Tunable assembly of heterogeneously charged colloids - Supplementary material

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The Coarse-Grained Model

For the particle-particle interaction, we employ the coarse-grained description of IPCs introduced in Ref.7. Figure S 1 represents a coarse-grained inverse patchy colloid (IPC) in the vicinity of a substrate. The model features a spherical, impenetrable colloid (of radius \( \sigma \) and central charge \( Z_c \)) carrying two interaction sites (each of charge \( Z_p \)) located at a distance \( e < \sigma \) in opposite directions from the particle center. The electrostatic screening conditions (expressed via the Debye screening length \( \kappa^{-1} \)) determine the range \( \delta \) of the pair interaction independently of the relative orientation of the particles. For each set \((\sigma, e, \delta)\) the patch size, defined by the opening angle \( \gamma \), is uniquely determined by Eqs. 10 and 11 of Ref.7. We fix the interaction range \( \delta = 0.4\sigma \) (corresponding to \( \kappa\sigma = 5 \) with the choice \( \kappa\delta = 2 \)) and \( \gamma \approx 60^\circ \) (corresponding to \( e = 0.32\sigma \)). The energy strengths appearing in Eq. 13 of Ref.7 depend on the choice for \((Z_c, Z_p)\) and are set by mapping

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(with the so-called “max” scheme) the coarse-grained potential to the analytical Debye-Hückel potential developed for IPCs in water at room temperature. The minimum of the equatorial-polar attraction, \(|\epsilon_{ep}|\), sets the energy unit. We consider two IPC-types, namely overall neutral particles, i.e. \(Z_{tot} = Z_c + 2Z_p = 0\), and overall charged units with \(|Z_c/2Z_p| > 1\); in the latter case we choose a non zero value for \(Z_{tot}\) such that the equatorial-equatorial repulsion is comparable to the polar-polar repulsion: \(Z_{tot} = -\frac{2}{3}Z_p\), i.e. the net particle charge is of the same sign as \(Z_c\). Figure S 2 reports the particle-particle potentials for both neutral and charged IPCs. We note that the induced dipole-dipole interactions between two colloids at contact scale as \(U_{dd}(r \approx 2\sigma) \approx Z^2_w/|\epsilon\sigma|\), where \(\epsilon\) is the dielectric permittivity of the solvent. For the values of \(Z_w\) employed here, \(U_{dd}\) is several orders of magnitude smaller than the Debye-Hückel interaction and thus can be safely ignored.

For the particle-wall interaction, we consider the coarse-grained description introduced in Ref. in full consistency with the particle-particle description. The interaction between a coarse-grained IPC and a neutral wall perpendicular to the z-axis is a steric interaction modeled as a hard repulsion taking place when the particle is located at distance \(z \leq \sigma\) from the wall. In the presence of a charged wall with surface charge \(\sigma_w = Z_w/4\sigma^2\), a screened electrostatic interaction must be added to the hard particle-wall repulsion. We consider walls that carry a surface charge with either the same sign as the patches (i.e., \(Z_wZ_p > 0\)) or the same sign as the bare colloid (i.e., \(Z_wZ_p < 0\)). We choose a very small value for \(Z_w\) as compared to \(Z_p\), i.e. \(Z_w = \pm\frac{5}{33}Z_p\). The specific value of the wall charge is such that, when \(Z_wZ_p > 0\), the corresponding minima of the particle-wall attraction of the two selected IPC-types are comparable to each other, being at the same time also comparable to the particle-particle bonding energy. We note that for \(\sigma\)-values ranging from a few nanometers to some micrometers, the chosen \(\sigma_w\) are well below one elementary charge per 60\(\AA^2\). Figure S 2 reports the particle-wall potentials for both neutral and charged IPCs in the presence of a substrate such that \(Z_wZ_p > 0\).

