

Direct Imaging of "Patch-Clasping" and Relaxation in Robust and Flexible Nanoparticle Assemblies

Ahyoung Kim, Kireeti Akkunuri, Chang Qian, Lehan Yao, Kai Sun, Zi Chen, Thi Vo,* and Qian Chen*



enables multifunctionality and directed self-assembly into nonclosely packed optical and mechanical metamaterials. However, experimental demonstration of such assemblies has been scant due to challenges in leveraging patch-induced NP–NP attractions and understanding NP self-assembly dynamics. Here we use low-dose liquid-phase transmission electron microscopy to visualize the dynamic behaviors of tip-patched triangular nanoprisms upon patch-clasping, where polymer patches interpenetrate to form cohesive bonds that connect NPs. Notably, these bonds are longitudinally robust but rotationally flexible. Patch-clasping is found to allow highly selective tip–tip assembly, interconversion between dimeric bowtie and sawtooth configurations, and



collective structural relaxation of NP networks. The integration of single particle tracking, polymer physics theory, and molecular dynamics simulation reveals the macromolecular origin of patch-clasping-induced NP dynamics. Our experiment-computation integration can aid the design of stimuli-responsive nanomaterials, such as topological metamaterials for chiral sensors, waveguides, and nanoantennas.

KEYWORDS: patchy nanoparticles, liquid-phase TEM, open self-assembly, scaling theory, molecular dynamics simulation

INTRODUCTION

Polymer patching on nanoparticles (NPs) is a potent approach to design complex nanostructures 1-5 such as nanomotors, directed assemblies, and robotics through multifunctionality and directional interactions.⁶ Unlike NPs of homogeneous surface that favor highly coordinated NP assemblies,⁷ patchy NPs allow low-coordination open structures.^{8,9} These open structures are predicted to have high reconfigurability, tunable photonic bandgaps,¹⁰ and negative Poisson's ratio,¹¹ properties useful for optical³ and mechanical metamaterials.^{12,13} However, current studies on patchy NPs are mostly limited to synthetic efforts due to a lack of understanding of the fundamental interactions governing their assembly mechanisms and dynamics. For example, synthesis of polymer-patched NPs exhibiting environmental and biological compatibility¹⁴ is often achieved through tuning the electrostatics repulsion between patches. Yet, such patchy NPs are limited in use for patch-induced self-assembly due to difficulties that arise from converting electrostatics repulsions into patch-patch attractions^{5,15} to mediate selfassembly for metamaterials fabrication. Furthermore, visual characterization of patchy NP dynamics to elucidate the necessary insights for subsequent theoretical developments has

been limited as both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) traditionally rely on dry or frozen samples, where information regarding NP dynamics is lost.^{16,17} Alternative, liquid based approaches aimed at characterizing the relevant molecular dynamics rely on ensemble spectroscopy methods,¹⁸ where configurations and interactions at the single NP-level are hard to access. Although liquid-phase TEM has successes in visualizing nanoscale dynamics of inorganic,^{19–22} organic,^{23,24} and hybrid materials,^{25,26} it has not been applied to polymeric patchy NPs. There is thus a lack of real-time and real-space observation of patch-induced NP behaviors in solution, crucial in understanding nanoscale patch–patch attractions.

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Figure 1. Patch clasp-induced nanoprism assembly. (a-c) Schematics of patchy nanoprism synthesis (a), assembly into a dimer and chain in liquid-phase TEM (b), and analogy to hand clasp (c). (d-g) TEM images of nanoprisms with false-colored patches (d, e) and assembly into bowties (f) overlaid with a local thickness l_t map of a patch (d) and a clasp (g). Images without false coloring are in Figures S1 and S2. (h, i) Schematics of surfactant–polyelectrolyte complexation before (h) and after patch clasp (i). Scale bars: 20 nm (d, g, inset of f), 100 nm (e), 200 nm (f).

Here we develop and implement protocols to image the formation and relaxation dynamics of flexible patchy NP assemblies under liquid-phase TEM, where selective patchpatch attraction is introduced to assemble open structures. Our in situ observation reveals that surfactant-polyelectrolyte complexation¹⁶ renders the charged polymer patches attractive, leading to flexible and robust bonds that differ from conventional, rigid inter-NP interactions (e.g., electrostatic, van der Waals). The observed patch-patch attraction is analogous to "hand-clasping" and is capable of linking NPs into bowties and branched networks. The real-time and real-space formation and relaxation dynamics of clasp-connected NPs are visualized under liquid-phase TEM at optimized low dose rates about 2 orders of magnitude lower than what were used for imaging inorganic NP assemblies^{27,28} to ensure polymer stability. Statistical analysis of single NP tracking reveals the flexibility of the patch clasps with nanoscale rotational freedom that is otherwise difficult to resolve. Polymer physics and molecular dynamics (MD) simulation aid the interpretation of our experimental results and verify the molecular origin of a range of clasp-induced dynamic behaviors, from how polymer patches recognize each other and undergo patch-specific penetration to how the extent of clasping determines the flexibility and structural integrity of NP bowties and networks. In situ imaging and corresponding simulations of networks further elucidate that a network-level structural relaxation of nanoprisms arises from the clasp flexibility. Such conformational changes in NP network keep the initial topological connection while relaxing the entire structure, making such networks useful for reconfigurable topological mechanical metamaterials.^{12,13} Lastly, we show

that the strategy of clasp-induced NP assembly can be extended to make a range of structures and motifs, including cyclics, branches, and triangular tiling lattices, all of which cannot be achieved without patch-specific attraction.

