

Harnessing Dynamic Covalent Bonds in Patchy Nanoparticles: Creating Shape-Shifting Building Blocks for Rational and Responsive Self-Assembly

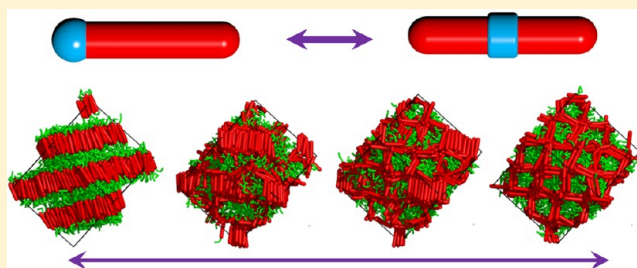
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S Supporting Information

ABSTRACT: Using computational modeling, we suggest and demonstrate a novel class of building blocks for nanoparticle self-assembly, that is, shape-shifting patchy nanoparticles. These nanoparticles are designed by harnessing dynamic covalent bonds between nanoparticles and patches decorated on them. The breaking and reforming of these bonds in response to their environment allow the patches to undergo a structural rearrangement that shifts the location or number of patches. Our simulations for the assembled superstructures and kinetic pathway of two types of these building blocks demonstrate that shape-shifting patchy nanoparticles delicately meet two emerging design concepts of next generation materials: rational self-assembly and responsive matter. In this context, these nanoparticles may enable new generations of materials with reconfigurable property as well as controllable topologies in a dynamical manner.

SECTION: Physical Processes in Nanomaterials and Nanostructures



In recent years, the request for next-generation materials has driven material design to the ability to reversibly adapt to their environment and possess a wide range of responses.^{1–8} Simultaneously, two powerful design concepts, responsive matter and rational self-assembly, have emerged and played a considerable role in this quickly developing area.^{3–6} The promising concept of responsive matter requires that intrinsic building blocks be able to reconfigure from one structure to another.^{3–6,8–10} For the concept of rational self-assembly, the building blocks should be carefully chosen and constructed to realize a high level of direction and control.^{11,12} A unique and emerging type of such building blocks is “patchy nanoparticles”, that is, the nanoparticles decorated with specific, anisotropic surface patterns of attractive and repulsive interactions.^{13,14} Through a unique design with respect to particle size and shape as well as the number and position of the “patches”, these particles can be successfully directed to self-organize into complex superstructures.^{12–18}

Almost all current patchy nanoparticles are static: once formed, they retain the same structure throughout their lifetime. This leads to the question: Can patchy nanoparticles be used to construct shape-shifting building blocks? If yes, then the shape-shifting patchy nanoparticles can delicately meet two material-design concepts stated above and thereby are a powerful and elegant alternative for the topological control of structures in a dynamical manner, with ordered, quasi-ordered, network-like, and discrete cluster morphologies. Given the fact that an impressive number of methods have been developed to fabricate patchy nanoparticles with different geometries in large quantity and that the responsive properties of some molecules

can also be introduced to surfaces, resulting in functional surfaces, patchy nanoparticles with reconfigurable patches create enormous possibilities for a new class of functional materials.^{19–25} However, little is known regarding this approach by experimental and theoretical methods. The primary challenge for this approach is then to ascertain precisely how the patchy nanoparticles can function as reconfigurable components and furthermore what structures and kinetics will present in the assembly of these types of nanoparticles.

Here we propose that the design of shape-shifting building blocks based on static patchy nanoparticles can be realized through incorporating the reversible chemistry that can be used to program a response that originates at the most fundamental (molecular) level. For illustrative purpose, we consider the dynamic covalent bonds that can break and reform under the appropriate conditions without irreversible side reactions.^{2,26,27} This class of bonds allows for the production of robust covalent molecules while maintaining a dynamic character that can only be accessed when specific external factors are present. Structural dynamic molecules have made use of a number of dynamic covalent bonds such as thermally activated alkoxyamine bonds and Diels–Alder adducts, chemosensitive hydrazones, and multiresponsive functionalities, such as the disulfide bond, that respond to pH, light, and redox conditions.²

