Programming Hierarchical Self-Assembly of Patchy Particles into Colloidal Crystals via Colloidal Molecules

Daniel Morphew, James Shaw, Christopher Avins, and Dwaipayan Chakrabarti*

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

E-mail: d.chakrabarti@bham.ac.uk

SUPPORTING INFORMATION

The present study demonstrates the self-assembly of triblock patchy particles into colloidal crystals with a two-level structural hierarchy. The results are presented here primarily for two sets of model parameters. The set of model parameters comprises $\epsilon_{\rm AA}$, $\epsilon_{\rm BB}$, α, β, s, and κ, where $\epsilon_{\rm ij}$ is the depth of the potential due to the patch i - patch j interaction when the two patches face each other, α and β are the half-opening angles for patch A and patch B, respectively, κ is the inverse Debye length and the parameter s controls the range of the patch-patch interactions. Here our focus is on the following parameter sets:

(1) $\epsilon_{\rm AA} = 5$, $\epsilon_{\rm BB} = 1$, $\alpha = 80^\circ$, $\beta = 40^\circ$, $s = 5$, and $\kappa = 100$;

(2) $\epsilon_{\rm AA} = 5$, $\epsilon_{\rm BB} = 1$, $\alpha = 85^\circ$, $\beta = 40^\circ$, $s = 1$, and $\kappa = 100$.

In the presence of a hierarchy of interactions, a two-step temperature-control protocol was shown to be successful to induce the self-assembly of the cubic diamond crystal with a two-level structural hierarchy. We therefore followed such a protocol for a system of $N = 500$

*To whom correspondence should be addressed

triblock patchy particles in virtual-move Monte Carlo (VMMC) simulations to assess the robustness of the assembly behavior over the parameter space, which is rather large. Some systematic variation of the parameters around the first set of parameters in particular was undertaken. Our results are summarized below in Supporting Table S1. We also undertook a series of VMMC simulations, where the system was subject to gradual cooling with the range parameter s set to 10, the other parameters remaining intact as in the first set of parameters; the patch-patch interactions are relatively short-ranged for $s = 10$. We again observed the formation of a cubic diamond crystal at low values of the reduced temperature. Since the ratio $\epsilon_{AA}/\epsilon_{BB}$ is crucially important for the success of the two-level self-assembly, we used $\epsilon_{BB} = 1$ and chose to vary ϵ_{AA}.

Table S1: A summary of systematic variation of the parameters undertaken in virtual-move Monte Carlo simulations following a two-step temperature-control protocol. One parameter was varied at a time with reference to the first set of parameter values, which appear in black along a row. The different values of a given parameter appear along a column and are color coded. The entries are in green if the formation of the cubic diamond crystal with a two-level structural hierarchy was observed in the simulations; the entries are in orange if the crystal formation was not observed but tetrahedral clusters were present in high yields ($> 90\%$); if even the tetrahedral clusters were not observed in sufficient yields, the entries are in red.

α	β	ϵ_{AA}	κ
60			
70	**30**		
75	**35**	**2.5**	**50**
80	**40**	**5**	**100**
85	**45**	**7.5**	**200**
90	**50**		