Our flexibly linked, open assemblies contrast with the prevalent densely packed NP assemblies favoring facet alignment between particles⁷ or "lock-and-key" motifs.²⁹ Densely packed NP assemblies⁷ not only are "closed" structures but have low flexibility in particle—particle bonds, limiting reconfigurability. Conversely, our patch-clasping design allows for extensive conformational change of the assemblies without bond breakage. As such, our NPs provide the ideal building blocks for bottom-up fabrication of dynamic architectures,³⁰ including nanoscale auxetics,¹³ waveguides,³¹ and nanoantennas.³²

RESULTS AND DISCUSSION

Tip-Patched Nanoprism Bowties Linked by Flexible and Robust Polymer Patch Clasps. Using gold triangular prisms with repulsive polymer patches, we assemble reconfigurable nanobowties and branched networks connected by longitudinally robust and rotationally flexible NP bonds, resembling hand clasps (Figure 1a–c). Such patch clasps are formed following our report on selective patch–patch attraction via surfactant–polyelectrolyte aggregation mechanism,¹⁶ which was conventionally applied to make coherent polymer films³³ and purify nucleotides.³⁴ Going beyond the previously observed static, dried single-patch prisms at the dimer-level,¹⁶ we reveal the real-time and real-space formation and relaxation dynamics



Figure 2. Patch clasp-induced bowtie assembly and disassembly dynamics. (a, b) Time-lapse liquid-phase TEM images (a) and corresponding schematics of a bowtie assembly and disassembly (b). (c, d) Center-to-center distance D (c) and tip-tip angle θ (d) of the prism pair in (a) (scatter plot, raw data; solid lines, averaged over 2.5 s). Dose rate: 0.14 e⁻ Å⁻² s⁻¹. (e) 2D distribution map of the nanoprism pair positions in stage ii with one prism positioned at the coordinate center. Scale bars: 50 nm.

of the bowties and multiclasp-connected networks by liquidphase TEM imaging (Figure 1b).

The gold nanoprisms (edge length, 67.8 ± 3.1 nm; thickness, 22.9 ± 2.3 nm, Figure S1, Supporting Information) are tipcoated with polymer patches (polystyrene-b-polyacrylic acid; PS-b-PAA) as our model patchy NP system (Figure 1a). Specifically, the polymers are PS_{154} -*b*-PAA₅₁, $M_p = 16,000$ for the PS block and $M_p = 3,700$ for the PAA block, with a polydispersity index of 1.04 (purchased from Polymer Source Inc.). These NPs are synthesized at a yield higher than 92% following our previous report¹⁵ (Figures 1a and S1, Methods). The tip-patched nanoprisms in their aqueous suspension are repulsive to each other, due to negatively charged PAAs on the patch surface¹⁵ (Figure 1d,e). However, upon incubation in an aqueous cationic surfactant solution,¹⁶ the patches of neighboring particles become attractive to one another and interpenetrate. The resultant self-assemblies of patchy prisms have highly selective patch-patch connections of 85.4% (Figures 1f, S2, and S3; incubated for 15 min in 50 μ M cetyltrimethylammonium bromide (CTAB); 493 patches in the TEM images counted) due to patch clasping, with 14.6% of the assemblies formed through patch–edge connections (Figure S3).

The tip-tip distance of the connected prism pairs by clasps (Figures 1f,g and S3, 16.4 ± 5.7 nm, 156 pairs analyzed) is 23% smaller than twice the maximum patch thickness $t_{\rm m}$ of

unassembled prisms (10.6 \pm 1.3 nm, 132 patches analyzed, Figures 1d and S3), suggesting molecular interpenetration³⁵ during patch clasp formation. The $t_{\rm m}$ of unassembled prisms after incubation in 50 μ M CTAB (9.23 \pm 1.12 nm, 102 patches analyzed, Figure S3) decreased by 13% compared to t_m before CTAB incubation, inferring that penetration of small cationic CTAB molecules shrinks negatively charged polymer patches. Meanwhile, the chord length *l* characterizing the lateral dimension of the patch on the prism surface $(18.1 \pm 1.8 \text{ nm})$ 132 patches analyzed) remains unchanged in the assembled compared to unassembled prisms after incubation in 50 μ M CTAB (18.4 \pm 1.9 and 18.5 \pm 1.7 nm, respectively, 102 patches analyzed, Figure S3). These analyses suggest that CTAB molecules in this incubation condition primarily impact the outer region of patches, with a negligible effect on the patch areas close to the surface of gold NPs. Thus, outside the clasping region, the patches, especially close to the gold NPs, remain mostly intact.

We find that other cationic surfactants, such as benzyldimethylhexadecylammonium chloride, cetylpyridinium chloride, and cetrimonium chloride, induce similar patch—patch connections in the prisms, showing the generalizability in surfactant-induced patch clasping (Figure S4 and Table S1). In contrast, when simple charge screening salt such as NaCl is used, instead of patch—patch connection, the van der Waals attraction

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Figure 3. Relaxation dynamics of bowties assembled through patch clasp. (a, b) Time-lapse liquid-phase TEM images of a reconfiguring dimer color-coded by the prism angle α (a) and the corresponding molecular schematics (b). Dose rate: 2.5 e⁻Å⁻² s⁻¹. (c) SEM image of postimaging patchy prisms on liquid-phase TEM chips. (d) Theory prediction of patch-patch interaction potential in a wet versus dry state. (e) Theoretical calculation of energy distribution for bowtie and sawtooth dimeric configurations. Scale bars: 100 nm (a) and 300 nm (c).

of gold NPs drives closely packed structures between gold surfaces with stars and slanting diamonds motifs¹⁵ (Figure S5). Thus, we attribute the patch clasping to the surfactant–polyelectrolyte aggregation that can be summarized as follows:^{33,34,36} (1) positively charged heads of CTAB molecules adsorb onto the negatively charged PAA blocks of the patch (Figure 1h); (2) accumulation of CTAB on the patches facilitates the aggregation of the hydrophobic tails of CTAB into micelles; and (3) CTAB tail aggregation bridges patches between neighboring NPs (Figure 1i).