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Full technical details of the simulation methods and the interactions considered in the present simulations can be found in the Supporting Information. In brief, the patchy nanoparticles are generated through generic coarse-grained bead-spring models interacting via empirical pair potentials, which greatly reduces the overall number of forces that must be calculated while retaining the basic surface interactions expected in the nanoscopic particles.¹³ We adopt the Bell model to describe the rupture and reformation of bonds due to thermal fluctuations. In fact, the Bell model has served as a useful framework for describing the reversible bonds formed in the model of self-healing materials, between biological cells, or between cells and surfaces.^{28,29} For illustrative purpose, we investigate two spontaneous shape transformations due to the patch change, as demonstrated by the schematic diagrams in Figure 1A. The left and right panels in Figure 1A,a display that

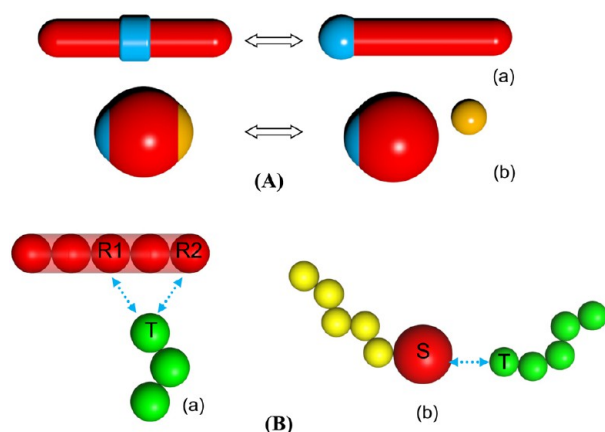


Figure 1. (A) Schematic diagrams showing patchy particles with tunable patches: (a) transition between nanorods with patches at the lateral site (left) and the end (right) and (b) transition between nanospheres with two patches (left) and one patch (right). (B) Models of nanorod (a) and nanosphere (b) used in the simulations. The tether bead labeled “T” can be linked to the beads of “R1” and “R2” in the nanorod and “S” in the nanosphere by dynamic covalent bond.

the position of a patchy nanoparticle on a nanorod shifts from the lateral site to the end of the rod, representing the first shape-shifting process considered: the transformation of patchy position. The left panel of Figure 1A,b shows the structure of a nanosphere with two lateral patches in the opposite sides, whereas in the right panel one of them drops off from the nanosphere. This represents the second shape-shifting process considered in the simulations: the change of patchy number. In general, both of these transformations are the most typical shape-shifting processes for each patchy nanoparticle with tunable patchy number. Other more complex shape-shifting processes may also be envisioned based on them.

The ability to control which dynamic bond is present in patchy nanoparticles is critical in designing tunable patches. Fortunately, the quickly emerging dynamic bonds give the chemist a molecular toolbox in designing tunable patchy nanoparticles. For example, there are two general classes of dynamic covalent bonds: “unsymmetrical” dynamic bonds where complementary functional components are required to react/bind ($A+B$ yields $A-B$, for example, an imine bond) or “symmetrical” dynamic bonds that form by the reaction/binding of similar functional components ($A+A$ yields $A-A$, for

example, a disulfide bond).² For the first transformation with the position transition of a patchy nanoparticle, the unsymmetrical bond with complementary functionalities or the synthetic application of unsymmetrical and symmetrical bonds may be particularly useful, whereas the symmetrical bond can be chosen to design the particles in the second transformation because only one component needs to be present to form the bond.

In the present simulations, the building blocks in the transformation of Figure 1A,a are represented by the lateral and end-tether nanorods, where the species of the same type tend to aggregate (Figure 1B,a). As stated above, this transformation might be produced by the unsymmetrical dynamic bond or the synthetic application of unsymmetrical and symmetrical bonds. The building blocks in the second transformation are represented through a ditethered nanosphere with two offsite tethered ligands (Figure 1B,b). The yellow tethers tend to aggregate and are linked to the nanosphere by a general covalent bond, whereas the green tethers tend to separate and are linked to the nanosphere by a dynamic covalent bond. Once the dynamic bond breaks, the ditethered nanosphere becomes a monotethered nanosphere, achieving the structural reconfiguration of building blocks, as demonstrated in Figure 1A,b.

