

# Shaping Phases by Phasing Shapes

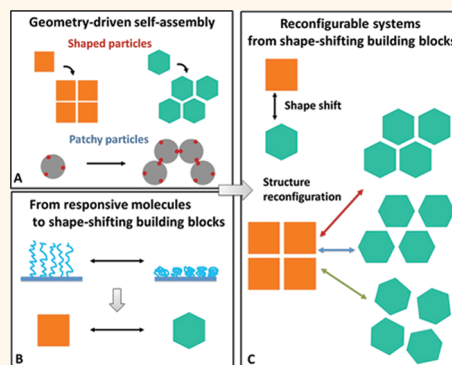
Oleg Gang\* and Yugang Zhang

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

In recent years, the landscape of material science has been drastically evolving due to the rapid development of two powerful design concepts: rational self-assembly<sup>1,2</sup> and responsive matter.<sup>3,4</sup> Rational self-assembly ultimately seeks to achieve *à-la-carte* structure formation with the ability to incorporate a diverse range of functional building blocks. Various approaches based on biorecognition, shape complementarity, and size and charge effects have been demonstrated in this quickly developing area.<sup>1,2,5–8</sup> Simultaneously, there has been considerable progress in the arena of responsive materials, which are capable of sensing external stimuli, fields, or molecular input and react accordingly by changing their microstructure and properties.<sup>3,4,9,10</sup> Both concepts aim to mimic different aspects of biological systems, which are able to manage a multi-scale and multicomponent self-organization in a dynamically challenging manner. Materials with such properties might reconfigure their internal structure to accommodate stress and temperature or self-arrange in different global forms depending on the response of building blocks. However, the sophistication of living systems requires a complex mechanism for responding to continuously changing environments and for adapting the changes within the systems. Although mimicking the abilities of biosystems to coordinate self-assembly and responsiveness in materials is still far in the future, both concepts are beginning to merge in nonliving systems built from reconfigurable components. Therefore, there is an emergent interest in uncovering how self-assembly processes are affected and modulated by reconfigurable properties of building blocks.

Structural self-organization is governed by a delicate balance of thermodynamic factors and the properties of the individual building blocks. Even in systems composed of the simplest blocks—spherical particles—the variation of basic parameters, such as free volume or particle size in mixtures,<sup>11</sup>

## ABSTRACT



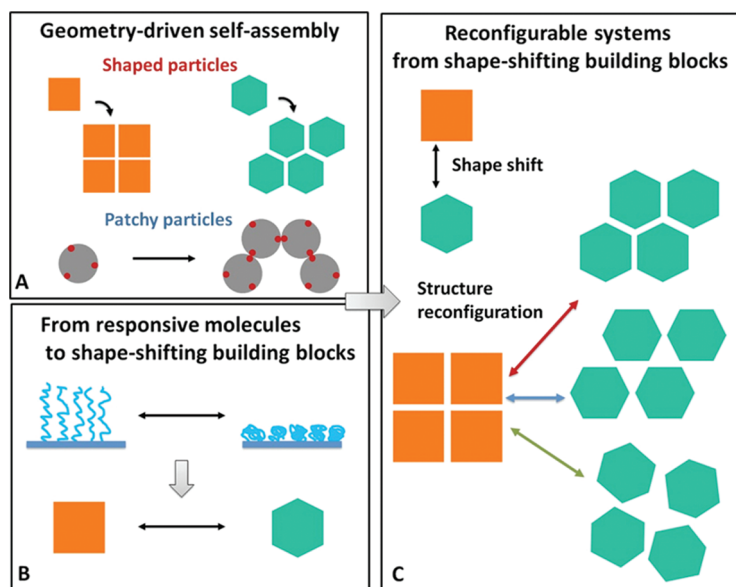
Incorporation of shape-shifting building blocks into self-assembled systems has emerged as a promising concept for dynamic structural control. The computational work by Nguyen *et al.* reported in this issue of *ACS Nano* examines the phase reconfigurations and kinetic pathways for systems built from shape-shifting building blocks. The studies illustrate several unique properties of such systems, including more efficient packings, novel structures that are distinctive from those obtained through conventional self-assembly, and reversible multistep shape-shifting pathways. The proposed assembly strategy is potentially applicable to a diverse range of systems because it relies on a change of geometrical constraints, which are common across all length scales. Recent developments in the areas of responsive materials and self-assembly methods provide feasible platforms for experimental realizations of shape-shifting reconfigurations; such systems might enable the next generation of dynamically switchable materials and reconfigurable devices.

