Supporting Information for “Bottom-Up with a Twist: A New Approach for Colloidal Crystal Assembly”

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FIG. S1: Difference in chemical potential of an adsorbed linear homopolymer with length, $M$, between the cubic and hexagonal tetrastack polymorphs composed of colloids with diameter, $\sigma_c$, at $k_B T = 1.0$. 

**S1. MONTE CARLO**
FIG. S2: Representative conformations of a star inside tetrastack polymorphs. Colloids are shown in red, and monomers in blue for a star polymer with $f = 8$ arms at $q \approx 1.3$. (a) In the cubic polymorph, the star is centered in an octahedral void (OV) whose base is outlined in white. For such a large star, its arms expand into the neighboring (smaller) tetrahedral voids (TV), whose bases are outlined in black. (b) Similarly, in the hexagonal polymorph a star of the same size also expands to access the free volume in neighboring voids. However, the star can now make use of the neighboring (large) OVs which are stacked in the $z$-plane as depicted. As a result, the star adopts a more prolate morphology than when adsorbed in the cubic polymorph. The voids are centered in the gaps visible in the upper panel of part (b), while a cross-section is shown in the lower panel.
FIG. S3: Difference in chemical potential between the cubic and hexagonal tetrastack polymorphs for stars of increasing size with full monomeric detail at different temperatures. Changing the temperature of the simulation makes only a marginal difference to $\Delta \mu$ when normalized by $k_B T$ (increased by approximately 8%), hence Monte Carlo results obtained at $k_B T = 1.0$ can still be fruitfully applied to molecular dynamics simulations where $k_B T = 0.155$. 
FIG. S4: Fitting the minimum in $\Delta \mu / k_B T$ at $q = 3$ for the coarse-grained star polymer model to a polynomial function in terms of the star’s functionality shows a non-zero intersection at $f = 0$. Where $g(f)$ is less than zero implies the star can weakly bias the formation of the cubic polymorph, though quantitatively it is an order of magnitude smaller than the preference which can be introduced around $q = 1.5$ toward the hexagonal polymorph. For this model, when $f > 8$ no preference for the cubic form can be induced by the star at any size ratio, $q$.

FIG. S5: Representative interparticle potentials between a colloid of diameter, $\sigma_c$, and a star with a certain functionality, $f$, and size ratio with respect to the colloid, $q$. These potentials are obtained by numerically integrating the mean force, $F(r)$, obtained from previous analytical theories as described in the main text.
FIG. S6: Right: Snapshot of a molecular dynamics simulation of a binary mixture of colloids and stars with $f = 30$ and $q = 1.5$. Only stars which are closer than $2\sigma_c$ to any colloids are shown. Colloids are semitransparent and stars are represented as black spheres with diameter $0.4\sigma_c$ to aid visualization. The colloids in the sample have crystallized into a hexagonal polymorph, which is stabilized by the presence of the stars. These can move more freely inside the crystallite thanks to canals which are not present in the cubic polymorph.
FIG. S7: Number of (left) hexagonal and (right) cubic particles as a function of time in annealing simulations of mixtures of colloids and stars. A particle $i$ is labelled as hexagonal (cubic) if its locally-averaged $q_4$, $\bar{q}_4(i)$, takes a value between 0.1 and 0.3 (0.45 and 0.6). All simulations were started by placing a purely cubic (black and green curves) or hexagonal (red curves) crystallite in a sea of star polymers with $f = 30$ and different size ratios. For stars with $q = 0.75$ (red and green curves) the number of particles of a specific type remained constant throughout the simulation, while the $q = 1.5$ sample (black curves) annealed to an almost perfect hexagonal crystallite.

FIG. S8: Number of elementary charges $Z$ required by each polymer star in order to generate a star-star interaction rescaled by a factor $\alpha$ with respect to the repulsion generated by neutral stars.
FIG. S9: Non-additivity parameter $\Delta$ as a function of $\alpha$ for (top) $f = 30$ and different values of $q$ and (bottom) $q = 1.5$ and different values of $f$. $\Delta$ increases monotonically with both $q$ and $f$ while it is a decreasing function of $\alpha$.

FIG. S10: The average bond-order parameter $\langle q_4 \rangle$ as a function of time for simulations performed at different values of the star-star repulsion rescaling factor $\alpha$. Stars have $q = 1.5$ and $f = 30$. These simulations have been carried out at two different polymer stars number density $\rho_s$: (left) $\rho_s = 0.193$ and (right) $\rho_s = 0.217$. The annealing power of the stars is highly dependent on both $\alpha$ and $\rho_s$, with $\alpha$ controlling the density range in which the annealing is most efficient. We note that the red curve in the right panel refers to a system in which part of the colloids are in a closed-packed structure and part in a tetrastack crystallite, signalling that, for this value of $\rho_s$, a pure tetrastack crystal requires a higher value of $\alpha$ in order to be stable.