We first observe the ordered superstructures prepared by performing thermodynamic self-assembly simulations from disordered initial states upon cooling at fixed volume fractions, where the structure of each building block is unchangeable (Figure S1 and its description in the Supporting Information). The equilibrium assembled superstructures of laterally and end-tethered nanorods are columnar square grid and lamellar structure, respectively. Either ditethered nanospheres or monotethered nanospheres can self-assemble into tubal superstructure, where yellow tethers form tube center and nanospheres organize into tube wall. Interestingly, the tubal structure formed from ditethered nanosphere presents a larger tube-by-tube distance. This can be identified from their radial correlation distribution $g(r)$ (Figure S1 in the Supporting Information). To understand the structural coordination at different length scales and the kinetic pathway, we focus on the first transformation, that is, the structural reconfiguration between laterally tethered and end-tethered nanorods. At temperature $T = 2.0 \epsilon/k_B$, which is below the disorder–order transition temperatures for both structures, we start the position transition of the rod patches (tethers) by tuning dynamic covalent bonds. The morphological evolution from columnar square grid structure to lamellar structure and vice versa is spontaneously obtained and is monitored by the parameters of the lateral and end-bond number, N_b , the system potential energy, U , and $g(r)$. If the fluctuations in these quantities are less than 5–10%, then we ascertain that the transformation is complete.

Starting with the square grid structure formed by laterally tethered nanorods, we initiate the rupture of the dynamic covalent bonds between rods and tethers at the rod middle (middle bonds). The separated tethers are set to have a predominant trend to reform bonds with rods at the rod end (end bonds). Figure 2a presents the snapshots of the morphological transition and Figure 2c–e provides N_b , U , and $g(r)$ as a function of time during the square grid-lamella transformation. Upon the rupture of middle bonds, the equilibrium square grid structure becomes unstable and the bilayer rod ribbons tend to be disordered. This morphological evolution advances gradually due to the kinetics of the rupture