quickly results in an intricate phase behavior, which is further complicated when interparticle interactions are introduced. Nevertheless, the self-assembly studies of the last few decades, from molecules to viruses and from nanoparticles to millimeter-sized objects, indicate that there are many common assembly scenarios despite system dissimilarities. The origin of such universal behavior often lies in a dominance of geometric effects over the details of specific interactions. For instance, the uniaxial anisotropy of simple asymmetric objects—rods—results in a competition between translational and rotational entropies and leads to a liquid crystal phase behavior, observed for molecules, nanoparticles, viruses, *etc.* In a broader sense,

\* Address correspondence to ogang@bnl.gov.

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**Figure 1.** (A) Self-assembly from geometric particles into static structures. Examples of 2D lattices formed by shaped (squares and hexagons) and patchy particles are shown. (B) Responsive molecules (a polymer brush is shown as an example) can be used to fabricate shape-shifting particles. (C) Representation of reconfiguration of a system structure due to the particle shape-shifting. Possible scenarios are shown: (red arrow) a structure as formed *via* self-assembly from the isotropic state (blue arrow), a unique structure which is not formed through self-assembly (shown in A), and (green arrow) a disordered structure.

the apprehension of geometrical effects as a powerful tool in organizing matter enables the establishment of common approaches for directing self-organization processes on different scales (Figure 1A).

Systems containing soft matter components, such as surfactants, polymers, and biomolecules, are often highly susceptible to environmental conditions, such as temperature, salt concentration, pH, electric or magnetic fields, and light.<sup>3,10</sup> In some cases, even a relatively small change in these parameters triggers a considerable structural reconfiguration. These effects are under active exploration for creation of “smart” materials that can respond and adapt according to the stimuli. Molecular responsiveness is often utilized to induce a functional change by exposing different chemical groups, altering conformation or length, *etc.*,<sup>3,9</sup> this provides enormous possibilities for material engineering (Figure 1B). For example, systems with designed wetting properties, volume/size/shape changes, substance release, stimuli-responsive aggregation behavior, regulated morphological transitions, and optical

response have been demonstrated.<sup>3,6,9,10,12–15</sup> Now, we can envision that when individual building blocks are composed of such responsive molecules, the particle's shape can be switched on demand (Figure 1C).

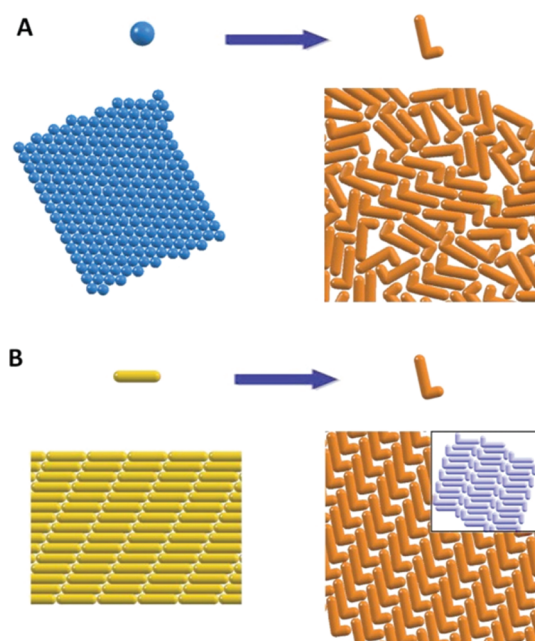
The fundamental question about properties of self-assembled systems composed of inherently changeable components is discussed in the molecular dynamics computational work of Nguyen *et al.* in this issue of *ACS Nano*.<sup>16</sup> A broad range of questions related to the phase behavior and kinetic pathways of reconfigurable systems built from shape-shifting building blocks is demonstrated in this study from Glotzer's group. Perhaps the most striking results are (i) observations of improved order fidelity and kinetically trapped structures that exhibit packings not accessible *via* a traditional self-assembly process from an isotropic state, and (ii) that predefined assembled structures can be formed *via* carefully chosen multistep shape-shifting processes. The study raises a number of intriguing questions related to potential use of these approaches for the design of materials from shape-shifting building blocks.

What are efficient shape-shifting pathways to drive system reconfiguration between particular lattice symmetries? What factors determine formation of ordered, porous (with voids), or fully disordered states during reconfigurations? What is the relationship between the time scales of shape-shifting and system reconfiguration?

