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# A Design Path for Hierarchical Self-Assembly of Patchy colloidal particles

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#### Abstract

Patchy colloidal particles are promising candidates for building blocks in directed self-assembly. To be successful the surface patterns need to be simple enough to be synthesized, while feature-rich enough to cause the colloidal particles to self-assemble into desired structures. Achieving this is a challenge for traditional synthesis methods. Recently it has been suggested that the surface pattern themselves can be made to self-assemble. In this paper we present a design path for hierarchical targeted self-assembly of patchy colloidal particles based on self-assembling surface patterns. At the level of the surface structure, we use a predictive method utilizing the universality of stripes and spots, coupled with stoichiometric constraints, to cause highly specific and functional patterns to self-assemble on spherical surfaces. We use a minimalistic model of an alkanethiol on gold as a demonstration, showing that even with limited control over the interaction between surface constituents we can obtain patterns that cause the colloidal particles themselves to self-assemble into various complex geometric structures, such as strings, membranes, cubic aggregates and colloidosomes, as well as various crystalline patterns.

uring the last decade, patchy colloidal particles have emerged as candidate building blocks for colloidal selfassembly. By altering the position of attractive areas, patchy colloidal particles can for example be used to mimic the anisotropic interactions between folded proteins, drawing inspiration from how certain proteins self-assemble into capsid shells enclosing the viral genome [1]. With an ambition towards self-assembling meta materials and nano-sized functional structures, examples of colloidal self-assembly insilico or in-vivo have grown to encompass kagome lattice systems to colloidal strings [2, 3] using equally varied techniques. In this paper we explore the idea of self-organizing surface patterns on the patchy colloidal particles. We demonstrate in-silico hierarchical self-assembly of a range of geometrical structures: different crystals, membranes, strings, colloidosomes of different size and cubic aggregates, all in the context of a single model system. By modifying parameters that determine the interac-

tions between the surface constituents, we are able to select which of the geometries that selfassemble. The parameter choices are based on a combination of more general design principles, also presented in this paper, and analytical predictions of the self-assembly processes on the surface [4].

Synthesization of large quantities of colloidal particles with attractive patches in specific directions and high specificity is difficult. The synthesis methods developed in the last decade [5] range from various coating techniques on thin films of colloidal particles on a substrate like dip-coating and glancing angle deposition [6], to techniques where colloidal particles are aligned using an external electric field combined with an evaporator [7], to multiphase colloidal particles where constituents are added or subtracted sequentially to produce highly anisotropic colloidal shapes [8]. A rather different method, suggested recently, is to let the surface coating itself self-assemble into desired patterns as a part of a hierarchical

self-assembly process. Experimental findings indicate that certain mixtures of alkanethiols adsorbed on gold nanoparticles phase separate into various morphologies depending on the properties of ligands and nanoparticles [9]. The results in this article support the idea of patchy colloidal particles with self-assembled coatings by showing that limited control over how the surface constituents interact is sufficient for targeted self-assembly of a wide range of surface patterns, and in extension, colloidal structures. An important advantage of forming the patterns this way is that there is no intrinsic difficulty in making patterns with many patches and high specificity. The method can therefore give access to many patterns that seem hard to come by using other techniques.

## I. A model system alkanethiol-on-gold

A proposed candidate for self-assembling patchy morphologies on spheres is the alkanethiol-on-gold system [9]. It consists of spherical gold nanoparticles coated with different species of alkanethiols. These alkanethiols organize into patterns due to a competition between their immiscibility and a mixing effect of entropic origin [10]. It has been shown in computer simulations that many different patterns can appear depending on the number of and distribution between alkanethiol types, with the common theme being that the pattens are combinations of stripes and spots [11, 12]. In [4] we showed that it is possible to predict which combination of spots and stripes that emerges in a spin model representation of the alkanethiol molecules. This explained the strong preference for spots and stripes as patterns more pure in terms of eigenfunctions to the interaction operator [4]. In this article we use the same mathematical relation to find parameters for which the spin model representation self-assembles into specific functional surface patterns. We will use the same spin model as in [4] as it has similar degrees of freedom and self-assembly behaviour as more detailed simulations of the system [11, 12].