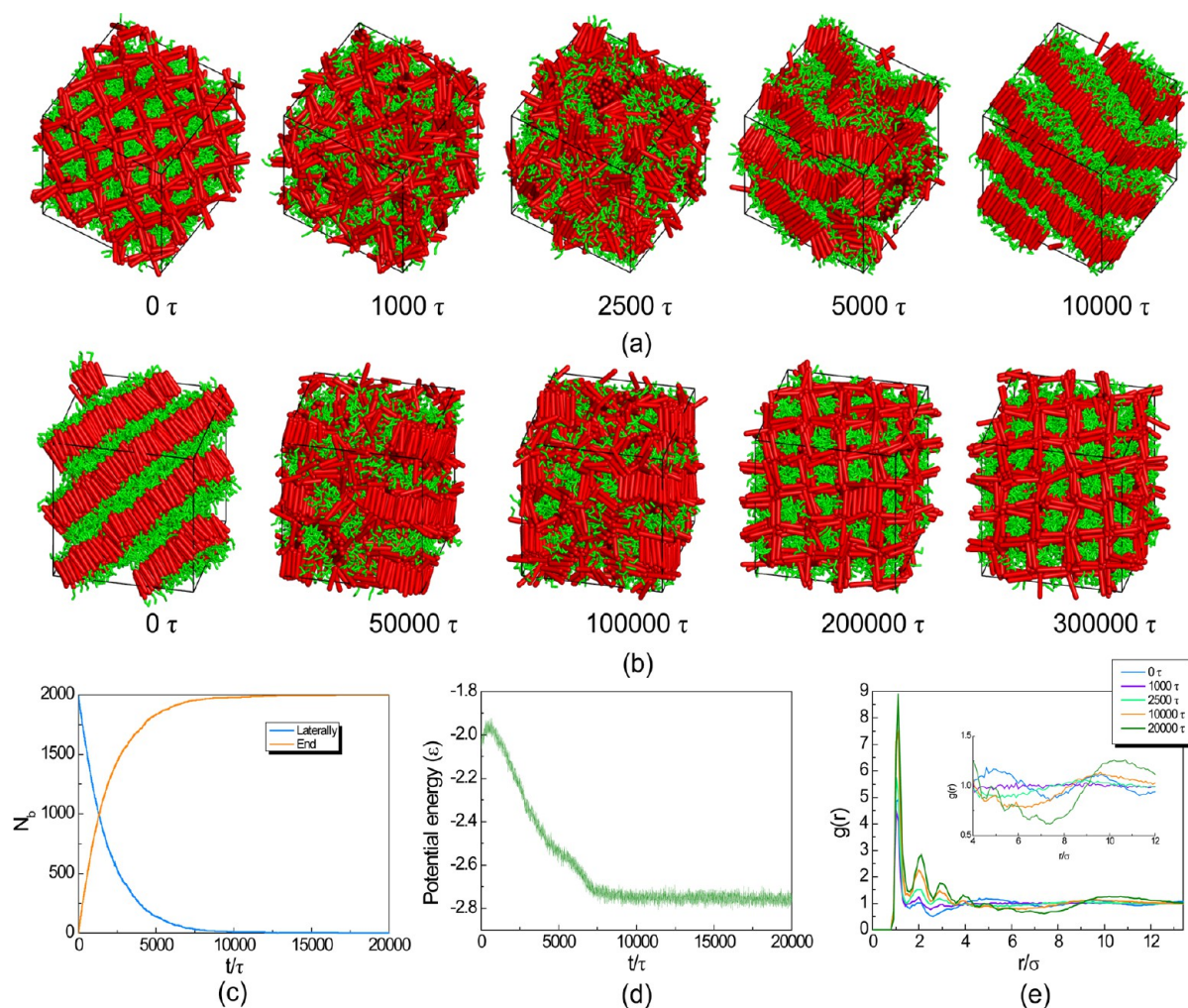


Figure 2. Transformations between columnar square grid structure and lamellar phase. (a) System snapshots for the transition from columnar square-grid structure (laterally tethered nanorods) to lamellar structure (end-tethered nanorods). (b) System snapshots for the transition from lamellar structure (end-tethered nanorods) to columnar square-grid structure (laterally tethered nanorods). The time steps are counted from the beginning of transformation. (c–e) The changes in the numbers of end (red) and lateral (blue) bonds, potential energy per particle, and radial rod–rod correlation functions during the transformation process of panel a.

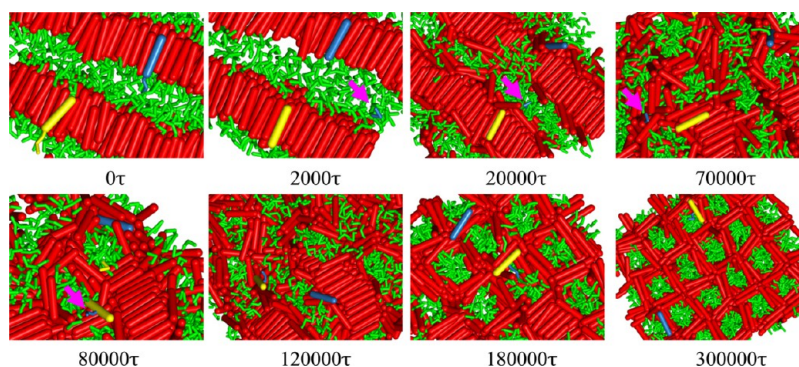


Figure 3. Coordination of structures at different levels during the transformation from lamellar phase to columnar grid structure. Two rods are marked in yellow and blue, respectively, and the tether of the blue rod will reform bond with the yellow bond. The pink arrows denote the tether of the blue rod.

of middle bonds and the reforming of end bonds (Figure 2c). With the increase in the number of end bonds, the nanorods finally organize into lamellar structure. As shown in Figure 2d, the system potential energy drops from a high value corresponding to the square grid to that corresponding to the

lamellar structure assembled from end-tethered nanorods. Figure 2e and its inset shows $g(r)$ clarifying the structural transformation, where the characteristic peaks of square grid at 5.0σ and 10.0σ gradually disappear with the formation of a characteristic broad peak of lamellar structure near 10.0σ .

