The emergence of valency in colloidal crystals through electron equivalents

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Abstract: Colloidal crystal engineering of complex, low symmetry architectures is challenging when isotropic building blocks are assembled. Here, we describe an approach to generating such structures based upon programmable atom equivalents (nanoparticles functionalized with many DNA strands) and mobile electron equivalents (small particles functionalized with a low number of DNA strands complementary to the programmable atom equivalents). Under appropriate conditions, the spatial distribution of the electron equivalents breaks the symmetry of isotropic programmable atom equivalents, akin to the anisotropic distribution of valence electrons or coordination sites around a metal atom, leading to a set of well-defined coordination geometries and access to three new low symmetry crystalline phases. All three represent the first examples of colloidal crystals, with two of them having elemental analogs (body-centered tetragonal and

high-pressure gallium), while the third (triple double-gyroid structure) has no known natural equivalent. This approach enables the creation of complex, low symmetry colloidal crystals that might find uses in various technologies.

The concept of valence electrons is central to chemical bonding theory, which defines how atoms form anisotropic bonding geometries in molecules and crystalline solids[1, 2]. In fact, the large number of low symmetry structures found in nature are a direct consequence of this valency. However, it is challenging to break symmetry in colloidal crystals because isotropic particle building blocks favor the formation of closely-packed phases[3-5]. Although progress has been made in using anisotropic particles and polyhedral templates to direct particle "bonding" interactions[6-13], these approaches are limited by the geometric shapes of building blocks that can be chemically synthesized.

Colloidal crystal engineering with DNA has emerged as a powerful approach to control nanoparticle superlattice symmetry, crystal habit, and lattice parameters, regardless of particle composition[14-18]. With this methodology, DNA-modified nanoparticles act as programmable atom equivalents (PAEs) that arrange themselves in three-dimensional space via a well-defined set of rules described by the complementary contact model (CCM)[19]. Recently, Girard *et al.*[20] made the remarkable finding that when reduced in size and DNA grafting density, small PAEs can behave as classical electron equivalents (EEs), allowing them to roam through and stabilize lattices defined by larger PAEs[20, 21]. However, it remains unclear whether these EEs can be programmed to dictate the symmetry of PAE lattices. If possible, new phases would become accessible and designable from isotropic building blocks by taking advantage of such particle valency.

Herein we describe an approach to reducing lattice symmetry in colloidal crystals by taking advantage of anisotropic distributions of "valence" EEs around PAEs concomitant with crystal lattice formation (Fig. 1a). In particular, we hypothesized that by controlling the relative densities of DNA grafted to the particle surfaces, we could establish a type of valency defined by EE distribution around PAEs (Fig. 1b) and that the symmetry breaking would be determined by: 1) the stoichiometric ratio of PAEs to EEs in a given lattice; 2) the local geometric configurations of the interstitial EEs (Fig. 1a); and 3) the delocalization and diffusion of EEs within the lattice (Fig. 1c). Through a combination of small-angle X-ray scattering (SAXS), electron microscopy, and molecular dynamics (MD) simulations, we show that the assembly of nine equilibrium phases is driven by the maximization of DNA hybridization. The flexible DNA shells and delocalization of EEs are responsible for stabilizing distorted EE local configurations and nonequivalent sites in certain lattices. Lastly, we report two enantiotropic phase transformations that rely on the redistribution of EEs upon thermal treatment. These findings reveal the role of EEs in enabling complex colloidal crystals and will further serve as design principles to engineer different phases.

EE-PAE stoichiometry in crystalline assemblies

To probe the role of EE-PAE stoichiometry, we synthesized PAEs and EEs by modifying 10-nm and 1.4-nm AuNPs with two types of single-stranded, propylthiolated DNA (ssDNA) (Supplementary Table 1), yielding particles with an average of 160 and 15 DNA ligands, respectively[20]. These ssDNA-modified PAEs and EEs were duplexed with specific numbers of linker strands that contain exposed 6-base sticky end overhangs that allow for DNA bond formation between PAEs and EEs via hybridization. Depending upon the number of input linker strands and EE-PAE stoichiometry (Supplementary Table 2), nine crystalline phases were

formed when PAEs and EEs were mixed, heated above their melting temperature, and then slow-cooled to form crystalline products[22], as characterized for crystals in solution by SAXS and for the silica-embedded samples by scanning transmission electron microscopy (STEM)[23] (Fig. 2). The sharp SAXS peaks and good agreement with simulated patterns suggest high crystal quality, and the typical crystal domain size is between ~400 nm to ~1.2 μm (Supplementary Table 4). However, the particle positions may be perturbed through the embedding procedures, resulting in the lattice distortion in the STEM images. The formation of specific phases is deliberately controlled by designed and sequence-specific DNA-DNA interactions, which is distinct from classical binary nanoparticle superlattices[4]. Three of the nine phases [BCT-2 (body-centered tetragonal), triple double-gyroid, and high-pressure gallium (HP-Ga)] have not been reported before from isotropic particles[24]. Among them, BCT-2 and HP-Ga formed when 10-nm AuNPs were duplexed with two types of linkers, one with a sticky end and a second type without a sticky end, to modulate the number of sticky ends on the PAE while maintaining the steric bulk of the PAE DNA shell (Supplementary Scheme 1 and Supplementary Table 2). For all other phases, a single type of linker, which contains a sticky end, was duplexed onto the PAE.

The EE-PAE stoichiometric ratio for each phase was quantified by dissolving pure-phase crystals containing dye-labeled EEs and measuring their concentration by UV-vis spectroscopy (see Methods). The input EE-PAE DNA linker and, therefore, sticky end ratio directly correlates with the EE-PAE stoichiometry observed in crystalline phases, providing a means to access distinct structures (Fig. 2j) deliberately. Across all phases, longer PAE-PAE distances and lower PAE volume fractions (Fig. 2k) are observed for phases generated from lower EE-PAE sticky end ratios, providing more spaces to host EEs, which is consistent with an increase in the EE-

PAE stoichiometry. Such a correlation is driven by the maximization of DNA sticky end hybridization, where unpaired PAE-EE sticky ends are unfavorable.