In the model system, the alkanethiols are represented as spherical particles interacting with a set of effective interactions. Between alkanethiols of different types  $\alpha$  and  $\beta$ , the interaction consists of a hard core with diameter  $\sigma_0$ , a soft shoulder potential with range  $\sigma_1$  (causing immiscibility), and a square-well potential of depth  $\epsilon$  (representing the mixing effect),

$$V^{\alpha\beta}(r) = \begin{cases} \infty, & \text{if } r < \sigma_0 \\ 1, & \text{if } \sigma_0 < r < \sigma_1 \\ -\epsilon, & \text{if } \sigma_1 < r < |L_{\alpha} - L_{\beta}| \\ 0, & \text{otherwise} \end{cases}, (1a)$$

where the  $L_{\alpha}$  are abstract parameters defined for each alkanethiol type, representing the different lengths or bulkiness of the tail groups. The interaction between alkanethiols of the same type is taken to be a simple hard-core repulsion.

$$V^{\alpha\alpha}(r) = \begin{cases} \infty, & \text{if } r < \sigma_0 \\ 0, & \text{otherwise} \end{cases}.$$
(1b)

Fig. 1 shows the shape limitation of the effective interaction functions between different alkanetiol types used later.



Figure 1: The model's interaction functions between different particle types consists of a shoulder potential reaching neighbouring particles, an attractive basin indirectly set by the relative length of the alkanethiol molecules and a hard core. By using the design principle presented in this article we find values for the depth of the attractive basin,  $\epsilon$ , and the reach of the alkanethiol molecules (or in 3, the height of the shoulder potential), that causes different functional patterns to self-assemble.

### II. Relating ground state to interaction functions

In [4] we formulate the problem of predicting the morphology of a particle system in terms of a Potts-like spin model [13]. Assuming that we have a model of the effective interactions between particle type  $\alpha$  and  $\beta$ , here described as a set of potentials  $V^{\alpha\beta}(r)$ , we can construct a Hamiltonian for this spin model as

$$H = \sum_{\alpha\beta}^{K} \sum_{ij}^{N} \Pi_{i\alpha} V_{ij}^{\alpha\beta} \Pi_{j\beta}$$
(2)

where *N* is the number of sites that can hold a particle, *K* the number of particle types,  $V_{ij}^{\alpha\beta} = V^{\alpha\beta}(|\vec{r}_i - \vec{r}_j|)$ , and  $\Pi_{i\alpha}$  is 1 if site *i* contains a particle of type  $\alpha$  and 0 otherwise.

The task is then to find the low-energy states of this Hamiltonian. While we cannot hope to solve it exactly for general interaction matrices  $V^{\alpha\beta}$ , if we relax the constraints and allow the state  $\Pi$  to take any real values while keeping its norm fixed we get a quadratic problem that is solvable. First the potentials  $V^{\alpha\beta}$ are diagonalized independently for each pair of particle types  $\alpha\beta$  by spherical harmonic functions, Fig. 2, this relies on that the interaction functions are isotropic [14]. With  $\Pi$  orthogonally decomposed into spherical harmonic functions with different *l*-degrees, the minimum of the Hamiltonian can be found by eigendecomposition of the  $K \times K$  matrix of every term in the Hamiltonian sum, one for each *l*-degree. The eigenvectors signify the relative magnitude of the *K* types that segregate at a length scale *l*, the eigenvalues are the energy associated to a segregation between the types with that relative magnitude. The result is an energy spectrum over different length scales *l* with *K* branches (one for each eigenvalue) whose minimum will be the ground state for the relaxed model.



Figure 2: Each part of the interaction matrix describing the interaction between two particle types  $\alpha$  and  $\beta$  are diagonized by spherical harmonic functions. This allows the Hamiltonian to be written as a sum over l-degrees (energies associated with equal degrees l but different orders m are degenerate) and the matrices' sizes to be limited by the number of particle types rather than the spin model resolution.

Each branch describes variation between two partitions of the particle types. To predict the behavior of the original model we combine the minima of enough branches to completely specify a particle configuration, excluding unphysical branches that do not describe separations between any types. An example is shown in Fig. 3 B, where the global minimum describes the phase separation of the blue particles and the next branch is needed to determine the behavior of the red and yellow particles, here a striped state. For further details see [4].