The fundamental question about properties of self-assembled systems composed of inherently changeable components is discussed in the molecular dynamics computational work of Nguyen *et al.* in this issue of *ACS Nano*.

Recently, the same group reported transformations in systems containing molecularly decorated particles: a length switching of rods, grafted with polymer chains,<sup>17</sup> induced transitions between square, honeycomb, and pentagonal grids, and bilayer morphologies. Their new study generalizes the results to 14 different types of particles in two-dimensional (2D) systems, including convex, rod-like, and branched shapes, and with different shape-shifting properties. We discuss several aspects of systems in which reconfiguration is induced by shape-shifting, namely, the efficiency of packing, observations of novel structures that do not have analogues in traditional self-assembly, reversibility, and kinetic pathways.

**Efficient Packing.** Nguyen and colleagues compare the assembly process for particles of different shapes, either self-assembled from an isotropic state of targeted shapes or



**Figure 2.** (A) Particle shape-shifting from spherical to L-shape induces system reconfiguration from a triangular lattice to a disordered structure with higher density than achieved by direct self-assembly of L-shape particles. (B) Novel structure with long-range order (not energetically favorable) is achieved by shifting particle shape from a rod to L-shape. The inset shows the energetic favorable state for L-shape particles. Reproduced from ref 16. Copyright 2011 American Chemical Society.

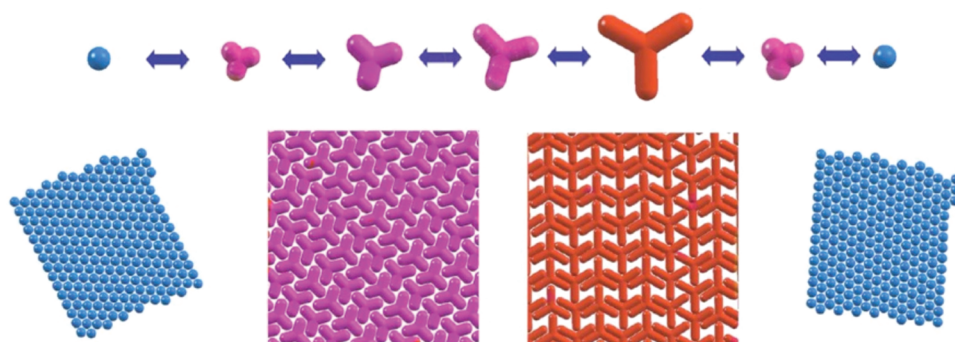
reconfigured through shape-shifting.<sup>16</sup> The latter approach allows for a more efficient assembly, exhibiting improved structural order and faster assembly time. The difference is particularly significant for non-convex-shaped particles, such as bent rods and branched particles, due to their susceptibility to steric restrictions. Self-assembly of these shapes typically requires long annealing times or use of external fields to overcome the substantial kinetic barrier. Order emerges spontaneously for anisotropic particles, like hockey sticks and sheared zigzags, when transformed from rods preordered in a smectic phase (Figure 2B), indicating the possibility of guiding particle packing. This ordering strategy also works for more complex-shaped particles with linear morphology, such as “bow” and “bull-head”, demonstrating that shape-shifting from a smectic arrangement of rods is a general and effective way to achieve order for this family of shapes.

**Novel Structures.** The shape-shifting strategy generates not only

thermodynamically stable structures but also novel arrangements with long-range ordering that are energetically unfavorable if self-assembled from an isotropic state. For example, the L-shaped particles obtained by “bending” rods form close-packed or porous ordered patterns (Figure 2B), depending on the length ratio of the branches, when starting from smectic packing. Both arrangements of L-shapes have higher potential energies than their corresponding ground states (inset in Figure 2B). The appropriate combination of the initial smectic states and a shape-shifting pathway facilitates the formation of porosity in these novel structures. Although such novel structures are kinetically trapped, the simulation results show that these structures are stable and reproducible. Therefore, this shape-shifting strategy is a particularly appealing kind of directed assembly, where the components are guided along the energy landscape into regions inaccessible to traditional self-assembly.