Valency defined by EE distribution

Having established that the average number of valence EEs is structure-dependent and can be controlled by the surface density of their DNA sticky ends, we next explored the EE spatial distribution for each phase, which defines the geometric shape of the EE valence shell. We hypothesized that EEs reside – in clusters or singly – at the Wigner-Seitz cell (W-S cell, also known as the Voronoi cell) vertices of the PAE lattices (Fig. 1a and Supplementary Table 3) because: 1) the W-S cell surface represents the interface at which EEs are equidistant between two or more neighboring PAEs; 2) at W-S cell vertices, one EE can interact with the most PAEs simultaneously to maximize DNA hybridization; and 3) W-S cell vertices define the largest distance between PAEs and EEs, minimizing steric repulsion between unpaired DNA strands and increasing EE configurational entropy. In this vein, the PAE coordination environment is defined by EEs at the W-S cell vertices, and the local geometry of an EE site is conversely defined by the polyhedral arrangement of its nearest PAE neighbors.

To test this W-S cell hypothesis, simplified particle models were built to study the colloidal assembly processes and equilibrium crystal structures *in silico* (Fig. 3, a–c, and Methods) using the HOOMD-Blue MD simulation toolkit[25]. In this model, PAEs and EEs are represented by rigid spherical cores (diameter: 10 and 1.4 nm) surrounded by soft DNA ligand shells (thickness: ~9 nm), where size parameters were selected to match experimental values similar to the procedures used in a previous study[11]. Although DNA strands may deform in real systems, the finite number of sticky ends on EEs are modeled as spatially uniform anchoring points that can bind to isotropic DNA shells on the PAEs for model simplicity[26], while their pair

potential is a Gaussian function with finite width to account for strand flexibility (Fig. 3a and Methods). To account for the compressibility of the DNA shells, an overlap index (ω_{PAE} and ω_{EE}) was assigned, which is correlated to the DNA grafting density on PAEs and EEs (Fig. 3, b and c, and Supplementary Fig. 35). Specifically, a low DNA grafting density allows for significant spatial overlap with other particles and is represented by a high ω value. In contrast, a high DNA grafting density corresponds to particles that behave like hard spheres with little distortion or overlap (low ω). By simulating crystal formation with different input parameters (ω_{EE}, ω_{PAE}, and the number of anchoring points on EEs), spontaneous formation of all nine different crystal structures from disordered fluid was observed, as confirmed by diffraction patterns, bond order diagrams, and direct visualization (Supplementary Table 5 and Supplementary Fig. 36, 38 to 41). The observed equilibrium phase behavior can be rationalized by calculating the relative stability of different crystals based on their overall packing density, where a higher overall packing density maximizes DNA bond formation. This model significantly expands the CCM to include structures such as these (FCC, FK-15, BCT-1, BCT-2, and gyroid) by considering the overlap of like particles (via the overlap indices ω_{EE} and ω_{PAE}) in addition to complementary particles. Stacking these packing density plots for each crystal lattice symmetry at a given set of overlap indices generates a landscape, in which the topmost structure has the highest packing density (lowest potential energy) and is predicted to be the equilibrium phase (Supplementary Fig. 45).

The sequence of symmetries realized experimentally when the EE-PAE sticky end ratio increases is reproduced well in MD simulations by simultaneously increasing the number of anchoring points on EEs and decreasing the magnitude of ω_{EE} (Supplementary Fig. 37). Isosurfaces of EE visitation frequency (Fig. 3d and Methods) reveal that the distribution of EEs

around a PAE has multiple well-defined local maxima, with a geometry that evolves from a 24-coordinated rhombicuboctahedron for the face-centered cubic (FCC) structure to an 8-coordinated cube for the simple cubic (SC) structure (Fig. 3d). The positions of these local maxima either agree with the PAE W-S cell vertex positions (Supplementary Table 3) or, in the cases of FCC and triple double-gyroid phase, correspond to groupings of several vertices in close proximity (Supplementary Fig. 10 and 11). Importantly, the simulated spacings between PAE-PAE and PAE-EE pairs (Au surface-to-surface) are consistent with SAXS measurements and the W-S cell analysis (Fig. 3e). The spacings between PAE cores and neighboring EE sites (derived from W-S cells) are nearly constant for all phases, and they match the length of a pair of DNA linkers hybridized through sticky ends.

Symmetry correlated with EE delocalization

The degree of EE delocalization correlates with their valence EE shell configurations across different lattice symmetries and allows the nine colloidal crystal PAE-EE phases to be categorized into three classes. In BCC and FCC phases, the number of sticky ends per EE is low, whereby a large number of "valence" EEs are recruited within a crystal, and the EEs are highly delocalized. Compared to other phases, these phases have a lower average spacing between neighboring EE sites (Fig. 3e) and more isotropic distributions of EEs around a PAE (higher sphericity[27] of the EE shell). Moreover, EEs show a strong mobility within the crystal[20], as quantified by the EE diffusivity in the simulation (Fig. 3f; see also Methods and Supplementary Fig. 47). In these "metallic" phases, a single EE does not have enough sticky ends to stabilize a tetrahedral interstitial site (Fig. 3d), which instead must be occupied by multiple EEs to form a collective bond, significantly increasing local EE disorder and macroscopic diffusion[20].

At intermediate sphericity and diffusivity, EEs are partially delocalized but still form clusters at EE sites. The clustering of EEs was determined in simulations by the time-averaged distribution of the number of EEs at each EE site (Supplementary Fig. 48). These "tetrahedral" phases are characterized by their near-tetrahedral EE local configurations but also appreciable EE diffusivity. In this group, EEs are mostly localized in clusters at the vertices of the W-S cells and can diffuse across multiple unit cells to form strongly delocalized, collective bonds.

In the remaining phases, low diffusivity correlates with low sphericity and high EE DNA grafting density. For SC, simple hexagonal (SH), HP-Ga, and triple double-gyroid, which all have a high EE-PAE sticky end ratio and high EE coordination numbers (≥6), we observed highly anisotropic PAE coordination geometries (Fig. 3d) and no long-range EE diffusion (Fig. 3g, right panel, and Movie S4). In this group, single EEs are largely constrained at local sites that bind multiple neighboring PAEs, showing strong covalent-like bonding characteristics; these "covalent" structures, from a building block standpoint, are not fully differentiated from conventional PAE-PAE binary crystals, highlighting the PAE-EE duality[20].

