Supporting Information:
Magnetic Coupling in Colloidal Clusters for Hierarchical Self-Assembly

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Cluster Property Comparison.

In Figures S1-S8 we showcase the data for the other cluster sizes investigated in this work and not singularly shown in the main text, namely $n = 2, [4, 10]$. It is important to recall however that this cluster data is summarised in Figure 5 of the manuscript as well. As a reminder to the reader, Figures S1-S8 describe and monitor cluster formation for each cluster size respectively and compare the evolution for sphere and cube clusters. The plot grid displays the data for each particle type in each column, cubes ($m = 4$) and spheres ($m = 2$). Each cluster property observable is plotted in each row as follows, second moment of the mass distribution $M_2$, total dipole moment of a cluster $M$, and the total magnetic interaction energy $U_m$. Each quantity is normalised to allow the data for different cluster sizes to be viewed on an equal footing. The evolution of each quantity is plotted in units of the simulation time-step $\Delta t$. The fifty replica compression runs performed for each type of cluster are shown in each plot, provided that the run completed successfully. The evolution of each replica was smoothed by calculating the moving average over 200 measures. The compression scheme used meant that the reduction in droplet size at each iteration was reduced as the simulation progressed. As the iteration length was kept fixed this equates to the confinement being applied more slowly as the system increased in density and thus facilitated the search for equilibrated structures.

The same conclusions reached in the manuscript with regards to the similarities and differences in cluster formation for cubes and spheres are applicable for the cluster sizes shown here, save for a few minor points which we will address shortly. The conclusion of the manuscript can be summarised as the ability of sphere clusters to repeatedly reproduce the same structural arrangements of the constituent particles but also their dipole configurations as well. Cubes struggle to achieve both, managing the former, not the latter. This summary holds true for $n = [4, 9]$, where we see a convergence of $M_2$, $M$, and $U_m$ for all replicas in the case of spherical particles, but multiple final values in $M$, and $U_m$ but not $M_2$ for cube clusters indicating the structural consistency but magnetic frustration. In the case of $n = 2$ we have some broader variations in the terminal values of $M$, and $U_m$ in the replicas, this can be attributed to the fact that, as the evaporation process comes to an end, the linearity of the
structure makes it less rigid and therefore more susceptible to deformations by the evaporating droplet. A similar observation can be made for the spherical cluster of $n = 10$, where $U_m$ has a bifurcation, a sign of two structures with different dipolar configurations. We attribute this to the fact that as the cluster size increases, the number of available microstates increases rapidly, making it harder for the system to consistently rearrange to the same final state, it seems the $n = 10$ is where this effect begins to manifest.

Cluster Aggregation

In this section we reproduce the monolayer snapshots in the full field of view for the clockwise case. This is shown in Figure S9. In contrast to the manuscript, here in Figure S9c-e we visualise the lattice pattern only and do not show the gradient transition. This choice holds for the subsequent figures as well. In Figure S10 we show the monolayer for the anticlockwise oriented cluster. As can be seen from the stills, the structure of the aggregated monolayer is akin to the clockwise variant as one would expect. However, moving to Figure S11 where we visualise the racemic mixture, one clearly notes that the monolayer is significantly less aggregated. The presence of the two enantiomers frustrates the self-assembly process resulting only in small areas of agglomeration between clusters of the same handedness. Given sufficient time one would expect the system to perform a kind of phase separation into distinct regions of each enantiomer. It is clear that when chirality is imposed on the system due to the strict two dimensional topology of the monolayer that enantiomerically pure systems offer the best route to hierarchical assembly.
Figure S1: Cluster Size: \( n = 2 \)
Figure S2: Cluster Size: $n = 4$
Figure S3: Cluster Size: $n = 5$
Figure S4: Cluster Size: $n = 6$
Figure S5: Cluster Size: $n = 7$
Figure S6: Cluster Size: $n = 8$
Figure S7: **Cluster Size: \( n = 9 \)**
Figure S8: Cluster Size: $n = 10$
Figure S9: **Monolayer Snapshot:** Clockwise trimers only at $\varphi_A = 0.4$ (a) Monolayer structure. (b) Dipole configuration, where the centre of mass of each cluster is indicated by the sliver sphere. (c) Dipole lattice with staggered kagome symmetry (see main text for details about the structure). (d) Particle lattice with bounce symmetry. (e) Lattice based on the cluster centre of mass with honeycomb symmetry.
Figure S10: Monolayer Snapshot: Anticlockwise trimers only at $\varphi_A = 0.4$ (a) Monolayer structure. (b) Dipole configuration, where the centre of mass of each cluster is indicated by the sliver sphere. (c) Dipole lattice with staggered kagome symmetry (see main text for details about the structure). (d) Particle lattice with bounce symmetry. (e) Lattice based on the cluster centre of mass with honeycomb symmetry.
Figure S11: **Monolayer Snapshot:** Racemic mixture of trimers at $\varphi_A = 0.4$ (a) Monolayer structure. (b) Dipole configuration, where the centre of mass of each cluster is indicated by the sliver sphere. (c) Dipole ‘lattice’. (d) Particle ‘lattice’. (e) Lattice based on the cluster centre of mass. (c-e) Lattice formation here is extremely limited and only occurs in isolated regions and has minimal extent.