Supplementary Information for "Inverse design of triblock Janus spheres for self-assembly of complex structures in the crystallization slot *via* digital alchemy"

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b_2-constrained alchemy with independent patch aperture fluctuations

Figure S1 shows the evolution of the alchemical variables during alchemical simulations where the aperture angles of the two patches (θ_1 and θ_2) are allowed to fluctuate independently of one another. For the system biased towards the kagome lattice (Figure S1a–d), θ_1 and θ_2 converge to the same value (approximately 37°) for all successful optimizations, reflecting the symmetry of the valence of each particle in the kagome lattice. In contrast, for the case of snub square, θ_1 and θ_2 converge to different values, approximately 67° and 38°. This difference reflects the asymmetric valence around each particle in the snub square lattice.

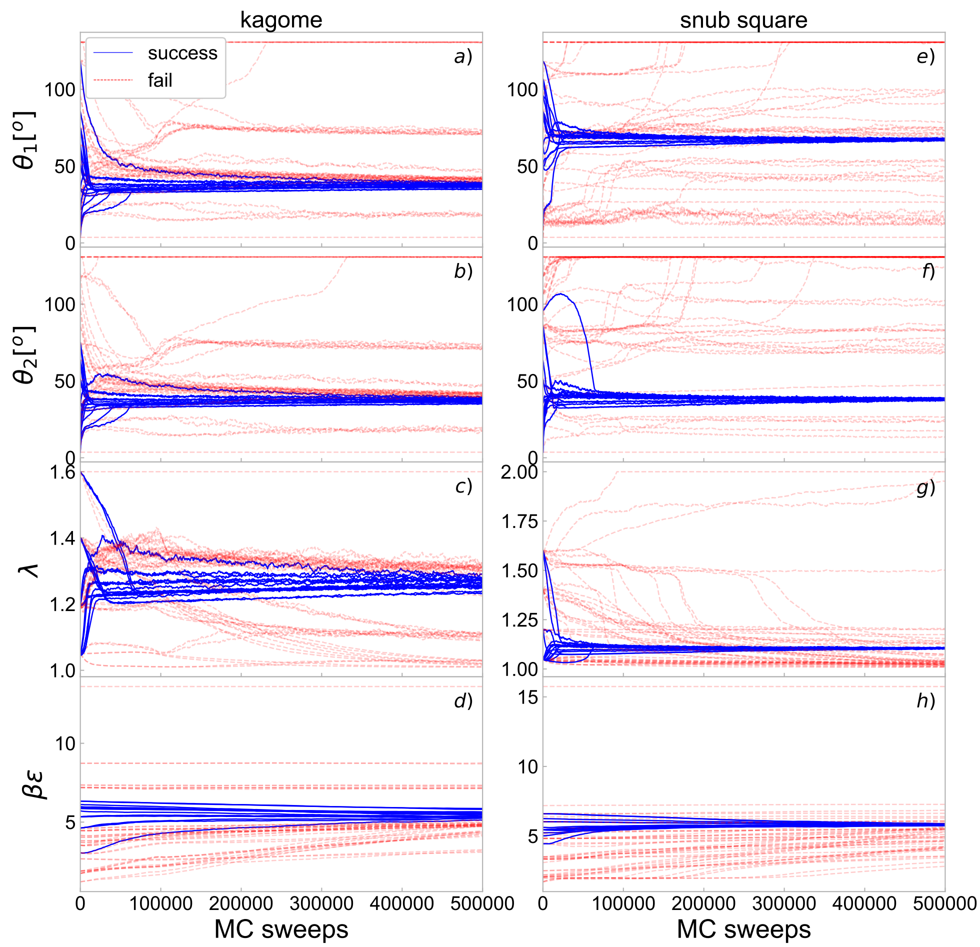

Fig. S1 Alchemical variables as a function of the MC sweeps when the equal-size aperture angle constraint is relaxed for kagome (a-d) at $(b_2, \phi_{\text{target}}) = (-9, 0.5)$, and snub square (e-h) at $(b_2, \phi_{\text{target}}) = (-19, 0.59)$.