**Reversible Reconfiguration.** The computational results indicate a high degree of reversibility of reconfigured structures obtained by shifting particle shapes. Indeed, the reversibility is observed in the simulation studies (Figure 3) for shape-shifting between different convex particles (squares, rhombuses, and pentagons) and for shifts from convex to nonconvex particles (square and Y-shapes, pentagons, and crosses). However, reversibility for nonconvex particles (hockey sticks, L-shaped, and zigzags) requires alignment of the major axis with the layer direction (Figure 3). Remarkably, using the reconfigurable approach, desired structures can be prepared *via* a designed multistep shape-shifting pathway. For example, ordered structures of zigzags can be achieved by transforming rods into zigzags. If it is experimentally difficult to bend two ends of rods directly into zigzags, then rods can first be bent into hockey sticks, resulting in a biaxial smectic structure. The subsequent bending of the hockey sticks at the longer end will lead to an ordered structure of zigzags. This finding might help in the future experimental realization of a reconfigurable system when a direct shift between desired shapes is not possible. A reversible reconfiguration occurs not only between close-packed states but also between close-packed and porous packings: shortening and lengthening of the branches of Y-shaped particles results in switching between close-packed and porous states, which resembles membranes opening and closing (Figure 3). The tunability of the pore size over a relatively large range (twice as large as a subunit bead comprising the particle in the simulation) is appealing for the design of stimuli-switchable materials for separation, purification, and drug delivery and for control of mechanical properties.

**Kinetics and Pathways.** The shape-induced structure reconfiguration was found to be a highly kinetics-dependent process where the final structural details are determined by the initial ordered structures, the



**Figure 3.** Reversible reconfigurations are found between different ordered states for multistep shape-shifting, including close-packed and porous states. Shifting involves both convex and nonconvex particles. Reproduced from ref 16. Copyright 2011 American Chemical Society.

shape-changing pathway, and the shape-changing rate. The initial ordered structures, such as a triangular lattice of spheres or a smectic structure of rods, help guide the packing of shape-shifting particles. This effect grants shape-shifting systems unique packing behavior in comparison to self-assembly from discrete particles. Generally, an initial triangular lattice helps to order convex and branch-shaped particles, and an initial smectic lattice facilitates not only convex and branched but also rod-like-shaped particles. For example, the directionality of rods in the smectic layers allows for “bending” rods, such as hockey sticks or L-shaped particles, so adjacent neighbors can be easily packed and biaxial smectic phases are formed (Figure 2B). On the contrary, similar shape-shifting from a triangular lattice of spheres results in a disordered state that is denser than that obtained by self-assembly (Figure 2A). The optimization of long-range order in the target structure can be achieved by appropriate pathways, especially for cases involving nonconvex particles. The authors establish a rule for an optimal shape-shifting pathway: the particle's orientation relative to its neighbors should be consistent with the local packing of the target structure. The dynamical aspects of reconfiguration were revealed by changing the rate of particle shape evolution. If this rate is too fast, the degree of order decreases on a global scale, although locally ordered

clusters might exist. On the other hand, when this rate is comparable to the system's relaxation rate, the system's transformation is similar to a traditional self-assembly process. Systems of convex particles show less sensitivity to the details of kinetics, as evidenced by their preferences for close packing.

The multistep shape-shifting strategy enables directing reconfiguration processes toward formation of a broad range of structures. Does a system's behavior depend on the fine details of the continuous shape changes, or is it mainly determined by coarse shape evolution? In other words, is it still necessary to examine how reconfigurability is modified by changes in the functional form of a shape-shift? This question is imperative for any practical implementations of the concept since the system design, as well as the choice of materials and specific molecular mechanisms, might affect the shape evolution to a large degree, even if the initial and final particle shapes are fixed.

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A number of recent studies have investigated systems with specific particle models in which shape evolution was described by an explicit functional form.<sup>11,18,19</sup> Although these studies typically address questions related to the self-assembly of target particles from an isotropic state rather than by the shape-shifting strategy, the findings provide insight into the factors governing packing. For example, a model with shapes continuously changing from spherical into elliptical was proposed by Batista *et al.*<sup>11</sup> They studied the structure of assemblies built directly from deformable spherical particles and observed more efficient packing in these assemblies than for rigid spherical particles. This system does not exhibit spontaneous transitions from the face-centered cubic (FCC) phase of sphere packing to the dense crystalline phase of ellipsoids, signifying a continuous pathway for both shape-shifting particles and a phase transformation. The assembly of particles with shapes continuously evolving from octahedron to sphere and to cube in a specifically defined functional form was studied by Torquato's group.<sup>18,19</sup> Both three-dimensional (3D) and 2D systems, formed respectively from so-called “superballs”<sup>19</sup> and “superdisks”,<sup>18</sup> were examined computationally. Interestingly, the requirement for the highest packing density results in a lattice symmetry transformation. The discontinuity of the phases for continuous shape changes was