Dynamic Formation, Breakage, and Relaxation of Patch-Clasps in Bowtie Assembly. Liquid-phase TEM imaging of the patchy NPs in a 50 μ M aqueous CTAB solution captures the patch "clasping" process, induced by highly selective patch-patch attraction. To prevent beam damage on the polymer patches, we optimize the electron dose rate to be sufficiently low (0.14 e^{-} Å⁻²s⁻¹, Methods) and confirm the integrity of polymer patches from post-mortem SEM characterization (Figure S6, Methods). Due to the low dose rate and low TEM contrast of polymers, we focus on the clasp-induced NP bonds, manifested as the dynamics of gold prisms connected by them. Comparisons of liquid-phase TEM images of assembled patchy NPs, single patchy NPs, and unassembled nonpatched NPs show consistency in the spatial resolution achieved by our imaging protocols (Figure S2). Single NP tracking of approaching prisms has three stages of patch-clasping (Figures 2a,b and S7, Movie S1). The first is "Approach and Jump". Namely, prism 1 approaches prism 2 by slow crawling, followed by a sudden jump into the tip-tip configuration at 27 s (Figure

2c,d). Such "Jump" from a distance is consistent with the extended interaction range of a water-solvated patch (as far as 40 nm or roughly 3 times the hydrodynamic radius of the chain).¹⁶ In the second stage "Reconfigure", the prism pair has a stable center-to-center distance *D* for 78 s (96.6 ± 2.6 nm; Figure 2c), inferring that prisms are robustly connected longitudinally (Movie S1, more examples in Figure S8). Meanwhile, the prism tip-tip angle θ fluctuates over time (Figure 2d). The two-dimensional (2D) distribution map of the prism pair in their relative positions^{37,38} (Figure 2e) summarizes such rotational flexibility in patch clasps. In the last stage, "Twist and Leave", the prisms twist against each other, eventually leading prism 2 to leave at 111 s. We attribute the disassembly of the prisms to the severe distortion of the patch clasp, as also found in other breakage events (Figures S9 and S10).

Liquid-phase TEM imaging of the relaxation dynamics of the bowties shows that patch clasps have rotational flexibility, while keeping the prisms longitudinally connected. Time-lapse liquid-phase TEM images of a preassembled dimer show that the prism orientation α (defined in Figure 3a) changes over time in each prism, suggesting rotational freedom of NPs at the patch clasp (Figures 3a,b and S11, Movie S2). Accordingly, the dimer conformation continuously interconverts between sawtooth-like (t_0 and t_0 + 6 s) and bowtie-like (t_0 + 3.2 and t_0 + 7.6 s) upon thermal fluctuation (more examples in Figure S8). However, the center-to-center distance remains stable for over 100 s (120.7 ± 5.9 nm, Figure S11), suggesting the longitudinal robustness of the patch clasp. Measured values of *D* sit at the high end in the histogram of dried state D_{dried} (up to ~106.0 nm, Figure S3).



Figure 4. Systematic analysis of the rotational flexibility of clasps given different extent of interpenetation. (a) Schematics of patch clasp with R_{sd} labeled. (b) Representative TEM images of patch clasps annotated with tip—tip distance *d* and neck width *n*. (c) Scatter plot and distribution of *d* and *n*. The Gaussian mixture model classifies prism pairs into "full" (green) and "partial" (violet) clasp groups. The green and violet shades show a density of scatter larger than 0.004 and 0.008, respectively. The theory prediction of neck width *n'* (solid line) and the average (dotted line) and standard deviation (gray shade) of $2t_m$ are presented for comparison. (d) Contour of patch clasps in (b) color-coded by the local surface curvature. (e–g) Distribution of local surface curvature (e), θ in experiment (solid lines) and simulation (shades) (f), and 2D projected patch area *a* (g) of the two groups, full clasp (green) and partial clasp (violet), in comparison with that of patches before merging (black dashed lines). Scale bars: 20 nm.

Note that such flexibility is not rendered by electron beam damage, as confirmed by post-mortem characterization of the patchy NPs in and out of the window (the region without electron beam illumination) (Figure 3c, Methods). Despite possible variations in our experiments in terms of the interaction between polymer patchy NPs and SiN_x chips, as well as electron dose rates, patch clasps consistently exhibit longitudinal robustness and rotational flexibility. Such flexible NP assemblies are strikingly different from the static configuration of assemblies between NPs without polymer patches.³⁹

To incisively probe the microscopic origins and underlying mechanisms of the observed patchy NP behaviors, we employ polymer scaling theory and MD simulations. First, to understand longitudinal robustness and patch—patch interaction range enabling clasp-induced NP bonding, we compute the patch patch interaction potential between patchy NPs in both their wet and dry states (Figure 3d, Methods). By inspection, the wet state has an interaction range that is roughly double in size compared to the dry state. This means that chains within solvated (wet) patches can extend further without significant energic penalty (compared to the collapsed, dry patches). We attribute this chain flexibility as the source for the observed longitudinal robustness between interacting patches. Specifically, chains can quickly reorganize to adapt to perturbations within the interpenetrating regime associated with interconversions between the sawtooth and bowtie patch configurations. This rapid reorganization will preserve the thermodynamically stable chain size within the interpenetrating regime, producing the observed longitudinal robustness between interacting NPs.

Next, to understand the fundamental driving forces governing the transition between the sawtooth and bowtie configurations, we compute the excess free energy of formation for both NP configurations (Figure 3e). Briefly, we employ our previously developed thermodynamic perturbation theory, which considers a noninteracting reference state of patchy NPs positioned and oriented in each respective configuration.40 An interaction potential U(r) is then assigned between all interacting monomers, where r is the center-to-center distance between two patches on the tips. Here, we employ a Lennard-Jones (LJ)type interaction potential to mimic the isotropic CTAB-induced aggregation between monomers while simultaneously accounting for steric repulsion between neighboring polymer chains. By defining a set of relative orientations between patchy NPs, a potential of mean force V(r) can then be computed between interacting particles. The excess free energy of formation is

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simply $\Delta G = -k_{\rm B}T \ln K$, where *K* is the equilibrium constant for the formation of any given configuration defined as

$$K = \frac{\rho^m}{m!} \int f^m(r) g(r) dr$$
⁽¹⁾

Here, g(r) defines the spatial configuration of interacting patchy NPs, ρ is the system density, *m* is the number of NPs in a given configuration, and f(r) is the Mayer *f* function:

$$f(r) = e^{-V(r)/(k_{\rm B}T)} - 1$$
(2)

