Emulsions have long been a foundational technology for the solution-phase synthesis of functional particles and materials. More recently, methods to create emulsions with complex internal droplet structure and assembly have opened up an entire new design space of complex droplets and soft solids with potential advantages for medicine, additive manufacturing and functional materials. However, limitations on current emulsification methods have prevented these advances from being translated to the nanoscale, where their true advantages lie. Nanoemulsions – metastable suspensions of nanoscale droplets – overcome these limitations through their scalable processing and metastable behavior. However, their engineering is complicated by emergent colloidal and interfacial behavior when droplets are driven to the nanoscale. In this seminar, I will summarize our recent work to show how interfacial molecular self-assembly can be used to control this emergent behavior to create complex nanodroplets, and exploit it for nanomaterials synthesis and assembly. In one example, we demonstrate the production of double nanoemulsions (i.e. nanodroplets in nanodroplets) whose morphology can be selected by fluid composition through the selection of co-surfactants with frustrated interfacial mechanics. In another example, we develop nanoemulsions with thermoresponsive droplet linkers that self-assemble into hierarchically structured soft solids, whose morphology and mechanical properties can be controlled through thermal processing in a similar as in biphasic hard materials. These complex emulsions provide new opportunities for templating colloidal particles, gels and soft solids with tailored structure and properties.