Local distortion of the EE sites

The formation of low symmetry phases requires the local coordination environment to be distorted and, in certain cases, split into multiple nonequivalent EE sites. These subtle differences in the EE local configurations are evidenced by local maxima in the EE density determined by STEM analysis and the EE visitation frequency derived from MD simulation (Fig. 4). We first consider the three "tetrahedral" phases – BCT-1, BCT-2 and the FK-A15 phase – as they all have similar tetrahedral EE sites (i.e., each EE site is surrounded by four PAEs) but distinct PAE arrangements. In all three phases, there may be one or multiple EEs at an EE site. In BCT-1, there is one W-S cell: a rhombo-hexagonal dodecahedron where one PAE is surrounded

by 18 EE sites (Fig. 4a). Two types of nonequivalent EE sites exist: a distorted tetrahedral 4d site and an irregular square pyramidal 4e site. In contrast, EEs within the BCT-2 lattice reside at distorted, tetrahedral 4d sites and octahedral 8j sites (Fig. 4b). PAEs are surrounded by 24 EE sites, rather than 18 as for BCT-1, leading to distinct scattering and lattice parameters despite having body-centered tetragonal symmetry.

In the third case, the FK-A15 unit cell has two types of W-S cells for PAEs: two PAEs reside in 20-coordinated pyritohedra of EE sites, and six PAEs are surrounded by 24 EE sites that define a truncated hexagonal trapezohedron, also known as the Weaire-Phelan structure (Fig. 4c). The absence of (110) and (220) scattering peaks (Supplementary Fig. 3) indicates that the A15 ($Pm\bar{3}n$) crystal realized here is a single-component system from the PAE perspective. There are three types of EE sites (6d, 16i, and 24k sites) within the A15 structure. All three types of EE sites comprise the 24-coordinated W-S cell, while only two (16i and 24k) comprise the 20-coordinated W-S cell, and all are tetrahedrally coordinated.

Additionally, we observed the DNA directed-assembly of PAEs into an intriguing triple double-gyroid structure in the cubic $Ia\bar{3}d$ space group (lattice parameter a = 108 nm). This is a rare space group that is found in ternary garnet-type inorganic minerals or in soft matter assemblies as single or double gyroids[28-30]. In this triple double-gyroid structure, there is a single coordination environment (W-S cell) of PAEs (48g), and it is an irregular 11-sided polyhedron with 10 vertices (Fig. 4d). PAEs are surrounded by three inequivalent octahedrally coordinated EE sites (16a, 16b, and 48f), resulting in a unique distorted octahedral close-packing of PAEs that has not been reported before in the colloidal domain. The 48 PAEs of the unit cell can be divided into 3 subgroups (Fig. 5a), each containing 16 PAEs. Connecting neighboring PAEs within any 1 of these 3 subgroups constructs a skeleton representation of a double gyroid

network (Fig. 5b and Supplementary Fig. 43)[31]. Consequently, the PAEs of the entire gyroid structure, including all three subgroups, sit at the nodes of the six intertwined gyroid networks (Fig. 5, c and d). Additionally, connecting EEs on all 16b EE sites gives an additional double-gyroid structure with a slight distortion (Supplementary Fig. 44). Together, the PAEs and 16b EEs comprise an 8-srs network structure[32] that exists in biological photonic crystals and often exhibits chiroptical properties[33]. This quadruple double-gyroid structure of PAEs and EEs is among the most topologically complex structures reported to date[34] and has not been reported in nanoparticle assemblies. These four examples illustrate that complex low symmetry phases arise from the distortion of EE local configurations, as confirmed by STEM experiments and MD simulations.

Reversible phase transformation

The nine phases described above were all obtained at ambient temperature from different structural configurations of PAEs and EEs. We hypothesized that since EE mobility increases with temperature[20], PAE lattice symmetry changes could be triggered with a deliberate change in temperature and the resulting EE redistribution (Fig. 6a). Importantly, *in situ* variable temperature SAXS experiments reveal that FCC and BCT-2 structures exhibit enantiotropic phase transformations (fully reversible, solid-state transformations without an intermediate liquid phase). Although similar phase transitions have been reported in binary compound colloidal crystals mediated by DNA[35-37], it is unknown how crystal lattice transforms between thermodynamic products in a PAE-EE system. Both FCC and BCT-2 transition to the BCC structure upon heating (Fig. 6, b and c), likely driven by the lattice entropy difference which favors BCC at increased temperatures. In the first case, a pure FCC sample annealed by the standard slow-cooling method was heated on a thermal stage at a constant rate of 0.25 °C/min

and monitored by SAXS (Supplementary Figs. 16 to 18). Distinct from conventional PAE-PAE assemblies that directly melt into an isotropic liquid state (Supplementary Fig. 19), a set of sharp BCC scattering peaks gradually emerge near 41 ºC accompanied by a reduction in the intensity of FCC features (Fig. 6b). The FCC to BCC transition is complete at 44 ºC, and the BCC structure persists up to 46 ºC before completely melting. The observed BCC phase exhibits high crystallinity, as evidenced by the sharp scattering peaks that are well resolved even at high angles. The absence of additional scattering peaks other than those of the BCC and FCC structures suggests that the transformation occurs via a solid-state nucleation-growth pathway rather than the theoretical Bain's pathway[38], which involves an intermediate BCT structure[39]. Indeed, MD simulation shows that nucleation of the BCC phase preferentially occurs through the slip of (111) facets near domain boundaries and subsequent growth into FCC crystallites (Fig. 6d, 6e and Movie S6) rather than through any intermediate phase. In this process, EEs must dynamically reconfigure their locations to induce and accommodate the structural transformation, supported by the EE density change between the crystalline phase and the surrounding solution, as observed in the MD simulation (Supplementary Fig. 49). The redistribution of EEs is further confirmed by accumulated EE positions during the phase transition (Fig. 6f). The *in situ* change in EE distribution (i.e., a change in PAE symmetry breaking in response to temperature) provides a novel route to rare colloidal crystal-to-crystal transitions[40, 41].

Outlook

In this work we report an approach to induce colloidal crystal symmetry breaking via the anisotropic distribution of EEs in colloidal crystals of PAEs engineered with DNA. In this PAE-EE system, the strength of local DNA bonding interactions can be regulated by two means:

temperature and the EE-PAE sticky end ratio. Weak interactions occur at high temperature or low EE DNA loading (e.g., 4 sticky ends/particle), where PAEs densely modified with DNA interact isotropically with many EEs, analogous to the spherical free-electron Fermi surface. Strong local interaction occurs at low temperature or high EE DNA loading, where the clustering of DNA bonds and stronger steric repulsion between EEs prevents their free diffusion and leads to symmetry breaking. Intermediate between these extremes, partial delocalization of EEs leads to symmetry breaking through localized, collective bonds involving multiple EEs. We note that the observed symmetry breaking in the PAE-EE system *via* EE redistribution is reminiscent of phase transitions in metals via charge exchange. For instance, some metallic elements, such as Li[42] and Mn[43], undergo a phase transformation from close-packed BCC or FCC to multiple low-symmetry structures as a result of significant frustration of the Fermi surface topology by strong local interactions[44]. Furthermore, certain mechanistic features are shared between this proposed mechanism and mesophase formation involving soft matter, which is typically driven by noncovalent interactions between spherical micelles formed by lipids[45], supramolecules[9], nanoparticle clusters[46], dendrimers[47], and block copolymers[48]. In these systems, local asymmetries originate from molecular flexibility, building block size dispersity, micellar size and shape polydispersity, and inter-micelle mass transfer, causing relaxation of cellular domains to unequal volumes with minimized contact surface and overall increased packing density[40, 49].