To generate sample configurations in the computation of K, we employ MD simulation (Methods) and a coarse-grained model of patchy NPs to rapidly generate 1,500+ sample configurations for patchy NP dimers. Computing ΔG for each configuration results in the energy histogram shown in Figure 3e, where two dominant peaks are observed. These two peaks correspond to the sawtooth and the bowtie motifs with an energy difference of ~0.2 $k_{\rm B}T$. This low energy barrier between the sawtooth and bowtie motifs is well within the level of the Brownian fluctuations of nanoparticles $(k_{\rm B}T)$ caused by stochastic motions of solvent molecules,⁴ providing a thermodynamic explanation for the rapid transition observed in situ between the two states in Figure 3a. As discussed in previous studies, the local heating effects under our electron beam dose rate conditions are negligible.⁴

Molecular Mechanism of the Formation and Rotational Flexibility of Polymer Clasps Dependent on Patch Interpenetration: Full vs Partial Clasping. Complementary to the NP-level dynamics revealed by liquid-phase TEM imaging, systematic image analysis provides the molecular picture of patch clasp formation and characteristics. Based on the staged assembly dynamics observed in situ (Figure 2a), we propose that the patch-clasps behave differently upon the extent of clasp or patch interpenetration (Figure 4a). Analysis of 156 clasps by TEM imaging reveals a range of tip-tip distance d $(16.4 \pm 5.7 \text{ nm})$ and neck width *n* of the patch clasps $(12.7 \pm 5.0 \text{ m})$ nm) (Figures 4b,c, S2, and S12). The *d* distribution has a single peak with a tail in the high d region, while n has a bimodal distribution, suggesting that two regions exist in terms of patchpatch interpenetration. To analyze the patch clasp shape distributions, we use Gaussian mixture model-based unsupervised machine learning⁴³ to classify the paired patches into two groups of similar instances (Supporting Information, Figure S13). One has d (14.1 \pm 3.1 nm) smaller than $2t_{\rm m}$, which we refer to as "full" clasping with an extended flat neck, and the other has $d (24.0 \pm 4.0 \text{ nm})$ larger than $2t_m$, which we refer to as "partial" clasping with a thin neck (Figures 4c and S13). The "full" clasping group has a steep increase in *n* upon a decrease in $d (-0.65 \pm 0.05 \text{ and } -0.22 \pm 0.06 \text{ for full and partial},$ respectively). Accordingly, the local surface curvature of 2Dprojection of patch clasps contours inFigure 4b differs in two groups. The local surface curvature distribution in Figure 4e shows that compared to before clasping, the clasping shifts the local surface curvature to more negative, in general. Meanwhile, the partial clasping exhibits even more negative surface curvature than the full clasping due to the thin and longitudinally extended neck.

We provide a physical interpretation for this transition between "partial" and "full" clasping using polymer scaling theory (Figure 4c, solid line; Supporting Information). We posit that the shift in n as a function of d is a direct result of the changing degree of confinement that polymer chains experience during clasp formation. Thus, the partial to full clasping transition is mediated by a reorganization of the local monomer concentration (*c*) dependent correlation blob size ξ to minimize polymer chains' free energy. To understand the molecular picture of clasp formation, we derive a set of self-consistent equations that solve for ξ as a function of *d* (Supporting Information). The theoretical neck width *n*' can then be simply derived as

$$n' \sim n_{\rm b}(c) \,\xi(c) \tag{3}$$

where $n_{\rm b}(c)$ is the number of correlation blobs occupying the neck in merging patches.

We show that n' (Figure 4c) provides similar predictions for a range of patch clasping in experiments and explains the partial to full clasping transition mechanism. First, the patches start to merge via a few chains at a distance $(d > 2t_m)$, where these chains stretch to maximize favorable chain-chain interaction and initiate clasp formation. This results in the thin neck observed for the "partial" clasping regime. Next, d decreases because the chains continuously relax to their equilibrium conformation and increase entropy, while maintaining the same extent of favorable monomer-monomer interactions. Thus, the two patches from each NP can get even closer $(d < 2t_m)$, with more polymer chains joining the existing clasp and experience stronger patch-patch interaction. This stronger interpenetration results in a rapid increase of n, making the "full" clasping neck motif. This mechanistic insight into clasp formation and transition is also consistent with the staged assembly dynamics observed in situ (Figure 2a): slow crawl at a distance and sudden jump to form a reconfigurable assembly of a prism pair.

Next, the extent of patch clasping determines not only the patch clasp shape but also their rotational flexibility. The tip–tip angle θ of the full clasping group θ_{full} (69.3 ± 32.2°) exhibits 52% larger range of relative fluctuation in θ than that of the partial clasping group θ_{partial} (87.6 ± 26.7°), indicating that NPs connected by fully clasped patches are rotationally more flexible (Figure 4f, solid lines). Theory prediction of the tip–tip angle in each group θ'_{full} and θ'_{partial} also reveals similar behaviors, which can be directly correlated to the neck width n' using the following equation:

$$\theta' \sim \sin^{-1} \left[\frac{(R_{\rm sd}^2 - n'^2)^{1/2}}{R_{\rm sd}} \right]$$
 (4)

where $R_{\rm sd}$ is the size of the polymer chain occupying the neck region (defined in Figure 4a, Supporting Information). The θ'_{partial} reflects stiffer clasp due to stretched chain configurations reducing chain mobility and a narrower clasp opening angle. Conversely, θ'_{full} reflects flexible clasp attributed to relaxed and thus more flexible chains, which account for increased clasp rotational freedom (Figure 4f, bar graphs). The theoretical prediction is in good agreement with our TEM image analysis (Figure 4f, solid lines). This theoretical prediction of clasp formation is also consistent with our liquid-phase TEM observation of extended "reconfiguration" in Figure 2a, occurring after the prism pair is close enough for full merging. We note that despite the different characteristics (i.e., shape and flexibility) in each clasp group, the 2D projected areas of full and partial clasping a_{full} and a_{Partical} are indifferentiable, inferring that the extent of clasping is not predetermined by the original patches but rather captured during the clasping process (Figure 4g). Moreover, both a_{full} and a_{Partical} remain similar to twice the 2D projected area of patches before clasping 2a (where a = 212.0



Figure 5. Extended assemblies of patch-patch assemblies and motifs. (a, c) Representative TEM images of various motifs with false-colored patches (a), corresponding topological reconfigurations (b), and corresponding structural motifs from MD simulation of patchy NPs assembly (c). TEM images without false coloring are in Figure S12. (d) Representative snapshot of patchy NP assembly MD simulation in dilute NP concentration. (e, f) Theoretical calculation of energy distribution for representative trimer (e) and tetramer motifs (f). Scale bars: 50 nm.