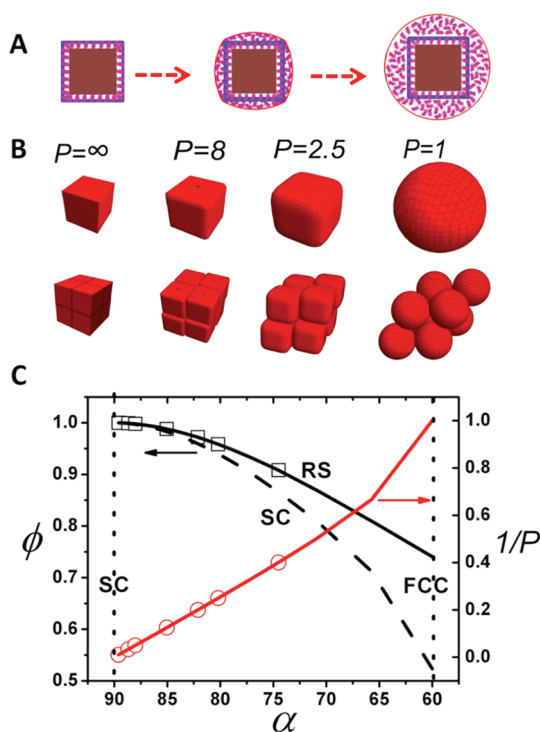


Figure 4. (A) Illustration of a cube shape-shifting from cube to quasi-sphere due to the ligand adsorption. (B, Bottom) Illustration of a phase transformation from SC to FCC via RS phase due to (top) the continuous particle shape-shifting from cube to sphere for experimentally determined values of deformation parameter  $p$ .<sup>15,19</sup> (C) Calculated  $1/p$  (red solid line) and volume fraction,  $\phi$ , for RS (black solid line) and SC (black dashed line) as a function of variable angle ( $\alpha$ ) in a rs lattice. The black and red symbols correspond to the experimental data. Adapted from ref 15. Copyright 2011 American Physical Society.

observed in both the 2D and 3D cases. For example, in 3D, the densest packing jumps from a distorted FCC lattice with three-fold rotational symmetry to a distorted FCC lattice with two-fold rotational symmetry at a certain quasi-sphere state when the particles are rounded from cubes to spheres.<sup>19</sup>

In the experimental arena, several types of stimuli-responsive shape-shifting particles were fabricated recently. For example, Yoo *et al.*<sup>14</sup> synthesized poly(lactide-co-glycolide) polymeric particles that are able to switch their shape from elliptical disks to spheres in response to temperature, pH, and chemical additives. This shape-shifting behavior was related to a change in the balance between polymer viscosity and interfacial tension. Gebhardt *et al.*<sup>12</sup> showed that polypeptide-based block copolymers can undergo a rods-to-spheres shape transformation due

to pH variation. However, experimental investigations of the relationship between shape-shifting building blocks and systems' reconfiguration properties are still in their early stages. One of the successful experimental realizations of this type of system was recently demonstrated by our group.<sup>15</sup> The approach is based on tailoring the well-defined shape of inorganic nanoparticles by a tunable shell that is composed from small mobile organic molecules (Figure 4A). Specifically, we investigated the phase behavior of a Pd nanocube (10 nm) system in a ligand-rich (dodecanethiol) solution as a function of *in situ* variation of the particle's shell. A continuous structural evolution from a simple cubic (SC) structure to an angle-variable rhombohedral structure (RS) was observed upon solvent evaporation (Figure 4C).<sup>15</sup> Such phase transformation was related to the system's attempt to accommodate a changing

particle shape from a cube to a quasi-sphere due to ligand adsorption (Figure 4A,B). A relationship between the particle shape and the lattice reconfiguration was established using the "superball" model.<sup>19</sup> The observed reconfiguration pathway is consistent with theoretical predictions based on the densest packing criteria, although a kinetically trapped state, evident in our study, manifests the role of physical reality with its molecular interactions and rheological effects. In the recent results from Hanrath's group,<sup>20</sup> the phase behavior of ligated PbSe nanoparticles was investigated using *in situ* grazing-incidence X-ray scattering. A body-centered cubic-to-FCC phase transition was observed upon solvent annealing. This phase transition was associated with the evolution of the particle's effective shape from cuboctahedrons to spheres due to a more extended state of the tethered ligand and a solvent layer increase between particles.

