Journal Name

ARTICLE

Electronic Supplementary Information
Self-assembly with colloidal clusters: facile crystal design using connectivity landscape analysis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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S1 Tetrahedral Cluster Sintering Extent

Directional binding on the faces of clusters is the result of distinct multivalent sites for docking of spheres. For tetrahedra, 4 trivalent sites are present—1 on each face of the cluster. In Fig. S1 (left), a trivalent binding site on one face of a tetrahedron is denoted by the red triangle, where each dotted circle at the vertices represents a contact patch between the cluster and a bond sphere. For low sintering extents the contact patches are well separated and lead to a unique, trivalent site for bond particles. With increasing sintering extent, σ'_B/σ_B, beyond about 0.53-0.56 (see main text), the 3 binding sites become merged, weakening the preferential nature of the trivalent bonding; Fig. S1 (right). This sintering constraint represents a hard boundary that cannot be crossed for all of the superstructures considered in the present study.

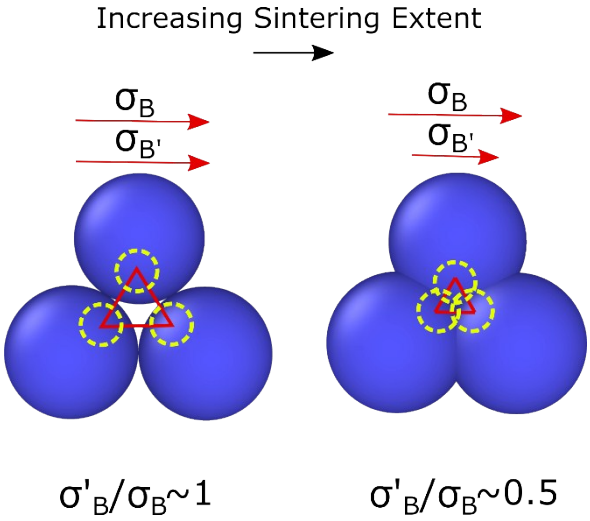

Fig. S1 Evolution of the trivalent binding site on the faces of tetrahedral clusters. The unique trivalent site is weakened once the sintering extent exceeds a critical value of about 0.5.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

S2 Connectivity Analysis

The expressions corresponding to the various pairs of coloured lines in the connectivity landscapes (Figs. 3-6 in the main document) are derived analytically by calculating the distances between different types of particles in the superstructure for a given set of particle sizes and then assessing the connectivity in the superstructure. The bounds for each connectivity zone are computed by introducing a parameter, α, whose value is 1.00 when a pair of particles is in hard contact and 1.15 when the distance between the particle pair corresponds to the fully-stretched limit of the DNA-mediated interaction between the particles. The 1.15 value is based on the maximum range of the DNA-mediated potential of about 60 nm, normalized by the 400-nm particle diameter considered in the present study.

S2.1 $MgCu_2$/$MgSnCu_4$

For the $MgCu_2$ and $MgSnCu_4$ superstructures (Sections 3.1 and 3.2 in the main document), σ_B represents the diameter of B particles, σ_{C1} and σ_{C2} represent the diameters of the two types of C particles. Particle size ratios are defined as $r_{CB}=\frac{\sigma_{C1}}{\sigma_B}$ and $r_C=\frac{\sigma_{c2}}{\sigma_{C1}}$. Note that for the $MgCu_2$ structure, $r_C=1$. The sintering parameter is defined as $s_B=\frac{\sigma_B^{'}}{\sigma_B}$ where $\sigma_B^{'}$ is the centre-to-centre distance of two B particles belonging to the same tetrahedral cluster.