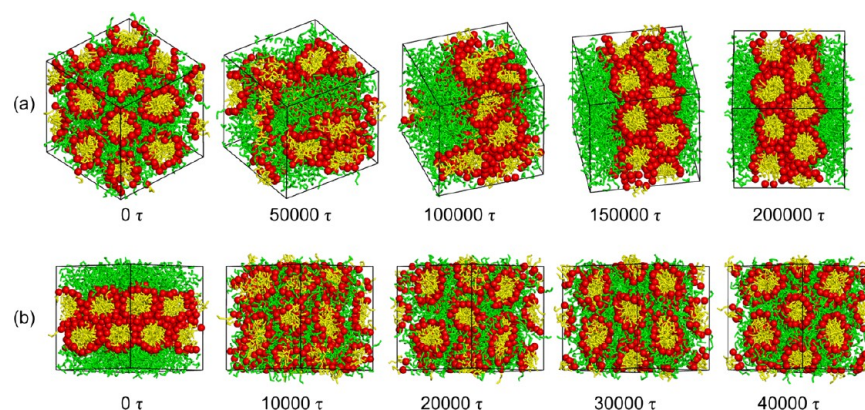


Figure 4. Transformations between tubal phase and compact tubal phase formed by tethered nanospheres. (a) System snapshots for the transition from ditethered nanospheres to monotethered nanospheres. (b) System snapshots for the transition from monotethered nanospheres to ditethered nanospheres.

Figure 2b and Figure S2 in the Supporting Information present simulation results of morphological transition and various characteristic parameters in the transformation from lamellar structure to square grid structure, where dynamic bonds at the rod end rupture and the separated tethers reform bonds with nanorods at rod middle. By comparing the time scales of two order–order transformations, it is interesting to find that the transformation from lamellar structure to square grid structure needs about $300\,000\tau$, much longer than that from square-grid structure to lamellar structure ($10\,000\tau$) at the same temperature. This significant difference demonstrates that the shape-shifting-induced structural reconfiguration is highly initial-structure-dependent. In practice, the lamellae-square grid transformation may be fastened by increasing system temperature. Indeed, our simulation results demonstrate that the transforming can be shortened to about $30\,000\tau$ if the temperature is increased to $3.0\ \varepsilon/k_B$ and subsequently decreased to $2.0\ \varepsilon/k_B$ (Figure S3 in the Supporting Information). A higher temperature is helpful to destroy the densely packing of the nanorods within a lamella and thereby facilitates the reconfiguration process (Figures S4–S6 and their description in the Supporting Information).

To gain insight into the effects of structural coordination in different length scales on the kinetic pathway and mechanism of system reconfiguration, we study the shape-shifting process of some certain nanorods during the assembling. For this purpose, a local region is selected from the lamellar structure in the initial stage, where two end-tethered nanorods, marked in yellow and blue, respectively, are chosen as tracking objects (Figure 3). We ascertain in advance that the tether at the end of the blue nanorod will separate and finally connect to the middle of the yellow nanorod. Figure 3 shows that the tethers on both of these nanorods separate from the rods upon bond rupture. The separated tethers move in the tether domain, whereas the yellow and blue nanorods are still kept within the lamellae due to the strong side-by-side rod attraction. One can note that a long period is needed for the blue tether to anchor near the yellow nanorod and to connect to the rod by forming a new bond. The snapshots reveal that two factors can account for the long period: the random motion of the tether in the tether domain and the dense packing of the nanorods within lamellae. The second factor may have a stronger effect because it strongly limits the diffusion of the tether to reach the middle position of rods, which can be validated from the plots of mean-square displacement (MSD) (Figure S7 in the Supporting Informa-

tion). Until $80\,000\tau$, a bond forms between the yellow nanorod and the blue tether, leading to the formation of a laterally tethered nanorod. The yellow rod is consequently dragged out of the lamella by the tether. Thus, the superstructure gradually evolves into square grid structure with the reorganization of the laterally tethered nanorods.

