

# Supporting Information

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## SI Text

**Simulation of Model Spherical Micelles (MSMs).** We perform molecular dynamics simulations in the canonical ensemble (constant number of particles, volume, and temperature) of the MSMs using the LAMMPS molecular simulation package (1) with periodic boundary conditions and reduced Lennard–Jones (LJ) units (2). The Nose–Hoover thermostat is used with  $T = 1.0$  and time step = 0.005. The simulations that we report in this work are performed at a nominal volume fraction,  $\phi \approx 0.54$ , computed assuming micelles are space-excluding spheres of diameter  $5.27\sigma$ .  $\phi \approx 0.54$  is chosen because it is comparable to the volume fraction of state points observed to form spherical micelles in previous simulations of tethered nanospheres (TNSs) (3). A cursory sensitivity analysis, performed by starting from an assembled sigma phase at  $k = 5$  and either slowing increasing or slowly decreasing the box size predicts that the sigma phase is physically stable within a range of nominal volume fractions  $0.47 \leq \phi \leq 0.57$ , for the specific MSM parameters used in this study. In practice, the effective micelle volume fraction will be lower than the nominal volume fraction, because the micelles have a bumpy, soft corona and will overlap to form dimers. For example, if we account for dimers, the volume fraction is reduced from 0.54 to 0.46 for a system with  $f_{\text{dimer}} = 0.25$ , assuming dimers are spherocylinders of length  $6.72\sigma$  and diameter  $5.27\sigma$ . In Fig. S1 we provide a schematic of the MSM, depicting the approximate micelle corona and core sizes, as well as the dimer to monomer size ratios, for the MSM simulations investigated in this paper.

As discussed in the main text, surface particles interact via the purely repulsive Weeks–Chandler–Andersen (WCA) potential, meant to capture excluded volume. The WCA potential follows the form (4)

$$U = \begin{cases} 4\epsilon \left( \frac{\sigma^{12}}{(r-\alpha)^{12}} - \frac{\sigma^6}{(r-\alpha)^6} \right) - U_s, & (r-\alpha) < r_c, \\ 0, & (r-\alpha) \geq r_c \end{cases}, \quad \text{[S1]}$$

where  $U_s = -\epsilon$  and the interaction cutoff  $r_c$  is set to  $2^{1/6}$ .  $\alpha$  is an adjustable shifting parameter, set to zero here. Surface particles are held to their scaffold sites with harmonic springs, defined as  $U(r) = kr^2$ , following the convention in LAMMPS (1). The general simulation procedure is as follows: Simulations are initialized by creating a random arrangement of MSMs under dilute conditions ( $\phi < 0.1$ ) with  $k = 10$ ; the system is then slowly compressed until the target box size is reached. Starting from the target box size, MSMs are simulated with  $k = 2$  and further allowed to disorder.  $k$  is then incrementally increased by 0.25 until the final value is reached (typically,  $k = 4$  to 5). For each value of  $k$ , the system is run for 10 to 50 million time steps (large systems are run for longer than small systems). Simulations are typically run for between 50 and 500 million total time steps. This procedure of slowly increasing  $k$  mimics the procedure used to simulate TNSs, discussed below. Note, our simulations did not span long enough time scales to observe tile rearrangements in the ordered solid phases.

**Simulation of TNSs.** We perform Brownian dynamics simulations in the canonical ensemble of the TNS system with periodic boundary conditions and reduced LJ units. The mono-TNS building block used consists of a chain of eight spherical beads of diameter  $\sigma$ , connected via finitely extensible nonlinear elastic (FENE) springs (3, 5). Each chain is attached with a FENE spring to a larger “nanosphere” of diameter  $D = 2.5\sigma$ . The potential energy

of the FENE spring is given by

$$U_{\text{FENE}}(r) = -\frac{1}{2}kR_o^2 \ln \left[ 1 - \left( \frac{r-\alpha}{R_o} \right)^2 \right], \quad \text{[S2]}$$

where  $k$  is the spring constant,  $r$  is the interparticle separation,  $R_o$  is the maximum allowable separation, and  $\alpha$  is an adjustable shifting parameter to account for excluded volume of the nanosphere. For this study,  $k = 30$  and  $R_o = 1.5$ , and  $\alpha = 0.75$  for the bond connecting the chain to the nanosphere, and zero otherwise. Tethers are treated as “solvent-phobic” and thus aggregate at sufficiently low  $T$ . To model this aggregation, the attractive LJ potential is used, given by Eq. S1, but with  $U_s$  set to the energy at the cutoff and  $r_c = 2.5$ . All other interactions are modeled by the purely repulsive WCA potential (Eq. S1, with  $U_s = -\epsilon$  and  $r_c = 2^{1/6}$ ), appropriately radially shifted to account for excluded volume; for tether-nanosphere interactions  $\alpha = 0.75\sigma$  and for nanosphere-nanosphere interactions  $\alpha = 1.5\sigma$ . Simulations are performed using the Brownian dynamics thermostat, where the volume fraction of the excluded volume of the individual beads is varied between  $0.25 \leq \phi \leq 0.30$ , the range where spherical micelles were predicted in previous work (3). This translates to a nominal micelle volume fraction of approximately 0.52, calculated assuming a characteristic diameter of  $12\sigma$  for the spherical micelles (approximated from the radial distribution function for micelle centers).