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Snub square design: pattern registration analysis

Figure S2 shows the final snapshot of self-assembly simulations performed with $\theta_L = 60°, 62°, 64°$ and $66°$, while keeping the smaller patch aperture angle fixed at $\theta_S = 38°$. The first three values are large enough to accommodate a maximum of three bonds per patch while the last one is slightly larger than the minimum required to accommodate four bonds per patch. From these pattern registration considerations alone, we would expect to observe the formation of a high quality snub-square lattice with the first three values of θ_L. However, this is not the case. Instead, we observe the formation of kagome/twisted kagome at $\theta_L = 60°$. Slightly increasing the aperture angle to $\theta_L = 62°$ results in a snub square/twisted kagome coexistence. Finally, we observe the assembly of a pure snub square lattice only when $\theta_L \in \{64°, 66°\}$, that is, when θ_L is close to or slightly larger than the minimum aperture required to accommodate a maximum of four bonds per patch. We also note that the snub square lattice obtained from the systems with $\theta_L \in \{64°, 66°\}$ exhibits a considerable number of defects, whereas the lattice obtained with the optimized parameters is relatively defect free (Figure 6, main text).

Fig. S2 Final snapshot of self-assembly simulations at $\theta_L = 60°, 62°, 64°$ and $66°$ with fixed $\theta_S = 38°$. Here, the upper left symbol θ_L^{XS} denotes how much larger θ_L is above the minimum for three-bonds-per-patch ($\approx 52°$) for $\lambda = 1.10$.

Bonds-per-patch analysis

The maximum number of bonds a given patch can form to other bonds is dictated by the aperture angle θ and patchy interaction range λ. The range of λ and θ values where patches can form at most n bonds is given by

$$C_{\min}^{(n)} \leq \lambda \sin\theta < C_{\max}^{(n)}.$$

In two-dimensions, $(C_{\min}^{(n)}, C_{\max}^{(n)})$ pairs are given by $(0, 1/2)$, $(1/2, 1/\sqrt{3})$, and $(1/\sqrt{3}, 1/\sqrt{2})$ for $n = 1$, 2, and 3, respectively. In 3D, these pairs are given by $(0, 1/2)$, $(1/2, \sqrt{3}/2)$, and $(\sqrt{3}/2, 1)$ for $n = 1$, 2, and 3, respectively.

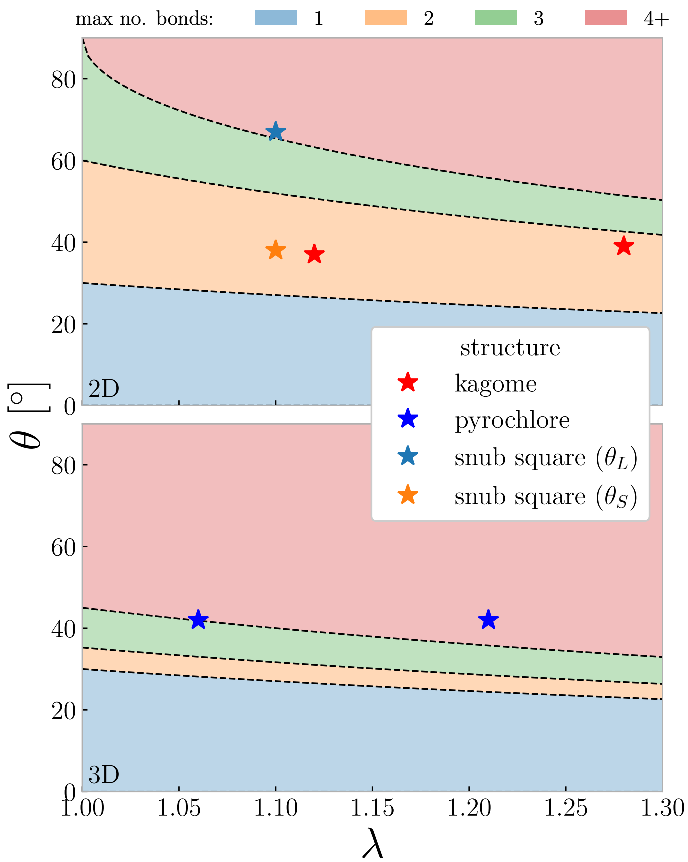

Fig. S3 The range of patch aperture angles θ that allow a maximum of 1, 2, 3, and 4 bonds per patch as a function of λ for 2D (top) and 3D (bottom). Optimized parameters for selected structures shown as colored stars.