#### III. A DESIGN PATH FOR TARGETED HIERARCHICAL SELF-ASSEMBLY OF PATCHY NANOPARTICLES

Since the self-assembling morphologies are closely tied to their energy spectra, we can use the spectra as intermediates between the parameters describing the coating and the resulting ground state. The theoretical model for what constitutes a ground state helps us decide on reasonable targets to aim for, patterns with stripes and spots that are symmetrically distributed over the surface. The locations of attractive patches in the target surface pattern should match the direction colloidal particles will bind in the target nano-particle configura-



Figure 3: The length scale that defines the segregation between different surface constituent types is given by the energy spectra. To fully understand the ground state morphology, stoichiometric constraints have to be taken into account as well. a) With two particle types of equal concentration, the ground state will be stripes. The wavelength is determined by the minimum in the energy spectrum. Here  $L_{blue} - L_{red} = 1.1$  radii (radius of the colloid),  $\epsilon = 0.1$ . b) With multiple particle types, the ground state is described by multiple minima in the energy spectrum, sufficiently many to account for the entire stoichiometry. The global minimum takes precedence and separates blue from red and yellow, the second minimum then determines the wavelength of the yellow-red striped part.  $L_{blue} = 0.44$ ,  $L_{red} = 0$ ,  $L_{yellow} = 0.88$  radii,  $\epsilon = 0.1$ . c) Here the dominating segregation is between red and the surrounding colors, but stripes cannot form due to stoichiometric constraints (red, blue and yellow have equal proportions), causing the red state to be spotty instead. Here  $L_{blue} = 1.1$ ,  $L_{red} = 0$ ,  $L_{yellow} = 1$  radii,  $\epsilon = 0.1$ .

tion. If the directions in which the colloidal particles are supposed to bind in aren't symmetrical, a combination of stripes, spots and janus patterns might do the trick, e.g. Fig. 7. The order in which the segregations takes precedence sets the order of the minima in the energy spectrum, similarly to how the order of the energy minima determines if blue makes a janus pattern relative to red and yellow (that in turn form stripes) or if red makes a pattern of spots relative to blue and yellow (that in turn makes a janus pattern) in Fig. 3 B and C. Decomposing the target pattern into spherical harmonics indicates if the pattern is reasonable (if the patterns are dominated by a few length scales) and at which length scales segregation should occur at. By tuning different parameter settings for the surface constituents until the effective interaction potentials transforms into an energy spectrum with the minima at the correct length scales we should obtain a system that self-assembles into the target pattern. We verify that there are no patterns with similar or lower energy levels by Monte Carlo simulations with simulated annealing of both the surface constituents and of a suspension of colloidal particles with the obtained functional

surface pattern.

The following sections cover examples of what is possible to design assuming different degrees of control over the energy spectrum and the interactions between surface constituents.

#### IV. SINGLE LENGTH SCALE COUPLED WITH STOICHIOMETRIC CONSTRAINTS

While the potentials of the model (Eqs. 1a and b) are clearly not realistic, striped patterns have been observed both in first principle simulations [11] and experiments [15]. There are fundamental theoretical reasons explaining why stripes are expected to appear universally [14]. This supports the idea that at least one (non l = 0) minimum in the energy spectrum can be selected for, the minimum that determines the length scale of the striped pattern. When combined with stoichiometric constraints, this is sufficient for causing hierarchical self-assembly of different crystal patterns.

Suppose, for example, that we want to cause patchy particles to self-assemble into a crystal pattern, a diamond or a cubic lattice. Simple patterns that achieve this are patches in each direction where a neighboring colloid should reside. For a diamond lattice, this means four patches equally distanced to each other on the surface of the nanoparticle, for a cubic lattice, the number of patches would be six. Expanding these patterns in terms of spherical harmonic functions shows that they are almost completely dominated by l = 0 modes, determining the stoichiometry, and l = 3 resp. l = 4 modes, deciding the length scale of the spotted pattern. By choosing parameters in the alkanethiol-on-gold model (or indeed, in an experimental setup) that causes the global minimum of the energy spectrum, as well as the stoichiometry, to coincide with the target pattern's will cause the target pattern to selfassemble, see Fig. 4 A. We verify that a group of particles with four or six attractive patches do assemble into respective lattice in Monte Carlo simulations with local moves using simulated annealing, Fig. 4 B-C.

# V. Single length scale coupled with stoichiometric constraints and segregating subtypes

Using only two particle types, the patterns tend to be spherically symmetric. The previous approach of selecting a single length scale usually falls short when trying to obtain more complicated (asymmetric) patterns. This issue can be remedied by introducing more types of surface constituents to a simple pattern of two types, e.g. the striped one in Fig. 3 A. Let us consider the introduction of very similar subtypes of one particle type; type *blue* is divided into type *blue* and *yellow*. These subtypes behaves identical at long range ( $L_{blue} = L_{yellow}$ ), but they are immiscible and tend to segregate, all else being equal. The system will strive towards segregating type *red* from the other in the earlier striped or spotted pattern, while also minimizing the subtype blue to yellow interfaces. If we choose a stoichiometry where the subtypes can completely occupy different spots and stripes that was previously *blue*, we can completely retain the ground state pattern, without any subtype interface. Such a pattern

must be a ground state.