Di-TNSs are modeled in much the same way as mono-TNSs described above. Chains composed of four beads of diameter  $\sigma$  are connected via FENE springs (Eq. S2). Two chains are connected to a single nanosphere of diameter  $D = 2.0\sigma$ , diametrically opposed. This planar angle of  $180^\circ$  between the chains is maintained by the use of a harmonic spring between the first beads of the two polymers, with  $k = 60$  and equilibrium separation set to  $3\sigma$ . The two polymer chains are chemically distinct. One chain is considered to be solvent-phobic (i.e., attractive), and thus is modeled by the LJ potential. The other chain is considered to be solvent-philic (i.e., nonattractive) and modeled by the WCA potential. Nanosphere-nanosphere interactions are modeled with the LJ potential, appropriately radially shifted to account for excluded volume ( $\alpha = 1.0$ ). All other interactions are modeled by the WCA potential, appropriately radially shifted ( $\alpha = 0.5$  for tether-nanosphere interactions). Simulations are performed at  $\phi = 0.20$ , as calculated from the excluded volume of the individual beads. In Fig. S2, we plot the asphericity histogram of the micelles formed by the di-TNS system. We note the asphericity histogram closely matches the result obtained for the mono-TNS system shown in Fig. 3D of the main text.

The general simulation procedure used is identical for both mono- and di-TNS. Systems start from a disordered mixture of TNS, well above the order-disorder temperature where little-to-no aggregation occurs ( $T = 2.0$ ). Systems are then incrementally cooled to their final temperature ( $T \approx 1.0$ ), where systems are run for several million time steps at each incremental temperature. The potential energy is monitored to ensure a steady state is reached before additional cooling. As the temperature is reduced, individual TNSs slowly aggregate into micelles; micelles form ordered structures at sufficiently low  $T$ . Simulations are typically run for a total of 40 million time steps. Multiple independent cooling sequences are performed to ensure reproducibility of results. Simulations of mono-TNS are performed for systems of 2,500 building blocks in cubic boxes (22,500 total beads) and 5,000 building blocks in boxes with aspect ratio

2:2:1 (45,000 total beads). Simulations of di-TNS are performed in cubic boxes for systems of 2,000 building blocks. See refs. 3 and 5–7 for additional details regarding the simulation of TNS. Note, our simulations did not span long enough time scales to observe tile rearrangements in the ordered solid phases.

**Free Energy of MSMs.** We investigate how surface particle mobility affects the stability of MSMs in various crystal structures (Fig. 4A) by calculating the change in Helmholtz free energy  $F$  as a function of the strength of the harmonic springs (i.e.,  $k$ ) that anchor particles to the micelle surface, using free-energy perturbation (FEP) (8). For each structure, the calculation is split into eight independent stages to avoid asymmetric bias (9), consisting of equilibrium simulations with spring constants  $k = 3, 4, \dots, 10$ . Within each stage, we compute the ensemble average:

$$F(k_j) - F(k_i) = -k_B T \ln \left\langle \exp \left( -\frac{U_{k_j} - U_{k_i}}{k_B T} \right) \right\rangle_{k_i}, \quad [\text{S3}]$$

which gives the free energy difference between stage  $i$  and  $j$ , where  $j = i \pm 1$ . Each stage consists of a molecular dynamics simulation (1) in the canonical ensemble at  $T = 1.0$  and micelle nominal volume fraction  $\phi \approx 0.54$  to match the simulations. The vertical offset between the curves for different structures is computed using a FEP variant of the standard Frenkel–Ladd lattice coupling expansion thermodynamic integration (TI) method for molecular systems (2, 10). We use FEP to adapt the method to the complex objects considered here. Although this method is nonstandard, it gives reasonable estimates of  $F$  that are consistent with our self-assembly results. We note this calculation only effects the vertical offset of the curves and not how  $F$  changes as a function of  $k$ .

**Free Energy of Sphere/Dimer Mixtures.** The free energy for mixtures of WCA spheres and dimers is evaluated using a three-step scheme based on the standard Einstein crystal TI method for spherical particles (2, 11, 12), plus an additional alchemical (13) step to convert a given fraction of the spheres into dimers. Because systems of WCA spheres do not act like harmonic crystals for many of the structures tested, we use the Dzugutov (DZ) (14) system as a convenient reference system that gives harmonic behavior. Computing the work required to change the particle interactions from the DZ potential to the WCA potential constitutes the third step of our scheme.

In the first step, we compute the free energy difference between a noninteracting harmonic (Einstein) crystal and a system of spherical particles interacting with the DZ potential using the standard Frenkel–Ladd method (2, 11, 12). We denote this free energy difference  $\Delta F_I = F_{\text{DZ}} - F_{\text{Ein}}$ .