We perform Monte Carlo (MC) simulations of IPC systems with \(N = 1000\) particles in the canonical ensemble at \(T^* = 0.10\) (temperature in reduced units, i.e., \(T^* = k_BT/|\epsilon_{EP}|\)) in a volume \(V = hL^2\), where \(L = 100\sigma\) and \(h = 2.9\sigma\) (tight confinement) or \(h = 4\sigma\) (loose confinement). Under
tight confinement particles are prevented from sitting on top of each other, while under loose
confinement two particles at contact can assemble along the z-axis. Each MC step consists on
average of $N$ trial particle moves, where the acceptance rule is given by the Metropolis criterion.
A particle move is defined as both a displacement in each Cartesian direction of a random quantity
distributed uniformly between $\pm \delta r$ as well as a rotation around a random axis of a random angle
distributed uniformly between $\pm \delta \theta$. The chosen values for the trial changes are $\delta r = 0.1 \sigma$ and
$\delta \theta = \delta r / 2 \sigma$ rad. Since the aggregation processes are studied out of equilibrium, we run for each
IPC-type 10 parallel MC runs, starting from different initial conditions. Each run lasts for a total
of $10^7$ MC steps. To test the charging-decharging processes, longer MC simulations for a total
of $10^8$ are run for smaller systems, i.e. $N = 400$ and $L$ leading to the same constant $\rho_{av}$. All
quantities shown in this paper are averages over the final $10^3$ MC steps, corresponding to 100
different configurations per independent run.
Figure S 1: Schematic representation of a coarse-grained IPC. The dark gray central sphere corresponds to the hard colloid, the yellow caps represent the polar patches, the light gray halo features the interaction sphere of the bare colloid. It is worth noting that IPCs are spheres: the yellow caps only feature the interaction sphere of the bare patches, whose centers are located inside the colloid. The unit vector $\hat{n}$ defines the particle orientation with respect to the direction $\hat{z}$, the normal to the bottom wall, shown in a light blue color.
Figure S 2: Panels A and B: representation of the coarse-grained particle-particle interaction for both overall neutral and overall charged IPCs with a broad patch extension. Panel A shows three characteristic particle-particle orientations for two IPCs at contact ($r = 2\sigma$), namely the polar-polar (pp), the equatorial-equatorial (ee) and the equatorial-polar (ep) configurations. In each of these configurations, the continuous black arrows indicate the translation direction of one IPC with respect to the other, while the dashed circles with one central dot represent the rotation of one IPC around an axis perpendicular to the plane. In the two top/bottom graphs of panel B, the radial/angular dependence of the particle-particle interaction between two IPCs in the three characteristic configurations is shown: the green/blue/red continuous/dashed/dash-dotted line corresponds to an initial configuration where the two colloids are at contact and have reciprocal orientation referred to as pp/ee/ep. Panels C and D: representation of the coarse-grained particle-wall interaction for both overall neutral and overall charged IPCs when the wall charge is such that $Z_w Z_p > 0$; when $Z_w Z_p < 0$, the particle-wall interaction curves can be obtained by simply inverting the signs of the displayed curves. Panel C shows two characteristic particle-wall orientations for an IPC at distance $r = \sigma$ from the wall, namely the polar-wall (pw) and the equatorial-wall (ew) configurations; the planar wall is reproduced in light blue on the left side with respect to the IPC; continuous arrows and dashed circles represent respectively the translational and rotational moves of the IPC with respect to the wall. In the two top/bottom graphs of panel D, the radial/angular dependence of the particle-wall interaction is shown: the turquoise/magenta continuous/dashed line corresponds to an initial configuration where the two colloids are at contact and have reciprocal orientation referred to pw/ew. All energies are in units of $|\varepsilon_{ep}|$ at contact.
The Order within the Aggregates

The spatial order of the particle arrangements can be quantified via the radial distribution functions, $g(r)$, depicted in panel A of Figure S 3. The fluid-like spatial arrangement of overall neutral particles observed when $Z_wZ_p > 0$ is confirmed by an almost structureless $g(r)$. For the other two cases of wall charge the corresponding $g(r)$ shows the typical peak pattern of triangular ($Z_wZ_p = 0$) and square ($Z_wZ_p > 0$) lattices, respectively. In a similar fashion, the formation of triangular lattices of overall charged particles irrespective of the substrate charge is fully confirmed in the $g(r)$.