+ 39.2 nm², a_{full} and a_{Partical} are 433.0 ± 69.2 nm² and 416.3 ± 52.6 nm², respectively), confirming that during the clasping there is no obvious change in the number of polymer chains.

Beyond Dimers: Self-Assembly, Energetics, and Structural Relaxation of Extended Patch-Patch Assemblies. The flexible nature of the polymer clasp leads to structural motifs with varied θ values, including linear, cyclic, and branched structures (Figure 5a). We can describe these NP assemblies as topologically organized systems of links and nodes⁴⁴ (Figure 5b). Through this lens, the mechanical properties or structural flexibility of each motif varies depending on its topological structure, which is dictated by the allowed motion of individual NPs within. Assuming that the assemblies are effectively 2D, we can apply Maxwell's counting⁴⁴ to determine the topological zero modes.^{12,13,45} Assembly structures with topological zero modes can be flexible because the prisms' motion does not require clasp breakage or energy input during structural relaxation. For example, in the three-membered cyclic structure, the clasps cannot rotate, and thus, it has no topological zero mode. On the other hand, the four-membered cyclic structure has one zero mode, and thus it can be twisted by the rotation of NPs at the clasps, while keeping the original topological structure (Supporting Information).

MD simulation using our coarse-grained model similarly produces the experimentally observed structural motifs from patchy NPs in the low concentration limit (Figures 5c,d and S14). To quantitatively characterize the energetics of this low density system, we generalize our free energy calculation for the bowtie and sawtooth configurations (Figure 3e) to compute the relative probability of finding different configurational motifs for clusters that contain only three or four NPs. Similar to the binary NP limit, we employ simulations to rapidly generate a distribution of configurations containing a predefined number of NPs. We then employ eq 1 to compute the free energy of each cluster and predict the relative probability of finding a specific configuration given a cluster size (Figure 5e,f). Results reveal that the rings and linear motifs are both thermodynamically favored (lower values of ΔG). All peaks in probabilities, however, correspond only to rings and linear motifs, with none present for close packed structures. As such, we conclude that open networks are thermodynamically preferred for patchy NPs as opposed to close-packed tiling lattices commonly observed in the NPs with isotropic polymeric grafting. Additionally, our



Figure 6. Relaxation dynamics of a branched network in liquid-phase TEM and MD simulation. (a) Time-lapse liquid-phase TEM images of a branched network overlaid with prism labels and NP trajectories. Dose rate: $0.36 \text{ e}^{-} \text{Å}^{-2} \text{ s}^{-1}$. (b) Schematics of the branched structure annotated with bond angles γ and D. (c, d) Average (scatter) and standard error of mean (gray shadow) of D (c) and γ (d). (e) Scatter plots of representative γ (averaged by 2 s interval). (f) Correlation matrix of p of γ for 732 s. The dotted boxes highlight branches A-B-C-D-E-F (top) and F-H-I-J-K (bottom). (g) MD simulation schematic of the branched structure with branching location F highlighted in blue. (h, i) Simulation time-series data of average D between adjacent NPs from MD (h) and average γ (i). Data from local time-series of simulation with rescaled time-range τ' to fit experimental scale. Shadows correspond to standard error of the mean. (j) Local time-series of variation in the three corresponding bond angles in simulation. (k) Corresponding correlation matrix p for the corresponding simulation duration. Scale bar: 100 nm.

calculations reveal a higher energy barrier between rings and linear motifs as compared to sawtooth versus bowtie structures. This implies that transitions between such configurations are less favorable, suggesting topological robustness in claspconnected NP assemblies.

Drawing upon the topological robustness in extended assembly structures, we probe their flexibility using liquidphase TEM to image branched NP networks, which reveals collective structural relaxation and correlated motions among 11 prisms within, originating from the clasp connections (Figure 6a,b and Movie S3). The branched network continuously reconfigures over the entire observation time of 732 s without clasp breakage as inferred by the stability in average *D* and the bond angle γ , the angle of adjacent NP bonds (Figure 6a, D = 78.4 ± 16.1 nm, γ = 136.3 ± 28.3°, annotated in Figure 6a). The individual *D* and γ vary significantly depending on the local connections or the NP-level valency, i.e., the number of patches connected to other prisms (Figures 6e and S15). For example, γ_{EFH} (147.8 ± 13.0°) has broader distribution, compared to γ_{HIJ} (107.0 ± 5.0°) and γ_{BCD} (162.0 ± 7.0°). We attribute the larger fluctuation in γ_{EFH} compared to others to the prism F, which connects with all three branches, and is thus influenced by each chain motion (Figure 6b).