This can be used to design hierarchical selfassembly of strings and membranes. Patterns with two patches at opposing sides of every nanoparticle would cause the self-assembly of a string, while a single attractive band at the equator would cause the self-assembly of a membrane. One way to self-assemble this pattern would be to choose parameters for a binary coating, where segregation occurs at length scale corresponding to l = 4 causing a striped pattern as the ground state. By differentiating type *blue* into subtypes *blue*, *yellow*, and green, we can ensure that e.g. yellow and green occupy each polar patch respectively, and blue occupies the equatorial stripe. If yellow and green are attractive, the polar patches will be too, causing self-assembly of strings. If *blue* is attractive, the nanoparticles will instead form membranes. Fig. 5 shows how this construction cause hierarchical self-assembly of string and membranes.

# VI. VARIOUS DEGREE OF IMMISCIBILITY COUPLED WITH STOICHIOMETRIC CONSTRAINTS

By controlling the strength of the energetic drive towards segregation, we can also cause hierarchical self-assembly of colloidosomes. A thin, circular, attractive band causes colloidal particles to self-assemble into a spherical shell, where the distance from the equator to the stripe determines the curvature. If the energy associated to the interface between a type red and a type *blue* is, for example, twice as large as the interfaces with type *yellow*, the *yellow* constituent will form a stripe separating the others. The features are represented in the energy spectrum as a large minimum at a low modulation number *l*, forcing two types to segregate to opposing sides and a much smaller minimum at the length scale corresponding to the width of the band that separates the two sides, see Fig. 6. Since the low *l* minimum is an order of magnitude larger than the second minimum, the ground state configuration will be one where type *blue* and *red* are separated



Figure 4: a) Phase separation at l = 3 together with a 4:1 ratio of blue:red surface constituents causes the ground state configuration to have four equally separated patches (solid line, left inset in a),  $L_{red} - L_{blue} = 1.33$  radii,  $\epsilon = 0.05$ ). With the minimum at l = 4 and a blue:red ratio of 3:1, the coating self-assembles into 6 patches instead (dashed line, right inset in a),  $L_{red} - L_{blue} = 1$  radius,  $\epsilon = 0.1$ ). On the colloidal scale, the small changes make the difference between a self-assembling diamond lattice b) or a cubic lattice c). Both surface patterns and the colloidal structures are obtained from Monte Carlo simulations using simulated annealing.



Figure 5: a) The global minimum causes segregation into two red stripes. The other three colors, being immiscible, fills in different segments caused by the red stripes. The inset in a) shows the self-assembled patchy particle from different directions. Depending on which segments are made attractive, the colloidal system self-assembles into different structures. With opposing ends attractive, we obtain strings b) and with an attractive central stripe, we obtain a self-assembled membrane c) when testing the interactions Monte Carlo simulations ( $L_{blue} = L_{yellow} = L_{green} = L_{red} - 1.1$  radii,  $\epsilon = 0.1$ ).

as much as possible. This differentiates the target pattern from e.g. one where *blue* and *red* forms a Janus sphere with *yellow* as an overlapping spotty pattern as can be seen in Fig. 4 C. The position of the attractive *yellow* stripe is only dependent on the stoichiometry and by adjusting the ratio between the surface constituents we can choose between colloidosomes with different curvatures, see Fig. 6.

#### VII. MULTIPLE MINIMA IN THE ENERGY SPECTRUM

We identify parameters in the alkanethiol-ongold model that cause self-assembly into colloidal particles with three orthogonal patches that are attractive, which will cause the colloidal particles to self-assemble into cubes. It turns out that this target requires a more complicated construction than the previous. The patches of the desired pattern are primarily described by l = 4 modes. With two polymer types, this minimum can cause a surface pat-

