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Supporting information

## Hierarchical self-assembly of 'hard-soft' Janus particles into colloidal molecules and larger supracolloidal structures

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Fig. s1 Calibration curve used to calculate primary particle concentration to absorbance.



**Fig. s2** Collated time lapse laser diffraction measurements of PS seed microspheres in (a) pure water and (b) aqueous PVP-K90 solution. Note that the smaller secondary peak arises from a small quantity of undispersed aggregate present from the start of the measurement. (c) Volume fractions of single particles measured at 2  $\mu$ m diameter during the laser scattering measurements as a function of time for particle suspensions in pure water (a) and PVP solution (b).



**Fig. s3** Primary 'hard-soft' particle concentration as a function of time over a range of mixing speeds.



**Fig. s4** Optical micrograph of a typical Janus particle suspension after PVP removal, whereby desorption of the PVP from the particles has led to irreversible flocculation, the PBA soft lobes stick and assemble to dimer, trimer, tetramer, pentamer and even higher ordered structures.



**Fig. s5** Optical micrographs of 'hard-soft' Janus particle dispersions after removal of PVP and assembly, Janus particles with varied PBA size were used, (a) conversion: 26%, PBA:PS volume ratio: 0.13:1; (b) conversion: 50%, PBA:PS volume ratio: 0.32:1; (c) conversion: 91%, PBA:PS volume ratio: 0.53:1.



Fig. s6 SEM image of a higher order particle cluster with hollow structure.