Supporting Figures

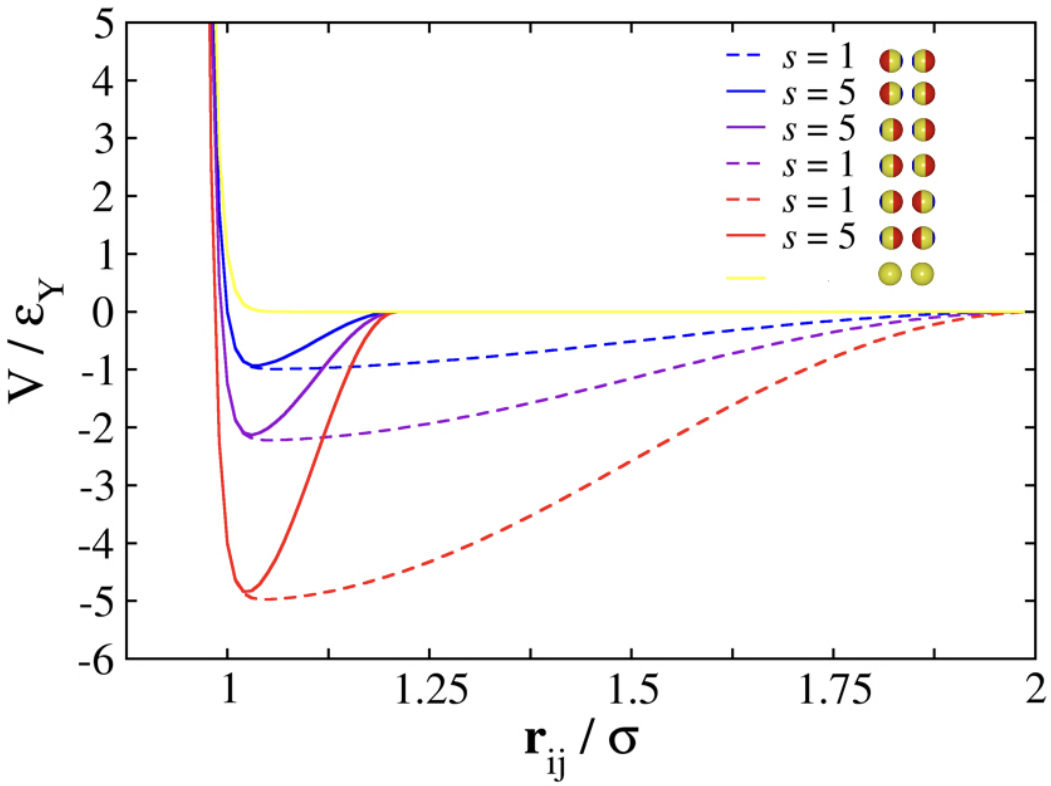

Figure S1: The effective pair potential for the patchy particles under consideration as a function of separation for three different orientations and two values of the potential parameter s. The following potential parameters are kept constant: $\epsilon_{\mathrm{AA}} = 5$, $\epsilon_{\mathrm{BB}} = 1$, $\alpha = 80°$, $\beta = 40°$, $\kappa = 100$. Here ϵ_{ij} is the depth of the potential due to the patch i - patch j interaction when the two patches face each other, α and β are the half-opening angles for patch A and patch B, respectively, κ is the inverse Debye length and the parameter s controls the range of the patch-patch interactions. The isotropic component, given by the Yukawa potential U_{Y}, is shown separately in yellow.

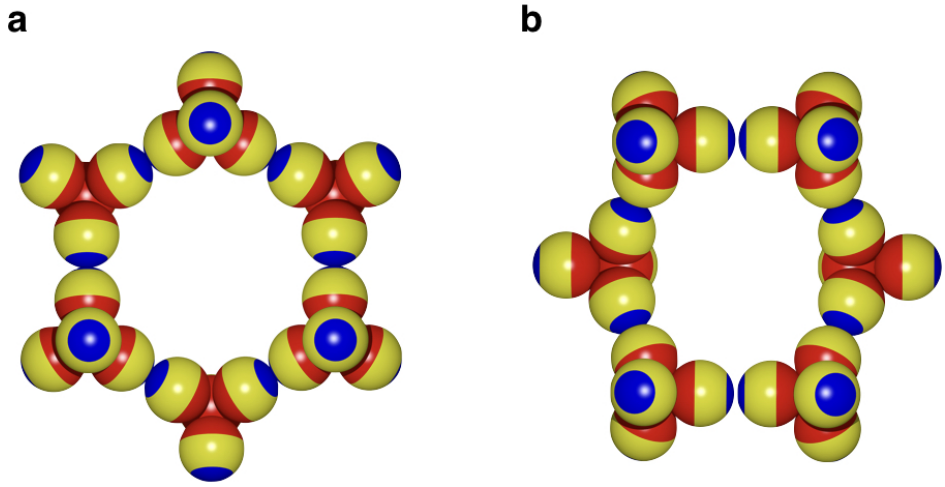

Figure S2: Two most stable structures for the 24-particle cluster of triblock patchy particles for the set of potential parameters: $\epsilon_{\mathrm{AA}} = 5$, $\epsilon_{\mathrm{BB}} = 1$, $\alpha = 80°$, $\beta = 40°$, $\kappa = 100$, and $s = 5$. The ring-like structures are formed with tetrahedral subunits in (a) 'chair' and (b) 'boat' conformations.

