive supramolecular materials for self- healing, compartmentalization and strain-stiffening applications
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Abstract:	Nature has unprecedented handle over the conformation and dynamics of its macromolecular morphologies. One of the precise example is the finite arrangement of amino acids in living system into a spatial organization by means of chain folding which results in higher order structures that can carry out specific functions like enzymatic catalysis in extremely efficient way. This intricate structure–activity relationships observed in biopolymers like proteins has been an inspiration for chemists and material scientists to understand the fundamentals of nature's design. This led us to design synthetic macromolecular architectures by bottom up approach biomimetic applications such as self-healing and compartmentalization. In the quest of designing such nanostructures with intelligent stimuli-response and adaptable nature, we developed single chain polymers utilizing controlled living polymerization and anchored with stimuli responsive moiety e. g. coumarin. We demonstrate intra-chain collapse of the extended coiled chain of the polymer to uniform sized nanoparticles in dilute condition mediated by photo-dimerization of coumarin under UV B light (max = 320 nm). At the crowded macromolecular solution the polymer folds in higher order nanostructures with polydispersed topologies that are far from condensed globule or partially swollen globule conformation. The flexo- rigid chain crosslinks has structural analogy with thermoplastic elastomers and prompted us to investigate the thermal and self-healing behaviour of polymers. They show autonomous and intrinsic self-healing at ambient condition, that can be modulated by the photo-crosslinking. Next, thermo-responsive single chain polymers were developed that exhibited chain collapse via coumarin cycloaddition along with host–guest interaction by cyclodextrin linker and act as nanocompartments in aqueous environment. The system was utilized for controlled loading of cargo molecules irrespective of their hydrophobicity and triggered their release over heating above lower critical solution temperature (LCST). Further, in a bid to design precise supramolecular materials with higher order morphology, we took cue from amyloid beta sheet assembly and developed coumarin tethered short peptide fragments to perform stimuli-responsive in out-of-equilibrium self-assembly to yield kinetically controlled 1D fibers and 2D nanosheets. Control over length and area distribution was realized by living supramolecular polymerisation on fiber and sheet seeds that plays important role in determining the mechanical stiffness of the resulting hydrogels. The peptide nanostructures were also envisioned as excellent exfoliating agents for inorganic hybrid materials e.g. MoS 2 . Finally, the strain-stiffening phenomenon, a ubiquitous characteristics of soft biological materials e.g. fibrin gels in blood clotting and actin filaments in cellular cytoskeletons that manifests on deformation in its microenvironment are mimicked in the synthetic peptide-polymer conjugates. Coumarin tethered short peptide fibers conjugated with thermo-responsive polymer system to form strain stiffening peptide-polymer network through dynamic covalent chemistry and demostrated mechanically nonlinear stiffness in elastic modulus with applied strain akin to natural ECM materials for tissue scaffold applications.
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