In conclusion, our strategy for symmetry breaking relies on the establishment of the new concept of "valence electrons" in the PAEs and EEs that comprise colloidal crystals. Such colloidal "bonding valency" is a fundamentally new paradigm for describing particle bonding resulting from attractive interparticle potentials and is analogous to the valence shell electron pair repulsion (VSEPR) theory that is foundational in chemical bonding. Importantly, the nine

crystals reported herein are only a small fraction of possible structures. Based on this approach, we expect more low symmetry and complex colloidal architectures to be discovered, including other Frank-Kasper phases, Laves phases, and quasicrystalline structures.

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Author contributions

C.A.M. and S.C.G. directed the research. S.W. performed synthesis and X-ray scattering experiments. S.L. performed MD simulations. J.S.D. and S.W. performed electron microscopy studies. S.W. and B.L. performed SAXS simulation. All authors contributed to data analysis and manuscript preparation.

Competing interests

The authors declare no competing interests.

Figure Captions

Fig. 1 | Assemblies of PAE-EE colloidal crystals and simulation models. a, Colloidal crystals synthesized from co-assembling PAEs and complementary EEs with different numbers of DNA linkers. Wigner-Seitz cell representation of the PAE sublattice is highlighted in red, and the local EE configuration is highlighted in blue. **b**, A zoomed-in view of local PAE coordination environment surrounded by EEs (left) and examples of anisotropic EE spatial distributions around a single PAE. **c**, A zoomed-in view of local geometric configuration of an EE site, where the arrangement of PAEs and relative EE diffusion is controlled by the strength of PAE-EE interaction.

Fig. 2 | Formation of nine distinct PAE-EE assemblies as controlled by DNA-based interaction. a-i, Top row of each panel: unit cell model (PAEs in color, EEs in light grey) and representative cross-sectional low-angle annular dark-field (LAADF) image for each crystal. Bottom row of the panel: structure factor $S(q)$ obtained from synchrotron-based SAXS experiments (color) and simulated SAXS patterns based on PAE crystals alone (grey). Scale bars are 50 nm for all images. **j**, A positive correlation is observed between PAE-EE stoichiometry and their surface sticky end density ratio (based on input linkers). Error bars were determined by testing at least three different input conditions to form the corresponding crystalline phases. **k**, Packing fraction of PAE AuNP core for each phase following the order of EE:PAE stoichiometry ratio.

Fig. 3 | MD simulations of the structural configurations and dynamics in equilibrium phases. a, Double-stranded DNA around PAEs and EEs are modeled by isotropic shells surrounding the particle cores. The finite number of sticky ends on EEs was modeled as spatially uniform anchoring points that can bind onto the isotropic DNA shells on the PAEs, representing DNA hybridization of ssDNA sticky ends. **b,c**, In three cases modeled in **b**, different pair potential functions are assigned for PAE-EE pairs without patch contact nor shell overlap (black), without patch contact but with shell overlap (grey), and with patch contact (red). **d**, The isosurface plots of EE visitation frequency in a PAE local environment (upper left insets), all EEs surrounding one PAE at the center (lower left insets) and local PAE coordination polyhedra (lower right insets) for the nine different crystals obtained from MD simulation for 10^7 timesteps. **e**, Interparticle spacing (surface-to-surface) for each phase obtained from experiments (black) and MD simulations (red). Experimental PAE-EE and EE-EE spacings are calculated based on the constructed W-S models assuming one EE residing at the geometric centroid of an EE site. Error bars in the simulation data indicate the standard deviations of the distribution of spacings obtained from at least a few hundred unit cells in equilibrium (Supplementary Table 5). **f**, A positive correlation is observed between EE diffusivity and the sphericity of local PAE coordination polyhedra. **g**, Trajectories of a single EE in the BCC (left), FK-A15 (center), and SC (right) phases for 10^6 MD timesteps. The trajectory in SC is confined within a single unit cell (inset).

Fig. 4 | Local structural analysis based on STEM and MD simulations. Structural characterization of four representative crystals: BCT-1 (**a**), BCT-2 (**b**), FK-A15 (**c**), and gyroid (**d**). For each panel: illustration of a single unit cell composed of PAE and EE sublattices with their corresponding local polyhedral coordination environments and Wyckoff positions (left); MD simulation snapshots of PAE-EE assemblies and EE spatial distribution around a single PAE

(middle); representative LAADF image of a single unit cell (EEs are highlighted by red dashed circles), and overlay of averaged-intensity LAADF images of identified EE spatial distribution along the [100] direction (right). Scale bars are 20 nm for all images.

Fig. 5 | Colloidal gyroid crystal structure. a, The 48 PAEs in a unit cell of the triple double-gyroid crystal can be divided into three subgroups, where each subgroup contains 16 PAEs. **b**, The PAEs in each subgroup are superimposable onto the vertices of skeletal graphs of a double gyroid structure. One of the three double gyroid structures viewed along 4-fold axis (left) and 3-fold axis (right). **c**, The PAEs in the whole gyroid crystal can be superposed onto the vertices of six intertwined gyroid networks.

Fig. 6 | Enantiotropic crystal-crystal phase transitions induced by redistribution of EEs. a, Schematic representations of crystal-crystal phase transformation at elevated temperature before complete melting into liquid phase. **b**, **c**, SAXS patterns for FCC and BCT-2 structures heated and cooled *in situ* resulting in phase transitions. Grey spectra show complete melting of lattices at high temperatures. **d**, MD simulation snapshots of the reversible FCC-BCC phase transition by system temperature change (red arrow = heating, blue arrow = cooling). PAEs are colored by the bond-order parameter (Q_4, Methods), where red and blue PAEs correspond to BCC and FCC, respectively. **e**, Local PAE coordination environment highlighted by a single unit cell (green or purple) during the phase transition in MD simulation. **f**, The spatial distribution of EEs over time for the FCC-BCC phase transition.