To quantify the orientational order of our particle arrangements we have evaluated probability distribution functions for different characteristic angles. Introducing the orientational vectors of two neighboring particles, $\hat{n}_1$ and $\hat{n}_2$, we define two-particle angles $\alpha$ and $\alpha_{xy}$ and the single-particle angle $\alpha_z$ via

$$\cos \alpha = \hat{n}_1 \cdot \hat{n}_2, \quad \cos \alpha_{xy} = \frac{\hat{n}_{1,.} \cdot \hat{n}_{2,.}}{||\hat{n}_{1,.}|| \cdot ||\hat{n}_{2,.}||}, \quad \cos \alpha_z = \hat{n}_i \cdot \hat{z},$$

(1)

$\hat{n}_{i,.}$ being the projection of vector $\hat{n}_i$ (shown in Figure S 1) onto the xy-plane. The orientational probability distributions are calculated taking into account only bonded IPCs with the same number of bonded interactions. By construction, when the probability distributions $P(\alpha)$ and $P(\alpha_{xy})$ have similar values, the particles are preferentially oriented in a direction parallel to the walls; otherwise, the difference between these functions provides information about how strongly the symmetry axes of the particles are tilted out of the horizontal plane. The respective probability distributions are summarized in panels B1-B3 of Figure S 3 for IPCs in their typical bonding environment, i.e., for triangular/square arranged domains only IPCs with six/four bonds are considered. In each panel schematic views of the corresponding unit cells are reproduced, highlighting the symmetry axes of the central particle and its first nearest neighbors.

For the grain-like particle arrangement (panel B1) $P(\alpha_{xy})$ is characterized by two maxima. The first one, observed at $\alpha_{xy} \approx 90^\circ$, corresponds to the T-shape arrangement of four out of six neighboring particles in the unit cell. From the fact that $P(\alpha) \sim P(\alpha_{xy})$ for $60^\circ \lesssim \alpha, \alpha_{xy} \lesssim 90^\circ$, ...
we conclude that the symmetry axes of such particles are predominantly oriented parallel to the substrate. The other maximum in $P(\alpha_{xy})$, observed at $\alpha_{xy} \sim 0$, corresponds to the orientation of the remaining two neighboring particles: the projected orientational vectors of such particles are essentially parallel to the projected orientational vector of the central particle. However, differences in $P(\alpha)$ and $P(\alpha_{xy})$ for $0 \lesssim \alpha, \alpha_{xy} \lesssim 60^\circ$ indicate that the orientational vectors of two neighboring particles are twisted with respect to each other.

For the flower-like particle arrangement (panel B2) the two distribution functions coincide for $\alpha, \alpha_{xy} \sim 60^\circ$. This confirms on a quantitative level that (i) the preferred angle between the orientational axes of two neighboring “petal” particles is compatible with a ring-like structure, and (ii) the orientational vectors of the petals are nearly horizontal. The fact that $P(\alpha)$ has a second, pronounced maximum at $\alpha \sim 90^\circ$ reflects the second, characteristic feature of the flower-like particle arrangement, namely the (essentially) “up-right” orientation of the central particle. The difference between $P(\alpha)$ and $P(\alpha_{xy})$ for $0 \lesssim \alpha \lesssim 40^\circ$ is due to the fact that the central particle of the flower-like structure fluctuates around the vertical, thus its orientational vector has always a non-zero projection on the xy-plane, which covers a broad spectrum of angles with the projections of the petals.

For the square-like particle arrangement (panel B3) the functions $P(\alpha)$ and $P(\alpha_{xy})$ essentially coincide; consequently the particle symmetry axes are oriented predominantly along the horizontal direction. The pronounced maximum of the two functions for $\alpha \sim 90^\circ$ confirms in an unambiguous manner that the first nearest neighbors of a particle are in a T-shape configuration.

Additional information about the orientational order within the crystalline domains can be gained by the combined probability distribution function $P(\alpha, \alpha_z)$ represented in panels C1-C6 of Figure S 3 in contour plots; data are shown for charged and neutral particles that condensate, respectively, in grain- and flower-like arrangements in the presence of a neutral substrate. The panels show, from left to right, results of $P(\alpha, \alpha_z)$ for two-, four-, and six-bonded particles. Panels showing data for the other particle charge/wall charge combinations are summarized for completeness in Figure S 4.
Data shown in panels C1-C3 of Figure S 3 fully confirm the specific features of a grain-like particle arrangement: fully bonded, six-fold coordinated particles whose symmetry axes are either perpendicular or parallel to each other, being at the same time oriented in the horizontal direction with respect to the confinement geometry. The pronounced maximum of $P(\alpha, \alpha_z)$ in the region where $\alpha, \alpha_z \sim 90^\circ$ for IPCs with six bonds provides evidence that the overwhelming part of the particles have an ideal, grain-like structural surrounding. Reduced in its intensity and blurred by a poorer statistics, essentially the same behavior of $P(\alpha, \alpha_z)$ is observed if we perform this probability analysis, considering only four- and two-bonded particles. This allows us to draw the following two conclusions: (i) precursors of the ideal grain-like particle arrangement are already anticipated in smaller aggregates formed by particles that are not-fully bonded; (ii) the information about the specific features of the grain-like arrangement is not only stored in particles located in the center of a domain, but also in particles that populate the boundary regions; thus as particles condensate on an existing cluster, they arrange immediately in such a way as to allow a continuous and undisturbed growth of the grain-like pattern within a domain.