The above simulation results demonstrate that by shifting the location of patches patchy nanoparticles with tunable patches can provide unique possibilities for the topological control of self-assembled structures in a dynamical manner. Another possible approach regarding this concept is to tune the patchy number. To demonstrate this approach, we choose ditethered nanosphere with two opposite tethers. As presented in Figure 1B,b, the yellow tethers are hydrophobic and the green tethers are hydrophilic. From the disordered initial state, the ditethered nanospheres can thermodynamically self-assemble into ordered structure with dispersed nanotubes (Figure S1 and its description in the Supporting Information). Each nanotube consists of a tube center of hydrophobic tethers and tube wall of nanospheres. The hydrophilic tethers are found to fill in the space among nanotubes. To realize the dynamical control for the patchy number, here the bonds between green tethers and nanospheres are modified into dynamic covalent bonds (Figure 1B,b). With the rupture of these dynamic bonds, the ditethered nanospheres become monotethered nanospheres that can organize into compact tubal structures, as shown in Figure S1 in the Supporting Information. In Figure 4a,b, we present the transformation from dispersed tubal structure to compact tubal structure upon the geometrical shifting from ditethered nanospheres to monotethered nanospheres and vice versa. One can find that the tube-by-tube distance can be dynamically tuned in these transformations.

The simulation study demonstrates a new class of nano building blocks that simultaneously meets two material-design concepts, that is, responsive matter and rational self-assembly. Experimentally, the progress of the synthetic chemistry of nanoparticles offers us more chances to design nanoparticles with various shapes and architectures.^{19–25,30–35} For example, the polyhedrons can be used as the building blocks to directly self-assemble into various topologies.³⁵ By decorating patches on some certain faces, edges, and vertices with dynamic covalent bonds, these nano building blocks may become more “smart” and can rationally self-assemble into precise topologies in a dynamical manner. Thus, the shape-driven assembly of shape-shifting patchy nanoparticles opens access to the

dynamically topological control of structures, with ordered, quasi-ordered, network-like, and discrete cluster morphologies, and to novel materials with tunable properties, such as reconfigurable materials, soft smart materials, self-healing materials, and so on. It should be emphasized that the technique demonstrated by the simulations is achievable in the experimental research. For example, the unsymmetrical bond (A+B yields A-B, for example, an imine bond) with complementary functionalities or the synthetic application of unsymmetrical and symmetrical bonds (A+A yields A-A, for example, a disulfide bond) may be used to design the first transformation with the position transition of a patchy nanoparticle, whereas the symmetrical bond can be chosen to design the particles in the second transformation because only one component needs be present to form the bond.² Actually, the responsive properties of some these molecules have been introduced to surfaces, resulting in functional surfaces, which provide useful guidelines for the experimental realization of shape-shifting patchy nanoparticles.^{22–25}

In summary, we proposed and theoretically demonstrated a conceptual framework capable of describing patchy nanoparticles of tunable patches on the basis of dynamic covalent bonds, where the Bell model was adopted to describe the rupture and reforming of dynamic covalent bonds. On the basis of this model, molecular simulation was employed to study the structure response, kinetic pathway, dynamical mechanism, and the coordination on different length scales during the directed self-assembly of these tunable particles. Our simulations predict that by harnessing dynamic covalent bonds into patchy nanoparticles, for example, lateral and end-tethered nanorods and di- and monotethered nanospheres and so on, the patches on the nano building blocks can be effectively “activated”, which offers their self-organizing process with responsive matter in addition to rational direction. In this context, the concept of shape-shifting building blocks is successfully generalized to patchy nanoparticles, with powerful potential in the material design. We further predict that the shape-shifting-induced structural reconfiguration is highly initial-structure-dependent and external conditions, such as temperature, can be used to tune the transformation kinetics. The findings indicate that adding dynamic patches to patchy nanoparticles can significantly broaden the shape-driven assembly of nanoparticles by opening access to unique structural organizations, to system reconfiguration pathways, and to novel materials with tunable properties.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of simulation methods and additional simulation results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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