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Methods

Synthesis of oligonucleotides

A MerMade 12 oligonucleotide synthesizer (Bio Automation) was used to synthesize oligonucleotides on a standard controlled pore glass (CPG) solid phase support. All

oligonucleotides were deprotected under conditions recommended by the manufacturer and then purified by reverse phase high performance liquid chromatography (HPLC). Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry and UV-vis spectroscopy were used to characterize the oligonucleotides and determine their concentrations, respectively. Supplementary Table 1 summarizes the oligonucleotides synthesized for this work.

DNA functionalization of AuNPs

10-nm unconjugated spherical AuNPs (Ted Pella) were used as received without further modification. Ultrafine AuNPs (~1.4 nm, nominal size) were purchased and used as received (non-functionalized Nanogold labeling reagents, Nanoprobes).

PAEs were synthesized by functionalizing 10-nm AuNPs with thiol-modified oligonucleotides following literature procedures[20]. Briefly, 100 nmol of the AuNP-bound strand A (see Supplementary Table 1) were treated with a solution of 100 mM dithiothreitol (DTT, pH = 8) for ~ 1 h and subsequently purified using NAP-10 size exclusion columns (GE Healthcare) to remove residuals. Then, sodium dodecyl sulfate (SDS) was added to the solution of AuNPs as surfactants reaching a concentration of 0.02 vol%, followed by the addition of purified thiolated DNA (~ 4–5 nmol of DNA per 1 mL of AuNPs). In order to increase the density of DNA on the particle surface, a "salt aging" process was performed by slowly adding a NaCl solution (5 M) to the solution of NPs over the next several hours for shielding against electrostatic repulsion between strands. As the final salt concentration reached 0.5 M NaCl, the NPs were allowed to settle overnight, followed by purification by passing through a 50 kDa cut-off centrifugal filter unit three times (4000–15000 rpm for 60 min) to remove any unreacted DNA, salt, or surfactant. Finally, these purified PAEs were concentrated by centrifugal filter unit to a stock solution (~

500 nM of particles) in 0.5 M NaCl solution, which is the salt concentration at which all subsequent assembly reactions took place. Similarly, EEs were synthesized by functionalizing 1.4-nm AuNPs with thiol-modified strand B (Supplementary Table 1). To prepare 1.4-nm AuNPs modified with fewer DNA strands, a reduced number of equivalents of DNA were added for functionalization. For instance, the addition of 6, 10, 40, and 80 molar equivalents of DNA per particle results in a loading density of 3, 6, 10, and 15 ssDNA strands/1.4-nm particle (on average) as measured by UV-vis spectroscopy (*vide infra*), respectively.

Quantification of single-stranded DNA (ssDNA) loading on 1.4-nm AuNPs

DNA loading of 1.4-nm AuNPs was measured by UV-vis spectroscopy after functionalization with dye-labeled DNA (dye-labeled strand 1, Supplementary Table 1), and extensive washing to remove unreacted DNA. The increased absorbance at 260 nm is due to the modification of the AuNPs with DNA. The DNA concentration was determined by measuring the extinction at 647 nm (for Cy5 dye, molar extinction coefficient = 250,000 $M^{-1}cm^{-1}$). The concentration of 1.4-nm AuNPs was determined using the corrected absorption at 420 nm (for Nanogold, molar extinction coefficient = 112,000 $M^{-1}cm^{-1}$) via subtraction of the Cy5 DNA baseline. Note that the solution was diluted before the measurement such that the target absorption was between 0.1 to 1.0. A summary of the extent of DNA functionalization is shown in Supplementary Scheme 1 and 2.

Synthesis of PAE-EE assemblies

In a typical experiment, stock solutions (see Supplementary Table 2 for representative concentrations and quantities) of ssDNA-functionalized PAEs and EEs (A or B) were combined

with their respective complementary DNA linkers (linker A or linker B) to yield two separate colloidal solutions (0.02% SDS and 0.5 M NaCl). Two alternative approaches were used to prepare the EEs (Supplementary Scheme 2). When dummy linker A' was used to synthesize BCT-2 and HP-Ga structures, they were premixed with regular linker A to ensure a uniform hybridization to PAEs. The colloidal solutions were incubated for 20 min on a thermal shaker (r.t., 750 rpm) to allow for linker hybridization, followed by the combination of 50 μL of each solution, which resulted in the formation of aggregates that settled out within minutes. Samples were heated to 47 ºC (above the melting temperature of colloidal crystals) and cooled at a rate of 0.1 ºC per 10 min to 20 ºC using a polymerase chain reaction (PCR) system. In principle, the crystal size and quality improve with slower cooling rate[22]. More synthetic conditions that yield these crystal structures can be found in the section "Synthetic Phase Space for Colloidal Crystals" in the Supplementary Information.

Small-angle X-ray scattering (SAXS)

Confirmation of all crystal structures in this work was done primarily using small-angle X-ray scattering. SAXS characterization was carried out at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) located in Sector 5 and 12-ID-B beamline of the Advanced Photon Source (APS) at Argonne National Laboratory following a literature report[20]. X-rays of wavelength 1.24 Å (10 keV) and 0.9322 Å (13.3 keV)$I(q)$were used at Sector 5 and 12, respectively, and the system was calibrated using silver behenate as a standard. In both beamlines, two sets of slits were used to define and collimate the X-ray beam, and parasitic scattering was removed via a pinhole. Typical exposure times between 0.1 and 0.5 s were used. The scattered X-rays were collected with a CCD detector, and one-dimensional scattering spectra

were obtained by radially averaging the images into scattering intensities, q, against the scattering vector, q. To clearly identify scattering peaks at high scattering vector $I(q)$, all experimental scattering intensity $S(q)$, were plotted and simulated on a logarithmic scale for this study. The structural factor, $I(q)$, of each phase was extracted from the experimental scattering intensity $I(q) = S(q) \times P(q)$, where$P(q)$, by subtracting the experimentally measured form factor $P(q)$ of 10 nm PAE particles.