Interestingly, the seemingly random individual prism motions are often highly correlated (Figures 6f and S15, Supporting Information). We quantify such behaviors by Pearson coefficient⁴⁶ p for a pair of γ (i.e., γ_1 and γ_2) defined as following, where p = 1 and p = -1 correspond to strong correlation and anticorrelation, respectively.

$$p = \frac{\sum (\gamma_1 - \overline{\gamma_1})(\gamma_2 - \overline{\gamma_2})}{\sqrt{\sum (\gamma_1 - \overline{\gamma_1})^2} \times \sqrt{\sum (\gamma_2 - \overline{\gamma_2})^2}}$$
(5)

The dotted boxes in Figure 6f indicate that the correlation of γ within each branch, *A-B-C-D-E-F* (upper right) and *F-H-I-J-K* (lower left), is particularly strong, whereas the correlation of γ from different branches (outside the two boxes) is much weaker. Taking a closer look into each pair, expectedly, the neighboring γ pairs $\gamma_{CDE} - \gamma_{DEF}$ and $\gamma_{EFG} - \gamma_{EFG}$ exhibit strong positive and negative correlations, respectively. Interestingly, the pairs

 $\gamma_{CDE} - \gamma_{EFG}$ and $\gamma_{ABC} - \gamma_{EFG}$ also show strong correlations (p = -0.87 and 0.94, respectively), although they are positioned apart by two and four NPs, respectively. Furthermore, the correlations in γ and D are not fixed but change over time (Figure S15). For example, the pair $\gamma_{EFH} - \gamma_{HIJ}$ is moderately anticorrelated for the first 375 s but becomes correlated in the remaining time from 375 to 732 s (p changes from -0.40 to 0.42). Likewise, γ_{EFH} develops strong anticorrelation with γ_{EFG} and γ_{CDE} , which does not exist in the initial stage of the relaxation (p change from -0.20 to -0.94 and from -0.08 to -0.76, respectively). Such long-range and dynamic correlations suggest that the motions of prisms propagate along the network, where each NP adapts its motion to the neighbors' positions via flexible and robust clasps.

To obtain a deeper insight into the relaxation dynamics of such assemblies, we simulate the assembled structure in Figure 6b, along with a few linear and branched chain topologies, using MD (Figure 7a). Because of the greater statistics accessible through simulation, we are also able to obtain long-time behavior of the system to assess equilibrium properties. We see good agreement of D and γ with experiment (Figures 6h,i and



Figure 7. Comparison of fluctuation in bond angles across chain topologies by MD. (a) Schematics of chains (from left to right): linear extended sawtooth; linear extended bowtie, randomly oriented linear chain, star-like chain with randomly oriented NPs (blue denoting the center NP of the star). (b) Comparison of γ across topologies over a span of 2000 simulation time unit τ . For comparison of global average values, refer to Figure S21. (c, d) Long-time p of γ for the extended bowtie (c) and star (d).

7b). The simulated global equilibrium values of D (82.9 \pm 0.9 nm), and γ (125.8 ± 2.3°), and that of average tip-tip angle θ $(57.2 \pm 2.8^{\circ})$ are also in concurrence (Figure S16). We also verify if the model exhibits a similar dynamical correlation between bonded NPs (Figure 6j), focusing on the same local time-series as in Figure 6h,i. We employ the same Pearson coefficient analysis used in experiments (Figure 6f) to quantify the collective motions of particles within the local simulation time-series. Additionally, we characterize the long-time behaviors of correlated motions of bonded particles by performing the analysis over the entire simulation run (Figure 7c,d). The data confirm that for any given patchy NP assemblies, (1) neighbors nearer to each other should influence each other's motion (relative to distant NPs), (2) inter-NP correlation decays to zero at long time scales, and (3) neighbors nearer to the branching location are more rotationally constrained, regardless of time scale.

In 2D, the relative orientation of any two NPs is "locked" (either in the same or opposite direction) due to the inability to rotate in/out of plane. We explicitly probe the effect of such topological constraints on the rotational dynamics in MD (Figure 7). As shown in Figures 7b and S16-S20, for an allsawtooth structure (Figure 7a, first), as expected, we have much higher values of γ on average (148.3 \pm 1.0°). On the other extreme, the all-bowtie structure exhibits a much smaller γ of 119.6 \pm 1.8° (Figure 7a, second). For a random mix between bowtie and sawtooth chain topology, we obtain an intermediate γ of 127.7 \pm 1.3° (Figure 7a, third). Therefore, chain topology plays a critical role in controlling the equilibrium bond angle between NPs. To further solidify our claims about NPs constraining the relative bond angle and NP orientations, we compute the corresponding Pearson correlation matrices for each respective chain topology. Figure 7c and Figure 7d highlight the long-time heatmaps for the linear bowtie and a three-arm branch (Figure 7a, fourth), respectively. For the bowtie, almost all pairs of neighboring NPs show negative correlation (Figure S17). Similarly, for the linear sawtooth, pairs of neighboring NPs show a positive correlation (Figure S18). For the branch, we see a correlation peaking around the branchpoint, indicating that the presence and the location of branching also impacts the equilibrium dynamics (Figure S20). Full characterization of both dynamics and rotational modes for each topology can be found in Figures S16-S20 (with representative rendering in Movies S4 and S5).

In summary, we show that chain topology can drastically affect the chain dynamics and the relaxation behaviors of the connected NP networks. In experiments, we show that by using different CTAB concentration and incubation time, we achieve different topologies of networks (Figures S22–S26). These results immediately suggest that tuning chain topologies can provide a powerful handle for inverse engineering of the relative bond orientations between NPs to target specific deformation modes of interest.

CONCLUSION

We visualize the real-time and real-space dynamics of patchy NP assemblies, connected by polymer patch—patch selective NP bonds using low dose liquid-phase TEM. The selective attraction between patches is achieved by a surfactant-induced polymer complexation mechanism, which interpenetrates polymer patches into patch "clasp". Patch-clasping allows rotationally flexible and longitudinally robust NP bonds to be leveraged to design structural networks capable of adopting

multiple stable configurations. We show that the clasp-induced NP assemblies exhibit a range of unique dynamics, including highly selective tip-tip assembly, interconversion between dimeric bowtie and sawtooth configurations, and collective structural relaxation of NP networks. Polymer scaling theory and MD simulations, integrated with single-NP tracking and machine learning based statistical analysis, reveal the molecular picture of a range of clasp-induced dynamic behaviors, from how polymer patches recognize each other and undergo patchspecific penetration to how the extent of clasping determines the flexibility and structural integrity of NP bowties and networks. All of these computational results quantitatively agree with our experimental results. Furthermore, we show that controlling the bonding topology of NPs relative to each other not only provides tunability in the equilibrium structure and rigidity but also influences the emergent network relaxation dynamics. Such robust yet flexible patch clasp-induced NP bonds are crucial for designing reconfigurable nanoauxetics, which can effectively absorb external shocks¹¹ at the nanoscale.