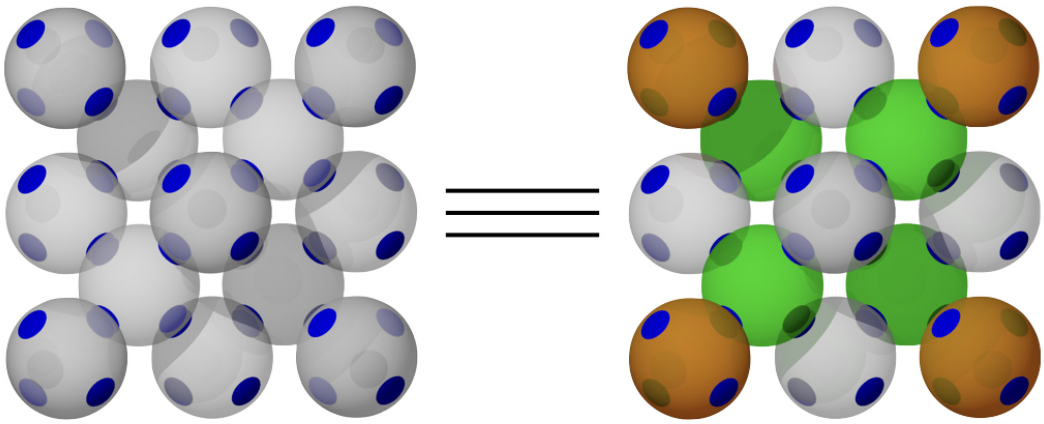

Figure S3: A perfect cubic diamond lattice formed by patchy particles, each with four patches in tetrahedral symmetry. On the right, the same structure is shown with color-coding to highlight distinct sites: vertex sites (orange), face-centered sites (grey), and tetrahedral sites (green).

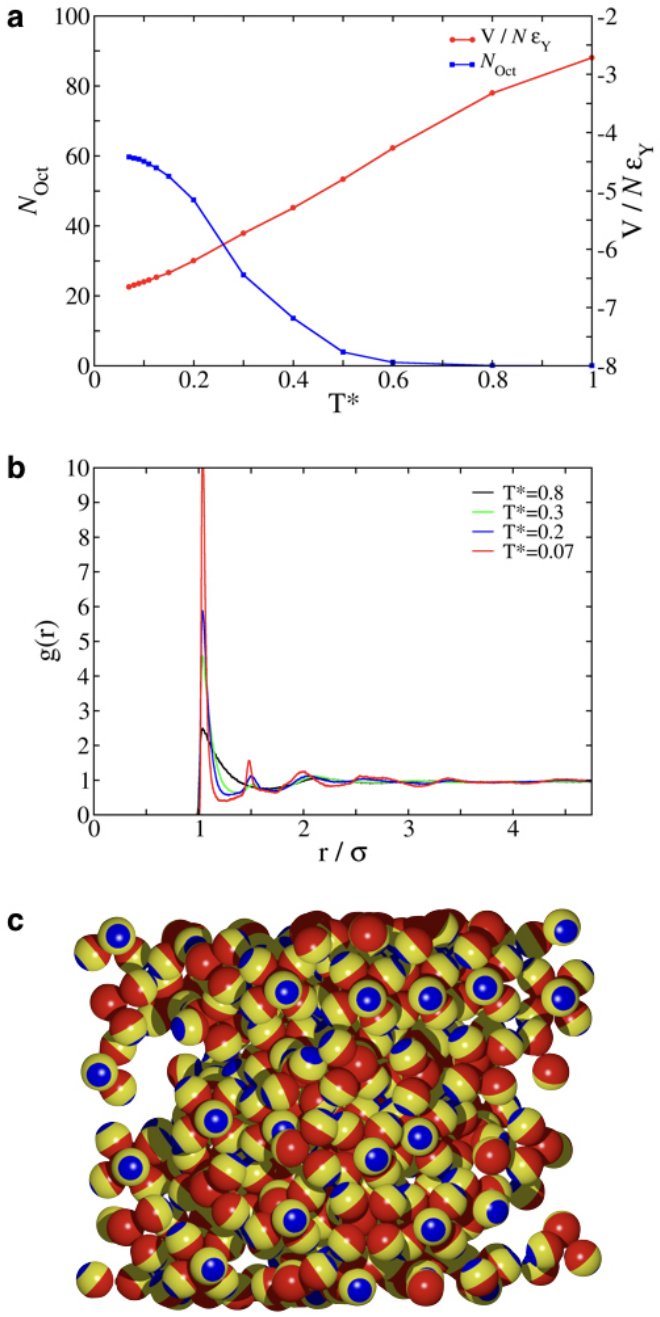

Figure S4: Self-assembly of patchy triblock colloidal particles. Here the half-opening angle of the stronger patch A is $\alpha = 80°$ instead of $\alpha = 85°$ with the remaining parameters as in the second set. (a) The average potential energy per particle in the reduced unit, $V/(N\epsilon_{\mathrm{Y}})$, and the number of octahedra formed, N_{Oct}, shown on two different scales, as a function of the reduced temperature $T^{\star}$ for an $N = 500$ particle system at the volume fraction $\phi = 0.3$. (b) The pair distribution function $g(r)$ for the patchy particles at four different reduced temperatures. (c) A snapshot of a typical low-temperature configuration, showing the presence of both octahedra and tetrahedra formed at the first level of assembly.