In situ SAXS measurements were conducted on a stage with thermal control, closely monitoring the temperature of each sample during the kinetics experiments. Large batches of annealed samples were prepared to maintain consistency. At the beginning of each experiment, the temperature was set to 25 °C, and an initial scan of the annealed sample was taken. In the initial melting period, the temperature was increased at a constant rate (0.25 °C/min), and scans were taken every 0.5 °C. The end point of the melting period was reached once no scattering peaks were observed in consecutive scans, and then the samples were held for 10 min to ensure complete melting. In the cooling period, the sample was cooled to room temperature at a constant rate (0.1 °C/min) and scans were taken at designated temperatures.

Modeling of nanoparticle superlattice SAXS data

One-dimensional SAXS spectra were simulated and indexed following a literature report for determining crystallographic symmetries and lattice parameters[50]. In a typical simulation, a unit cell model was first constructed composed of spherical particles arranged in a selected symmetry and lattice parameters, such that all peaks are matched. Next, particle size was adjusted within a small range (diameter = 9.5 ± 0.5 nm) and a polydispersity factor (5-10 %) to ensure a good background fit. Lastly, the average crystalline domain size, Debye-Waller factor (DWF), and the

microstrain parameter were empirically adjusted to fit the peak width and relative peak intensities across the entire spectrum.

Silica encapsulation of the assemblies

Immobilization of colloidal crystal assemblies in the solid state was achieved by silica encapsulation following a literature report[23]. Briefly, *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMSPA) (2 μL, 7.2 μmol) was added to the assemblies in 0.5 mL of 0.5 M NaCl solution, and the mixture was stirred for ~30 min before the addition of triethoxysilane (TES) (4 μL, 21.7 μmol). The suspension was vigorously stirred for 24 h at room temperature, followed by three rounds of centrifugation and resuspension in water to remove excessive silica. The samples for morphological characterization with electron microscopy were solvent-exchanged with ethanol and drop-cast onto a TEM grid.

Resin embedding of silica-encapsulated assemblies and ultramicrotomy

Ultramicrotomy was adopted for obtaining cross-sectional views of the silica-encapsulated assemblies. The samples were embedded in a resin following a literature report[20]. Briefly, ~5 mg of silica-encapsulated assemblies were embedded in 0.2 mL of 4% gelatin. The gelatin sample was dehydrated upon immersion in anhydrous ethanol solutions of increasing concentration (30% → 50% → 70% → 80% → 90% → 100%). Next, the sample immersed in 100% ethanol was solvent exchanged with acetone twice for 10 min. In acetone, the gelatin was embedded in EMBed-812 resin (Electron Microscopy Sciences) following the standard protocol provided by the manufacturer. The samples were held at 65 °C for 16−20 h to polymerize and solidify the resin, and the resin was then sectioned into 80-nm slices (Leica EM UC7). For samples

assembled from PAEs (sizes ≥ 2 nm), TEM grids with ~20-nm carbon films were used to enhance sample stability. For samples involving EEs (sizes below 2 nm), TEM grids without carbon films were used. Instead, after the cross-sections were transferred onto the grid, a 3-5 layer graphene membrane [grown from chemical vapor deposition (CVD) on Cu foil, ACS Material, LLC] was coated onto the grid through a wet transfer method[51].

Scanning transmission electron microscopy (STEM)

Silica-encapsulated cross-sectional samples were loaded onto a double-tilt sample holder and imaged in STEM mode on a JEOL JEM-ARM300F electron microscope. Low-angle annular dark field (LAADF) imaging was performed with a collection angle from 30 to 120 mrad. The images were then processed and analyzed following published methods[20]. Briefly, images were first denoised using the block-matching and 3D filtering (BM3D) algorithm[52] and then meshed and segmented into repeating unit cells based on the periodicity and orientation of the lattice identified by 2D auto-correlation function (ACF) analysis. Note that this repeating unit cell represents the smallest repeating unit in the 2D projection of the lattice and is not necessarily identical to the crystal unit cell. The EE locations in selected repeating unit cells (based on lattice quality defined by PAEs) were labeled using the TrackMate package and then stacked with the averaged unit cell LAADF image. The local densities of the EEs were calculated by counting neighboring EE numbers in a circular area (radius: r_s) surrounding each EE location (with periodic boundary conditions) divided by the area of the repeating unit cell. A uniform distribution density (σ_{uni}) was defined as the total number of EEs in a stack divided by the area of the repeating unit cell for normalizing the computed local densities.

Morphological characterization of silica-encapsulated samples was performed on a Hitachi HD-2300A equipped with a field emission gun (FEG) operated at 200 kV and a secondary electron (SE) detector.

Simulation setup

Simulations of this study were performed using molecular dynamics (MD) implemented in the HOOMD-blue simulation package[25, 53, 54]. HOOMD-blue can be performed either on the central processing units (CPUs) or on the graphics processing units (GPUs), but it is highly optimized on GPUs. As such, most simulations of the present work were performed on NVIDIA Tesla P100 GPUs[55].

We developed a simplified model of PAEs and EEs to simulate a large number of particles on a reasonable timescale. A PAE with a large number of DNA ligands is modeled as a sphere that has an isotropic interaction with EEs and other PAEs. The EE model contains two parts: attractive patches and a spherical body on which the patches reside on. The patches are uniformly positioned around the EEs where the sum of the distances between them is maximized. The purely repulsive Weeks-Chandler-Andersen (WCA) pair potential[56],

$$V(r) = \begin{cases} 4\varepsilon_{\mathrm{WCA}}\left[\left(\frac{\sigma_{\mathrm{WCA}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{WCA}}}{r}\right)^{6}\right] - 4\varepsilon_{\mathrm{WCA}}\left[\left(\frac{\sigma_{\mathrm{WCA}}}{r_{\mathrm{cut}}}\right)^{12} - \left(\frac{\sigma_{\mathrm{WCA}}}{r_{\mathrm{cut}}}\right)^{6}\right], & r < r_{\mathrm{cut}} \\ 0, & r \geq r_{\mathrm{cut}} \end{cases} \quad \text{(Eq. 1)}$$

is applied to the PAE–PAE, PAE–EE body, and EE body–EE body interactions (Fig. 3B-C), where r is the center-to-center separation distance between two particles. The σ_{WCA} between *i* and *j* particles is determined by the radius of each particle and the overlap parameters (ω_{ij}), $\sigma_{\mathrm{WCA\_}ij} = (1 - \omega_{ij}) \times (r_i + r_j)$. The $r_{\mathrm{cut}} = \sigma_{\mathrm{WCA}} \times 2^{1/6}$ and the $\varepsilon_{\mathrm{WCA}}$ are 1.0 for all systems. The shifted Gaussian model is applied to the PAE–EE patch interaction:

$$V(r) = \varepsilon_{\text{Gauss}} \exp\left[-\frac{1}{2}\left(\frac{r-r_0}{\sigma_{\text{Gauss}}}\right)^2\right] \quad \text{(Eq. 2)}$$

where $\varepsilon_{\text{Gauss}} = -0.7$ and $\sigma_{\text{Gauss}} = 0.5$ are the depth and width of the potential, respectively. The quantity r_0 indicates the position of the minimum in the potential energy function. In this system, we take $r_0 = r_{\text{PAE}} \times 2^{1/6}\,\sigma$ to minimize the potential energy when the surface of a PAE is in contact with the center of the patch on an EE. The shifted Gaussian pair potential is truncated for separation beyond $V(r) < 10^{-2}$. We controlled the number of patches ($4 \leq N_{\text{patch}} \leq 12$) on EEs as a simulation parameter to mimic the estimated number of ligands on EEs in the experiments.