Our experiment—computation integration and fundamental understanding of patch-clasp-induced inter-NP bond (directional, flexible, and robust) can be extended to other patchy NPs¹⁶ to aid the design of stimuli-responsive nanomaterials, such as topological metamaterials for chiral sensors, waveguides, and nanoantennas.^{10,12,44} Along this line, we expect that future studies in structure-dependent dynamic behaviors and ondemand, controllable reconfigurability^{17,30} of NP assemblies can facilitate the advancement of these applications.

METHODS

Materials. All chemicals were used without further purification after purchase: gold(III) chloride trihydrate (\geq 99.9% trace metals basis, HAuCl₄·3H₂O, Sigma-Aldrich), cetyltrimethylammonium chloride (CTAC) (>95%, C₁₉H₄₂ClN, TCI), sodium iodide (99.999%, NaI, Sigma-Aldrich), L-ascorbic acid (BioXtra, ≥99.0%, Sigma-Aldrich), sodium hydroxide (99.99%, NaOH, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB) (BioXtra, \geq 99.0%, C₁₉H₄₂BrN, Sigma-Aldrich), polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) (PS₁₅₄-*b*-PAA₅₁, $M_{\rm n}$ = 16 000 for the PS block and $M_{\rm n}$ = 3700 for the PAA block, $M_{\rm w}/M_{\rm n}$ = 1.04, Polymer Source Inc.), 2-naphthalenethiol (2-NAT, 99%, Sigma-Aldrich), N,N-dimethylformamide (DMF) (anhydrous, 99.8%, Sigma-Aldrich), acetone (\geq 99.5%, Fisher Chemical), sodium chloride (99.3%, NaCl, Fisher Scientific), benzyldimethylhexadecylammonium chloride (BDAC) (\geq 97.0%, CH₃(CH₂)₁₅N(Cl)(CH₃)₂CH₂C₆H₅, Sigma-Aldrich), cetylpyridinium chloride (CPC) (>98.0%, C21H38ClN·H2O, TCI), Spin-X centrifuge tube filters (cellulose acetate membrane, pore size 0.22 µm, nonsterile, Corning Inc.), and 2-(2-[2-(11-mercaptoundecyloxy)-ethoxy]-ethoxy)-ethoxy-ethoxy-ethoxy-ethoxy-acetic acid $(\geq 95\%, HS(CH_2)_{11}(OC_2H_4)_6OCH_2COOH, Prochimia Surfaces)$ were purchased and used without further purification. Nanopure water (18.2 MΩ·cm at 25 °C) purified by a Milli-Q Advantage A10 system is used throughout the work.

Characterizations of Patchy NPs and Their Assembly. The UV–vis spectra of the prisms and separated impurities were measured by using a Scinco S-4100 PDA spectrophotometer with a quartz cuvette (path length = 1 cm, VWR). Harrick Plasma PDC-32 (maximum RF power of 18 W, Harrick Plasma) was used for plasma treatment of TEM grids. A JEOL 2100 Cryo TEM with a LaB₆ emitter at 200 kV was used to characterize the tip-patch prisms before and after patch formation. A Hitachi S-4800 scanning electron microscope (SEM) was used to characterize the dimension and monodispersity of the prisms before assembly and postimaging of the SiN_x chips after liquid-phase TEM experiments. The liquid-phase TEM imaging was conducted on a Hitachi 9500 TEM with a LaB₆ emitter at 200 kV by using a liquid flow holder (Hummingbird Scientific).

Synthesis of Polymer Patchy Prisms. The polymer patchy nanoprisms were synthesized following our previous report.¹⁵ First, the gold nanoprisms were synthesized and purified following a literature method.^{7,16} Next, in an 8 mL glass vial, the 2-NAT solution (3 μ L, 2 mg/mL in DMF) was mixed with 817 μ L DMF. 100 μ L of stock solution II and 100 μ L of water were added into the vial dropwise using pipet while vortexing the solution in the vial. The PS-b-PAA solution $(80 \,\mu\text{L}, 8 \,\text{mg/mL} \text{ in DMF})$ was added into the vial, followed by mixing on the vortex. The β of the reaction mixture, defined as the ratio of 2-NAT molar concentration to optical density (OD) of the prisms at λ_{max} is 75 nM. The vial was capped tightly with a Teflon-lined cap and sonicated for 5 s, parafilm-sealed, and heated at 110 °C in an oil bath. The solution was left undisturbed for 2 h during heating. The reaction mixture in the vial was cooled down to room temperature in the oil bath, which typically took 80 min. The solution was transferred to a 1.5 mL microcentrifuge tube and 400 μ L of water was added into the tube. The solution was centrifuged three times (5000, 4500, and 3600 rpm for 20 min each) to remove the residual 2-NAT and PS-b-PAA from the assynthesized patchy prisms. After each centrifugation, 1.48 mL of the supernatant was removed and the 20 µL sediment was dispersed with 1.48 mL of water. After the last round of centrifugation, 10 μ L of the sediment was diluted by 190 μ L of water. A total of three reaction vials were prepared at the exact same condition and the products were combined into one tube in this step. We estimate the polymer grafting density to be \sim 2.4 chains/nm² for the covered surface area of the tips, based on our previous thermogravimetric analysis of patchy prisms synthesized in similar conditions.¹⁵ The patchy prism solution was then filtered through the centrifuge tube filters at 2600 rpm for 10 min to remove the micrometer-scale PS-b-PAA films, if any exists. The penetrated patchy prism solutions were collected and diluted by water to make stock solution III of 1.1 OD at λ_{max} . For the TEM imaging, 8 μ L of sediment solution was drop-casted onto a TEM grid treated with oxygen plasma (1 min at low radio frequency power) and left dry in the air for 3 h. The patchy prism solutions were stable for at least 6 months. The full detail of synthesis is in Supporting Information.