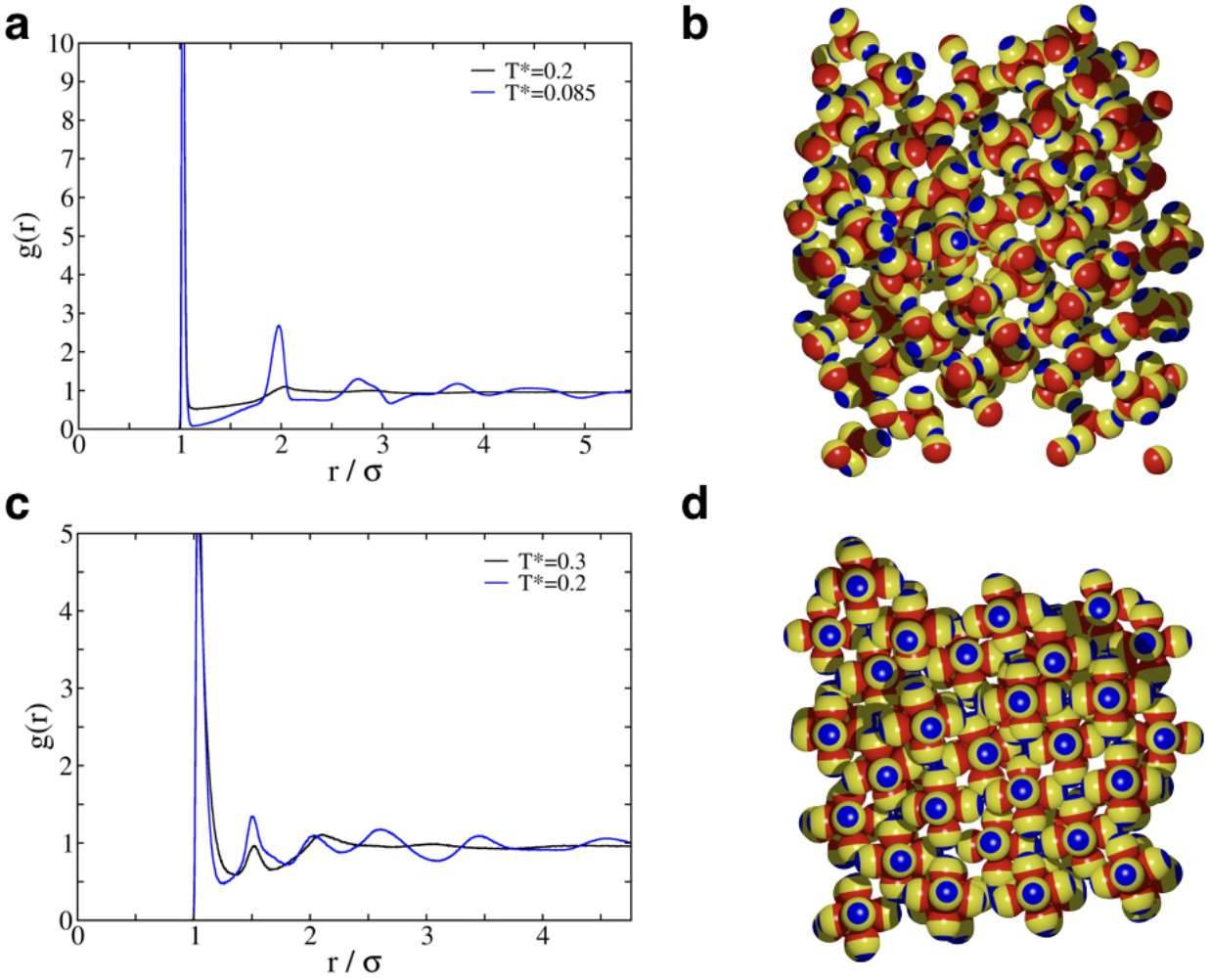

Figure S5: The two-level hierarchical self-assembly of triblock patchy particles into colloidal crystals observed in the presence of polydispersity in patch sizes. (a) The pair distribution function $g(r)$ for the patchy particles at two different reduced temperatures for the first parameter set with allowance for polydispersity in both patch sizes. (b) A snapshot of a typical configuration at $T^\star = 0.085$, illustrating a two-level structural hierarchy into a cubic diamond crystal via tetrahedra. (c) The pair distribution function $g(r)$ for the patchy particles at two different reduced temperatures for the second parameter set with allowance for polydispersity in both patch sizes. (d) A snapshot of a typical configuration at $T^\star = 0.2$, illustrating a two-level structural hierarchy into a body-centered cubic crystal via octahedra.