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Figure 6: a) The dominating global minimum separates red and blue to opposing sides of the colloid. The second minimum at l = 7 encourages an even yellow stripe of a thickness determined by the stoichiometry. By adjusting the stoichiometry, the distance to the yellow stripe and the equator can be tuned. b) A large distance from stripe to the equator will cause an attractive yellow stripe to force self-assembly of small colloidosomes. c) A smaller distance will cause the curvature of the surface of the colloidosomes to be lower and the container to be larger. All cross color particle interactions are shoulder potentials from  $\epsilon = -1$ ,  $L_{blue} = 0$ ,  $L_{yellow} = 0.17$  and  $L_{red} = 0.33$  radii , but interactions between yellow particles and the other colours are weaker (by a factor of 0.4). Without the large energy difference between red-blue interface compared to the other interfaces, it is difficult to find parameters that allow for a thin yellow stripe, as this goes against the principles of the design path (Many spherical harmonic overtones are required to define a thin stripe).

tern with 6 orthogonal patches, Fig. 4. To only obtain 3 patches, a third type is introduced with the intention of creating a Janus sphere with the patches on one of its two sides. The third polymer length *L<sub>vellow</sub>* is chosen so that the interaction potentials between the three different types, each different versions of Fig. 1, are equivalent to an energy spectrum exhibits a minimum at l = 1 that separates the third type from the previous two. An important property of the pattern is the specificity of the attractive patches. The three red patches are designed to be small in order to increase the precision of the bond between two colloidal particles, which prevents other geometric structures with bonds in similar directions to assemble. To achieve this we use a third minimum that also separates *blue* and *red* from *yellow* at approximately double frequency  $l = 2 \times 4$ . The yellow regions that separates *blue* and *red* makes those patches thinner/smaller. If we try to reduce the patch sizes by stoichiometry alone, i.e. small red patches separated by a large yellow region, other patterns described by fewer components of the basis tend to form instead.

All three features are present for the alkanethiol-on-gold model if we choose  $\epsilon = 0.15$ ,  $L_{blue} = 1.1$ ,  $L_{yellow} = 0$  and  $L_{red} = 0.66$  radii. Choosing a stoichiometry of 21% blue particles, 8% red particles and 71% yellow particles yields patches sufficiently small and with correct spacing, see the energy spectrum in the inset in Fig. 7. The spacing and patch size can be adjusted to some degree by slight changes in the stoichiometry. We verify the design by a Monte Carlo simulation of a colloidal suspension. In Fig. 7 we see a low energy configuration where several cubes have self-assembled.

It is not obvious from the beginning how the stripes and spots of the red and blue types would be arranged, but the theory predicts that the pattern should be dominated by as few Fourier modes as possible. [16] derives a limited set of such aggregate patterns defined by single spherical Bessel functions, among which our blue-red pattern can be found. The patterns in this set are good candidates as parts of a self-assembling surface patterns.



Figure 7: With greater control over the energy spectrum, more complex functional patterns can be made to self-assemble. a) Here three minima in the energy spectrum together encode for a pattern of three orthogonal red patches with high specificity. The first minimum concentrates red and blue to one side. The second minimum causes red patches to be separated by blue regions with a desired distance. The last minimum causes red and blue regions to be separated by yellow, allowing for a higher specificity. The parameters that caused this energy spectra are  $\epsilon = 0.15$ ,  $L_{blue} = 1.1$ ,  $L_{yellow} = 0$  and  $L_{red} = 0.66$  radii and ensure that the self-assembled surface pattern shown in inset from front and right have red patches in the correct positions. b) Surface patterns and cubic aggregates obtained from Monte Carlo simulations with simulated annealing when the red patches are assumed to be attractive show that the pattern causes self-assembly of cubic aggregates.

#### VIII. SIMULATION METHODOLOGY

We verify that the deduced parameter choices do cause self-assembly as intended using Monte Carlo simulations. The surface patterns shown in insets in Fig. 3-7 have been ob-

tained by swapping position of random pairs of surface coating constituents, and rejecting the change with a probability proportional to  $e^{-\Delta E/k_bT}$ .  $\Delta E$  is the change in surface configuration energy given by parameter choices and the corresponding interaction potentials, Fig. 1, during the annealing  $k_bT$  decays exponentially during  $5 \times 10^7$  iterations until the configuration freezes. The initial temperature was set high  $((k_B T)_{start}^{-1} \simeq 1)$  to ensure a slow relaxation through the metastable temperature range. There are only a few distinct regular tilings of a spherical surface. Therefore the surface sites' position was obtained by a Monte Carlo simulation with particles performing random short moves interacting with short range trapezoid-like potentials until a zero energy configuration was found (the interaction range chosen so that the surface would barely accommodate the 880 particles).