Constraint	Equation
blue	$r_{CB}=\sqrt{\frac{4}{3}s_B^2+\frac{3}{2}(\alpha+\frac{2}{3}s_B)^2}-1$
yellow	$r_{CB}=\frac{\frac{\alpha}{\sqrt{24}}(1+r_C)s_B+\frac{1}{2}+\sqrt{(\frac{\alpha}{\sqrt{24}}(1+r_C)s_B+\frac{1}{2})^2-(\left(\frac{\alpha}{2}(1+r_C)\right)^2-\frac{1}{4})(\frac{9}{6}s_B^2-1)}}{\frac{\alpha^2}{2}(1+r_C)^2s_B-\frac{1}{2}}$
orange	$r_{CB}=\frac{\frac{\alpha\sqrt{6}}{8}(1+r_C)s_B+\frac{3}{8}r_C+\sqrt{(\frac{\alpha\sqrt{6}}{8}(1+r_C)s_B+\frac{3}{8}r_C)^2-(\left(\frac{\alpha}{2}(1+r_C)\right)^2-\frac{3}{16}{r_C}^2)(\frac{9}{8}s_B^2-\frac{3}{4})}}{\frac{\alpha^2}{2}(1+r_C)^2-\frac{3}{8}{r_C}^2}$
pink	$s_B>0.57$

Table S1: Blue lines bound a region where B-B and C-C connectivity are accommodated simultaneously, yellow and orange lines bound similar regions for B-C (B-C1 and B-C2, respectively, for the yellow and orange cases) and C-C connectivity. The pink boundary represents the sintering limit described in Section S1 above.

S2.2 Diamond Configuration

For the diamond configuration (Section 3.3 in the main document) formed by closed sintered tetrahedra and spheres, the relevant geometric parameters are $s_B=\frac{\sigma_B^{'}}{\sigma_B}\ and\ r_{CB}=\frac{\sigma_C}{\sigma_B}$. The geometric constraint expressions shown graphically in Figure 5 of the main document are listed in Table S2.

Constraint	Equation
blue	$r_{CB}=\sqrt{\alpha^2+s_{B\text{-}1}^2}$
red	$r_{CB}<\frac{2}{\sqrt{2+s_B^2}}-1$
pink	$s_B>0.57$

Table S2: Blue lines bound a region where B-B and C-C connectivity are accommodated simultaneously. The red line delineates the boundary at which defective sites are formed in the superstructure that are energetically degenerate with the correct sites for docking bond spheres. In this context, correct sites represent the trivalent sites on a single cluster face, while the defective trivalent sites are formed at the interstices between adjacent clusters. The pink line represents the cluster sintering constraint described in Section S1.

S2.3. Zincblende Configuration

For the zincblende configuration (Section 3.4 in the main document) formed by open sintered tetrahedra and spheres, the relevant geometric parameters are $s_B = \frac{\sigma_B}{\sigma_B}, r_{CB} = \frac{\sigma_B}{\sigma_C}$, and $r_{CA} = \frac{\sigma_C}{\sigma_A}$. The geometric constraint expressions shown graphically in Figure 6 of the main document are listed in Table S3. Note that in Figure 6 of the main document, $r_{CA} = 1$.

Constraint	Equation
blue	$r_{CB} = \sqrt{\frac{3}{2\alpha(1+r_{CA})}}\ (1+s_B)$
yellow	$r_{CB} = \frac{\frac{4}{\sqrt{24}}\alpha(1+r_{CA})s_B + 2 + \sqrt{(\frac{4}{\sqrt{24}}\alpha(1+r_{CA})s_B + 2)^2 - (6{s_B}^2 - 4)(\alpha^2(1+r_{CA})^2 - 1)}}{2\alpha^2(1+r_{CA})^2 - 2}$
cyan	$r_{CB} \geq \frac{\sqrt{\frac{3}{2}}s_B - 1}{r_{CA}}$
pink	$s_B > 0.57$

Table S3: Blue lines bound a region where B-B and A-C connectivity are accommodated simultaneously and the yellow lines bound a region where B-C and A-C connections are simultaneously present. The pink and cyan lines represent different constraints on the extent of cluster sintering (see main document).