The idea to combine a WCA potential and the shifted-Gaussian potentials first arose in a previous publication[11], where a PAE is modeled as a rigid core surrounded by a DNA shell composed of two layers of DNA: a double-stranded DNA (ds-DNA) layer and a single-stranded DNA (ss-DNA) layer. In the experiments, it is the ss-DNA oligomers that bind with ss-DNA oligomers on other particles. The ds-DNA, which is significantly more rigid than ss-DNA, effectively serves to expand the core of the PAE while retaining the overall shape of the gold nanoparticle core. With this knowledge, we then modeled the ds-DNA layer as rigid and non-attractive, and the ss-DNA layer as flexible and with a short-range attractive interaction. Because of the rigidity of the ds-DNA layer, these layers are unlikely to have significant overlap. We chose to model this layer by a steep and purely repulsive WCA potential to inhibit overlap of the ds-DNA layers on neighboring PAEs. We modeled the ss-DNA part by a negative Gaussian potential with a minimum at a distance corresponding to the expected bonding distance of the PAEs as obtained from the experiments. The ss-DNA layer flexibility in our model is controlled by the width of the Gaussian σ_{Gauss} and the strength of the DNA binding interaction is controlled by its depth $\varepsilon_{\text{Gauss}}$. We observed that small changes in width of the shifted-Gaussian ($\sigma_{\text{Gauss}} =$

0.3 and 0.7) gives similar assembly outcomes at a slightly shifted temperature ($\Delta T \sim -0.02$ and $+0.02$).

It is notable that our model is not as sophisticated as other detailed and/or coarse-grained models in the literature[57-59] yet reproduces all experimentally observed phases in the present study as well as the previous study[11]. These observations confirm that once particle shape, interaction strength, and interaction distance are accounted for, the self-assembly process is surprisingly robust.

Overlap parameters

In an atomistic model of the PAE[57, 60], the ligand layers would be somewhat compressible and overlap. In our patch particle model, to control the amount of overlap between particles, we introduced an overlap parameter (ω) in the simulation. The amount of overlap of a particle is defined by $\omega = l/r$, which is a ratio between the thickness of the overlap region that is allowed to overlay with other particles (l) and the radius of the particle (r) (Supplementary Fig. 35A). As such, $\omega = 0$ defines that overlap is not allowed on the particle, and $\omega = 1$ defines that the particle can be fully overlapped with other particles. In principle, the overlap parameter between two particles (ω_{ij}) should be solely determined by ω_i and ω_j, but we introduced a constant coefficient c_{ij} for allowing us to slightly adjust the overlap specific types of pairs (Supplementary Fig. 35B). As such, the general formula of ω_{ij} is defined as:

$$\omega_{ij} = \frac{l_i + l_j}{r_i + r_j} - c_{ij}\frac{(r_i - l_i) + (r_j - l_j)}{r_i + r_j} = \frac{\omega_i r_i + \omega_j r_j - c_{ij}[(1-\omega_i)r_i + (1-\omega_j)r_j]}{r_i + r_j} \quad \text{(Eq. 3)}$$

For $c_{ij} = 0$, the ω_{ij} is determined by ω_i and ω_j only. We kept $c_{\mathrm{PAE-EE}} = 0.05$ and $c_{\mathrm{EE-EE}} = 0$ as constants for all calculations and simulations in this work. In addition, the value

of $c_{\mathrm{PAE-PAE}}$ is changed when we modulate the rigidity of PAE shells due to the dummy linkers. The values of the simulation parameters used in this work are listed in Supplementary Table 5.

Overlapping packing model

An overlapping packing model (OPM) compares the maximum packing density of various crystals where overlap between particles is allowed. The overall packing density ϕ of the PAE-EE binary system is defined as $\phi = (N_{\mathrm{PAE}} \times v_{\mathrm{PAE}} + N_{\mathrm{EE}} \times v_{\mathrm{EE}})/V_{\mathrm{Box}}$, where N, v, and V_{Box} are the number of particles, volume of a particle, and total volume of a system, respectively. In this study, we compared the maximum packing density of nine PAE-EE crystals depending on the PAE overlap (ω_{PAE}) and the EE overlap (ω_{EE}).

Steps for calculating the maximum packing density of an input lattice for a given set of overlap parameters are:

1. Assign an input lattice with a low-enough packing density such that no overlap exists between any particle. In this study, the initial packing density was set to $\phi = 0.1$.
2. Assign the radius of each type of particle (r_{PAE} and r_{EE}) and the overlap parameters (ω_{PAE}, ω_{EE}, and c).
3. Slightly compress the crystal with a proper scale. We compressed the system 0.5% in the length scale in each step.
4. Calculate the PAE-PAE, EE-EE, and PAE-EE distances that are averaged by the number of the nearest neighbor.
5. Check if:

- $d_{\mathrm{PAE-PAE}} < (1 - \omega_{\mathrm{PAE-PAE}})(r_{\mathrm{PAE}} + r_{\mathrm{PAE}})$
- $d_{\mathrm{EE-EE}} < (1 - \omega_{\mathrm{EE-EE}})(r_{\mathrm{EE}} + r_{\mathrm{EE}})$
- $d_{\mathrm{PAE-EE}} < (1 - \omega_{\mathrm{PAE-EE}})(r_{\mathrm{PAE}} + r_{\mathrm{EE}})$

6. If all three conditions are false, go back to step 3. Otherwise, go to the next step.
7. Calculate the packing density of the current state. This is the maximum packing density of the input lattice for a given set of overlap parameters.