In a similar manner, data displayed in panels C4-C6 of Figure S 3 confirm the specific features of the flower-like particle arrangement: the pronounced maximum of $P(\alpha, \alpha_z)$ for $\alpha \sim 60^\circ$ and $\alpha_z \sim 90^\circ$ corresponds to the specific mutual orientation of the symmetry axes of two neighboring petals of the flower-like pattern, while the peak appearing at $\alpha \sim 90^\circ$ and $\alpha_z \sim 0^\circ$ corresponds to the up-right particles in the center of the flowers. Also in this case, the specific features of the bonding pattern are essentially reflected in the contour plots of $P(\alpha, \alpha_z)$ for two- and four-bonded particles, with the exception of the peak corresponding to vertically oriented IPCs, which appears only when a particle has more than two bonds.
Figure S 3: **Panel A**: radial distribution functions, $g(r)$, for both neutral (main panel) and overall charged (inset) particle systems under tight confinement and close to differently charged substrates, as labelled. The $g(r)$ are shifted with respect to each other in order to help the visualization. **Panels B1-B3**: orientational probability distributions $P(\alpha)$ (dashed lines) and $P(\alpha_{xy})$ (continuous lines) as function of $\alpha$ and $\alpha_{xy}$, respectively, where $\alpha$ and $\alpha_{xy}$ are defined in Eq. 1. The orientational probability distributions are calculated for tight confinement cases taking into account bonded IPCs in their typical bonding environment, i.e., the number of bonded interactions per particles is six for IPCs forming triangular arranged domains (panels B1 and B2) and four for IPCs forming square domains (panel B3). Magnified views of isolated units of typical IPC aggregates are shown in the upper part of the corresponding panel: the grain-like triangular arrangement (labelled “g-triangles”) occurs in the case of charged IPCs close to a neutral substrate, the flower-like triangular arrangement (labelled “f-triangles”) is observed in the case of neutral IPCs close to a neutral substrate, the square-like particle arrangement (labelled “squares”) emerges in the case of neutral IPCs when $Z_wZ_p > 0$. Bars and points are added to indicate the orientations of the particles parallel or perpendicular to the confining walls. **Panels C1-C6**: contour plots of the combined probability distributions $P(\alpha, \alpha_z)$ as function of $\alpha$ and $\alpha_z$, where $\alpha_z$ is defined in Eq. 1. Only results for $Z_wZ_p = 0$ and in tight confinement are reported (the other wall charge cases are summarized in Figure S 4): the top/bottom row refers to overall charged/neutral IPCs, as labelled; from left to right: contour plots for two, four and six bonded IPCs, as labelled.
Figure S 4: Contour plots of the combined probability distributions $P(\alpha, \alpha_z)$ as function of $\alpha$ and $\alpha_z$, where $\alpha$ and $\alpha_z$ are defined in Eq. 1; from left to right: contour plots for IPCs with two, four and six bonds, as labelled. The top/bottom box refers to neutral/charged IPCs close to differently charged substrates, as labelled. In each box, top and bottom rows correspond to $Z_wZ_p < 0$ and $Z_wZ_p > 0$, respectively.
Effect of the pH changes

By suddenly inverting the charge of the substrate a fully reversible transformation between disordered monomers and square-like crystalline domains can be triggered, as shown in Figure S 5.

Figure S 5: The particle-particle, $e_{cc}$, and the particle-wall, $e_{cw}$, energies per particle (left panel) and the two-dimensional order parameters $\Phi_4$ and $\Phi_6$ (right panel) as functions of time (i.e., MC steps) for sudden inversions of the substrate charge occurring at the vertical dashed lines, as labelled.