Assembly of Patchy Prisms Using Surfactant-Polyelectrolyte Complexation. The patchy nanoprisms were assembled on the TEM grids for the direct characterization under TEM. In our typical assembly experiments, $6-8 \mu L$ of stock solution III was placed on a clean side of the parafilm. The aqueous CTAB solution was added into the droplet of stock solution III on the parafilm to make the desired CTAB concentration (detailed assembly conditions are summarized in Table S2). The mixture was quickly mixed by pipetting the droplet thoroughly 10 times. The mixture droplet was then transferred onto an oxygen plasma-treated TEM grid by pipet and kept undisturbed under a glass Petri dish (10 cm in diameter) for the desired amount of time (Table S2). Two vial caps filled with water were placed next to the TEM grids under the Petri dish, and the Petri dish was pressed hard on the parafilm to seal the assembly environment thoroughly and minimize the drying of the mixture droplets. After the desired amount of reaction time, clean filter paper was gently placed on the grid to quickly remove all of the liquid and to quench the patchy prism assembly. The remaining liquid on the grid was removed further using another piece of filter paper gently pressed on the grid. The assembly of patchy prisms using other cationic surfactant molecules (i.e., CPC, CTAC, and BDAC) and NaCl (Figures S4 and S5) was done following the same procedure as above, by replacing CTAB with other chemical compounds. The detailed assembly conditions for each reagent are summarized in Table S1.

Liquid-Phase TEM Imaging of Prisms Connected by Patch Clasps. In a typical experiment, SiN_x microchips were oxygen-plasmacleaned for 27 s at a low RF level (Harrick Plasma Cleaner PDC-23G). The patchy prisms were assembled directly on SiN_x microchips, and throughout the sample preparation and imaging, they were kept in liquid. Specifically, the 3 μ L of solution III was placed on the clean side of the parafilm and mixed with 1 μ L of 0.2 mM CTAB solutions. The solution on the parafilm was quickly and thoroughly mixed by pipetting the solution 10 times. The mixture droplet was then transferred using a pipet onto an oxygen plasma-treated SiN_x microchip that is placed at the bottom (window: $50 \ \mu m \times 200 \ \mu m \times 50 \ nm$, 250 nm or 100 nm spacer, Hummingbird Scientific) and covered with a glass Petri dish (10 cm in diameter). The solution on the chip was kept undisturbed while patchy prisms were allowed to self-assemble via surfactant—polyelectrolyte complexation. Two vial caps filled with water were placed next to the microchip under the glass Petri dish to minimize the drying of the droplet. Note that the Petri dish was pressed hard on the parafilm to keep the humid environment. Thirty minutes later, 3 μ L of this assembly solution was pipetted to lower the liquid thickness without disturbing the liquid coverage on the window area. The sector-shape cut filter paper was used to absorb the solution quickly and gently further to thin the liquid layer on the window area. The solution on the bottom chip was then covered with the top chip (window: $30 \,\mu$ m × 50 nm). 50 μ M CTAB solution containing carboxylate-terminated thiol molecules ($0.6 \,\mu$ M) was flown through the liquid flow holder for 30 min at 5 μ L min⁻¹ prior to imaging.

The liquid-phase TEM movies were captured by a UltraScan (US) 1000 CCD and K2 camera with an exposure time of 0.1-1.5 s. A spot size of Micro 1 was used with the precalibrated current to ensure the low dose rate to image patchy nanoprisms without damaging polymer patches (Figure S6). Note that the dose rate was controlled by manipulating beam current, electron beam size, magnification, and the first condenser lens (C1). The dose rate was calculated from the total pixel intensity of an acquired image with samples out following eq 6. The conversion factors were measured as 17.6 and 36.5 counts per e⁻ for US1000 CCD and K2 direct detection camera, respectively.

dose rate =
$$\frac{\text{total pixel intensity}}{\text{acquisition area } \times \text{ exposure time}} \\ \times \frac{1}{\text{conversion factor}}$$
(6)

Postimaging Characterization of Liquid-Phase TEM Chips under SEM. In a typical characterization, after liquid-phase TEM imaging of patchy nanoprism assemblies, SiN_x microchips were gently disassembled on a clean surface. The sample on the chips was fully dried in the air before being imaged under SEM at 10 kV.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.3c09710.

Materials and methods, image and data analysis, polymer physics theory and MD simulation, Tables S1–S3, Figures S1–S27, and Movies S1–S5 captions (PDF)

Movie S1 showing patch clasping-induced assembly and disassembly process (AVI)

Movie S2 showing dimer assembled by a rotationally flexible polymer patch clasp (AVI)

Movie S3 showing reconfiguration of branched network (MPG)

Movie S4 showing relaxation of branched structure (MPG)

Movie S5 showing relaxation of extended linear sawtooth structure (MPG)

AUTHOR INFORMATION

Corresponding Authors

- Thi Vo Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States; o orcid.org/0000-0002-0953-4143; Email: tvo12@jhu.edu
- Qian Chen Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, United States; Department of Chemistry, Beckman Institute for Advanced Science and Technology, and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, United States;

orcid.org/0000-0002-1968-441X; Email: qchen20@ illinois.edu

Authors

- Ahyoung Kim Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, United States
- Kireeti Akkunuri Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States; occid.org/0009-0005-5307-477X
- Chang Qian Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, United States
- Lehan Yao Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, United States; orcid.org/0000-0003-1945-833X
- Kai Sun Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, United States
- Zi Chen Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts 02115, United States; orcid.org/0000-0001-5927-0249

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.3c09710

Author Contributions

The manuscript was written through contributions of all authors. A.K. and Q.C. designed the experiments. A.K., C.Q., and Q.C. performed the experiments, and A.K., L.Y., and Q.C. performed experimental data analysis. K.A. and T.V. constructed polymer scaling theory and performed MD simulations. K.S. and Z.C. provided topological mechanical insights and discussions. Q.C. and T.V. supervised the work.

Notes

The authors declare no competing financial interest.

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