In the second step, we compute the work required to change a given fraction,  $f_d$  of the spherical particles in the system into dimers. We consider a system with the energy function

$$U(\lambda)_{\text{II}} = (1 - \lambda)U_{\text{pure}} + \lambda U_{\text{mix}}. \quad [\text{S4}]$$

The free energy required to change the system of DZ spheres (pure) to a mixture of DZ spheres and dimers (mix) is the integral over the derivative with respect to the so-called switching parameter  $\lambda$ :

$$\Delta F_{\text{II}} = \int_0^1 d\lambda \left\langle \frac{\delta U(\lambda)}{\delta \lambda} \right\rangle_\lambda = \langle U_{\text{mix}} - U_{\text{pure}} \rangle_\lambda. \quad [\text{S5}]$$

The third step is to compute the work required to change the potential from DZ to the WCA potential. We consider a system with the energy function

$$U(\lambda)_{\text{III}} = (1 - \lambda)U_{\text{DZ}} + \lambda U_{\text{WCA}}. \quad [\text{S6}]$$

The free energy difference for changing the interaction potential is given by integrating over the derivative with respect to the switching parameter  $\lambda$ :

$$\Delta F_{\text{III}} = \int_0^1 d\lambda \left\langle \frac{\delta U(\lambda)}{\delta \lambda} \right\rangle_\lambda = \langle U_{\text{WCA}} - U_{\text{DZ}} \rangle_\lambda. \quad [\text{S7}]$$

For all calculations, we run 20 independent MC simulations for different values of  $\lambda$  to estimate  $\delta U(\lambda)/\delta \lambda$ , and obtain  $\Delta F$  by numerical integration. Simulations are selectively carried out where  $|\delta^2 U(\lambda)/\delta \lambda^2|$  is the largest. For systems that contain dimers, each simulation begins with a compression run with particles constrained to their lattice positions allowing rotations and swaps before equilibrating at constant density. The total free energy for a sphere/dimer mixture is given by

$$F = F_{\text{Ein}} + \Delta F_I + \Delta F_{\text{II}} + \Delta F_{\text{III}}. \quad [\text{S8}]$$

This formula is used to evaluate  $F$  for the WCA system, shown in Fig. 4B.

**Isosurface Generation.** Representative configurations from self-assembly simulations are plotted as time-averaged isosurfaces to coarse-grain over thermal fluctuations and produce a clearer picture of the structure. To generate the isosurfaces, we replace the centroids of the MSMs (or aggregating tethers in the case of TNS) with a normalized Gaussian of width  $1.5\sigma$ , mapped to a voxel grid composed of cells of length  $1\sigma$ , to achieve a degree of spatial coarse-graining. We then average the voxel data for ten configurations generated within a time window that is much shorter than diffusion timescales. This voxel data is then used to create isosurfaces within the Visual Molecular Dynamics software program (15), with an isovalue typically ranging between 0.1 and 0.2 for MSMs and between 4 and 6 for the TNS systems.

**Clarifying Figures.** In Fig. S3, we plot representative snapshots of various sigma structures formed with the DZ potential, MSM model, and mono- and di-TNS models. For all systems, we observe a characteristic tiling constructed of squares and triangles from at least one perspective. Fig. S3A and B depict point particle systems simulated using the DZ potential. Fig. S3A shows a system of 60 point particles (i.e., an ideal number for forming the sigma structure), with coordinates obtained by quenching to zero temperature using LAMMPS. Fig. S3B is identical to S3A, however with 54 particles (i.e., a nonideal number of particles for the sigma structure), highlighting slight changes to the tilings as a result of reduced number of particles. Fig. S3C shows the MSM system, Fig. S3D shows the mono-TNS system, and Fig. S3E shows the di-TNS system. Fig. S3C corresponds to Fig. 2D in the main text, and Figs. S3C and D correspond to Fig. 2B and F from the main text, respectively. The slight differences we observe between the various systems is likely related to nonidealities in system size, as we highlighted in the comparison between Fig. S3A and B.

In Fig. S4, we plot multiple views of simulations of 360 building block systems in boxes with aspect ratio 1.28:1.28:1 calculated for the DZ system (Fig. S4A) quenched to zero temperature using LAMMPS and the MSM system (Fig. S4B). Fig. S4A highlights the fact that small systems often will demonstrate nonideal arrangements of the tilings due to boundary effects, even for the known quasicrystal forming DZ system. Fig. S4B corresponds to the system plotted in Fig. 2E in the main text, where the  $xz$  plane demonstrates quasi-12-fold symmetry (diffraction pattern shown in Fig. 2E in the main text), and the  $xy$  and  $yz$  planes demonstrate periodic ordering. Note, the simulation coordinate system is not always coincident with ordering in the system and, as such, labeled orientations are approximate in both Figs. S3 and S4.