For all nine crystals found in this study, we carried out the OPM calculation for $0 \leq \omega_{\mathrm{PAE}} \leq 0.30$, and $0 \leq \omega_{\mathrm{EE}} \leq 0.55$ with 0.01 intervals, $c_{\mathrm{PAE-EE}} = 0.05$, $c_{\mathrm{PAE-PAE}} = 0$, and $c_{\mathrm{EE-EE}} = 0$. Supplementary Fig. 45a–c shows three example results (BCC, BCT-2, and gyroid) of the OPM calculation where ω_{PAE} and ω_{EE} vary. By stacking all 3D plots for the nine crystal structures (Supplementary Fig. 45d), we can identify the structure that has the maximum packing density for a given set of overlap parameters (Supplementary Fig. 45e; see also Supplementary Fig. 45f for a cross section at a fixed ω_{PAE} value). Note that ϕ can be larger than 1.0 because there exists a significant amount of overlap between particles at the maximum packing state.

Crystallization simulations

For the assembly simulations, the number of PAEs is fixed (N_{PAE} = 500), and the number of EEs (N_{EE}) varies from 500 to 8000. This system size is large enough to contain a few hundred unit cells of the crystal structures in this study. We kept the packing fraction of PAEs constant ($\phi_{PAE} = N_{\mathrm{PAE}} \times v_{\mathrm{PAE}}/V_{\mathrm{Box}} = 0.05$), where v_{PAE} is the volume of a PAE. For each MD timestep, $\delta\tau = 0.005$ is applied for all systems. Brownian dynamics are applied, and all simulations are conducted under periodic boundary conditions.

As an initial setup, we place the PAEs and the EEs in a large simulation box (ϕ_{PAE}~0.01) with no overlap between the particles and assign a random orientation to the EEs[61]. Then, we compress the system to a target density ($\phi_{PAE} = 0.05$) and equilibrate the system at a constant temperature (T^*) by checking the potential energy of the system every $10^3\tau$. If the T^* is lower than T_m^*, a supercooled liquid cluster, where the PAEs and the EEs are mixed, is formed. Once the system overcomes the nucleation barrier within the simulation time, spontaneous crystallization occurs, as identified by a drop in the potential energy of the system, the diffraction patterns, and the bond-order diagrams. Typically, nucleation of the crystals was observed around T^*/T_m^*~0.9 within 10^8 MD timesteps (τ), which takes around 48–72 GPU h. A typical assembly simulation process is shown in Supplementary Fig. 36.

Phase identification from simulation results

In order to identify the crystal structures obtained in the MD simulations, we used diffraction patterns of PAE crystals, bond orientational order diagrams (BOD) of PAEs, and direct visualization of simulation snapshots (Supplementary Figs. S36, S39-S41). The diffraction patterns were calculated by FFTs of the PAEs configurations in real space. The BOD shows a stereographic projection of the accumulated orientation of the nearest-neighbor bonds along a crystal symmetry axis. In order to get references for the structural information, we constructed the ideal structures of the nine PAE lattices observed in experiments and obtained the BODs and the diffraction patterns from a main zone axis (Supplementary Fig. 38). We used them as references to identify the crystal structures obtained from MD simulations.

For the FCC-BCC transition simulation (Fig. 6D-E, S49 and Movie S6), we used the rotationally invariant Steinhardt bond order parameter (Q_l)[62, 63] that associates a set of spherical harmonics with every bond between particle i and its neighbors j. We denote

$$Q_{lm}(\vec{r}) = Y_{lm}(\theta(\vec{r}), \phi(\vec{r})) \quad \text{(Eq. 4)}$$

where $\vec{r}$ is the vector of the bond that connects from i to j, and $Y_{lm}(\theta, \phi)$ are spherical harmonics. To determine the local environment, we averaged over all nearest neighbors

$$\bar{Q}_{lm} = \langle Q_{lm}(\vec{r}) \rangle \, . \quad \text{(Eq. 5)}$$

To remove local orientational order, one should use the rotationally invariant combination

$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}|^2 \right]^{1/2} . \quad \text{(Eq. 6)}$$

We used Q_4 to distinguish between BCC ($Q_4 < 0.1$) and FCC ($Q_4 \geq 0.1$) phases (*35*). Only the bonds between PAEs are considered when the Q_4 is calculated.

PAE-EE phase diagram simulation

We first performed MD simulations by changing the number of patches on the EE, $4 \leq N_{\text{patch}} \leq 12$, and the amount of overlap of the EEs, $0 < \omega_{\text{EE}} < 0.5$, while keeping $\omega_{\text{PAE}} = 0$ and $c_{\text{PAE-PAE}} = 0$ (Supplementary Fig. 37). We observed spontaneous formation of gyroid, SH, BCT-1, A15, and BCC lattices as we increase the ω_{EE} and decrease the number of EE patches (Supplementary Fig. 36, S39-S41). This observation agrees well with the experiments where gyroid and SH were found with high EE grafting density, that BCT-1 and A15 were found with intermediate grafting density, and that FCC and BCC were found with high grafting density. Note that FCC was self-assembled when there are excess amount of EEs ($N_{EE} \geq 25 \times N_{PAE}$). When we increase ω_{PAE} by 10% in the high grafting EE density region ($0 < \omega_{\text{EE}} < 0.1$), we observed the formation of the SC phase. In the low grafting EE density region ($0.35 < \omega_{\text{EE}} <$

0.50), when we increased the EE concentration, we observed a phase transformation from BCC to FCC. In the range of $0.05 < \omega_{\mathrm{EE}} < 0.15$ and $0.30 < \omega_{\mathrm{EE}} < 0.40$, when we decreased $c_{\mathrm{PAE-PAE}}$ 5%, which effectively increased the rigidity of the PAE shell, we observed that HP-Ga and BCT-2 phases were well stabilized, consistent with experiments. Within the range that self-assembly could occur, we selected a specific parameter set for each phase (Supplementary Table 5) that matches with thermodynamic and dynamic properties observed in experiments. A schematic diagram of the phase transition behavior in the parameter space described above is shown in Supplementary Fig. 37.

Data availability

Data generated or analysed during this study are provided as Source Data or included in the Supplementary Information. Further data are available from the corresponding authors upon request.

Code availability

Source code for HOOMD-blue is available at https://github.com/glotzerlab/hoomd-blue. Source code for SAXS simulation is available at https://sites.google.com/site/byeongdu/software. Lattice segmentation and analysis codes for electron microscopy images are available at https://github.com/SequoiaDu/ImageLatticeAnalysis.

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