Self-assembly of the patchy particles themselves was also modelled using simulated annealing. The self-assembly was simulated in a box  $(20 \times 20 \times 20 \text{ radii})$  with periodic boundary conditions with around 60 particles susceptible to Brownian motion, with random moves of 1/100 radii and random rotations by a small angle. The interaction was modelled based on a square potential well giving a stickiness to the patches. More precisely, the potential energy between two particles was set to -1when two patches on the surface of the particles where within a distance of 1/10 radii. The surface of the particles was approximated as perfect circles with size and location obtained from the assembly of the surface constituents. This allows efficient modelling of particle interactions using simple geometric calculations (scalar products of vectors defining the centre point of the patches). We assume an increase in bond strength for more precisely aligned patches would only improve the self-assembly process. In these simulations  $(k_b T)_{start}^{-1} \simeq 10$ with the temperature dropping around 20% during annealing (simulation lengths on the order of  $2 \times 10^9$  sweeps). All patchy colloids simulations was done on low density systems in order to minimise the risk of gelation, and can

be considered to be colloidal aggregations. The design of the functional patterns ensure that the target geometric configuration is a ground state, i.e. all patches are connected. This means that the few defects found in the figures can be corrected using a sufficiently slow annealing from a temperature capable of breaking patch bonds.

The robustness of the self-assembly of colloidal particles very much depend on how the functional surface pattern was designed (most notably the patch size), how patches interact and which geometric structure one tries to achieve. For example the cubic aggregate configuration competes with long strings of paired particles, with the only difference in configuration energy comes from the unconnected ends of the strings. A low density colloidal suspension easily self-assembles into the desired cubic aggregates due to the lack of material to create long strings whereas at higher density the defect rate would be much higher. For the cubic lattice however, a high density of colloidal particles would only increase the rate at which the lattice assembles as there is no competing structures.

#### IX. DISCUSSION AND CONCLUSIONS

We introduce a design path for self-assembly of target patterns on the surface of spherical colloidal particles. We utilize that self-assembling systems have a strong tendency to form patterns with stripes and/or spots, which are used as functional patches on the next level when the colloidal particles self-assemble into target geometries. The central idea behind the first step in the design path is to match the essential features (the minima) of the energy spectrum of the effective interactions, to the maxima in the Fourier spectrum (an expansion in spherical harmonic basis functions) of the target surface pattern. By doing this the interactions are tuned to cause self-assembly of the target surface morphology. What structures can be made to self-assemble depend on the degree of influence we have over the interactions between surface constituents and the stoichiometry of the surface coating and we give examples of what is possible to self-assemble with different degree of control over the adhesion molecules' interactions.

The surface stoichiometry can be set by altering the molecular concentration in the solvent from which the adhesion molecules are adsorbed onto the colloidal particles [17]. There will be some variation in the stoichiometry in a large batch of self-assembling colloidal particles. Assuming the adsorption events are independent, this variation is described by a multinomial distribution. Obtaining relatively (to the size of the colloid) small patches comes at the cost of using either larger colloidal particles, smaller adhesion molecules, or accepting a larger amount of deviating colloidal particles during synthetization. We found that the sensitivity of the final configuration to changes in the stoichiometry varies from pattern to pattern. For the cubic lattice, assembled from colloidal particles with 6 patches, fig. 4, the colloidal pattern is very resilient to variation in the stoichiometry. We found in simulations that the correct configuration of patches form when the surface coverage of the patch forming constituent is within 11% to 35%. This interval is much larger than the standard deviation of 1.5% of the 900 adhesion molecules per colloid we use for simulations and the number of defective colloidal particles will be negligible (risk of deviating pattern is  $10^{-13}$ ). The intervals in which the correct patterns self-assemble have been obtained by multiple simulated annealing of a range of surface compositions to find in which range the target pattern is the most energetically favourable.

A more complicated pattern will be susceptible to stoichiometric changes. The window for when the cubic aggregate forming colloidal particles have the correct pattern is between 5,7% and 8% coverage of the type that forms attractive patches. With a standard deviation of 0.9% for the amount of this surface type, again assuming a multinomial distribution around the target stoichiometry, 90% of the colloidal particles would end up with the correct surface pattern. A simple model for alkanethiol molecules on gold nanoparticles shows that only a few parameters is sufficient for hierarchical selfassembly of a wide range of geometries, for example diamond lattices, colloidosomes and cubic aggregates.

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