## OUTLOOK AND FUTURE CHALLENGES

The geometry-driven approach for organizing matter has emerged as a practical strategy due to its applicability to a broad range of systems and different scales. The phase control orchestrated by local geometrical constraints of particle arrangements can be realized either by particle shapes or by placing binding spots at specific locations on a particle's surface, with so-called patchy particles<sup>21</sup> (Figure 1A). The locking mechanism of proteins illustrates that even a combination of both approaches can be successfully implemented. The recent computational work on packing of Platonic and Archimedean solids,<sup>22,23</sup> in which ordered and quasi-crystalline structures were observed, demonstrates that shape-driven assembly can result in a complex organization. New simulations by Glotzer's group on the packing of tetrahedral particles show that even subtle changes in shape can cause profound changes in the resulting ordered structure.<sup>24</sup>

Moreover, not only the whole particle shape but also specifically shaped particle regions can control local arrangements, as shown for colloids with “key” and “lock” shape complementarity.<sup>25</sup> On the other hand, much attention, particularly in theoretical studies, has been focused on the concept of patchy particles,<sup>21,26–28</sup> where the number and location of binding sites determine the interparticle connectivity. Interestingly, the primitive models of colloidal patchy particles were found to correlate well with findings for atomic and molecular systems; for example, a water-like structure was captured by a model with tetrahedral connections.<sup>29</sup> Hence, these findings demonstrate that geometry-driven self-assembly approaches might be a powerful and elegant alternative to tailoring interaction potentials, which is typically required for the formation of complex phases.

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Adding a new, dynamical dimension, as shown in the work from Glotzer's group, can significantly broaden geometry-driven assembly by opening access to unique structural organizations, to system reconfiguration pathways and structural fluidity, and, potentially, to novel materials with tunable properties. There is a range of questions that are waiting to be addressed in respect to “coordination” of shape-(symmetry)-shifting and a system's structural response and reconfiguration, rheological limitations for system transformations, physical

mechanisms to control a particle's shape, and requirements on reconfiguration into quasi-crystal organization. The particle's softness might be another important parameter, in particular, for experimental systems made from real materials. The softness can render shapes in contact and contribute to a shape polydispersity; both effects are relevant for experimental systems. The significant shape fluctuations on relevant time scales and across ensembles might hinder or promote reconfigurations. Another aspect is the natural extension of these ideas to 3D systems, which raises a new set of questions. Moreover, in principle, the concept of shape-shifting building blocks can be generalized to patchy particles, where locations and a number of patches can be shifted. This approach might provide unique possibilities for the topological control of structures in a dynamical manner, with ordered, quasi-ordered, network-like, and discrete cluster morphologies. The realization of this approach by theoretical or experimental methods is yet to be explored. The coalescence of these ideas will perhaps enable scientists to find more universal rules for geometry-driven assembly processes.

Although direct experimental realizations appear tempting yet distant at the present time, there are already a broad range of materials and approaches that can be utilized for the fabrication of shape-shifting building blocks, including foldable materials, biomolecular constructs, shape-memory polymers, photodeformable colloids,<sup>30</sup> and different classes of nanomaterials.<sup>3,4,9,10,31</sup> In the latter area, recent advances in the fabrication of shaped particles and their superlattices provide an experimental platform<sup>5,32,33</sup> for the exploration of geometry-driven nanoparticle reconfigurations. Nanoparticles are typically decorated with organic molecules, which might restrict their use as model systems in studies on the packing of solids. However, responsive shells formed by molecules tethered to a particle open possibilities for shape-shifting and modulation of

pure geometrical forms and their assemblies.<sup>3,6,34</sup>

The concept of a reconfigurable and dynamically induced system state by shape-shifting of its components is an appealing route for materials design, with endless possibilities to link scales in a predictable manner: molecules affect blocks, blocks affect macrosystems. The practical realization of these ideas might enable new generations of switchable materials and devices. Beyond this, the effects of local constraints and the relationship between the evolving structure of building blocks and system evolution as a whole have deeper implications for the topological control of life and death of cells<sup>35</sup> and society structuring from evolving social groups.<sup>36</sup>

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